REDOX KINETICS STUDY FOR CHEMICAL-LOOPING COMBUSTION, WATER AND CO\textsubscript{2} SPLITTING USING NICKEL AND CERIUM-BASED OXYGEN CARRIER

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SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

AT THE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

SEPTEMBER 2016

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Submitted to the Department of Mechanical Engineering on August 12, 2016 in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

Chemical-looping (CL) is a novel and promising technology for several applications including oxy-combustion for carbon capture, hydrogen production and CO₂ reuse. In this process, oxygen carriers are utilized to cyclically adsorb and release oxygen producing two separated exhaust streams with desirable products. A rotary reactor design with micro-channel structure was developed in the Reacting Gas Dynamics Lab (RGDL) at MIT, which exhibits superior performance over conversional designs. Preliminary simulation identified OC redox kinetics and material characteristics as keys to the success of CL technology.

This thesis examines the fundamentals of the reduction and oxidation (redox) processes with the aim of achieving fast and reliable reaction kinetics for CL applications. Experiments are conducted in a button-cell fixed-bed reactor with an on-line mass spectrometer. The time-resolved kinetics are modeled with consideration of thermodynamics, surface chemistry, transport mechanism, and structural evolution. Our approach, combining well-controlled experiment and detailed kinetics modeling, enables a new methodology for identifying the rate-limiting mechanism, examining the defect electrochemistry, and designing alternative materials for chemical-looping technology.

Redox study with nickel thin foils reveals that structural evolution is the determining factor. Nickel oxidation starts via nucleation of oxide grains, which overlap and annihilate the fast diffusion paths. The model shows that the reaction is limited by the decreasing ionic diffusivity.
To achieve practical redox repeatability, NiO fine particles supported on YSZ nanopowder is tested, and superior kinetics and cyclic stability are observed. Fast oxygen exchange is achieved from 500 to 1000°C with sufficient utilization of the carrying capacity within 1 min. Improvement is attributed to the enhanced ionic diffusivity with YSZ.

The use of ceria nanopowder exhibits an order of magnitude H₂ production rate improvement as compared to the state-of-the-art. Ceria reduction is slow with a threshold temperature of 700°C. The model reveals that the charge transfer is the rate-determining step for H₂ production. Improving H₂ splitting requires: (i) reducing the defect formation enthalpy, and (ii) accelerating charge-transfer. The addition of Zr lowers the threshold temperature to 650°C with 60% improvement in the rates, resulting from 40% decrease in the defect formation enthalpy. Doping ceria with Pr³⁺ further lowers the threshold temperature to 600°C while doubling the peak rate. The model reveals that the high concentration of surface defects achieved from either approach promotes adsorbate formation, thus accelerating the splitting steps. Similar conclusions are obtained for CO₂ splitting. Using the derived kinetics, H₂-syngas co-production with CH₄ as fuel is examined. Two important stages are identified: the formation of the complete products on oxidized surface, and syngas on the reduced surface. CH₄ reduction is found to be rate-limited by the slow fuel cracking reaction. To accelerate the kinetics, a novel perovskite-nickel composite OC is examined, in which nickel effectively catalyzes reduction, leading to an order of magnitude faster kinetics at 600-700°C.

This project has clearly demonstrated that using novel materials, CL technology can provide an efficient solution to oxy-combustion based CO₂ capture, and H₂/syngas co-production. Specifically, the use of NiO/YSZ achieves fast kinetics, robust stability and sufficient OC utilization from 500 to 1000°C, enabling complete CO₂ capture with minimum energy penalty. The ceria-, and perovskite-based OCs exhibit over an order-of-magnitude faster kinetics compared to the state-of-the-art, enabling improved H₂ production/CO₂ reduction efficiency isothermally at 600-700°C. In-depth understanding gained on the redox fundamentals will shed light on the design and fabrication of new materials as well as optimization of the CL applications.
Acknowledgements

First, I would like to express my utmost thanks to my supervisor Professor Ghoniem. No words can describe how grateful I am to be able to work with him here at MIT. His expertise and support have guided me through the past six years. His serious attitude on scientific research has set up a high standard for my future work, and his wisdom, not only on research, but also the way to face, think, and solve challenges, will benefit me and encourage me in my whole career life.

I would also like to express my gratitude to Professor Bilge Yildiz, for being a great support, and especially for the opportunity to collaborate on the H₂O splitting project, and providing the profound insights over the years. I am also grateful to Professor Kripa K. Varanasi for being on my PhD Thesis committee and for his interests and valuable input and constructive suggestions to my research.

This work would not have been possible without the help and guidance from Professor Mruthunjaya Uddi, who taught me hand-by-hand on how to do the experiments, and has always been the “go-to” person whenever experiments run into trouble. I am so grateful to have him by my side over the years throughout so many difficult stages of this research.

I would like to thank Dr. Santosh Shanbhogue for many great advices for experiments. I also want to thank Dr. Nikolai Tsvetkov for the help with material preparation and valuable discussions on some modeling challenges.

A big thanks to all my friends in RGD lab: Xiaoyu, and Georgios, who have been with me through many unfortunate incidents in the lab; to Nwike and Claire, who were once the team of chemical-looping; to Richard, Lei, Cristina, Guang, Soufien, Dan, Ping, Patrick, Simcha, Addison, etc, for friendship and support, which surely makes the journey lots of fun. Many thanks to Lorraine, Leslie Regan, and William F. DiNatale for their support throughout my stay here.
I am also thankful for the friends I have from all the places I have lived. I did have a great time working on a few projects with amazing people here at MIT. To my teachers and mentors from MIT, I thank them for their efforts in making the journey challenging and fruitful.

I appreciate the sponsorship from Masdar Institute, KAUST, and BP for the support of my PhD research.

Finally, I would like to thank my parents, my wife and our daughter. They have been with me every step of the way.
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Chapter 1

Introduction

1.1 Chemical-looping Combustion with CO₂ Capture

It has been widely accepted that fossil fuel combustion is a major contributor to the rise of CO₂ concentration in the atmosphere and global warming. One approach to reduce anthropogenic CO₂ emissions, apart from improving energy efficiency and using alternative sustainable energy sources, is carbon capture and sequestration (CCS), in which CO₂ is separated from flue gases, liquefied, and injected in geological formations, such as depleted oil or gas fields. Of these steps, CO₂ capture remains the most challenging part from an economic point of view since obtaining carbon dioxide in high purity still accounts for the major share of the cost of state-of-the-art CCS technologies. Over the past decade, extensive research focus has been placed on three general processes for capturing CO₂ from combustion in power plants: post-combustion capture, pre-combustion decarbonization and oxy-combustion. A schematic comparison of the three methods is shown in Figure 1-1. One of the key issues that limit the applications of CCS approaches is the large energy penalty during the separation process.
Recently, a new approach for CO₂ capture has been widely investigated. This approach was named “chemical-looping combustion (CLC)”[1]. In CLC, combustion is decomposed into two steps (Figure 1-2): fuel is oxidized by a metal oxide in a fuel reactor to generate CO₂ and steam; the reduced metal oxide is then regenerated by air in an air reactor. The reactions in each step can be written as:

Reduction: \( \text{Me}_x\text{O}_y + \text{fuel} \rightarrow \text{Me}_x\text{O}_{y-1} + m\text{H}_2\text{O} + n\text{CO}_2 \) \hspace{1cm} (1.1)

Oxidation: \( \text{Me}_x\text{O}_{y-1} + \text{air} \rightarrow \text{Me}_x\text{O}_y + \text{N}_2 + \text{unreacted O}_2 \) \hspace{1cm} (1.2)
The flue gas from the reduction step contains only CO\(_2\) and H\(_2\)O where CO\(_2\) can be readily captured after steam condensation. During this two-step process, the looping medium (Me\(_x\)O\(_y\)) adsorbs oxygen during the oxidation step and releases it to oxidize fuel during the reduction step, and as a result, it is named “oxygen carrier” (OC). Due to the fact that fuel directly reacts with a pure oxygen source (in this case, lattice oxygen in Me\(_x\)O\(_y\)), this process belongs to oxy-fuel combustion.

The summation of energy released from these two reactions gives exactly the same amount as the direct combustion:

\[
C_nH_{2m} + \text{air} \rightarrow mH_2O + nCO_2 + N_2 + \text{unreacted } O_2
\]  

(1.3)

The major advantages of CLC as compared to other CCS methods are related to the simplification of separation: with the use of OCs as the medium to transport the pure oxygen, the direct contact between air and fuel is circumvented and hence energy-intensive gas separation processes are avoided. Thus, CLC is also categorized as an unmixed combustion process to emphasize this advantage.
The first application of the chemical-looping (CL) concept in industry may date back to the late 19th and early 20th century, when this concept was prompted by the lack of effective chemical conversion/separation techniques in the generation of products. A steam-iron process was proposed for hydrogen production using iron oxide as an intermediate to oxidize syngas: [2, 3]

\[
\text{Fe}_3\text{O}_4(s) + 4\text{CO}(g) \rightarrow 3\text{Fe}(s) + 4\text{CO}_2(g) \quad (1.4)
\]

\[
3\text{Fe}(s) + 4\text{H}_2\text{O}(g) \rightarrow 4\text{H}_2(g) + \text{Fe}_3\text{O}_4(s) \quad (1.5)
\]

Owing to the poor regenerability and the low product yield, this method was gradually replaced by less costly reforming methods with oil and natural gas as feedstock. Later in mid-1950s, the idea of chemical looping was proposed in a patent by Lewis and Gilliland from Massachusetts Institute of Technology to produce pure CO\(_2\) for the beverage industry using two inter-connected fluidized-bed reactors (Figure 1-3) [4], which is widely acknowledged as the first application of CL strategy.

![Figure 1-3 Schematic representation of Lewis and Gilliland CO\(_2\) production process [4]](image)

In 1980s, the name “chemical-looping” was proposed by Richter and Knoche [1, 5] for the first time, prompted by the need to increase the reversibility of combustion processes and therefore
improve the thermal efficiency of power plants [1, 5]. The studies explored the idea of supplying low-temperature heat to the endothermic reaction in the fuel reactor, thereby upgrading the heat produced in the high-temperature air reactor. However, little attention was drawn to this proposal at that time owing to the difficulties associated with the inter-connected two-reactor system.

In 1994, Ishida and Jin [6] suggested for the first time that CLC could be used as a way to separate and thus capture CO₂ in a power plant. Since then, its development almost entirely concentrates on its capability of inherent CO₂ separation from combustion of carbonaceous fuel. With growing interests in environmental issues and better understandings of greenhouse gas emissions on climate change, the CO₂ separation feature from CLC has drawn significant attention. Since the beginning of the 21st century, research on CLC has been growing exponentially with research institutes all over the world playing critical roles. Among them, Chalmers University of Technology of Sweden, Instituto de Carboquímica (CSIC) of Spain, Vienna University of Technology of Austria, Korean Institute of Energy Research of Korea, Southeast University of China, Eindhoven University of Technology of Netherlands, SINTEF Materials & Chemistry of Norway, Ohio State University, University of Connecticut, and Massachusetts Institute of Technology have put forth significant efforts in designing and operating lab-scale or sub-pilot scale reactors to demonstrate and exploit the merits of this promising technology. Various prototypes (see Section 1.3) with power output up to 150 kW and over 4000 operation hours have already been documented in the literature [7]. The experiences from these successful applications are expected to lead to a wider commercial deployment of CLC.
Given the potential efficiency enhancement compared to current available CCS technologies, both experimental and computational studies have been carried out towards a better understanding of the fundamentals of the redox process within CLC. Experiences have been gained from the initial proof-of-concept investigations, and conclusions are summarized in several review papers [8-11]. While successful, CLC technology still faces many challenges from different aspects, mostly on identifying and optimizing the oxygen carrying materials with aim of reaching fast redox chemistry, high oxygen carrying capacity, and sustained cyclic regenerability.

1.2 Chemical-looping H2O/CO2 Splitting Technology as Carbon-Neutral Energy Solution

Despite the significant progress in CCS and the promising results from the preliminary prototype demonstration, significant challenges still remain, mostly in the process economics, safety, and long-term stability. Exploring and developing alternative approaches, such as H2 production from H2O splitting, or CO2 splitting and reuse technologies, is thus motivated by energy needs and environmental concerns, and offers novel and promising carbon-neutral energy solutions. This section summarizes two possible carbon-neutral energy solutions based on chemical-looping technology: (1) water splitting and H2-syngas co-production, and (2) CO2 splitting.

1.2.1 Water splitting and H2-syngas co-production

Hydrogen is an important environment friendly energy carrier because of its high gravimetric energy density and zero emission. Moreover, hydrogen finds wide applications in a variety of industries, including crude oil refining, chemical production, aerospace, metal refining, food processing and electronics manufacturing. Hydrogen consumption in the refining industry is
growing rapidly with a growth rate around 3.5% annually through 2018 [12]. The hydrogen generation market is expected to be worth $152.1B by 2021 [13]. Currently, steam methane reforming (SMR) is the major hydrogen production method. However, SMR leads to significant greenhouse gas emission (see Figure 1-5), and it has already reached its maximum efficiency (70-85%) [14]. The growing demand for clean and cost-efficient hydrogen sources has led to significant efforts to develop alternative technologies [15-17].

![Comparison of H₂ production cost via different methods. Unit, gallon gasoline equivalent H₂. Data valid as of Jan. 2016. Data source is refs. [14, 18, 19].](image)

Break-down of the hydrogen production cost for SMR¹ is shown in Figure 1-6, which illustrates the potential opportunities for developing alternative technologies:

¹ Note here that the cost shown in Figure 1-4 and Figure 1-6 does not include the transportation and dispensing cost, which can lead to additional $1–$2 per gge.
1) **Improve System Efficiency:** The requirement of high-temperature steam (700°C-1000°C [20]) in SMR restricts the system efficiency. Novel catalysts with fast kinetics for CL-based process effectively reduces operating costs as well as feedstock requirement.

2) **Reduce Capital Cost:** SMR requires expensive reformers as well as serial of complex post-processing reactors, including water-gas shift (WGS), pressure swing adsorption (PSA) reactors. Novel rotary CL reactor with compact, and economical design (see Section 1.3) effectively cuts the capital cost associated with reformer, system assembly, WGS, and PSA.

3) **CO₂ Capture and Sequestration:** CL process offers an intrinsic CO₂ separation with limited energy penalty, which enables CO₂ tax credit; the reuse of CO₂ to produce syngas (ready for gas-to-liquid process) enables by-product gain.

![Well-to-Wheel Emissions (SMR)](image)

Figure 1-5 Well-to-wheel CO₂ emission during the SMR process, data source: ref. [17]
Figure 1-6 Break-down of hydrogen production cost. Data source: ref. [17]; feedstock price adjusted to natural gas price as of Jun 1st 2016.

Among a variety of options (see Figure 1-4), thermo-chemical water splitting (TCWS) has recently attracted significant attention, because of its potential for high conversion efficiencies with limited emissions [21-24]. This approach is based on a two-step mechanism using a metal oxide (such as ceria or iron-based materials) to dissociate H$_2$O into H$_2$, and heat to reduce the metal oxide:

\[
\text{reduction step: } \quad \text{Me}_x\text{O}_y \rightarrow \text{Me}_x\text{O}_{y-1} + \frac{1}{2}\text{O}_2 \quad (1.6)
\]
\[
\text{oxidation step: } \quad \text{H}_2\text{O} + \text{Me}_x\text{O}_{y-1} \rightarrow \text{H}_2 + \text{Me}_x\text{O}_y \quad (1.7)
\]

The reduction step proceeds at higher temperature (above 1400 °C) to form oxygen deficiency and release O$_2$, while the oxidation step takes place at lower temperature (below 1000°C) to dissociate H$_2$O and generate H$_2$. During this process, the metal oxide undertakes the role of an oxygen carrier: it transports oxygen between the two steps, remaining intact at the end of the
cycle. Various studies have examined different material options for TCWS, and a brief summary is presented in Section 1.5. Although exhibiting remarkable potentials, major challenges are related to the need for expensive high quality heat and large temperature swing which can render the process less efficient.

An immediate extension of TCWS is reactive chemical-looping water splitting (RCLWS), in which the reduction step is replaced by a fuel reduction reaction:

\[
\text{Reduction step with fuel: } \text{Me}_x\text{O}_y + \text{CH}_4 \rightarrow \text{Me}_x\text{O}_{y-1} + \text{CO} + 2\text{H}_2 \quad (1.8)
\]

The utilization of a fuel ensures enhanced defect creation kinetics at lower temperature with significantly improved extent of OC reduction, and hence larger oxygen carrying capacity. The required high quality heat and large temperature swing could be replaced by an isothermal redox operation, hence leading to a much reduced cost, enhanced stability [25-28], and improved system efficiency [29, 30]. In contrast to TCWS, the net reaction, combining eqs. (1.7) and (1.8), is a fuel reforming reaction, where a fuel is selectively oxidized to form hydrogen and syngas. In the case of natural gas, the syngas stream has a $\text{H}_2:\text{CO}$ close to 2:1, ideal for the production of $\text{H}_2$ (after shift), methanol, or liquid fuel via Fischer-Tropsch process with $\text{CO}_2$ separation. With the abundance and low price of natural gas, RCLWS offers a simple and promising solution for co-producing hydrogen and syngas.

The advantages of CL $\text{H}_2\text{O}$ splitting as compared to SMR $\text{H}_2$ production technology are mainly the following: 1) the use of oxygen carrier enables direct gas-solid reactions, thus leading to a fast reduction and oxidation kinetics at lower temperature (see Chapter 11); 2) the overall methane reforming reaction is effectively split into a two-step process, with pure $\text{H}_2$ (after condensation)
produced from oxidation, and syngas with $H_2:CO$ ratio of 2:1 from reduction (see Chapter 10), eliminating the need for complicated post-possessing steps, such as water-gas shifting and gas-separation; 3) the use of OC in a rotary-based CL reactor (see Section 1.3) offers a compact and simple $H_2$ production solution, potentially reducing the transportation and dispensing cost. In addition, the use of a suitable OC in the fuel conversion (reduction) step improves the equilibrium constant, leading to possible enhancement in fuel conversion at low temperature (see Chapter 7, Section 7.10). The lower operating temperature, coupled with the reduction and oxidation cycling, reduces the coking potential and improves the system stability (see Chapter 10 and Chapter 11). These merits enable CL as one of the most promising carbon-neutral $H_2$ production technology.

1.2.2 CO$_2$ splitting

Inspired by the thermo-chemical $H_2O$ splitting technology, thermo-chemical CO$_2$ splitting has attracted significant interests very recently. The process is analogous: CO$_2$ is catalytically dissociated into CO with the use of oxygen-deficient metal oxide (also referred to as oxygen carrier, OC):

\[
\text{Oxidation: } \quad CO_2 + Me_xO_{y-1} \rightarrow CO + Me_xO_y
\]  

(1.9)

The surface defect acts as the oxygen sink, enabling CO$_2$ dissociation at low temperature (<1000°C, in contrast to the direct thermolysis reaction). Similarly, oxidation is followed by a reduction step, where the oxygen deficiency is regenerated from the healed surface by either heating the metal oxides with concentrated solar irradiation (eq. (1.6), \textit{thermo-chemical CO}_2 \textit{splitting}), or reducing the OC with fuel (eq. (1.8), \textit{reactive chemical-looping CO}_2 \textit{splitting}). The net reaction combining the reduction and oxidation (redox) steps becomes CO$_2$ thermolysis, i.e.,
CO₂ ⇌ CO + ½ O₂, or the dry reforming reaction, i.e., CO₂ + CH₄ ⇌ 2CO + 2H₂, respectively. The OC remains intact as it catalyzes and facilitates the dissociation of CO₂ through this two-step process. The transfer of oxygen between the redox steps exploits the oxygen non-stoichiometric capacity of the metal oxide by mediating the oxygen fugacity in the reactive environment, by either heating or flowing fuel, which drives the two-way ionic exchange between the gas and the solid. Promising results have been demonstrated on the efficient production of CO/syngas [31-34], which are the key precursors to the synthesis of liquid fuel and commodity chemicals.

As compared to dry reforming process, the major advantages of CL CO₂ splitting are, similarly as with H₂O splitting, that improved kinetics can be achieved at lower temperature with higher fuel conversion and lower coking risks, that desirable syn-gas composition can be achieved with the CO-rich stream separated, and that compactness and simplifity of the CL reactor potentially lowers the cost.

1.3 State-of-the-art Reactor Design and Applications

The CL technology inevitably involves periodic cycling of the solid OCs to the reduction or oxidation gaseous environment; therefore, an efficient alternating mechanism is the key to the successful operation. Research on CLC reactors has almost exclusively concentrated on an interconnected fluidized-bed reactor with OCs in a form of particles pneumatically circulated between a fuel reactor and an air reactor [35-42]. A cyclone in the top and a loop-seal in the bottom are used to complete the loop. Advantages of the fluidization-based design include perfect mixing, thermal robustness, and steady and continuous operations [43]. However, major
challenges are related to the particle circulation process [35, 44]: (1) energy is required for fluidization leading to large pressure drop, which compromises the system efficiency; (2) recovery of OC solid and separation of CO$_2$ rely critically on an efficient cyclone; (3) advanced filtering component is necessary for fine particles removal from the flue stream before delivering the hot gas to power generation unit (e.g., gas turbine in a combined cycle); (4) agglomeration and particle collision are potential threats to the longevity of the system. These issues become more pronounced at harsh conditions (elevated temperature and pressure) thus must be carefully addressed in a successful deployment of fluidized-bed CLC system. Although a great variety of industrial applications using fluidized bed reactors have been reported, complexities involved within the multiphase, multi-scale reactive flow requires tremendous efforts in the system design, optimization and up-scaling.

Alternative systems, such as a moving-bed reactor [2, 45, 46], a fixed packed-bed reactor [44, 47, 48] or a rotating packed-bed reactor [49, 50], have also been proposed and investigated. Fan and co-workers [2, 45, 46] suggested utilizing a moving bed for the fuel reactor. Compared to fluidized-bed reactors, the moving-bed system requires a smaller geometry, owing to the enhanced gas-solid mixing patterns. Similar technical difficulties still exist in the particle circulation process as in the fluidized-bed design. To avoid particle transport, Noorman and co-workers [44, 47, 48] devised a packed-bed reactor, in which the alternation of redox conditions is achieved by periodic switching of the gas feed streams. The design easily prevails in the compactness and the easiness of operation, although effective control of high volume gas flow at harsh conditions and the redox induced large temperature swing remain two major concerns that require further research and development. In an attempt to overcome the challenges with
switching, Dahl et al [49, 50] examined the feasibility of a rotating packed bed reactor: an annulus packed bed containing OC particles rotates when fuel and air streams are introduced radially outwards through the reactor. However, gas leakage that accompanies the rotational motion of the OC particles seems unavoidable [35].

Recently, a rotary reactor design with micro-channel structures was proposed in the Reacting Gas Dynamics Lab (RGDL) at Massachusetts Institute of Technology [25-28, 51]. As shown in Figure 1-7a, the reactor consists of a rotary wheel and two stationary chambers at the top and bottom of the wheel. The wheel rotates continuously through four sectors (Figure 1-7b): fuel, air, and two purging sectors. The rotary wheel consists of a large number of micro-channels (Figure 1-7c) with the OC coated onto their inner wall. As shown in Figure 1-7d, the channel wall has two solid layers with one being a highly porous OC layer and the other being a bulk dense ceramic layer with high thermal inertia and conductivity. The OC layer usually consists of an active metal oxide which reacts with the fuel and air alternatively, as well as an inert ceramic substrate which helps maintain the pore structures and chemical reactivities of the OC. As seen in Figure 1-8, pressurized feed gas (fuel, air or steam) flows through the reactor, reacts with the oxygen carrier (OC) while it is heated to high temperature. In the fuel sector, the fuel is diluted with CO₂ to effectively lower the operating temperature while in the air sector air is used to re-oxidize the OC. Two purging sectors are implemented between the fuel and the air sectors to sweep the residual gases. Flue streams from a large number of channels merge into two separate streams from the fuel zone and the air zone (see Figure 1-8b), respectively, and then drive turbines in the downstream, as described in ref. [25]. The advantages of the rotary CLC reactor compared to the existing options are that (1) the complexity in alternation is reduced to a
minimum, (2) the operation is continuous with regulated flow and minimum energy loss, and (3) the design is compact and feasible for both large-, and small-scale applications. These merits enable it as one of the most promising approaches to commercially and economically realize the CO₂ separation from combustion and H₂/syngas production from H₂O/CO₂ splitting. Potential challenges may exist on handling the axial temperature gradient and gas sealing near the bearings and outer pressure case during rotation. Nevertheless, these challenges are expected to be less significant, given the slow rotational motion (1~2 rpm). Design experiences and engineering details from gas turbines can be naturally inherited.

Figure 1-7. Schematic diagram of rotary CLC system design [25]: (a) front view, (b) bottom view, (c) individual channel structure, and (d) the oxygen carrier coated on the surface.
1.4 Problem Statement and Thesis Motivation

The application of any aforementioned reactors critically depends on the OC loaded in the CL system. Thus far, the selection of the OC has been acknowledged as one of the most important parts of chemical-looping technology. The thermal, physical, chemical characteristics of OCs directly determine the size and configuration of the reactor, bed inventory, power output as well as pre-, post-CL processing procedures, the overall cyclic efficiency and the economics. Previous computational fluid dynamics (CFD) simulation has demonstrated that the redox kinetics of the oxygen carrier materials is the key to the overall reactor performance [27, 28]. As a demonstration, Figure 1-9 shows the sensitivity of the fuel conversion on the design parameters for the case of the rotary reactor [27]. Here three different materials are tested, and clearly, for all cases the performance of the reactor (in this case, fuel conversion efficiency) is mostly affected by the redox characteristics of the OCs. As a result, a critical knowledge of the OC characteristics, including redox fundamentals, the cyclic stabilities, and interactions with support or dopant, is needed for the purpose of reactor design and optimization.

Figure 1-8 Schematic illustrations of the reactor with inlet and exit flue streams. Panel (a) is the isometric projection of the reactor, and panels (b) and (c) are the gas species concentration at the exit and the inlet of the reactor for two cycles.
The redox study on metal-based materials is nothing new. Historically, extensive experiences have been gained, both experimentally and computationally, on the redox characteristics of metal oxide/metal pairs\(^2\), such as NiO/Ni, and CeO\(_2/\)Ce\(_2\)O\(_3\), with focus on applications such as alloys and metallurgy, three-way catalyst, etc. A great knowledge has been well documented on the physical, chemical, and electrochemical properties of these materials with aim of achieving the specific properties for these applications, i.e., corrosion resistant, oxygen storage and CO/NO\(_x\) removal. Driven by the needs from new applications, including solid oxide fuel cells, electrolyzers, and chemical-looping, etc., the redox properties of these “old” materials have drawn more and more “new” attentions. Despite the experience and knowledge previously gained on these materials, many important questions rise, resulting from the discrepancy in operating conditions, characteristic scale of reaction, and the requirement on the samples, as listed in Table 1-1. More importantly, with the rapid advancement in the microtechnology and nanotechnology, more and more emphasis has been zoomed-in on a surface-oriented, microscopic picture of the thermal, electrochemical, and redox conversion process, aiming at specially designing and engineering the properties of the surface towards specific needs.

Efforts have been initiated on exploring the material options suitable for chemical-looping combustion and H\(_2\)O/CO\(_2\) splitting technology. Studies involved a variety of possible carrier materials including nickel, ceria, iron, copper, etc. Advanced in-situ techniques, such as X-ray adsorption spectroscopy (XAS) [52], X-ray diffraction (XRD) [53], environmental transmission electron microscopy (TEM) [54, 55], full-field transmission X-ray microscopy (TXM) [56], and X-ray photoemission spectroscopy (XPS) [57, 58], have been applied to probe the structural dynamics, examine the different stages of the redox conversion, and explore ion-incorporation

\(^2\) Note, metal oxide refers to OC at oxidized state, while metal corresponds to the reduced state.
and the adsorbate-defect interactions under a redox environment. Density functional studies compared the preferable sites and surface orientations for gas-surface interactions, and examined surface defect formation and the energy landscape of the redox process [59-66]. Specifically engineered nanostructures were also proposed and evaluated, and significantly improved performances were discovered [18, 19, 67, 68]. Empirical equations based on simplified kinetic models have been obtained, and a preliminary understanding of the redox processes has been acquired [69-73]. A brief overview of these studies is summarized in the next section. However, for the purpose of CL reactor design and its commercial application, the efforts are still far from sufficient, and a much closer examination, both experimental and theoretical, on the surface-oriented redox processes is technologically important for the design and optimization of the CL processes.

| Table 1-1 Comparison between the conventional metal redox study and CL study |
|-----------------------------|---------------------------------|
| Area of applications       | Conventional study | Novel applications |
| Metallurgy,                 | metallurgy,           | solid oxide fuel cells, |
| three-way catalyst         | three-way catalyst     | electrolyzers, chemical-looping |
| Time scale of reaction      | hours or even days     | seconds |
| Sample used                 | fresh                | after cycling at new equilibrium state |
| Desirable sample            | corrosion resistant,  | fast cycling, high capacity, |
|                           | stability            | electric properties |
| Focus of study              | bulk properties,      | surface chemistry, |
|                           | phase diagram,        | ionic and electronic transport, |
|                           | thermodynamics        | structural dynamics, size effect |
activation energy $E_{CH4}$
pre-exponential factor $k_{CH4,0}$
pressure coefficient $a_{CH4,0}$
reaction order $n_{CH4,0}$
activation energy $E_{O2}$
pre-exponential factor $k_{O2,0}$
pressure coefficient $a_{O2,0}$
reaction order $n_{O2,0}$
channel width $d$
solid layer thickness $\delta_{bulk}$
solid layer thickness $\delta_{OC}$
fuel fraction at inlet vol\%
cycle period $r$
operating pressure $P$
inlet temperature $T_{in}$
air flow velocity $u_{air}$
fuel flow velocity $u_{fuel}$
fuel purge velocity $u_{fuel,p}$
air purge velocity $u_{air,p}$

Figure 1-9 Sensitivity of fuel conversion on the reaction kinetics, design and operational conditions for three commonly used OCs, i.e., Fe, Cu, Ni

The motivations for this thesis are thus summarized in the sequence of relative importance:

- The fundamental surface redox pathway is not well understood. The details that are involved in the interactions of mobile ions, and electrons between the bulk and the surface, along with the gaseous reactants, adsorbates and electrostatic fields, as well as the morphological and microstructure surface evolutions, are highly complex. An in-depth knowledge of these factors not only sheds light on the design and optimization strategies for CL technology, but also provides critical inputs for other important fields, such as fuel cell, electro-catalyst, etc.
• Kinetic data reported in the literature are based on highly simplified models, which are less capable of representing the redox behavior in a sufficiently accurate and thermodynamically consistent manner. The fitted mechanism lumps the effects of surface chemistry, transport, and the surface morphological and structure evolutions, and the obtained kinetic parameters are highly case specific, and offer limited insights towards material optimization. Orders of magnitude discrepancy in the derived kinetic parameters are reported among various studies [35] (see Table 1-2).

• Few studies have reported time-resolved reactivity under conditions relevant for CL application (temperature, gaseous composition). In even fewer studies, detailed data on the conversion were published as a function of varying temperature and concentrations. With the lack of kinetics data, many important questions remain by and large unresolved, such as the impact of the redox-cycle treatment on the equilibrium state of the material, the OC structure and its effect on the redox kinetics, the synergy effect between the OC and the binder, etc.

1.5 Literature Review on Kinetics Study of Oxygen Carrier

This section conducts a brief literature review on the kinetics study of OCs to lay out the background for the thesis. The discussion here compares the approaches, both experimental and computational, that are attempted to examine the redox kinetics for CLC and CL H₂O/CO₂ splitting. Summary of the results from the kinetics study is also included for comparison. The review work here is by no means a comprehensive coverage of all available studies on CL in the literature. For a more detailed literature view, refs. [2, 8, 11, 35, 59, 74] are excellent resources to refer to.
1.5.1 Redox Measurement

Many experiments have been carried out based on mass-gain method using thermo-gravimetric analyzer (TGA) to measure the kinetics of OC redox reactions. In TGA, OC samples are loaded onto a spring balance. As reaction proceeds, weight changes of the OC samples are continuously monitored. The kinetics can be then interpreted based on the mass-gain profile as a function of time. Limitations of TGA are mainly related to the less flexibility of the system, and the lack of sensitivity on fast redox dynamics (especially at the beginning of the reaction).

Gas-consumption based experiments have also been used for CL kinetics study. In these experiments, the effluent gas is admitted into an on-line residual gas analyzing system, commonly consisting of a gas chromatography mass-spectrometer (GCMS). The measured difference between the feed and the exhaust streams are then interpreted to obtain the OC kinetics. A fixed-bed reactor (FxB) is usually used in this type of experiment, which is capable of sampling a larger amount of OC at more flexible redox conditions. Gas flow rate is usually restricted below a certain level in order to acquire appreciable difference between the feed and exhaust. Concerns may also be related to the non-uniformity of gas concentration within the reaction zone. Gas-consumption based experiments can be coupled with TGA to enable a more responsive and accurate monitoring of the redox system. Other reactors, such as fluidized-bed reactors (FzB), or temperature-programmed reduction (TPR), or oxidation (TPO) with linear temperature ramping, are also useful in redox kinetics study, although additional complexity may exist on data interpretation. A comparison of experiments in the literature is briefly summarized in Table 1-2.
1.5.2 Kinetics Modeling

Different empirical models for gas-solid reactions have been used to evaluate the redox process. As will be discussed in details in Chapter 3, the redox reaction usually consists of gas-phase diffusion, surface chemistry, solid-state diffusion, and phase change and structural migration [26]. The empirical models usually emphasize one step using simple expressions with other contributions neglected. Some commonly applied models may include the unreacted shrinking-core model (SCM), and nucleation and nuclei growth models (NGM). A brief comparison is summarized as follows and the obtained kinetic parameters are listed in Table 1-2.

- SCM considers a diffusion-controlled mechanism such that reaction occurs only on the interface that delimits product layer and unreacted core, and core shrinks as reaction proceeds.
- Nucleation and nuclei growth model (NGM) assumes that the structural and morphological evolutions dominate the reaction. The conversion starts with creation of active sites, followed by their growth, development, and saturation.

Other models are also available, following more or less a similar approach as in SCM or NGM. For instance, Avrami-Erofeev Model (AEM) simplifies the NGM by assuming that the conversion is dominated by surface sites creation. Power law model (PLM) or modified volumetric model (MVM) which treats the solid reactant as another gas in the Arrhenius expression, is another simplified version of the NGM. Changing grain size model (CGSM) spatially resolves the gaseous species diffusion-reaction equations through the OC sample while treating each active site with a SCM. A simplified version of CGSM is named diffusion-reaction model (DRM), in which the diffusion-reaction process within each metal oxide grain is modeled using an effectiveness factor.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Equipment</th>
<th>d (mm)</th>
<th>Model</th>
<th>( E_a ) (kJ/mol)</th>
<th>( n )</th>
<th>( H_2 )</th>
<th>( CO )</th>
<th>( CH_4 )</th>
<th>( O_2 )</th>
<th>Ref</th>
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<td>NiO</td>
<td>TGA</td>
<td>1-3</td>
<td>SCM</td>
<td>82(1.0)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17(1.0)</td>
<td>131(-)</td>
<td>[75]</td>
</tr>
<tr>
<td>Bentonite</td>
<td>TGA</td>
<td>0.08</td>
<td>SCM</td>
<td>-</td>
<td>37(-)</td>
<td>-</td>
<td>-</td>
<td>131(1.0)</td>
<td></td>
<td>[76]</td>
</tr>
<tr>
<td>Bentonite</td>
<td>TGA</td>
<td>0.11-0.15</td>
<td>VVM, SCM</td>
<td>-</td>
<td>57(-)</td>
<td>2.4(-)</td>
<td></td>
<td></td>
<td></td>
<td>[77]</td>
</tr>
<tr>
<td>NiAlO4</td>
<td>TGA</td>
<td>0.090.21</td>
<td>CGSM</td>
<td>-(1.0)</td>
<td>-</td>
<td>-(0.75)</td>
<td>-(1.0)</td>
<td></td>
<td></td>
<td>[78]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.09-0.25</td>
<td>CGSM</td>
<td>26(0.5)</td>
<td>25(0.8)</td>
<td>78(0.8)</td>
<td>7(1.0)</td>
<td></td>
<td></td>
<td>[79]</td>
</tr>
<tr>
<td>MgAl2O4</td>
<td>TGA</td>
<td>0.125-0.18</td>
<td>CGSM</td>
<td>-</td>
<td>-</td>
<td>114(0.4)</td>
<td>40(1.0)</td>
<td></td>
<td></td>
<td>[80]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TPR, TPO</td>
<td>0.07</td>
<td>RNM</td>
<td>53(-)</td>
<td>-</td>
<td>-</td>
<td>45(-)</td>
<td></td>
<td></td>
<td>[81]</td>
</tr>
<tr>
<td>Co-Al2O3</td>
<td>TPR, TPO</td>
<td>0.07</td>
<td>RNM</td>
<td>45(-)</td>
<td>49(-)</td>
<td>44(-)</td>
<td></td>
<td></td>
<td></td>
<td>[81]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>FzB</td>
<td>0.01-0.11</td>
<td>RNM</td>
<td>-</td>
<td>-</td>
<td>44(1)</td>
<td>-</td>
<td></td>
<td></td>
<td>[82]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TPR</td>
<td>0.13-0.43</td>
<td>DRM</td>
<td>96(-)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>[83]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.09-0.11</td>
<td>CGSM</td>
<td>28(0.6)</td>
<td>28(0.8)</td>
<td>55(0.4)</td>
<td></td>
<td></td>
<td></td>
<td>[84]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>FzB</td>
<td>0.14</td>
<td>MVM</td>
<td>26(1.0)</td>
<td>27(1.0)</td>
<td>77(1.0)</td>
<td>-</td>
<td></td>
<td></td>
<td>[85]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.1-0.3</td>
<td>PLM</td>
<td>5(0.4)</td>
<td>5(0.6)</td>
<td>5(0.2)</td>
<td>22(0.7)</td>
<td></td>
<td></td>
<td>[86]</td>
</tr>
<tr>
<td>NiO</td>
<td>TGA</td>
<td>0.1</td>
<td>AEM</td>
<td>-</td>
<td>-</td>
<td>84(-)</td>
<td></td>
<td></td>
<td></td>
<td>[87]</td>
</tr>
<tr>
<td>SiO2</td>
<td>TGA</td>
<td>0.8-1.2</td>
<td>CGSM</td>
<td>-</td>
<td>-</td>
<td>41(1.0)</td>
<td>-</td>
<td></td>
<td></td>
<td>[88]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.1-0.3</td>
<td>CGSM</td>
<td>33(0.6)</td>
<td>14(0.8)</td>
<td>60(0.4)</td>
<td>15(1.0)</td>
<td></td>
<td></td>
<td>[89]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>FzB</td>
<td>0.34-0.5</td>
<td>DRM</td>
<td>58(1.0),</td>
<td>44(1.0)</td>
<td>60(1.0)</td>
<td></td>
<td></td>
<td></td>
<td>[90]</td>
</tr>
<tr>
<td>NiO</td>
<td>TGA</td>
<td>0.12</td>
<td>NGM</td>
<td>20(0.7)</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td>[91]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.09-0.11</td>
<td>CGSM</td>
<td>30(0.55)</td>
<td>16(0.8)</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td>[84]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.1-0.5</td>
<td>CGSM</td>
<td>20(0.5)</td>
<td>11(0.8)</td>
<td>106(0.5)</td>
<td>-</td>
<td></td>
<td></td>
<td>[92]</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>Bentonite</td>
<td>0.11-0.15</td>
<td>VVM, SCM</td>
<td>-</td>
<td>29(-)</td>
<td>6.0(-)</td>
<td></td>
<td></td>
<td></td>
<td>[77]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.09-0.25</td>
<td>CGSM</td>
<td>24(0.5)</td>
<td>20(1.0)</td>
<td>49(1.3)</td>
<td>14(1.0)</td>
<td></td>
<td></td>
<td>[79]</td>
</tr>
<tr>
<td>Al2O3</td>
<td>TGA</td>
<td>0.09-0.11</td>
<td>CGSM</td>
<td>22(0.85)</td>
<td>19(1.0)</td>
<td>25(0.2)</td>
<td>-</td>
<td></td>
<td></td>
<td>[84]</td>
</tr>
</tbody>
</table>

### 1.5.3 Oxygen carrier for CLC

Nickel oxides have been suggested as one of the most promising OCs for CLC because of its very fast reactivity, high oxygen capacity, high conversion yield to achieve complete combustion product (CO\(_2\) and H\(_2\)O), and great chemical stability. Metallic nickel catalyzes the fuel decomposition, thus the reduction step usually undergoes a fast autocatalytic reaction pathway. Major criticisms are its high cost and toxicity. Pure dense nickel usually exhibits limited capacity, because of the inadequate contact between solid and gas as well as the slow solid-state diffusion
step. YSZ was initially suggested as structural substrate [93, 94], which maintains the structure, and enhances the dispersion of nickel. Later, Ishida and Jin [95, 96] suggested Al₂O₃ as a good binder with a much lower cost. But the reactivity decreases with cycles because of the formation of the less reactive spinels NiAl₂O₄. Later, NiAl₂O₄ was suggested [97, 98] as a binder which enhances the regenerability. MgAl₂O₄ was also reported with improved nickel dispersion and a better reactivity [99]. Adanez et al [100] compared NiO supported by sepiolite, TiO₂, Al₂O₃, SiO₂, ZrO₂, and concluded that sepiolite, TiO₂, Al₂O₃ as binder generally provides a faster reactivity as compared to others.

Other potential options for CLC have also been proposed and evaluated in the literature:

- Cu-based oxygen carriers exhibit high oxygen carrying capacity. Copper is abundant, non-toxic and much cheaper than nickel in nature, although the reactivity is slower. Major issues include low melting point (1085 °C). Chuang et al. [101] reported the influence of preparation methods using CuO/Al₂O₃ as oxygen carriers, and concluded that co-precipitated carrier generally merits over other candidates and shows a high carrying capacity after cycles. SiO₂ and TiO₂ were considered by several researchers as promising support binders for Cu [100, 102-105].

- Iron is a cheap, abundant, non-toxic metal oxide. The multiple oxidation states make iron suitable for both CLC and CLWS. The reactivity with CH₄ is lower compared to nickel or copper, in the absence of metallic iron. Deactivation effect is severe, which leads to decreasing yield over cycles. Fe₂O₃ supported on different binders has been studied [100, 106-110]. Fe₂O₃ with MgAl₂O₄, ZrO₂ and Al₂O₃ shows good reactivity.
1.5.4 Oxygen carriers for H₂O/CO₂ splitting

Several studies have examined various metal oxides candidates for H₂O/CO₂ splitting, including ceria, copper, ferrites, tungsten, perovskites, etc. The reported H₂/CO production rates and production yields are summarized in Table 1-3, Table 1-4, and Table 1-5. It is generally observed that the use of ceria as an OC leads to higher splitting kinetics production because of its fast surface kinetics, high ionic diffusivity, large oxygen carrying capacity, and robust structural stability. The ability of ceria to accommodate high surface active site concentrations facilitates a relatively quick surface ion-incorporation process [111, 112]. The large non-stoichiometry capacity allows it to effectively adsorb, and release oxygen as it responds to the operating conditions. This property has been exploited in a large number of applications [113, 114], including three-way catalyst, solid oxide fuel cells and electrolyzers. For the same reason, CeO₂ has been suggested as one of the most promising OC candidates for CL H₂O/CO₂ splitting, and a base line for the development of alternative materials.

In an attempt to improve low temperature redox kinetics, zirconia is often suggested as a dopant to promote reducibility [115]. Zr⁴⁺ cation remains isovalent and redox inactive [116], and therefore its addition does not involve the creation of any charge compensating defects [117]. Instead, the undersized Zr⁴⁺ cation induces structural distortion [118], leading to lower defect formation energy [119] and enhanced oxygen mobility [120]. The relaxation in the bond energy facilitates the reduction of Ce⁴⁺ to the larger Ce³⁺ ion [121]. The long-term structural stability is also improved with the addition of Zr [122, 123]. These merits have led to wide applications of the ceria-zirconia oxide system (CZO) in other areas [115, 118, 124, 125], including three-way catalysis, water-gas shift, solid oxide fuel cells, methane reforming, etc. Similar effects were also
observed with the addition of isovalent dopant Hf$^{4+}$.

**Table 1-3** Total and peak H$_2$ production rates for two-step thermo-chemical water splitting

<table>
<thead>
<tr>
<th>Temp °C (Red/Ox)</th>
<th>Tot. H$_2$ prod. (μmole/g)</th>
<th>Peak H$_2$ rate (μmole/g/s)</th>
<th>Feed H$_2$O (%)</th>
<th>Oxygen Carrier</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500/800</td>
<td>278</td>
<td>6.8</td>
<td>44-52</td>
<td>CeO$_2$</td>
<td>[31]</td>
</tr>
<tr>
<td>1500/1500</td>
<td>126</td>
<td>1.0</td>
<td>15</td>
<td>CeO$_2$ (with Rh)</td>
<td>[126]</td>
</tr>
<tr>
<td>1350/1000</td>
<td>32</td>
<td>0.15</td>
<td>40</td>
<td>CeO$_2$</td>
<td>[127]</td>
</tr>
<tr>
<td>1500/1150</td>
<td>414</td>
<td>4.2</td>
<td>50, 84</td>
<td>CeO$_2$</td>
<td>[128]</td>
</tr>
<tr>
<td>1350/1000</td>
<td>28</td>
<td>-</td>
<td>81</td>
<td>CeO$_2$</td>
<td>[129]</td>
</tr>
<tr>
<td>1500/750</td>
<td>161</td>
<td>-</td>
<td>83</td>
<td>CeO$_2$ (10% Pr)</td>
<td>[130]</td>
</tr>
<tr>
<td>1400/1050</td>
<td>338</td>
<td>-</td>
<td>5.8</td>
<td>CeO$_2$ (25%Zr 1%Gd)</td>
<td>[131]</td>
</tr>
<tr>
<td>1300/800</td>
<td>109</td>
<td>-</td>
<td>30</td>
<td>Ce$<em>{0.15}$Zr$</em>{0.85}$O$_2$</td>
<td>[132]</td>
</tr>
<tr>
<td>1400/1050</td>
<td>467.7</td>
<td>-</td>
<td>38.3</td>
<td>CeO$_2$ (50% Zr)</td>
<td>[133, 134]</td>
</tr>
<tr>
<td>1500/500</td>
<td>210</td>
<td>-</td>
<td>84</td>
<td>Ce$<em>{0.8}$Ho$</em>{0.2}$O$_2$</td>
<td>[135]</td>
</tr>
<tr>
<td>1500/1000</td>
<td>153</td>
<td>-</td>
<td>83</td>
<td>CeO$_2$ (10% Mn)</td>
<td>[136]</td>
</tr>
<tr>
<td>1290/1000</td>
<td>62</td>
<td>16.4</td>
<td>21</td>
<td>CeO$_2$ (20% Zn)</td>
<td>[137]</td>
</tr>
<tr>
<td>1200/900</td>
<td>57</td>
<td>-</td>
<td>81</td>
<td>Ni$<em>{0.5}$Mn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>[129]</td>
</tr>
<tr>
<td>1190/900</td>
<td>2120</td>
<td>9.4</td>
<td>56</td>
<td>Zn:Fe-O</td>
<td>[138]</td>
</tr>
<tr>
<td>1700/575</td>
<td>4270</td>
<td>9.1</td>
<td>56</td>
<td>FeO</td>
<td>[139]</td>
</tr>
<tr>
<td>1400/1000</td>
<td>195</td>
<td>-</td>
<td>5.8</td>
<td>La$<em>{0.5}$Sr$</em>{0.5}$MnO$_3$</td>
<td>[140]</td>
</tr>
<tr>
<td>1350/1000</td>
<td>307</td>
<td>1.3</td>
<td>40</td>
<td>LaAlO$_3$ (with Sr, Mn)</td>
<td>[127]</td>
</tr>
<tr>
<td>1400/1000</td>
<td>407</td>
<td>5.6</td>
<td>-</td>
<td>La$<em>{0.5}$Ca$</em>{0.5}$MnO$_3$</td>
<td>[141]</td>
</tr>
</tbody>
</table>

*Note some studies tested various material compositions for repeated cycles. The highest values are chosen and listed here for comparison. The conversion of H$_2$ production unit from mL/g to μmole/g utilizes ideal-gas law at standard temperature and pressure (25°C 1 atm).

**Table 1-4** Reported total and peak H$_2$ production rates for CLWS

<table>
<thead>
<tr>
<th>Temp °C (Red/Ox)</th>
<th>Tot. H$_2$ prod. (μmole/g)</th>
<th>Peak H$_2$ rate (μmole/g/s)</th>
<th>Feed H$_2$O (%)</th>
<th>Oxygen Carrier</th>
<th>Reducer</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>800/800</td>
<td>3460</td>
<td>4.8</td>
<td>77</td>
<td>Fe$_2$O$_3$</td>
<td>CH$_4$</td>
<td>[142]</td>
</tr>
<tr>
<td>900/900</td>
<td>4140</td>
<td>8.1</td>
<td>30</td>
<td>Fe$_2$O$_3$</td>
<td>H$_2$</td>
<td>[143]</td>
</tr>
<tr>
<td>900/900</td>
<td>8900</td>
<td>34</td>
<td>31</td>
<td>Fe$_2$O$_3$ (with 5% CeO$_2$)</td>
<td>H$_2$+CO</td>
<td>[144]</td>
</tr>
<tr>
<td>800/800</td>
<td>47</td>
<td>0.36</td>
<td>5.5</td>
<td>Cu (with Co Pr)</td>
<td>H$_2$</td>
<td>[145]</td>
</tr>
<tr>
<td>650/350</td>
<td>150</td>
<td>-</td>
<td>20</td>
<td>CuO</td>
<td>H$_2$+CO</td>
<td>[104]</td>
</tr>
<tr>
<td>900/800</td>
<td>11300</td>
<td>-</td>
<td>20</td>
<td>CuFe$_2$O$_4$</td>
<td>CH$_4$</td>
<td>[146]</td>
</tr>
<tr>
<td>900/700</td>
<td>12000</td>
<td>-</td>
<td>31</td>
<td>Cu$<em>{0.7}$Fe$</em>{2.3}$O$_4$/Ce–ZrO$_2$</td>
<td>CH$_4$</td>
<td>[147]</td>
</tr>
<tr>
<td>900/800</td>
<td>2780</td>
<td>-</td>
<td>31</td>
<td>CuFe$_2$O$_4$/ZrO$_2$</td>
<td>CH$_4$</td>
<td>[148]</td>
</tr>
<tr>
<td>900/800</td>
<td>2130</td>
<td>-</td>
<td>31</td>
<td>CuFe$_2$O$_4$/CeO$_2$</td>
<td>CH$_4$</td>
<td>[148]</td>
</tr>
<tr>
<td>900/800</td>
<td>3000</td>
<td>-</td>
<td>47</td>
<td>Ni$<em>{0.36}$Fe$</em>{2.64}$O$_4$ (with ZrO$_2$)</td>
<td>CH$_4$</td>
<td>[149]</td>
</tr>
<tr>
<td>750/750</td>
<td>3500</td>
<td>3.8</td>
<td>20</td>
<td>WO$_3$ (with CeO$_7$, ZrO$_2$)</td>
<td>CH$_4$</td>
<td>[150]</td>
</tr>
<tr>
<td>800/500</td>
<td>840</td>
<td>0.29</td>
<td>2.4</td>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$ (with Pt)</td>
<td>CH$_4$</td>
<td>[151]</td>
</tr>
<tr>
<td>850/700</td>
<td>500</td>
<td>1.1</td>
<td>83</td>
<td>CeO$_2$</td>
<td>CH$_4$</td>
<td>[152]</td>
</tr>
<tr>
<td>850/700</td>
<td>1580</td>
<td>1.3</td>
<td>83</td>
<td>Ce$<em>{0.7}$Zr$</em>{0.3}$O$_2$</td>
<td>CH$_4$</td>
<td>[153]</td>
</tr>
<tr>
<td>800/800</td>
<td>326</td>
<td>0.65</td>
<td>27</td>
<td>10wt% CeO$_2$/ZrO$_2$</td>
<td>CH$_4$</td>
<td>[154]</td>
</tr>
<tr>
<td>800/700</td>
<td>1020</td>
<td>1.0</td>
<td>83</td>
<td>CeO$_2$ (30%Fe$_2$O$_3$)</td>
<td>CH$_4$</td>
<td>[155]</td>
</tr>
</tbody>
</table>
### Table 1-5 Reported total and peak CO production rates using ceria or ceria-zirconia as OC

<table>
<thead>
<tr>
<th>Temp °C (Red/Ox)</th>
<th>Oxygen Carrier (OC)</th>
<th>Tot. CO (µmole/g)</th>
<th>Peak rate 8 (µmole/g/s)</th>
<th>Feed CO₂ (%)</th>
<th>Reducer</th>
<th>OC surface area (m²/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500/800</td>
<td>CeO₂</td>
<td>280</td>
<td>6.8</td>
<td>50%</td>
<td>thermal</td>
<td>-</td>
<td>[31]a</td>
</tr>
<tr>
<td>1400/1000</td>
<td>CeO₂, Ce₀.₇₅Zr₀.₂₅O₂</td>
<td>105, 241</td>
<td>-</td>
<td>50%</td>
<td>thermal</td>
<td>-</td>
<td>[156]</td>
</tr>
<tr>
<td>1400/1000</td>
<td>CeO₂, Ce₀.₇₅Zr₀.₂₅O₂, Ce₀.₉Zr₀.₁O₂</td>
<td>100, 242, 130</td>
<td>-</td>
<td>50%</td>
<td>thermal</td>
<td>-</td>
<td>[157]b</td>
</tr>
<tr>
<td>1600/1000</td>
<td>CeO₂</td>
<td>219</td>
<td>1.9</td>
<td>60%</td>
<td>thermal</td>
<td>6.0</td>
<td>[158]c</td>
</tr>
<tr>
<td>1527/827</td>
<td>CeO₂</td>
<td>89</td>
<td>0.4</td>
<td>8.3%</td>
<td>thermal</td>
<td>-</td>
<td>[32]d</td>
</tr>
<tr>
<td>1200/850</td>
<td>CeO₂</td>
<td>37</td>
<td>4.0</td>
<td>25%</td>
<td>thermal</td>
<td>3.95</td>
<td>[159]</td>
</tr>
<tr>
<td>1500/800</td>
<td>CeO₂</td>
<td>180</td>
<td>1.6</td>
<td>38.5%</td>
<td>thermal</td>
<td>0.095</td>
<td>[160]</td>
</tr>
<tr>
<td>1400/800</td>
<td>CeO₂, Ce₀.₇₅Zr₀.₂₅O₂</td>
<td>180, 430</td>
<td>45, 1.5</td>
<td>100%</td>
<td>thermal</td>
<td>1.7, 2.1</td>
<td>[161]</td>
</tr>
<tr>
<td>1500/1500</td>
<td>CeO₂</td>
<td>90</td>
<td>2.5</td>
<td>100%</td>
<td>thermal</td>
<td>-</td>
<td>[162]e</td>
</tr>
<tr>
<td>1400/1000</td>
<td>CeO₂, Ce₀.₅Zr₀.₅O₂</td>
<td>55, 272</td>
<td>-</td>
<td>100%</td>
<td>thermal</td>
<td>-</td>
<td>[163]</td>
</tr>
<tr>
<td>1100/500</td>
<td>CeO₂</td>
<td>600</td>
<td>8</td>
<td>0.5-40%</td>
<td>H₂</td>
<td>-</td>
<td>[69]f</td>
</tr>
<tr>
<td>827/827</td>
<td>CeO₂</td>
<td>934</td>
<td>24.8</td>
<td>4%</td>
<td>H₂</td>
<td>10.2</td>
<td>[164]</td>
</tr>
</tbody>
</table>

*a data from Fig. 3; b CO production rates at the third cycle; c data from Fig. 6 based on ceria felt; d data from Fig. 2, H₂O (47%) is also fed; e data from Fig. 9; f peak rate is from the highest rate in Fig. 4, total production corresponds to δ = 0.1; g conversion of CO production unit from mL/g to µmole/g utilizes ideal-gas law at standard temperature and pressure (25°C 1atm)

Oxygen deficiency in ceria can alternatively be induced with the addition of lower valent substituents, such as Gd³⁺, La³⁺, or dopants whose valence varies with temperature and pO₂, such as Pr⁴⁺/Pr³⁺, Tb⁴⁺/Tb³⁺. The substituents carry effective negative charge, i.e., Gd⁺Ce, leading to the generation of high concentration defects on the surface [117, 165, 166], which thus facilitates the splitting reactions via a more favored adsorption/activation process. The structural relaxation or effects modulating the chemical bonding between oxygen and cerium ions are usually considered as local, whereas substitution with dopants that altered the electrical band-gap of the materials are sometimes referred to as global effect [59, 87].

### 1.6 Thesis Objective and Outline

The ultimate goal of this project is to develop a low cost, CO₂ reduction, and hydrogen and syngas co-production technology based on chemical-looping technology and state-of-art composite materials. Using novel and promising metal oxides as an “oxygen carrier (OC)”, CL
offers an efficient energy solution to CO₂ capture, and carbon-neutral H₂ production. The merits in cutting capital and production costs, improving conversion efficiency, and reducing CO₂ emissions will bring tremendous benefits to the energy industry.

1.6.1 Research Objective

This thesis aims identifying the optimal materials for CL oxy-fuel combustion and H₂O/CO₂ splitting processes, respectively. To achieve the objective, the fundamentals of the redox processes for CLC and CL H₂O/CO₂ splitting must be carefully examined and the complex microscopic interactions of mobile ions, electrons between the bulk and the surface, along with the adsorbates and electrostatic fields must be thoroughly explored. Experimental studies are carried out to evaluate the kinetic processes, and sub-models are developed to evaluate important kinetic steps. The results of kinetics measurement shall help answer the following questions:

- What is the reaction mechanism under the operating conditions relevant for CL?
- How do redox cycles impact the structures of the carrier materials?
- What is the optimal size/thickness for the carrier materials?
- How does structural substrate improve the performance of the carrier materials?
- What is the desirable dopant and how does it benefits the redox processes?

Specifically, the study can be split into two sub-tasks, and the objective for each task is as follows:

**Redox Study on Carrier Materials:**

As introduced in section 1.5, nickel-, and ceria-based are widely suggested as promising candidates for CLC and CL H₂O/CO₂ splitting, respectively. Thus, this study focuses on these
two OCs. Pure samples in the form of foil/powders are tested, and the size/thickness of the samples will be varied. The detailed microscopic ion-incorporation as well as the morphological evolution during the reaction processes is evaluated. Based on the results, the intrinsic reaction mechanisms are modeled.

Redox Study on the OC with dopant or support

Inert substrate provides structural support to allow for better cyclic stability. Characteristics of the support, i.e., surface area, ionic diffusional promotion, electrochemical properties, elastic strains, structural stability, etc, affect the redox kinetics of the OC. The aim of this study is to explore the dopant and support options for redox improvement. Specifically, the effect of YSZ as support for nickel-based OC for CLC, and Zr-, Pr- as support for ceria-based OC for CL H2O/CO2 splitting are evaluated. In addition, preliminary evaluations on alternative materials, including bi-metallic or perovskite-based OCs will be included.

1.6.2 Thesis Outline

The thesis is broken into 12 chapters. Chapter 2 details the experimental setup for the kinetics measurement. Chapter 3 presents the theory, and the overall modeling framework covering four major aspects: thermodynamics, surface chemistry, transport, and phase change and structural evolutions. Chapter 4 details the kinetics study with nickel foils as OC for CLC, with the focus on understanding the determining role of surface evolution on the redox kinetics. Chapter 5 examines NiO/YSZ as OC, focusing on the understanding the effect of YSZ support on the improved redox kinetics. Chapter 6 and Chapter 7 examine the surface chemistry and the defect equilibria for undoped ceria, and ceria zirconia, respectively, for CL H2O splitting, while Chapter
8 extends the measurements to CO₂ splitting. Chapter 9 examines the prasedynium-doped ceria and evaluates the effect of surface vacancy on redox kinetics for CL H₂O/CO₂ splitting. Chapter 6 - Chapter 9 use H₂ as a surrogate fuel to simplify the modeling, while Chapter 10 applies the ceria-based OCs to CH₄-fueled kinetics study. Alternative promising materials, specifically perovskite-based OCs, are examined and compared in Chapter 11. Chapter 12 summarizes the findings and conclusions from this thesis, and also provides recommendations for the future work in designing and optimizing the OCs as well as applying them in the scope of reactor design and performance optimization.

1.7 Bibliography

[13] Hydrogen Generation Market by Generation & Delivery Mode (Captive, Merchant), Technology (Steam Methane Reforming, Partial Oxidation, Gasification, and Electrolysis), Application (Refinery,
Ammonia Production, and Methanol Production), & Region - Global Forecast to 2021.
Marketsandmarkets, March 2016, in.


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Chapter 2
Experiments

The design of the experiments aims at providing time-resolved measurements of high temperature redox kinetics with sufficiently fast response and high accuracy. The selection of the reactor system, oxygen carriers, operating conditions, and measurement protocols are to ensure chemistry-controlled conversion processes with sufficiently high signal-to-noise ratio. With the detailed kinetics measurement, the fundamentals of redox reaction mechanism can be revealed. In this chapter, I will summarize details of the experimental system design, the preparation and characterization of the OC samples, as well as data acquisition and interpretation. The reactor system used in this thesis was upgraded from a previous design as introduced in ref. [1]. The critical changes are explained in details in this chapter.

2.1 Experimental System

2.1.1 Overview of the design and diagnostics

The experimental system is a button-cell fixed bed reactor, which consists of a gas flow delivery system, a reactor system, a real time flue gas analysis system with an on-line quadrupole mass-spectrometer (QMS), and a central control system as shown in Figure 2-1. The system layout and
schematics of the reactor are shown in Figure 2-2. Four Brooks GF40 MultiFlo digital thermal mass flow controllers (MFC) are used for the gas flow control. The reactor is made of a quartz tube positioned inside an ATS 3210 split tube furnace that provides an isothermal environment up to 1100°C. The central reactor consists of an outer, and an inner concentric quartz tube with an expanding section. Gases flow through the center tube, impinge on the bottom of the outer tube, and exit reversely through the exhaust. Capillary probes made of quartz are used to sample minute amounts of gases, before and after reactions. A quadrupole mass spectrometer (HPR20 from Hiden Analytical Inc.) is used to analyze the flue gas composition. The QMS has a response time of less than 300 ms and a wide bandwidth of species detection capability.

Figure 2-1 Novel button-cell fixed bed CL reactor system, consisting of a gas delivery, a control unit, a central reactor tube, and a real time flue gas analysis system with an on-line mass-spectrometer.
2.1.2 Gas flow delivery

Four Brooks GF40 MultiFlo digital thermal mass flow controllers (MFC) are used for the gas flow control. MFC 1 controls the flow of oxidizer, while MFC 3 controls the flow of fuel. MFC 2 controls the purging flow. MFC 4 is used to regulate auxiliary gas, including supplemental O₂ oxidation in the ceria-based study to ensure complete oxidation, or CO₂ flow in the case of Ni-
based study to suppress carbon deposition. The key specifications and the typical flow ranges are summarized in Table 2-1.

**Table 2-1 Key specifications of GF40 MFC [2]**

<table>
<thead>
<tr>
<th></th>
<th>MFC1 (oxidizer)</th>
<th>MFC2 (Ar)</th>
<th>MFC3 (fuel)</th>
<th>MFC4 (auxiliary)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow range</td>
<td>0 – 200 sccm</td>
<td>0 – 1000 sccm</td>
<td>0 – 200 sccm</td>
<td>0 – 1000 sccm</td>
</tr>
<tr>
<td>Control range</td>
<td>2-100% of S.P.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow accuracy</td>
<td>+1% S.P. 35-100%, +0.35% F.S. 2-35%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valve shut down</td>
<td>&lt; 1% of F.S. (normally closed valve)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Response time</td>
<td>&lt; 1 sec. (within 2% for steps 0-10 through 0-100%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) MFC 1 Air (21%O₂ in Ar) 
(b) MFC 2 Purging (Ar) 
(c) MFC3 Fuel (10%H₂ in Ar) 
(d) MFC4 Carrying gas (Ar)

Figure 2-3 MFC flow calibration: comparison of MFC set-points and flow rates measured in a bubble flow meter. x-axis is MFC set-point, and y-axis is the flow rate measured in the bubble flow meter. The correlations are included in each plot.
The accuracy of MFCs is tested using a bubble flow meter, with which the actual flow is measured by timing the motion of bubble front. A comparison is shown in Figure 2-3. The accuracy for Ar flow in MFCs 2 and 4 are within 1.5%, while the deviations for MFCs 1 and 3 are slightly larger, resulting from the addition of O2 or H2 in Ar, which slightly alters the flow properties. Nevertheless, the discrepancy is small.

![Schematics of the steam generator and water bath](image)

Figure 2-4 (a) Schematics of the steam generator. (b) Photo of the water bath. The 3-way solenoid valve is controlled by PC-1.

For the H2O splitting study, steam is produced through the steam generator, as depicted in Figure 2-4. Ar is slowly bubbled (flow rate in MFC 1: 10 ~ 150 sccm) through a 1 gallon bottle filled with de-ionized water maintained at fixed temperature (i.e., 80°C ±0.5°C in a base case) in an insulated heat bath. The temperature of the water bottle is controlled with 1/6 DIN Temperature Controller (CN740 from Omega). All connecting stainless steel tubes are insulated and heated above 140°C to avoid water condensation, with two additional temperature controllers monitoring the temperature at the exit of water flask, and the inlet of the central tube above the furnace. Additional thermocouples are also used to monitor the temperature along the feeding
lines. The produced flow carries H$_2$O according to the saturation pressure, as shown in Figure 2-5. To ensure minimum leakage and repeatable H$_2$O generation curves, a by-pass line is also included. A 3-way solenoid valve is switched between the feeding line and the by-pass line in accordance with the reaction cycles, automatically controlled by PC-1. Thus, in a typical H$_2$O splitting study, steam mixture is continuously generated at a steady state, and the produced steam is either admitted into the reactor system for the H$_2$O splitting (oxidation) step, or flown to the exhaust. To achieve the desirable H$_2$O concentration, the steam mixture is further diluted with Ar (MFC2).

![H$_2$O saturation curve (at 1 atm)](image)

Figure 2-5 H$_2$O saturation curve (at 1 atm) [3].

2.1.3 Central reactor system

The reactor is made of a quartz tube positioned inside an ATS 3210 split tube furnace (2640W/11.5 amps @ 230 VAC, single phase) that provides an isothermal environment up to 1100°C. As shown in Figure 2-2 (b), the reactor consists of an outer tube, 12" (305 mm) long, 1" (25.4 mm) outer diameter, OD, and 0.85" (21.6 mm) inner diameter, ID, and an inner concentric
¼" (6.4 mm) OD quartz tube with an expanding section of ¾" (19.1 mm) OD, 1.5" (38.1 mm) long. Gases flow through the central tube, impinge on the bottom of the outer tube, and exit reversely through the exhaust. OC samples in the form of powders or disks are embedded in quartz wool and placed at the bottom of the outer quartz tube. The outer quartz tube is pressed closely against inner tube with a minimum clearance (<5 mm). Schematic drawings and photos for both OC disks and powders are shown in Figure 2-6 and Figure 2-7.

Figure 2-6 (a) schematics of the reaction zone (expansion section) with embedded OC disks. (b) Photo of fresh OC disks embedded in quartz wool placed inside a quartz holder prior to inserting to the inner tube expansion section. (c) photo of OC disks inside the reactor after redox cycling.

Figure 2-7(a) schematics of the reaction zone (expansion section) with dispersed OC powder. (b) Photo of outer quartz tube with quartz wool (OC powder embedded within). Note in panel (b),
the inner tube is removed. Exhaust gas is connected through a ½" (6.4 mm) stainless steel tube via a pressure gauge and a needle valve, which slightly pressurizes the system (~0.2 psi above atmospheric pressure), to maintain an overall positive pressure within the system. Capillary probes made of quartz (0.53 mm ID, 0.80 mm OD) are used to sample minute amounts of gases, before and after reactions. The probe sampling the exhaust flow is located close to the outer tube, around 1~2 mm above the top of the expansion section of the inner tube, as shown in Figure 2-6 and Figure 2-7. Probe 2 is connected to the QMS, while probe 1 is used as a reference.

The layout of the reactor with the expansion section, small clearance between inner and outer tube, and location of the sampling probe is to ensure that the measured gaseous concentration exactly represents the local environment to which the OC is exposed. Ref. [1] examined the spatial distribution of the gaseous reactant based on an earlier design of the reactor, as shown in Figure 2-8, and concluded that with flow rate as low as 20 sccm, the species concentration in the reactor zone is relatively uniform, especially near the outer region (blue dotted area). The observed minor deviation in the inner area (red dashed region) results from a direct bypass of the feed stream. Therefore, the homogeneity was further improved by (cf. Figure 2-8) (1) adding the expansion section, which reduces the exit horizontal clearance from 10mm to 1.2mm, (2) lowering the height of reaction zone (from the bottom of the inner tube to the bottom of the outer tube) from ~15 mm to ~5 mm, (3) dispersing the sample powder in quartz wool; and (4) raising the feed flow rate from 20 sccm to ~ 300 sccm. Based on the current setting, the gas residence time through the control volume till probe 2 is estimated to be less than 300 ms, much shorter than chemistry.
2.1.4 Data acquisition with QMS

The residual gas analysis is performed using a QMS (HPR20 from Hiden Analytical Inc.). A small quantity of the sampled gas mixture passes through an ionization source as atoms and molecules are ionized by electrons to form detectable ion particles. The charged species then undergoes a filtering process, through which the particles with a pre-defined mass-to-charge ratio are selected. The multiplier voltage (1600 – 2400 V) controls the magnetic field of the mass filter, which determines the number of ionized charges counted by the detector. The entire process proceeds in a high vacuum (~10^-6 torr) environment and the charged particles freely pass through electric quadrupole. The QMS has a response time of less than 300 ms and a wide bandwidth of species detection capability. The photos of the QMS system are shown in Figure 2-9.
Species monitored by QMS is labeled by its molecular weight and ionization charges. This, however, gives rise to potential issues when multiple species trigger a similar reading. For instance, both $\text{N}_2$ and CO exhibit reading of 28, i.e., one $\text{N}_2$ or CO molecules with molecular weight of 28 and one charge. In addition, complex molecules become energetically unstable after being ionized, and break up into smaller pieces. As an example, $\text{N}_2$ can be fractured into two N, each of which produces a reading of 14, while $\text{CH}_4$ can be fragmented into $\text{CH}_2$ which gives the same reading. Figure 2-10 shows the peaks that can be detected in a typical $\text{H}_2/\text{O}_2/\text{Ar}/\text{N}_2/\text{H}_2\text{O}$ environment. Carefully selecting the best detection peaks as the representation of each species in the redox system with minimum interference is the key to the accurate measurement. The redox environments of interests with the corresponding choice of peaks are listed in Table 2-2. One situation that requires special attention is that when both CO$_2$ and CO co-exist in the system, the reading of peak 28 also contains the contributions from CO$_2$ fragmentation. As a result, in calculating the concentration of CO, the contribution of CO$_2$ to the 28 peak is removed by
subtracting the reading of 44 (i.e., CO₂) multiplied by a fragmentation ratio (i.e., reading of 28 divided by that of 44 resulting from CO₂), as will be shown in details below.

Figure 2-10 An illustration of the spectrum detected in the QMS in a typical environment (H₂, H₂O, Ar, N₂, O₂). Panel (a) summarizes the peaks that may present in the readings, and panel (b) shows the fragmentations of each gaseous molecules.

<table>
<thead>
<tr>
<th>Experiment scenario</th>
<th>Feeding species</th>
<th>Species: detection peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation with O₂</td>
<td>O₂, Ar</td>
<td>O₂: 32, Ar: 40</td>
</tr>
<tr>
<td>Oxidation with H₂O</td>
<td>H₂O, Ar</td>
<td>H₂O: 18, H₂: 2, Ar: 40</td>
</tr>
<tr>
<td>Oxidation with CO₂</td>
<td>CO₂, Ar</td>
<td>CO₂: 44, CO: 28, Ar: 40</td>
</tr>
<tr>
<td>Reduction with H₂</td>
<td>H₂, Ar</td>
<td>H₂: 2, H₂O: 18, Ar: 40</td>
</tr>
<tr>
<td>Reduction with CO</td>
<td>CO, Ar</td>
<td>CO: 18, CO₂: 44, Ar: 40</td>
</tr>
<tr>
<td>Reduction with CH₄</td>
<td>CH₄, Ar</td>
<td>CH₄: 15, CO: 28, CO₂: 44, H₂: 2, H₂O: 18, Ar: 40</td>
</tr>
<tr>
<td>Leakage test</td>
<td>Ar</td>
<td>N₂: 28, Ar: 40</td>
</tr>
</tbody>
</table>

The detected counts of selected peaks are then to be used to calculate the mole fraction, Xᵢ, of each species in the flow, as:

\[
\text{Corrected Signal of Species } i = \frac{R_i - B_i}{\eta_i} \tag{2.1}
\]
\[ X_i = \frac{\text{Corrected Signal of Species } i}{\sum_j \text{Corrected Signal of Species } j} \]  

(2.2)

Here, \( R_i \) is raw peak counts, corresponding to the peak readings at conditions of interests. \( B_i \) is background counts, accounting for readings of specific peak resulting from background noise (or leakage/impurities near the detector), and it is obtained based on the readings when only inert gas is flown. \( \eta_i \) is the calibration factor, obtained in prior to each experiment to account for the different sensitivities of the detector to different particles. For a system with \( N \) species, only \( N-1 \) calibration factors are complete to fully characterize the species sensitivity. A common practice is to set the calibration factor of the major species, most commonly inert carrying gas (e.g., Ar), to be unity.

To obtain the calibration factor, gas mixture with known composition is fed to the QMS, and these factors are then varied to minimize the difference between the measured concentrations and the unknown mixture, as:

\[ G = \min_{\eta_i} \left\{ \sum_{i=1, N-1} \left( X_{i, measured} - X_{i, 0} \right)^2 \right\} \]  

(2.3)

The selection of calibration gas should well represent a typical gas mixture observed in the redox reactions. For instance, in the case of \( \text{H}_2\text{O} \) splitting test with 26% \( \text{H}_2\text{O} \) (Ar balance), a typical condition may be 10% \( \text{H}_2\text{O} \), 5% \( \text{H}_2 \), with Ar balance. However, one can expect a more difficult calibration process in a case with multiple species, e.g., \( \text{CH}_4 \) reduction. An alternative method is to calibrate each minor species with respect to the major species (i.e., inert balance gas), individually. For instance, the preceding case can also be calibrated with a mixture of 10% \( \text{H}_2\text{O} \)
(with Ar balance) for H₂O calibration, and a mixture of 5% H₂ (with Ar balance) for H₂ calibration.

In those scenarios where multiple species produce overlapping readings, the fragmentation factor is then calculated. Here CO₂ splitting is taken as an example, in which CO₂ can be fragmented to produce readings of 28. The fragmentation factor for CO₂ is obtained during calibration:

1) feed only CO₂ (Ar balance) into the system,

2) compare the reading of 28 with respect to that of 44, as:

$$\text{fragmentation factor of CO}_2 = \frac{R_{28} - B_{28}}{R_{44} - B_{44}}$$  \hspace{1cm} (2.4)

With the fragmentation factor of CO₂ obtained, the corrected signal of CO (in an CO/CO₂ environment) is calculated as:

$$\text{Corrected Signal of CO} = \frac{(R_{28} - B_{28}) - (R_{44} - B_{44}) \times \text{fragmentation factor of CO}_2}{\eta_{CO}}$$  \hspace{1cm} (2.5)

Here $R_{28}$-$B_{28}$ consists of signals from both CO and CO₂. Eq. (2.5) is then substituted into eqs. (2.2) to obtain the mole fraction.

Readings from the detector commonly drift slowly with time, due to the degradation of detector as well as other factors, including pressure, power supply fluctuation, impurities, etc. Calibrations in prior to and after each test are recommended to ensure a desirable accuracy. For the sake of consistency, one inert carrying species (e.g., Ar, or He) is used throughout the entire measurement as the major species. All other species are then calibrated with respect to the major species.
2.1.5 Central control system

The gas delivery system, reactor furnace, and data acquisition with QMS are all controlled by a central control system (PC-1). The MFC units continuously update flow rates as an analog voltage signal, which are translated into a digital signal via a National Instrument (NI) data acquisition device, NI USB-6120. The feedback from PC-1 to the MFC units goes through a NI-9123 voltage output module connected to a cDAQ-9171 single-slot chassis. The NI USB-6120 data acquisition device is also used to control the 3-way solenoid valve and trigger the automatic data sampling by the QMS. The connection from NI USB-6120 to QMS is via a RS232 cable.

Figure 2-11 shows the connections and communications between devices and PC-1. Two thermocouples (K-type) are also connected to NI USB-6120 device to allow for real-time monitoring of temperature along the gas flow delivery system. The ATS split furnace is also controlled by PC-1, the temperature of which can be monitored and controlled in real-time in accordance with the designed experiments.

Figure 2-11 Control system flow diagram between data acquisition devices and the analog instruments [1]. Gray lines correspond to newly installed improvement to allow sampling automation.
The input and output control which interfaces with the NI data acquisition device is realized via a Matlab GUI, which was upgraded from a previous control system [1, 4] to allow for much improved automation. Figure 2-12 below shows the GUI. The top panel is a direct control of the 4 MFCs. The middle panel “simple cycle mode” enables a simple automatic cyclic looping following a sequence of “purge, oxidize, purge, reduce” at specified runtime for each step. Script model in the bottom panel enables a programmable measurement sequence. Figure 2-13 shows an example of a script (based on excel spreadsheets) for programmed measurement sequence. The script is also capable of interfacing with the furnace temperature control, allowing for an automatic temperature ramping with data acquisition. The 3-way valve and the QMS trigger are controlled in the top left and the middle left.

![Matlab graphic user interface control panel.](image)

Figure 2-12 Matlab graphic user interface control panel.
2.1.6 System Evolution and Experiment Protocol

The performance of the button-cell reactor system was tested for accuracy and flow responses. Figure 2-14 compares the measurements to the set concentrations of O₂ and H₂ under steady state, and a perfect match is observed within a wide range of composition. This demonstrates the accuracy of MFC in delivering the correct gas flow and that of QMS in detecting the flue stream composition. Figure 2-15 shows the flow response as the feed stream is switched (at t = 0) from Ar purging to O₂ (Ar balance). The time interval between t = 0 and 90% set point value is listed in Table 2-3. As the feed stream is switched, the QMS measures the change of the gas concentrations in the reactor. The delay in the MS readings indicates the flow response in the system. The delay includes the time taken by MFCs to ramp up the flow to the set value, the time for the gas to flow through the reactor and displace the existing gas volume, and the time for the flow to go through the sampling probe to the MS. Increasing the flow rate effectively reduces the flow residence time within the reactor, and leads to faster response. Nevertheless, the response time does not change much beyond a flow rate of 250 sccm (as seen in Table 2-3) where the delay is mainly caused by the MFCs and sampling probes. Therefore, a total flow rate above 250 sccm is adequate to ensure a fast response. The flow residence time in the reaction zone, as outlined in Figure 2-6(a), is also included in Table 2-3. For flow rate higher than 250 sccm, the residence time within the reaction zone is less than 400 ms.

Figure 2-13 Script for programmable measurement sequence.
Table 2-3 Flow response time with different set flow rate.

<table>
<thead>
<tr>
<th>Set flow</th>
<th>150sccm</th>
<th>250sccm</th>
<th>350sccm</th>
<th>450sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow response time through the reactor</td>
<td>28s</td>
<td>18s</td>
<td>16s</td>
<td>15s</td>
</tr>
<tr>
<td>Flow residence time in the reaction zone</td>
<td>600ms</td>
<td>350ms</td>
<td>250ms</td>
<td>200ms</td>
</tr>
</tbody>
</table>

Note, the calculated flow residence time in the reaction zone is based on the geometry outlined in Figure 2-6(a) at 900°C

Too high flow rate, on the other hand, should be avoided, since high flow rate adversely affects the signal-to-noise ratio for compositional measurement. A fast flow is usually accompanied by a less conceivable difference between inlet (probe 1) and exit (probe 2), leading to a lower concentration of product, and hence possibly higher uncertainty in the measurements. For a typical case, the flow rate in the range of 250 – 350 sccm provides sufficiently high signal-to-noise ratio, while maintains a fast system response.

Figure 2-14 Species concentration calibration: comparison of set-points and measurements from QMS. x-axis is set-point of feed mixture, and y-axis is the concentration measured in QMS. The correlations are included in each plot.
Figure 2-15 Comparison of flow response at different flow rate. \( \text{O}_2 \) is fixed at 10.5 sccm, and Ar is varying with total flow of 150 sccm (black), 250 sccm (red), and 350 sccm (blue). \( \text{O}_2 \) flow is initiated at \( t = 0 \).

The experiment protocol based on the button-cell fixed bed reactor is shown in Figure 2-16. Experiment usually starts with a blank test as a control group to rule out any potential issues, such as leakage issue, carbon deposition, etc. Minute amount of (typically 50~100 mg) sample is loaded into the reactor, pre-treated at highest temperature with redox cycling until a new equilibrium is established and the redox kinetics becomes stable. During the pre-treatment, samples usually undergo noticeable morphological and structural evolutions resulting from a combined effect of thermal sintering and chemical stresses during redox reactions. The new equilibrium state commonly exhibits a larger crystalline grain, hence a lower surface area, with modified surface structure. More distinctive structural changes may be observed when phase change takes place during the redox cycling, especially in the case of pure metal (e.g., nickel) oxidation, as will be discussed in Chapter 4. After periodic stationary state is reached, the redox measurement for kinetics study starts from high temperature. In each cycle, a typical cycling
sequence consists of various stages: purge, reduction, purge, and oxidation. Each operating condition is repeated for at least three times, and results are averaged to reduce the noise. As temperature ramps down, the measured kinetics slows down, and eventually becomes indistinguishable from the background noise at low temperature (e.g., 500°C as in Figure 2-16). Depending on the needs, experiments with different oxidation and reduction conditions are also carried out to evaluate the effects on the reactivity.

Figure 2-16 Experimental protocol using the button-cell fixed-bed reactor with the online QMS
2.3 Oxygen Carrier Preparation and Characterization

Oxygen carriers tested in this study include nickel-based materials for CLC, ceria-based and perovskite-based materials for CL H₂O/CO₂ splitting. A summary is listed in Table 2-4.

Table 2-4 List of OC samples tested in this thesis

<table>
<thead>
<tr>
<th>Chemical-looping combustion study</th>
<th>Chemical-looping H₂O/CO₂ splitting study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni foils</td>
<td>CeO₂, Ce₀.₅Zr₀.₅O₂, Pr₀₂Ce₀.₈O₂</td>
</tr>
<tr>
<td>NiO/YSZ nano-powder</td>
<td>LSCF, LSCF-Hf, PSCFN, LSCC</td>
</tr>
<tr>
<td></td>
<td>LSCF-Ni</td>
</tr>
</tbody>
</table>

Commercial thin foils and fine particles are used for the base tests for CLC, and CL H₂O/CO₂ splitting, respectively. The usage of OCs with simple form factors, such as foils and particles, enables a direct evaluation of the rate-limiting kinetics mechanism of the redox process:

- **CLC study with nickel foils**: the surface chemistry with nickel is generally fast, in line with the highly catalytic reaction process in presence of metallic nickel nuclei [5]. The conversion process is rather limited by a solid-state diffusional process: the transport of oxygen ions in the reduction step, and the diffusion of the nickel ions in the oxidation step. As a result, the phase-change and the structural evolutions critically determines the diffusional pathways and hence the redox kinetics. The usage of nickel foils ensures a one-dimensional development of oxide grains, hence enabling a direct observation of the structural evolution. The use of foils also eliminates the possible intra-particle agglomeration, thus providing a precise control of the sample geometry. Samples with different thickness are studied.
• CL H₂O/CO₂ study with ceria nano-powders: CeO₂ is known to maintain its fluorite structure even under large non-stoichiometry at elevated temperatures [6]. The electronic and ionic diffusivities ($D_{\text{Ce}_c}$, $D_{\text{v}_0}$) of ceria are very high, and bring the bulk defects to dynamic equilibrium during the redox process. Thus, the redox process with ceria is most critically determined by surface chemistry. The usage of fine nano-powders with large surface area ensures a surface-limited-process, hence enabling a direct observation of the ion-incorporation process on the surface.

With the preliminary experiences obtained from the studies with nickel-foils and ceria-powders, extensions are made by adding dopant/support to the OCs in an attempt to further enhance the redox characteristics:

• NiO supported on YSZ nano-particles (referred to as NiO/YSZ) are prepared following a mechanical mixing approach: 1) commercial nickel particles (size <1μm) are mixed with YSZ (3mol% yttria) fine nano-particles (size 30-60 nm), with organic additives (e.g., ethylene glycol) as binding agents; 2) the formed mixture is thoroughly mixed, stirred at 150°C for 1 hr till all the sample is completely dried; 3) the obtained sample is grinded, and then calcined at 1000°C for 8 hrs. The usage of YSZ allows for a much improved ionic diffusivity, resulting in a much improved redox kinetics and degree of conversion.

• Commercial Ce₀.₅Zr₀.₅O₂ (referred to as CZO) and Pr₀.₂Ce₀.₈O₂ (referred to as PCO) nanoparticles are used for the tests for CL H₂O/CO₂ splitting. Several perovskite-based OC samples are also tested, including (La₀.₆Sr₀.₄)₀.₉₅Co₀.₂Fe₀.₈O₃ (referred to as LSCF), Pr₀.₄Sr₀.₆Co₀.₂Fe₀.₇Nb₀.₁O₃ (PSCFN), and La₀.₆Sr₀.₄Cr₀.₈Co₀.₂O₃ (LSCC).
LSCF as OC is further modified with Hf: The Hf deposition was performed by treatment of the 1 g of LSCF powder in the 40 ml of 0.1 mM aqueous solution of HfCl₄ at 70 °C while stirring until water evaporates. The obtained powder was grinded and additionally dried at 150 °C for 20 min.

Ni-modified LSCF is also included for testing, the preparation of which follows a similar mechanical mixing method as with Ni/YSZ.

Table 2-4 summarizes all the samples employed in this thesis. SEM images of the freshly prepared samples are shown in Figure 2-17, Figure 2-18, Figure 2-19, and Figure 2-20.

(a) Nickel foil
(b) NiO/YSZ

Figure 2-17 SEM images of the fresh nickel-based samples (a) nickel foils, (b) NiO/YSZ powder. In panel (b), the smaller particles are YSZ nano-particles, and larger particles are NiO.
Figure 2-18 SEM images of the fresh ceria-based samples (a) CeO\textsubscript{2}, (b) CZO, (c) PCO.

Figure 2-19 SEM images of the fresh LSCF-based samples (a) LSCF, (b) Hf-modified LSCF, (c) Ni-modified LSCF.

Figure 2-20 SEM images of the fresh (a) PSCFN (b) LSCC samples.
The morphology and the average particle/grain size of the sample before and after the redox treatment are characterized with a JEOL 6700 scanning electron microscopy (SEM) system, and the composition is examined by the energy-dispersive X-ray spectroscopy (EDS). The crystal structure of the samples is examined by XRD analysis (Cu Ka, 45 kV and 40 mA, PANalytical X'Pert Pro Multipurpose Diffractometer, Almelo, The Netherlands) performed at room temperature in air. The BET surface area is measured using a surface area and porosity analyzer (ASAP 2020 from Micromeritics).

2.4 Data Interpretation

In order to derive the kinetics based on the flue stream composition, we consider a control volume as outlined in Figure 2-6 and Figure 2-7. Because of the high feed flow, the gas residence time through the reaction zone is much shorter than the characteristic time of chemistry (Table 2-3). Thus, the reactant partial pressure on the sample surface is essentially identical to that measured in the QMS.

The element conservation equations within the control volume are generally expressed as:

\[ \dot{n}_{in} \sum_{i=1}^{N} X_{in,i} a_{i,j} = \dot{\omega}_j + \dot{n}_{out} \sum_{i=1}^{N} X_{out,i} a_{i,j} \quad \text{element } j = \text{Ar, C, H, O} \quad (2.6) \]

where \( \dot{n}_{in} \) and \( \dot{n}_{out} \) are the total molar flow rate (unit, mole s\(^{-1}\)) at the inlet and exit, respectively. \( X_{in,i} \) and \( X_{out,i} \) are the mole fraction of species \( i \), and \( a_{i,j} \) is the number of element \( j \) in species \( i \). \( \dot{\omega}_j \) is the consumption of element \( j \) from reaction (unit, mole s\(^{-1}\)). The above derivations assume a quasi-steady state and neglect the accumulation or depletion effect in the control volume. This is valid as the flow residence time is much shorter than the characteristic time of the redox.
conversion. The derivations in the case of CH\textsubscript{4} reduction are shown below as an example, and the equations for other cases are summarized in Table 2-5.

The reduction with CH\textsubscript{4} can be written as:

\[
\text{CH}_4 (g) + O_{OC}(s) \rightarrow \text{CO}(g) + \text{CO}_2 (g) + \text{H}_2 (g) + \text{H}_2\text{O}(g) + C(s) \quad (2.7)
\]

Here O\textsubscript{OC} represents lattice oxygen from the OC, and C(s) corresponds to the possible carbon deposition in the system. The reaction is accompanied by a change in the flow rate, as more molecules (CO, CO\textsubscript{2}, H\textsubscript{2}, H\textsubscript{2}O) are generated with the consumption of one CH\textsubscript{4} molecule. The outgoing molar flow rate is obtained via Ar element balance, \( \dot{n}_{out} = \dot{n}_{in}X_{in, Ar} / X_{out, Ar} \). The element conservations for C, H and O become:

\[
\begin{align*}
\text{C:} & \quad \dot{n}_{in} X_{in,CH_4} = \dot{n}_{out} \left( X_{out,CO} + X_{out,CO_2} + X_{out,CH_4} \right) + \dot{N}_c \quad (2.8) \\
\text{H:} & \quad \dot{n}_{in} \left( 4X_{in,CH_4} \right) = \dot{n}_{out} \left( 4X_{out,CH_4} + 2X_{out,H_2} + 2X_{out,H_2O} \right) \quad (2.9) \\
\text{O:} & \quad \dot{\omega}_{\text{red}} = \dot{n}_{out} \left( X_{out,CO} + 2X_{out,CO_2} + X_{out,H_2O} \right) \quad (2.10)
\end{align*}
\]

Where \( \dot{N}_c \) is the carbon deposition rate, and \( \dot{\omega}_{\text{red}} \) is the oxygen removal rate during reduction.

Based on the above equations, \( \dot{N}_c \) and \( \dot{\omega}_{\text{red}} \) can be derived as:

\[
\begin{align*}
\frac{\dot{N}_c}{\dot{n}_{out}} &= \frac{1}{2} X_{out,H_2} + \frac{1}{2} X_{out,H_2O} - X_{out,CO} - X_{out,CO_2} \quad (2.11) \\
\frac{\dot{\omega}_{\text{red}}}{\dot{n}_{out}} &= X_{out,CO} + 2X_{out,CO_2} + X_{out,H_2O} \quad (2.12)
\end{align*}
\]

Note here, eqs. (2.8) and (2.9) are combined to derive \( \dot{N}_c \) to allow for a better accuracy, instead of subtracting \( \dot{n}_{out} X_{out,CH_4} \) from \( \dot{n}_{in} X_{in,CH_4} \), which leads to large uncertainty.
The conversion of the OC, or the accumulative change of oxygen non-stoichiometry, \( X \), can then be calculated by integrating the oxygen consumption rate:

\[
\text{Reduction with CH}_4: \quad X_{\text{red}}(t) = X_{\text{red},0} - \frac{1}{n_O} \int_{t=0}^{t} \dot{\omega}_{\text{red}} dt
\]  

(2.13)

where \( n_O \) is the maximum amount of oxygen in the OC, calculated based on stoichiometry. \( X_{\text{red},0} \) is the oxygen non-stoichiometry obtained from the previous oxidation step.

The derivations of other redox cases follow a similar method, and the results are summarized in Table 2-5.

2.5 Bibliography

<table>
<thead>
<tr>
<th>Case</th>
<th>Element conservation relations</th>
<th>Derived OC kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation $O_2$/Ar</td>
<td>$\dot{O}<em>O + \dot{n}</em>{out}(X_{out,O_2} + X_{out,CO} + 2X_{out,CO_2}) = \dot{n}<em>m X</em>{in,O_2}$</td>
<td>$\dot{\omega}<em>x = 2\dot{n}<em>m \left( X</em>{in,O_2} - X</em>{out,O_2} \frac{1 - X_{in,O_2}}{1 - X_{out,O_2}} \right)$</td>
</tr>
<tr>
<td>Oxidation $O_2$/Ar (w/ carbon)</td>
<td>$\dot{O}<em>O + \dot{n}</em>{out}(2X_{out,O_2} + X_{out,CO} + 2X_{out,CO_2}) = 2\dot{n}<em>m X</em>{in,O_2}$</td>
<td>$\dot{\omega}_x = 2\dot{n}<em>m X</em>{in,O_2}$</td>
</tr>
<tr>
<td>Oxidation $H_2O$/Ar</td>
<td>$\dot{H}<em>H + \dot{n}</em>{out}(X_{out,H_2O}) = \dot{n}<em>m X</em>{in,H_2O}$</td>
<td>$\dot{\omega}_x = \dot{n}<em>m X</em>{out,H_2}$</td>
</tr>
<tr>
<td>Oxidation $H_2O$/Ar (w/ carbon)</td>
<td>$\dot{H}<em>H + \dot{n}</em>{out}(X_{out,H_2O} + X_{out,CO} + 2X_{out,CO_2}) = \dot{n}<em>m X</em>{in,H_2O}$</td>
<td>$\dot{\omega}_x = \dot{n}<em>m X</em>{out,H_2}$</td>
</tr>
<tr>
<td>Oxidation $CO_2$/Ar</td>
<td>$\dot{C}<em>C + \dot{n}</em>{out}(X_{out,CO_2} + X_{out,CO}) = 2\dot{n}<em>m X</em>{in,CO_2}$</td>
<td>$\dot{\omega}_x = \dot{n}<em>m X</em>{out,CO}$</td>
</tr>
<tr>
<td>Oxidation $CO_2$/Ar (w/ carbon)</td>
<td>$\dot{C}<em>C + \dot{n}</em>{out}(X_{out,CO_2} + X_{out,CO}) = \dot{n}<em>m X</em>{in,CO_2}$</td>
<td>$\dot{\omega}_x = \dot{n}<em>m (2X</em>{in,CO_2})$</td>
</tr>
<tr>
<td>Reduction with $H_2$/Ar</td>
<td>$\dot{\omega}<em>{red} = \dot{n}</em>{out}X_{out,H_2}$</td>
<td>$\dot{\omega}_{red} = \dot{n}<em>m X</em>{out,H_2}$</td>
</tr>
<tr>
<td>Reduction with $CO$/Ar</td>
<td>$\dot{\omega}_{red} = \dot{n}<em>m X</em>{in,CO}$</td>
<td>$\dot{\omega}_{red} = \dot{n}<em>m X</em>{out,CO}$</td>
</tr>
<tr>
<td>Reduction with $CH_4$/Ar</td>
<td>$\dot{\omega}_{red} = \dot{n}<em>m (2X</em>{in,CO_2})$</td>
<td>$\dot{\omega}<em>{red} = \dot{n}<em>m (2X</em>{in,CO_2} + 2X</em>{out,CO_2})$</td>
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Chapter 3

Modeling Framework

The modeling of CLC, Chemical-looping Reforming (CLR), CL H₂O/CO₂ processes involves the descriptions of key phenomena associated with the redox conversion processes: thermodynamics, surface chemistry, transport mechanism, and structural evolution. In a typical CL system, one or a few of these elements control the overall conversion process. An in-depth understanding of redox fundamentals is technologically important for identifying the rate-limiting mechanism, and hence the insights gained from the modeling practice will shed light on the design and optimization of the CL process. This chapter lays out the modeling framework adopted to describe the redox kinetics in CLC, CLR, and CL H₂O/CO₂ splitting processes on the basis of electrochemistry. Sub-models for each component are developed and presented in details.

3.1 Overview of the modeling framework

Redox reactivity is one of the most important properties of the OC, as it directly determines the conversion of fuel in the gas phase. The reaction process involves the interactions between the gaseous reactants and the solid lattice. Generally, the overall redox reactions are written as

\[
\text{Reaction: } A \text{ (g)} + v_r \text{B (s)} \leftrightarrow v_p \text{C (s)} + D \text{ (g)}
\] (3.1)
where $A$ represents fuel for reduction, and $O_2$ for oxidation. $B$ represents the active sites from the solid, and $v_r, v_p$ are the stoichiometric coefficients. Modeling of the redox conversion involves consideration of four major aspects (as shown in Figure 3-1):

- **Thermodynamics**: the phase and defect equilibrium from thermodynamics dictates the equilibrium state of the gas-solid system under specific condition. The off-equilibrium bias determines the driving force for the kinetic process.

- **Surface chemistry**: surface reaction consists of a series of intermediate steps, including adsorption and dissociation, charge transfer, association and eventually desorption of product.

- **Transport**: gas-phase transport includes external and internal (through OC pores and voids) diffusion of gaseous reactant and product. Solid phase diffusion includes the diffusion of charged species.

- **Structural evolution**: phase change occurs during redox conversion with growth of oxide grains and migration of metallic grains, which is accompanied by evolutions of surface sites and transport pathways.

Figure 3-1 Schematics of the modeling framework and its inter-connections.
3.2 Thermodynamics

3.2.1 Defect (chemistry) equilibrium

The aim of thermodynamic treatment of defect chemistry is to define the equilibrium state of the OC solids, in terms of the precise composition (including defects) as a function of state variables, i.e., temperature and concentration. The thermodynamics description of the real OC solids includes the contributions of chemical bonds and defects [1]:

\[
\text{perfect solid } \leftrightarrow \text{ real solid } \quad (3.2)
\]

\[
G_{\text{real}} = G_{\text{perfect}} + \Delta G_{\text{defect}} \quad (3.3)
\]

where \( G \) is the total free energy of a solid system, and \( \Delta G_{\text{defect}} \) represents the change induced by defect formation, which includes contributions from bond relaxation (\( \Delta G_{\text{bond}} \)), vibrational relaxation (\( \Delta G_{\text{vib}} \)), and configuration relaxation (\( \Delta G_{\text{cfg}} \)), as:

\[
\Delta G_{\text{defect}} = \Delta G_{\text{bond}} + \Delta G_{\text{vib}} + \Delta G_{\text{cfg}} \quad (3.4)
\]

The redox reactions with nickel involves the formation of cation vacancy, \( V_{\text{Ni}}^{\ast} \), compensated by electron holes, \( h^{\ast} \), while those with ceria-based OCs are anion vacancy, \( V_{\text{O}}^{\ast*} \), and polarons (localized electrons), \( Ce_{\text{Ce}}^{\ast} \). The creation of a defect vacancy is accompanied by the removal of an internal ion, either \( \text{Ni}^{2+} \), or \( \text{O}^{2-} \), which requires energy to break-up chemical bonds, i.e.:

\[
\Delta G_{\text{bond}} = N_{V} n_{\text{bond}} E_{\text{bond}} > 0 \quad (3.5)
\]

where \( N_{V} \) is the number of vacancy, \( n_{\text{bond}} \) is the number of bonds that are affected by the defect formation, and \( E_{\text{bond}} \) is the bond energy. For a typical solid system, \( \Delta G_{\text{bond}} \) is about a few eV per vacancy (e.g., 4.7 eV for CeO\(_2\) [2], and 2.3 eV for NiO [3, 4]).

\[\text{A more rigorous derivation should further address the relaxation of the structure in the presence of defect. As a result, part of the binding energy is recovered via by the re-arrangement of the local ensemble. For the purpose in this section, however, this effect is factored into } E_{\text{bond}}.\]

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The formation of a defect, on the other hand, leads to a slight relaxation of the crystal structure, inducing an increase in the local vibrations free energy:

\[-\Delta G_{\text{vib}} / T \approx \Delta S_{\text{vib}} = -N_{v} n_{vib} k_B \ln \frac{v_{\text{vib}}}{v_0} > 0 \quad (3.6)\]

where \(\Delta S_{\text{vib}}\) is the induced entropy change, \(k_B\) is Boltzmann constant, and \(T\) is temperature. \(v_{\text{vib}}\) is the new vibrational frequency \(< v_0\) of the \(n_{\text{vib}}\) neighbor atoms. Assuming that the vibrational frequency is halved with the creation of a vacancy, \(-\Delta G_{\text{vib}}/T\) is estimated to be \(0.1\sim1\) meV K\(^{-1}\) per vacancy (e.g., 0.43 meV K\(^{-1}\) for CeO\(_2\) [2], and 0.61 meV for NiO [3]).

The third term is decisive for the existence of defect: it describes the enormous increase in the number of possible sites, and hence the entropy of the solid system:

\[-\Delta G_{\text{cfg}} / T = \Delta S_{\text{cfg}} = k_B \ln \Omega > 0 \quad (3.7)\]

where \(\Delta S_{\text{cfg}}\) is the induced entropy change, and \(\Omega\) is the total number of possible configurations with the same energy, calculated as:

\[
\ln \Omega = \ln \left( \frac{N!}{N_v! (N-N_v)!} \right) \approx -N_v \ln \frac{N_v}{N} - (N-N_v) \ln \frac{N-N_v}{N} \quad (3.8)
\]

where \(N\) is the total number of positions. Derivation here uses the Stirling approximation for large numbers: \(\ln N! \approx N \ln N - N\). \(N_v\) can be further connected to the defect concentration (or defect fraction to be more precise), \(X_v = N_v/N\).

The total free energy of the real solid, with the contributions of the binding energy, vibrational and configurational relaxation, can be re-written as:

\[\text{The calculated values here use the entropy of defect formation after adjusting for the entropy of gaseous O}_2.\]
Figure 3-2 schematically shows the variation of the total free energy, $G_{\text{real}}$, as a function of the number of defect vacancy. The chemical potential of the *defect element* is thus defined by differentiation:

$$
\mu_{\nu} = \frac{\partial G_{\text{real}}}{\partial N_{\nu}} \bigg|_{T,N} = \mu_{\nu}^0 + k_B T \ln \frac{N_{\nu}}{N} \frac{N - N_{\nu}}{N} \left( N_{\nu} \ln \frac{N_{\nu}}{N} + (N - N_{\nu}) \ln \frac{N - N_{\nu}}{N} \right)
$$

(3.9)

where $\mu_{\nu}^0 = n_{\text{bond}} E_{\text{bond}} + n_{\text{vib}} k_B T \ln \left( \nu_{\text{vib}} / \nu_0 \right)$ is the free energy of defect formation. From eq. (3.10), it is interesting to notice that the chemical potential of the "defect element" includes not only the contributions from the vacancy, but also the configurational entropy of the normal sites, $1 - X_{\nu}$, echoing the fact that the formation of one defect requires the replacement of a normal site by a vacancy.

Figure 3-2 Schematics of the free energy contributions by defect formation. The total number of sites is constant.
The thermodynamic equilibrium is established at minimum free energy, i.e., \( \mu_r(N_{r,eq}) = 0 \), which can be re-arranged to obtain:

\[
\frac{X_V}{1-X_V} = \exp \left( -\frac{\mu^0_V}{k_B T} \right)
\]  

(3.11)

where \( X_V \) is fraction of vacancy. A close examination of eq. (3.11) reveals that the equilibrium relationship essentially describes the law of mass action for the following defect formation reaction:

\[ \text{nil} \leftrightarrow \text{defect site} - \text{normal site} \]  

(3.12)

with the defect site and the normal site treated as individual species, i.e., in the case of O-deficient OC, \( V_{O''} \) and \( O_{O'} \). The corresponding chemical potential for each species can thus be defined as,

\[
\mu_i = \mu^0_i + k_B T \ln X_i, \; i = V_{O''} \text{ and } O_{O'}
\]  

(3.13)

Thus,

\[
\mu_V = \mu_{V''} - \mu_{O'}
\]  

(3.14)

In the case with non-uniform electrical field, the chemical potential of defect is replaced by the electro-chemical potential:

\[
\tilde{\mu}_i = \mu_i + z_i e \phi
\]  

(3.15)

where \( e \) is the unit charge of an electron, \( \phi \) is the electrostatic field, and \( z_i \) is the effective charge. The chemical potential for electron or hole defect can be defined similarly.

---

\(^5\) eq.(3.12) is essentially equivalent to eq. (3.2).
When external equilibria are established in presence of gaseous reactant, the defect formation reaction and the corresponding law of mass action can be naturally extended as 6:

\[
\text{O-deficient OC (ceria): } O_2^\circ + 2Ce_{ce}^\bullet \rightleftharpoons \frac{1}{2}O_2 + V_{O}^{\bullet\bullet} + 2Ce_{ce}^\circ
\]  

(3.16)

\[
\frac{p_{O_2}^{1/2}[V_{O}^{\bullet\bullet}][Ce_{ce}^\circ]}{[O_2^\circ][Ce_{ce}^\bullet]^2} = K_{\text{ceria}} = \exp \left(-\frac{\mu_{\text{ceria}}^0}{RT}\right)
\]

(3.17)

cation-deficient OC (NiO): \( \frac{1}{2}O_2 \rightleftharpoons \frac{1}{2}O_2^\circ + V_{Ni}^{\bullet\bullet} + 2h^\circ \)  

(3.18)

\[
\frac{[O_2^\circ][V_{Ni}^{\bullet\bullet}][h^\circ]^2}{p_{O_2}^{1/2}} = K_{\text{nikelel}} = \exp \left(-\frac{\mu_{\text{nikelel}}^0}{RT}\right)
\]

(3.19)

where eqs. (3.16) and (3.18) describes the defect formation processes in an oxygen-deficient OC (n-type, e.g., ceria), and a cation-deficient OC (p-type, e.g., NiO), respectively. The brackets here denote the fraction of solid species \( \chi_i \) for simplicity. The defect formation reaction here involves the creation of the vacancy defect, charge-balanced by the compensating electron or hole defect. Thus \( \mu_{\text{ceria}} \) or \( \mu_{\text{nikelel}} \) essentially involves the free energy of both vacancy and electron (holes).

Figure 3-3 shows the defect equilibria of ceria in \( O_2 \) environment as an example. As seen here in Figure 3-3, defect formation favors high temperature and low \( p_{O2} \), in line with the positive defect formation energy and the inverse \( O_2 \) pressure dependence, as seen in eq. (3.17). As an OC is cycled between a reducing and an oxidizing environment, the oxygen deficiency (\( \delta \)) is adjusted along the isotherms in accordance with the corresponding \( p_{O2} \) in the reactor, hence producing the driving force for the surface chemistry.

\[ ^{6} \text{The electrostatic term is canceled out.} \]
Figure 3-3 Defect equilibria of CeO₂ in O₂ environment, based on the equilibrium parameters derived from Chapter 6. Dashed lines are the pO₂ established during the reduction and oxidation steps, respectively, and the difference in the corresponding defect fraction indicates the driving force for reaction.

3.2.2 Transport equilibrium

The formed defect in equilibrium with the external gaseous environment is further connected between the material bulk phase and the surface via transport equilibrium (see Figure 3-4). The movement of a vacancy between location x₁ and x₂ within the solid system can be described as the exchange of positions between defect and normal sites (with O-deficient OC as an example):

\[ V_{o}^{-} (x_1) + O_{o}^{-} (x_2) \leftrightarrow O_{o}^{-} (x_1) + V_{o}^{-} (x_2) \]  \hspace{1cm} (3.20)

By re-arranging eq. (3.20), we obtain equivalently:

\[ V_{o}^{-} (x_1) - O_{o}^{-} (x_1) \leftrightarrow V_{o}^{-} (x_2) - O_{o}^{-} (x_2) \]  \hspace{1cm} (3.21)
Here, the transport equilibrium is restated in terms of the “defect element”, i.e., the structural defect minus the original normal site [1]. Thus at equilibrium, the chemical potential of the defect vacancy is identical between $x_1$ and $x_2$, i.e., $\bar{\mu}_t(x_1) = \bar{\mu}_t(x_2)$. By substituting eq. (3.15),

\[
\frac{[V^*_O(x_2)]}{1-[V^*_O(x_2)]} \frac{[V^*_O(x_1)]}{1-[V^*_O(x_1)]} = \exp \left( -\frac{1}{k_B T} \left( \frac{\mu^0_{O^*} - \mu^0_{O^*} + 2e\phi}{x_2} - \left( \frac{\mu^0_{O^*} - \mu^0_{O^*} + 2e\phi}{x_1} \right) \right) \right)
\]

Eq. (3.22) describes the law of mass action for the transport equilibrium of defect elements within the solids. The movement of an electron defect can be expressed similarly as

\[
[Ce'_C(x_1)] - [Ce'_C(x_2)] \leftrightarrow [Ce'_C(x_2)] - [Ce'_C(x_1)]
\]

\[
\frac{[Ce'_C(x_2)]}{1-[Ce'_C(x_2)]} \frac{[Ce'_C(x_1)]}{1-[Ce'_C(x_1)]} = \exp \left( -\frac{1}{k_B T} \left( \frac{\mu^0_{Ce^*} - \mu^0_{Ce^*} - e\phi}{x_2} - \left( \frac{\mu^0_{Ce^*} - \mu^0_{Ce^*} - e\phi}{x_1} \right) \right) \right)
\]

1.2 \ O_2(g) gas

surface

$V^*_O - O^*_O$

Vacancy conc.

$[V^*_O]$ bulk

Figure 3-4 Schematics of the transport equilibrium and the vacancy distribution within the solids.

Within the majority part of the OCs, the defect formation free energy, $\mu^0_{V^*} = \mu^0_{O^*} - \mu^0_{O^*}$, and $\mu^0_{e} = \mu^0_{Ce^*} - \mu^0_{Ce^*}$, remain mostly constant, with the only exception near the surface, where the defect formation energy can be dramatically lower [5-8], resulting in a pronounced surface defect.
segregation phenomenon. The underlying reasoning is explained here using ceria as an example. Creation of one vacancy in the bulk phase involves breaking up 4 Ce-O bonds, but fewer on the surface; therefore defects are more energetically favored on the surface. The vacancy-induced relaxation is more pronounced in the bulk, because more adjacent atoms are relaxed, and the relaxation from its dense-packed crystal is more dramatic. Therefore, for the transport equilibrium of oxygen vacancy between the surface and bulk,

\[ V_{O}^{*} (bulk) - O_{O}^{0} (bulk) \leftrightarrow V_{O}^{*} (surface) - O_{O}^{0} (surface) \] (3.25)

\[ \Delta \mu_{V}^{0} = \mu_{V}^{0}\bigg|_{surface} - \mu_{V}^{0}\bigg|_{bulk} = \Delta h_{V}^{0} - T \Delta s_{V}^{0} \] (3.26)

both \( \Delta h_{V}^{0} \) and \( \Delta s_{V}^{0} \) are negative. Similar conclusions can be drawn for the transport equilibrium of electrons, with \( \Delta h_{e}^{0} < 0 \) and \( \Delta s_{e}^{0} < 0 \), as experimentally observed in ref. [9]. The surface-bulk segregation effect is important in a process controlled by the surface kinetics, as the more pronounced surface defect concentration plays a critical role in the redox reactions.

3.2.3 Phase equilibrium

In the system of NiO/Ni for CLC, phase equilibrium can be established between the nickel core and the nickel oxide scale. Each phase at the interface possesses a mixture of elements \([1, 10]\): Ni possesses a finite solubility of oxygen (NiO\(_{6}\), \( \delta \ll 1 \)), and NiO possesses a finite amount of extra nickel (Ni\(_{1+\epsilon}O\), \( |\epsilon| \ll 1 \)). The phase equilibrium dictates that at thermodynamic equilibrium the chemical potential of nickel must be identical in either phase:

\[ \text{Ni in "NiO"} \leftrightarrow \text{Ni in "Ni"} \] (3.27)

Or equivalently,

\[ Ni_{Ni}^{*} \leftrightarrow Ni + V_{Ni}^{*} + 2h^{*} \] (3.28)
Here Ni denotes nickel atom in nickel core. The equilibrium relation thus yields\(^7\),

$$\left[ \frac{Y_{Ni}^n}{[Ni_{Ni}]} \right] = \exp \left( -\frac{\mu_{NiO-Ni}}{k_B T} \right)$$  \hspace{1cm} (3.29)

In the case where the NiO phase is also in equilibrium with the external gas environment, eqs. (3.19) and (3.29) are coupled to determine the equilibrium state of the triple-phase (Ni, NiO, gas) system.

### 3.3 Defect surface chemistry

Surface chemistry takes place under off-equilibrium conditions. The intrinsic rate of reaction (unit, mole m\(^{-2}\) s\(^{-1}\)) for eq. (3.1) can be written as:

$$r = S_{oc} \hat{\rho}_{OC,s} \left( k_f p_A [B]^n - k_b p_D [C]^m \right)$$  \hspace{1cm} (3.30)

where \(k_f\), \(k_b\) are the rate coefficient for the forward and the backward reactions (unit, s\(^{-1}\)), following a general Arrhenius express. \(S_{oc}\), \(\hat{\rho}_{OC,s}\) are the surface area (m\(^2\)), and the surface molar density (mole m\(^{-2}\)). \(p_A\) and \(p_D\) are partial pressure of reactant and product. B, and D in brackets denote the solid species fraction on the surface. The terms enclosed in the parenthesis represent the off-equilibrium bias, which drives the surface chemistry. In case of a first-order irreversible reaction, with kinetics controlled conversion, eq. (3.30) can be simplified and connected with the bulk phase oxygen carrying capacity, as

$$- \frac{1}{\nu} \frac{dN_B}{dt} = S_{oc} \hat{\rho}_{OC,s} k_f p_A (1 - X_B)$$  \hspace{1cm} (3.31)

\(^7\) Here we use the fact that the activity of nickel in nickel phase is (almost) unity.
where $N_B$ is the total moles of $B$, i.e., $N_B = (1 - X_B) \hat{\rho}_{oc} S_{oc} d_{oc}$, for OC grain with size of $d_{oc}$, and a molar density of $\hat{\rho}_{oc}$ (moles m$^{-3}$). $X_B$ is the conversion of solid. After integrating eq. (3.31), we obtain the characteristic conversion time under simple kinetics control as:

$$-\ln(1 - X_B) = t / \tau_r, \quad \tau_r = \frac{d_{oc}}{av k_f p_A} \tag{3.32}$$

where $a$ is the lattice constant of surface unit cell, i.e., $\hat{\rho}_{oc,s} = a \hat{\rho}_{oc}$. 

![Figure 3-5 Schematic illustrations of the adsorption and dissociation processes for (a) NiO reduction with CH$_4$ (b) Ni oxidation with air](image)

As the reactant approaches the grain surface, gaseous molecules adsorb onto the lattice crystals, dissociate, and catalyze on the metal ion along the surface. The activated gaseous species on the surface enables succeeding charge transfer and desorption processes. This process is schematically depicted in Figure 3-5. For adsorption to occur spontaneously, a net decrease in free energy is required, in addition to the decrease of entropy; thus the adsorption process is always exothermic and hence favored at low temperature \[10\]. The heat of adsorption is typically a few eV (e.g., around $-2$ eV for H$_2$O \[11\] and $-2.3$ eV for CO \[12\] on CeO$_2$). The detailed
adsorption and dissociation processes are complicated [13-15], and highly dependent on the
types of vacancies [16], surface orientation [17, 18], the sequence of the charge transfer [16, 19],
etc. For the sake of kinetics modeling, a two-step Eley-Rideal type mechanism is usually
adequate for capturing the essence of the surface dynamics with the formation of adsorbates:

\[
A \text{ (g)} + S \text{ (s)} \leftrightarrow AS \text{ (s)} \quad (3.33)
\]

\[
r_1 = S_{\infty} \hat{\rho}_{\infty,s} \left( k_{1,f} P_A[S] - k_{1,b} [AS] \right) \quad (3.34)
\]

\[
AS \text{ (s)} + \nu_r B \text{ (s)} \leftrightarrow \nu_p C \text{ (s)} + D \text{ (g)} \quad (3.35)
\]

\[
r_2 = S_{\infty} \hat{\rho}_{\infty,s} \left( k_{2,f} [AS][B]^\nu - k_{2,b} [C]^\nu P_D \right) \quad (3.36)
\]

where \( S \) is an active site for adsorption, and \( AS \) represents the adsorbate. \( k_{1,f}, k_{1,b} \) are the forward
and backward rate constant of reaction, respectively. In the case of CL \( \text{H}_2\text{O}/\text{CO}_2 \) splitting, eq.
(3.33) may represent \( \text{H}_2\text{O}/\text{CO}_2 \) adsorption over surface oxygen vacancy (with \( S \) denoting oxygen
vacancy) with the formation of hydroxyls or carbonates, while eq. (3.33) is the following charge
transfer step (with \( B \) being the electrons). In the case of nickel reduction in CLC, \( S \) may
represent nickel nuclei for adsorption of fuel or \( \text{O}_2 \). If we further assume that the adsorbate, \( S \), is
in quasi-steady state,

\[
\frac{d[AS]}{dt} = \left( k_{1,f} P_A[S] - k_{1,b} [AS] \right) - \left( k_{2,f} [AS][B]^\nu - k_{2,b} P_D [C]^\nu \right) \approx 0 \quad (3.37)
\]

which yields:

\[
[AS] = \frac{k_{1,f} P_A[S] + k_{2,b} P_D [C]^\nu}{k_{1,b} + k_{2,f} [B]^\nu} \quad (3.38)
\]

\[
\frac{r}{\hat{\rho}_{\infty,s} S_{\infty}} = \frac{k_{1,f} k_{2,f} P_A[S][B]^\nu - k_{1,b} k_{2,b} P_D [C]^\nu}{k_{1,b} + k_{2,f} [B]^\nu} \quad (3.39)
\]
In the case with a much faster adsorption reaction, eq. (3.39) is reduced into eq. (3.30) with \( k_f = K_1 k_2 S \), where \( K_1 = k_{f,1}/k_{f,2} \). If we further assume that the total number of active sites (including empty and occupied sites) is constant, thus the fraction of \( AS \) or \( S \) follows a Langmuir isotherm:

\[
[AS] = \frac{K_1 p_A}{K_1 p_A + 1}, \quad [S] = \frac{1}{K_1 p_A + 1}
\]

(3.40)

The net rate of reaction, eq. (3.39), thus becomes:

\[
\frac{r}{\hat{\rho}_{oc,s} S_{oc}} = \frac{K_1 k_{2,f} p_A [B]^\nu}{K_1 p_A + 1} - k_{2,b} P_D [C]^\nu
\]

(3.41)

In comparison to eqs. (3.30)-(3.32), eq. (3.41) reveals that the reaction rate may saturate at high \( p_A \), owing to the limited number of active surface sites for adsorption. The characteristic time of conversion for an adsorption controlled process may be written in the following revised form:

\[
\tau_{\tau, ads} = \frac{d_{oc} (K_1 p_A + 1)}{av \sqrt{K_1 k_{2,f} p_A}}
\]

(3.42)

Eqs. (3.39) and (3.41) will be used in later chapters in the modeling of ceria-based, and nickel-based reactions, respectively.

### 3.4 Transport mechanism

Transport of species is driven by the spatial gradient of chemical potentials. Both gas-phase diffusion and solid state diffusion take places in the reactor.

#### 3.4.1 Gas phase diffusion

Gas phase diffusion is mainly composed of the external diffusion and the internal diffusion, as shown schematically in Figure 3-6. As shown in panel (a), in the process controlled by external
diffusion, the concentration of gaseous reactant drops from its bulk value to zero within the gas film adjacent to OC. In this case, the rate of OC conversion can be expressed as:

$$-\frac{1}{v_r} \frac{dN_B}{dt} = S_{oc} h_m C_A, \quad X_B = t / \tau_{d.conv}, \quad \tau_{d.conv} = \frac{\rho_B d_{sc}}{v_r h_m C_A}$$

(3.43)

where $X_B$ is the conversion of solid OC, $C_A$ is the concentration of A, and $h_m$ is the mass transfer coefficient, estimated from Sherwood number, i.e., $h_m = Sh_d D_M/d_h$, where $d_h$ is the hydraulic diameter.

Figure 3-6 Schematic illustrations of the reacting OC under the control of (a) the external diffusion, (b) the internal diffusion.

In the case that internal diffusion controls (panel (b)), a slowly shrinking unreacted core is expected, inside which the solid reactant B remains unreacted. The rate of conversion follows the famous Wagner’s parabolic scaling theory [20]:

$$-\frac{1}{v_r} \frac{dN_B}{dt} = S_{in} D_{e} \frac{C_A}{(d_{sc} - z_{un})}, \quad X_B^2 = t / \tau_{d,gas}, \quad \tau_{d,gas} = \frac{\rho_B d_{sc}^2}{2v_r C_A D_{e}}$$

(3.44)
where $z_{un}$ is the thickness of unreacted core, and $D_e$ being the effective diffusivity.

The design of the button-cell reactor system, the selection of the OC samples and the test conditions ensure that the gas-phase diffusion is much faster as compared to the intrinsinc chemistry, thus leaving the gas-phase diffusional resistance outside the modeling framework. Eqs. (3.43) and (3.44) are used to evaluate the gas-phase mass-transfer resistances.

---

3.4.2 Solid state diffusion

The formation of solid product (metal for reduction and metal oxidation for oxidation) separates the reactants (gas and solid), and hence further conversion requires the solid state diffusion of reactants through the product layer (Figure 3-7): driven by the chemical-potential gradients, the adsorbed ions (e.g. $H^+$, $O^{2-}$) may transport into the grain lattice via defects to the unreacted core surface; the ions within the core (i.e., $Ni^{2+}$, $Ce^{3+}$, $O^{2-}$) may migrate outwards across the product
layer, and enter the gas-solid surface to form chemical bonds with the adsorbed molecules. Using the oxygen-deficient OC (i.e., ceria) as an example, the bulk-phase defect diffusion may be described as:

\[
\frac{\partial C_{i}^{\ast}}{\partial t} + \frac{\partial J_{i}^{\ast}}{\partial x} = 0
\]

(3.45)

\[
\frac{\partial C_{e_1}}{\partial t} + \frac{\partial J_{e_1}}{\partial x} = 0
\]

(3.46)

where \( C_i \) is the molar concentration, and \( J_i \) the flux of the defect. The flux densities are expressed using the Nernst-Planck equation:

\[
J_{i}^{\ast} = -\frac{C_{i}^{\ast} D_{i}^{\ast}}{k_B T} \frac{\partial \tilde{\mu}_i}{\partial x}
\]

(3.47)

\[
J_{e_1} = -\frac{C_{e_1} D_{e_1}}{k_B T} \frac{\partial \tilde{\mu}_e}{\partial x}
\]

(3.48)

where \( D_i \) is the diffusion coefficient, \( R \) the universal gas constant, and \( T \) the temperature. \( \tilde{\mu}_i \) and \( \tilde{\mu}_e \) are the electro-chemical potential of vacancy and electron defects, respectively, which can be expressed as (similarly as in eq. (3.14)):

\[
\tilde{\mu}_i = \tilde{\mu}_{i_0} - \tilde{\mu}_{o_0}
\]

(3.49)

\[
\tilde{\mu}_e = \tilde{\mu}_{e_1} - \tilde{\mu}_{e_1}
\]

(3.50)

Substituting eqs. (3.13) and (3.15) yields

\[
\frac{\partial [V_{o}^{\ast}]}{\partial t} = \frac{\partial }{\partial x} \left[ \frac{[V_{o}^{\ast}] D_{o}^{\ast}}{k_B T} \left[ \frac{\partial \left( \mu_{i_0}^0 - \mu_{o_0}^0 \right)}{\partial x} + k_B T \frac{\partial \ln \left[ \frac{[V_{o}^{\ast}]}{[O_{o}^{\ast}]} \right]}{\partial x} + 2e \frac{\partial \phi}{\partial x} \right] \right]
\]

(3.51)

\[\text{In fact, for p-type metal-deficient oxide (e.g., oxide of nickel, copper, iron), anion diffusion is slow, and usually cation diffusion dominates the transport process, while for n-type oxygen-deficient oxide (e.g., ceria), anion diffusion is the dominating mass transfer mechanism. The conduction mechanism can switch from p-type to n-type (or vice versa) depending on the operating conditions.}\]
Further coupled with Poisson equation for the electrostatic field,

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \phi}{\partial r} \right) = -\rho e \left( 2[V_o^{**}] - [C'_{Ce}] \right)$$  \hspace{1cm} (3.53)

Eqs. (3.51)-(3.53) formulate the complete description of the defect transport. In the case with defect at dilute limit ([V_o^{**}], [C'_{Ce}] < 1), and in the region away from the surface double layer with constant defect formation free energy, we can re-write the above equations as

$$J_{V_o} = \frac{\hat{\rho}_{OX} [V_o^{**}] D_{V_o}}{k_B T} \left[ k_B T \frac{\partial}{\partial x} \ln[V_o^{**}] + 2e \frac{\partial \phi}{\partial x} \right]$$  \hspace{1cm} (3.54)

$$J_{C'_{Ce}} = -\frac{\hat{\rho}_{OX} [C'_{Ce}] D_{C'_{Ce}}}{k_B T} \left[ k_B T \frac{\partial}{\partial r} \ln[C'_{Ce}] - e \frac{\partial \phi}{\partial x} \right]$$  \hspace{1cm} (3.55)

If we further assume electro-neutrality (charge neutral and zero net current), and hence eliminate the electrostatic potential, we obtain the classic Fick’s law of diffusion:

$$J_{V_o} = -\tilde{D} \frac{\partial C_{V_o}^{**}}{\partial x}, \text{ where } \tilde{D} = \frac{3D_{V_o} D_{C'_{Ce}}}{D_{C'_{Ce}} + 2D_{V_o}}$$  \hspace{1cm} (3.56)

$\tilde{D}$ is the chemical (or ambipolar) diffusion coefficient. Similar expression can be obtained for nickel oxidation:

$$J_{V_{Ni}} = -\tilde{D} \frac{\partial C_{V_{Ni}}^{**}}{\partial x}, \text{ where } \tilde{D} = \frac{3D_{V_{Ni}} D_{V_{Ni}}}{D_{V_{Ni}} + 2D_{V_{Ni}}}$$  \hspace{1cm} (3.57)

At quasi-steady state under the control of bulk-phase diffusion, the growth of oxide scale also follows the parabolic scaling law [20]:
\[ X_{\text{eff}}^2 = t / \tau_{d,\text{bulk}} \times \tau_{d,\text{bulk}} = \frac{\bar{p}_n d_g^2}{2 \nu C_A D} \] (3.58)

Eq. (3.58) shares exactly the same expression as with eq.(3.44). Indeed, the collapse and clustering of metallic nuclei [14] and the associated growth stresses between the unreacted core and the product layer [21] may form cracks, voids and hence porous product layers, enabling both gas-phase diffusion and the solid-state diffusion. Additionally, higher dimensional defects (line defect or grain boundary defect) enables short-circuit solid-state diffusion: diffusion along the grain boundaries (characteristic time, \(\tau_{d,\text{gb}}\)) can be order-of-magnitude faster than the bulk-phase ambipolar diffusion (\(\tau_{d,\text{bulk}}\)), leading to much accelerated scale growth rate. Figure 3-8 schematically illustrates these different diffusion pathways in the case of nickel oxidation.

![Figure 3-8 Schematic description of different diffusional pathways](image)

Modeling the hybrid diffusion process usually assumes that different diffusional pathways proceed in parallel, thus the effective growth rate follows [10]:

\[
\frac{1}{\tau_{d,\text{effective}}} = \frac{f_{\text{gas}}}{\tau_{d,\text{gas}}} + \frac{f_{\text{gb}}}{\tau_{d,\text{gb}}} + \frac{1 - f_{\text{gas}} - f_{\text{gb}}}{\tau_{d,\text{bulk}}}
\] (3.59)

where \(\tau_{d,\text{effective}}\) is the effective conversion characteristic, and \(f_i\) is the volume fraction of different diffusional pathways. The evolution of each pathway with conversion is determined by the structural evolution, as addressed next.
3.5 **Structural evolution**

As conversion proceeds, the structures of the OC evolve with time, resulting from sintering and the stresses associated with migration and agglomeration of ions. The structural evolution in the case of ceria leads to an enlarged particle but maintains the cubic fluorite phase and crystal structure. In the case with doped-ceria [9] or LSCF-based perovskites (see Chapter 11), the redox cycling may also cause a phase segregation near the surface, leading to element enrichment (or depletion), resulting from the differences in the elastic ($\mu^0$ in eq.(3.13)) and electrostatic ($ze\phi$, as in eq. (3.15)) driving forces between the dopant and the OC. In the case of nickel, phase change accompanies the conversion, leading to dramatic morphological and structural changes. These factors significantly influence the redox kinetics, and their contributions must be carefully addressed in the kinetics study.

3.5.1 Particle enlargement and cyclic repeatability

For ceria-based samples, particle enlargement is observed after redox cycling, resulting from a thermal sintering effect. Figure 3-9 shows the SEM images of the fresh (panel a) and aged (panel b) CeO$_2$ nano-powder. Therefore, before taking redox measurements, the samples are pre-treated at highest operating temperature for adequate cycles till cyclic stable kinetics is obtain, allowing for sufficient material degradation and structural relaxation. Particle size ($d_{oc}$) and surface area ($S_{oc}$) after pretreatment are carefully measured and used for the kinetics modeling.

3.5.2 Morphological and structural changes
The structural evolutions during nickel redox reactions are related to the structural difference between metal and oxide. Pilling and Bedworth rule [22], defined as the ratio between the molar volume of oxide and that of metal, is commonly used to categorize the chemical stresses,

\[ \text{PBR} = \frac{V(\text{NiO})}{V(\text{Ni})} = 1.65 > 1 \]  

(3.60)

Thus, compressive stresses develop and a protective oxide is formed over nickel core during oxidation. With the growth of oxide grain, the fast diffusional pathway along the dislocations or grain boundaries are significantly attenuated, leading to a more rapid decrease in the reaction rate as opposed to the parabolic law. This effect is attributed to the diminishing fast diffusional paths, resulting from the growth of oxide grain. To model this, the volume fraction of grain boundary, \( f_{gb} \), can be related to the oxide grain size, \( D \), as,

\[ f = 2d_{gb} / D, \quad D^2 = D_0^2 + \frac{(t-t_0)}{\tau_{d,\text{grain}}} \]  

(3.61)

where \( d_{gb} \) is the width of grain boundary. Here \( D \) is assumed to grow following a parabolic law. With the use of characteristic grain growth constant, \( \tau_{d,\text{grain}} \), the grain growth with diminishing
fast paths can thus be modeled semi-empirically. Under repeated cycling, cracks and voids are formed, which also shrink and disappear. Similar methods can be used for the modeling of $f_{gas}$.

The reduction of nickel, on the other hand, leads to an increasing number of nickel nuclei, which acts as an active site for surface adsorption. As a result, an autocatalytic process of NiO reduction has been observed, especially at low temperature, where NiO slowly reacts to form metallic nickel nuclei, which leads to autocatalytic fuel conversion [23, 24]. Semi-empirical models, such as Avrami-Erofeev Model (AEM) [25] is commonly suggested to model the evolution of surface sites with conversion.

3.5.3 Phase segregation and transformation

In the case of CL H$_2$O/CO$_2$ splitting using LSCF-based perovskite, we observe the phase transformation during redox reactions to Ruddlesden-Popper (RP) phase, and eventually to Co/Fe oxides at large nonstoichiometry. Phase segregation is also observed, with large variations of chemical composition across the OC sample. The modeling of this effect is not included in this thesis, and will require further study.

3.6 Summary

The modeling framework for the redox reactions of ceria-, and nickel-based systems is summarized below. In the following chapters, the kinetics modeling for each OC material follows the general modeling framework, with modified derivations to account for the process under the control of one or a few specific key steps.
Equilibrium

O-deficient OC (ceria): \( O_0^* + 2Ce_{Ce}^x \overset{\text{cera}}{\longleftrightarrow} \frac{1}{2} O_2 + V_{O}^{**} + 2Ce_{Ce}^\prime \)  \( \text{(3.16)} \)

\[
\frac{p_{O_2}^{1/2} \left[ V_{O}^{**} \right] [Ce_{Ce}^\prime]^2}{\left[ O_0^* \right] [Ce_{Ce}^x]^2} = K_{\text{cera}} = \exp \left( - \frac{\mu_{\text{cera}}^0}{RT} \right) \tag{3.17}
\]

cation-deficient OC (NiO): \( \frac{1}{2} O_2 \overset{k_{\text{cact}}}{\longleftrightarrow} O_0^* + V_{Ni}^* + 2h^* \)  \( \text{(3.18)} \)

\[
\frac{\left[ O_0^* \right] [V_{Ni}^*] [h^*]^2}{p_{O_2}^{1/2}} = K_{\text{nichel}} = \exp \left( - \frac{\mu_{\text{nichel}}^0}{RT} \right) \tag{3.19}
\]

Surface Chemistry

\( A \ (g) + S \ (s) \leftrightarrow AS \ (s) \)  \( \text{(3.33)} \)

\[
\begin{align*}
    r_1 &= S_{\alpha_c} \hat{\rho}_{\alpha_c} \left( k_{1_f} p_A [S] - k_{1_b} [AS] \right) \\

    AS \ (s) + v_t B \ (s) &\leftrightarrow v_p C \ (s) + D \ (g) \text{ (3.35)}
\end{align*}
\]

\[
\begin{align*}
    r_2 &= S_{\alpha_c} \hat{\rho}_{\alpha_c} \left( k_{2_f} [AS][B]^r - k_{2_b} [C]^r p_D \right)
\end{align*}
\]

Transport

\[
\frac{\partial [V_{O}^{**}]}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{[V_{O}^{**}] D_{V_{O}}}{k_B T} \left[ \frac{\partial \left( \mu_{V_{O}}^0 - \mu_{O_0}^0 \right)}{\partial x} + k_B T \frac{\partial}{\partial x} \ln \left[ \frac{V_{O}^{**}}{O_0^*} \right] + 2e \frac{\partial \phi}{\partial x} \right] \right\} \tag{3.51}
\]

\[
\frac{\partial [Ce_{Ce}^\prime]}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{[Ce_{Ce}^\prime] D_{Ce_{Ce}}}{k_B T} \left[ \frac{\partial \left( \mu_{Ce_{Ce}}^0 - \mu_{Ce_{Ce}^x}^0 \right)}{\partial x} + k_B T \frac{\partial}{\partial r} \ln \left[ \frac{Ce_{Ce}^\prime}{Ce_{Ce}^x} \right] - e \frac{\partial \phi}{\partial x} \right] \right\} \tag{3.52}
\]

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( \varepsilon r^2 \frac{\partial \phi}{\partial r} \right) = -\bar{\rho} e \left( 2[V_{O}^{**}] - [Ce_{Ce}^\prime] \right) \tag{3.53}
\]

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Structural evolution

\[
\frac{1}{\tau_{d,\text{effective}}} = \frac{f_{\text{gas}}}{\tau_{d,\text{gas}}} + \frac{f_{\text{gb}}}{\tau_{d,\text{gb}}} + \frac{1-f_1-f_2}{\tau_{d,\text{bulk}}} \tag{3.59}
\]

\[
f_i = 2d_i / D, \quad D^2 = D_0^2 + \frac{(t-t_0)}{\tau_{d,\text{grain}}} \tag{3.61}
\]

3.7 Bibliography

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Chapter 4

Redox Study of Nickel Foils for Chemical-looping Combustion: Kinetics and Structural Evolution

This chapter presents a detailed redox study of thin nickel foils with an emphasis on the structural evolution and the connection to the measured redox kinetics, applicable towards CLC. Pure nickel thin foils are tested in the temperature range 800-1000°C. Samples with different thicknesses (2.5 μm, 10 μm, and 100 μm) are subjected to alternate redox cycles using synthetic air (O₂+Ar) and H₂/Ar mixture respectively. SEM images clarify the stages and key features of the redox conversion. The oxidation starts via the anisotropic nucleation of the oxide grains, followed by a rapid growth of the grain driven by the short-circuit diffusion of Ni ions. As the oxide grains overlap and saturate the surface, the defects are annihilated and the fast diffusion paths are attenuated. Large faceted oxide grains are formed over the fully oxidized surface of thick foils, while the thin foils are more irregular loosely packed with smaller cellular-like grains, rich with defects which facilitate the reactions. The reduction process is initiated by the loss of oxygen atom on the outer surface, forming dense nickel clusters blocking the interior NiO. Macropores are also formed on the surface to accommodate the volume loss due to density differential between NiO and Ni, and collapse to form larger voids providing the direct gas-diffusion passages. Redox reactivity is measured in real-time using an on-line quadrupole mass-spectrometer (QMS). The oxidation rate is found to be 3-5 times faster as compared to reduction,
and is highly sensitive to O₂ concentration, but only weakly depends on the temperature. The oxidation undergoes three stages: (1) fast surface reaction stage; (2) surface assisted diffusion stage; and (3) slow bulk diffusion stage. The reduction is more sensitive to temperature but almost independent of the H₂ concentration. A nucleation-growth model is developed to characterize the oxidation process. The model reveals that the growth of the oxide grain follows a parabolic law, with the rate constant decreasing remarkably during the early stage I. The observed structural difference among the three foils contributes to the difference in the oxide grain growth. The reduction is characterized as a one-step reaction, with the consideration of the adsorption/desorption process, and the decreased accessibility of the residual oxygen. The model reveals that the surface of nickel is nearly completely saturated with adsorbed hydrogen, and the reaction is less affected by H₂O. The activation energy is found to be 20kJ/mol for oxidation and 30kJ/mol for reduction. The results establish a baseline for developing supported nickel oxygen carrier, and also provide guidance for the design and the practical application of the chemical-looping technology.

4.1 Introduction

Previous studies have showed that the characteristics of the OCs are critical in determining the performance of the CLC reactor. Parametric study (ref. [1]) on nickel-, copper-, and iron- based designs concluded that nickel exhibits key advantages, such as its fast kinetics at low operating temperature, and large oxygen carrying capacity. However, detailed knowledge of the reduction and oxidation (redox) kinetics of Ni, the structural evolution, and the operational stability is still lacking.
The redox process of pure nickel is considered as one of the simplest examples of high-temperature corrosion/reduction of pure metals. Many previous works were devoted to this model system with a focus on metallurgical applications and catalyst characterization [2-8]. Despite the apparent simplicity, the conversion process involves complex morphological and structural evolutions and many parameters, such as surface treatment, structural support, metal purity, and surface orientation are known to greatly affect the redox kinetics [5]. Advanced in-situ techniques, such as in-situ X-ray diffraction [9], environmental transmission electron microscopy (TEM) [10, 11], and full-field transmission X-ray microscopy [12], have been developed lately to examine the different stages of the redox conversion. Nevertheless, important questions still remain, mostly regarding the microstructural evolution and its connection to rate-controlling mechanism. Moreover, most of these studies worked with the fresh or pre-treated samples with an emphasis on the long-term corrosion-resistance behavior. The redox chemistry under fast redox cycling (CLC) is still not well understood.

Recently, there is a growing effort towards a better understanding of the nickel redox kinetics under fast cycling, originating from the growing interests in CLC. Several studies have examined suitable nickel/support combinations for the fluidized-bed operations and have measured the kinetics under relevant conditions [13-24]. A variety of physical models have been tested to describe the redox process (e.g., shrinking core model, Avrami model, etc, [24]). The obtained kinetics, however, scatter over an order of magnitude, between 7 to 131 kJ/mol for oxidation, and 5 to 96 kJ/mol for reduction (Table 4-1). The discrepancy may largely result from the inconsistency between the sample pre-treatment, microstructure and surface morphology, as well as the characterization and modeling techniques. Simple models, such as shrinking core model,
or Avrami model, may break down especially at the initial stage of conversion where the microstructure of scale is highly complex and the interplay between surface kinetics and different fast-diffusion pathways is of remarkable importance. An in-depth understanding of the characteristic features of NiO/Ni microstructure, subsequent structural evolution, and its relation to the rate-controlling chemistry is necessary.

Thus, the objectives of this chapter are to explore the structural evolution of the nickel-OC and its relationship to the surface chemistry, to extract the redox kinetics under CLC-relevant conditions, and to examine the effect of the redox pre-treatment on the conversion process. Pure nickel thin foils are tested in a button cell reactor in the temperature range 800-1000°C. The usage of nickel thin foils enables direct observations of the grain growth and evolution, and effectively isolates the intrinsic chemistry from the external effects, such as gas-phase diffusion,

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Equipment</th>
<th>Temperature</th>
<th>Reduction (H₂)</th>
<th>Oxidation (O₂)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
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<td>-</td>
<td>2.4</td>
</tr>
<tr>
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<td>TGA</td>
<td>750°C</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
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<td>TGA</td>
<td>600-950°C</td>
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<td>7</td>
</tr>
<tr>
<td>MgAl₂O₄</td>
<td>TGA</td>
<td>800-1000°C</td>
<td>-</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>TPR, TPO</td>
<td>200-700°C</td>
<td>53</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
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<td>TPR, TPO</td>
<td>200-700°C</td>
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<tr>
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</tr>
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<td>20</td>
<td>0.8</td>
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<tr>
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<td>800-950°C</td>
<td>5</td>
<td>0.4</td>
<td>22</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>TGA</td>
<td>800-950°C</td>
<td>5</td>
<td>0.4</td>
<td>22</td>
</tr>
</tbody>
</table>
or particles agglomeration, and synergy effect, thus leading to an in-depth understanding of the conversion stages and redox fundamentals. Samples with different thicknesses (2.5 μm, 10 μm, and 100 μm) are subjected to alternate redox cycles using synthetic air (O₂+Ar) and H₂/Ar mixture respectively. H₂ is used as the reducing gas instead of CH₄ to rule out coke formation. The reaction kinetics was determined by quantifying the flue stream composition using an on-line quadrupole mass-spectrometer (MS). The microstructures of the Ni foils were examined using SEM before and after reactions. Kinetic models have been developed to describe the structural evolutions during the redox process. The effect of the thickness on the reaction rates and the structural changes of samples are explored. The obtained results on the redox kinetics and cyclic regenerability of the nickel OC provide critical insights towards the design, fabrication, and optimization of the OC for CLC.

4.2 Experiment

The experimental setup consists of a gas delivery system, a control unit, a central quartz reactor tube, and a real time flue gas analysis system with an on-line mass-spectrometer. The schematics of the system layout are shown in Figure 2-2 and Figure 2-6. Commercial high purity (99.95% purity) nickel foils from Sigma Aldrich are used as the OC. Three different thicknesses are tested: 2.5 μm, 10 μm, and 100 μm. Key properties of the nickel sample are summarized in Table 4-2. In each test, pure nickel foil samples are placed vertically, embedded in quartz wool in the expanding section of the inlet tube. Fuel (H₂/Ar mixture) and air (synthetic) are alternately introduced into the reactor, with concentration varying between 2% and 8%. The total flow rate into the reactor is maintained constant at 250 sccm (standard cm³ per min) for the base case. Each cycle follows a sequence of oxidation (10 min), purging (10 min), reduction (30 min), and
purging (10 min). In each reaction phase, the MS measures the flue gas species composition for the initial 10 min, after which the reactivity approaches zero. To ensure sufficient regeneration, the reduction is continued for an additional 20 min before the next cycle. The evolution of the sample microstructure is examined using JEOL 6700 SEM after reactions.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of foils</td>
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</tr>
<tr>
<td>Number of foils</td>
<td>20</td>
</tr>
<tr>
<td>Weight of fresh samples</td>
<td>22 mg</td>
</tr>
<tr>
<td>Diamete, ( d_{foil} )</td>
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</table>

<table>
<thead>
<tr>
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<th>Value</th>
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</thead>
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</tr>
<tr>
<td>Molar density, ( \bar{\rho}_{Ni} )</td>
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</tr>
<tr>
<td>Lattice constant</td>
<td>0.352 nm</td>
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<tr>
<td>Melting point</td>
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<tr>
<td>Oxidation energy, ( \Delta h^{0}_{ox} )</td>
<td>-239.70 kJ/mol Ni</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxidized NiO</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, ( \rho_{NiO} )</td>
<td>6.67 g cm(^{-3} )</td>
</tr>
<tr>
<td>Molar density, ( \bar{\rho}_{NiO} )</td>
<td>( 8.93 \times 10^4 ) mol m(^{-3} )</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>0.4176 nm</td>
</tr>
<tr>
<td>Melting point</td>
<td>1955 °C</td>
</tr>
<tr>
<td>Reduction energy, ( \Delta h^{0}_{red} )</td>
<td>-2.1 kJ/mol NiO</td>
</tr>
</tbody>
</table>

The redox cycles modify the sample micro-structure (as shown in the next section), and as a result, the measured reaction rates vary during the initial several cycles. Figure 4-1 shows the oxidation of the 10 μm samples for the initial 50 cycles. Panel a compares the measured O\(_2\) concentration with varying cycles, and panel b shows the evolution of the total O\(_2\) consumption. The O\(_2\) consumption rate increases remarkably during the initial 3 cycles for a fresh sample, decreases rapidly over the following 10-15 cycles, and eventually stabilizes after 20 cycles. Thereafter, the measured concentration profiles overlap, and the difference is within noise level. Therefore, the nickel samples are pre-treated for at least 50 cycles at 1000°C to reach periodic stationary states. Afterwards, the measurements are taken starting from 1000°C till 800°C with a step of 100°C. Each operating condition is repeated for at least five times, and the results are
averaged to reduce the noise. Experiments with different oxidation and reduction conditions are also carried out to evaluate their effects on the redox reactivity.

![Image](https://via.placeholder.com/150)

**Figure 4-1** Cyclic measurement of (a) $O_2$ concentration and (b) total $O_2$ consumption for 50 cycles. Gray lines in panel b are for guiding the eyes.

### 4.3 Structural and Surface Evolution

Figure 4-2 shows images of nickel samples before and after 50 redox cycles. Morphological and structural changes are evident: the redox cycles reshape the samples (panels b-c), form macrostructures (panels d-e), and bring the samples into a new cyclic equilibrium state between reduction and oxidation. The 2.5μm foil crumbles and forms the skeleton structures with cross patterns. The metallic nickel (panel b) agglomerates and forms thin layers wrapping over the quartz wool rods, leaving open voids formed in between. The thin film (panel c) becomes highly convoluted, twisted, and completely embedded within the quartz wool. For the 10 μm samples, the diameter shrinks and the surface wrinkles, but the foil stays mostly in its disk shape. The 100 μm foils, in contrast, remain mostly intact after repeated cycles (panels f-g), although the surface becomes less smooth. The redox cycles are further repeated up to 100 cycles, and the
morphology of the samples remains the same. All nickel samples are confined within the quartz wool and no loss of samples is observed.

Figure 4-2: Images of nickel foil samples. Panel (a) shows the fresh 10 µm foils before reactions. Images on the right side show the samples with thickness of 2.5 µm (b, c), 10 µm (d, e), and 100 µm (f, g) after 50 redox cycles. The top panels (b, d, f) are reduced samples before a redox cycle, and the bottom panels (c, e, g) are after 10 min oxidation.

Figure 4-3(a)-(c) examine the surface of the 2.5 µm, 10 µm, and 100 µm foils after 10 min oxidation. Panels (d)-(f) are a further zoom-in near grain boundaries for each sample. Facetted oxide grains are randomly distributed on the surface with the size of 1-3 µm. Each grain exhibits layered structure with a series of edges in parallel. The boundaries between adjacent grains with different orientations lead to a short-circuit diffusional pathway, which enables a rapid growth of the scale during the initial stage of oxidation. Thick foils tend to develop large grains (~3 µm) with uniform, smooth and well-saturated surface. The grains are well connected and smoothly packed over the entire sample surface with fewer and thinner boundaries embedded slightly underneath the surface (panel f). In contrast, thin foil surface is highly irregular with smaller cellular-like grains (1-2 µm) loosely packed over the surface. With thin foils, the grains are less developed, with saw-toothed and fractured edges clearly observed on each grain surface (see
Grain boundaries are highly abundant, well dispersed and interconnected over the entire surface. Large pores and voids are also observed on thin foils (more evidently on the 2.5 µm sample), which directly expose its interior to the reacting environment. Similarly, Manukyan et al [7] observed pore-free facetted grains (size 1-3 µm) with saw-toothed grain edges for 100 µm nickel wire after 2.5 min oxidation at 1300°C. Peraldi et al [5] reported both porous cellular grains associated with a thin layer oxide (≤1 µm), and smooth facetted grains on a well-developed oxide scale (≥5 µm).

Figure 4-3 SEM images of (a) 2.5 µm, (b) 10 µm, and (c) 100 µm NiO after 10 min oxidation. Panels (d)-(f) are zoomed-in images on the edges and connections of the grains.

Figure 4-4 compares the internal microstructures of 2.5µm, 10µm, and 100µm nickel samples after 10 min oxidation. The oxidized foils are fractured and SEM images are taken on the cross-sections of the sample. The thickness of the 100µm remains almost unchanged, while that of 2.5 µm and 10µm sample foil almost doubles to about 5 µm and 20µm, respectively. Consequently,
the surface area of 2.5 µm and 10µm foils reduces. Thermal and chemical stresses generated during the repeated redox cycles lead to formation of a simplex porous structure with interconnected grains, similar to as reported in ref. [5]. Comparing to 2.5 µm foils, the internal structure of the 10µm sample is denser and more compact. Voids and cracks are formed near the center for the 2.5µm sample dividing the foil into two parts in symmetry, while a portion of the center of the 10µm foil remains relatively dense, connecting the scales on both sides. For 100 µm sample, however, the reactive area is mostly localized to the two sides of the foil, leaving the majority of the bulk intact. The oxide scales on each side are less than 5 µm in thickness, and are prone to break and peel off from the bulk phase resulting from the stresses associated with redox reactions.

Figure 4-4 Comparison of internal microstructures of (a) 2.5 µm, (b) 10 µm, and (c) 100 µm NiO after 10 min oxidation. Different scales are used for clarity.

Figure 4-5 shows the SEM images of the fully reduced surface. Similar structures are observed among different foils. Smooth nickel grains are observed with the size around 5~10 µm, larger and smoother as compared to the oxidized surface. Grains are slightly larger on the thin foils with the boundaries less defined, indicating stronger ionic migration and defect annihilation during the reduction. The pores and voids, on the other hand, are evident on the surface,
providing direct gas-phase diffusion paths. The size of pores ranges from 200 nm to 4 µm, and they are more abundant with the thinner foils.

Figure 4-5 SEM images of (a) 2.5 µm, (b) 10 µm, and (c) 100 µm Ni after fully regeneration.

Figure 4-6 illustrates the dynamic evolution of the surface morphology and microstructure for 100µm foil during one conversion (oxidation-reduction) cycle. The conversion starts with anisotropic growth of oxide grains over the nickel core (panels a-b). The grains are loosely packed over the nickel surface with the planer outer surfaces randomly oriented. Surface defects, grain boundaries, open pores and voids are abundant, which enable a rapid growth of oxide scale. As the oxidation continues, the grain overlaps and saturates the surface; the grain boundary saturated and defects are gradually annihilated. After 10 min, dense oxide scale is formed with well-developed oxide crystals covering the entire nickel core (panel c). The fast-diffusion paths are thus significantly attenuated, and the further growth of oxide is mainly constrained by the bulk phase diffusion of Ni^{2+}. Peraldi et al [5] reported a similar process where the oxidation starts with simplex microstructures with cavities and evolves into a dense and more compact structure.
Figure 4-6 Evolution of the surface morphology and micro-structures through one redox cycle for 100µm foil: (a) fully reduced, (b) 15 sec oxidation, (c) 10 min oxidation, (d) onset of reduction (~3 sec), (e) 15 sec reduction.

The reduction process is initiated by the loss of oxygen atom on the outer surface, leaving behind highly irregular surface with layered structures (see the edges in panel d). Macropores (50~100 nm) are formed to accommodate the volume loss that results from the reduction process. As reduction continues, metallic nickel nucleates and clusters to form nickel grains, smoothing out the irregular oxide grain surface (panel e). The formed nickel clusters inhibit the further conversion by blocking NiO from H₂. Pores collapse to form larger voids (100~200 nm) on the surface, which create the gas-diffusion passage into the interior. Eventually, the foil is completely reduced with large dense nickel grains covering the surface (panel a). Fewer large pores (>200 nm) are found on the reduced surface, as showed in Figure 4-5. Similar porous
structure and evolution paths were reported previously. Jeangros et al. [11] observed the formation of macropores which collapse and disappear with the conversion. Manukyan et al [30] reported the formation of mesoporous channels throughout nickel grains, more evidently at high temperature.

![SEM images of 10µm foil at (a) 15 sec oxidation, and (b) 15 sec reduction.](image)

Figure 4-7 SEM images of 10µm foil at (a) 15 sec oxidation, and (b) 15 sec reduction. The 2.5µm foil exhibits similar microstructures.

2.5 µm and 10µm foils undergo similar stages of redox conversion. However, important differences should be emphasized (Figure 4-7): the surface of thin foils becomes more convoluted during the conversion; layered or recessed surfaces are distributed and surrounded by interconnecting ridges and trenches (size ~ 100 nm). The ridges are found within the grain boundaries area and hence its occurrence is strongly dependent on the defect structures. Such oxide ridges were also observed previously [5, 31], and its growth is associated with a rapid outward diffusion process and an easier annihilation of defects near the grain boundaries. As a result, the abundance of defects on the thin foils facilitates the formation of this complex microstructure, in contrast to the smooth planer surfaces of the 100 µm foil. The growth of the oxide via ridges also demonstrates the importance of the fast diffusion paths during the initial
stage of conversion. Nevertheless, the ridged structure disappears after complete reduction or oxidation. During the oxidation of the thinner foils, some of the interfacial defects between grains are not sufficiently annihilated; instead, pores and cracks are formed, facilitated by thermal-chemical stresses and structural inhomogeneity, leading to a direct exposure of the interior, as observed in Figure 4-3(a)-(b) and Figure 4-4(a)-(b), also reported in refs. [5, 10, 32].

Evidently, distinctive morphological and microstructural features are observed for nickel foils treated under the sample condition with only differences in their thickness. Therefore, it demonstrates the important inter-connections among the bulk phase, surface defects, and the evolution of the microstructures. Facilitated by the abundance of nickel cations from the bulk, the growth of the oxide scale on the 100 μm foil is smooth and complete, forming well-developed faceted grains with the saturations of the grain boundaries and the depletion of the pores and voids. In contrast, the sparseness of the cation in the bulk of the thin foils constrains the development of oxide grains, leading to the formation of a porous and pseudo cellular structure. The abundance of the defects on the surface enables fast ionic diffusion, and leads to improved kinetics as compared to the 100 μm foil (as showed later). The obtained kinetics of the nickel redox reaction is linked to the observed structural evolutions, and insights can be gained towards designing of OC for CLC applications.

4.4 Experimental Results

The oxidation and the reduction reactions can be written as:

\[
\text{Oxidation: } \quad 2\text{Ni} + \text{O}_2(g) \rightarrow 2\text{NiO} \quad (4.1)
\]

\[
\text{Reduction: } \quad \text{NiO} + \text{H}_2(g) \rightarrow \text{Ni} + \text{H}_2\text{O}(g) \quad (4.2)
\]
In the reduction step, the production of one mole of H₂O is counter-balanced by the consumption of one mole of H₂, thus maintaining the total flow rate constant. In contrast, the oxidation consumes \( \frac{1}{2} \) mole of O₂, leading to reduced flow rate. By considering the species balance, we can express the reaction rates as:

\[
\text{Oxidation: } \omega_{O_2} = \dot{n}_{\text{ax,in}} \left( x_{O_2,\text{in}} - x_{O_2,\text{out}} \frac{1 - x_{O_2,\text{in}}}{1 - x_{O_2,\text{out}}} \right) = \frac{P^0 \dot{V}^0}{R T^0} \left( x_{O_2,\text{in}} - x_{O_2,\text{out}} \frac{1 - x_{O_2,\text{in}}}{1 - x_{O_2,\text{out}}} \right) \tag{4.3}
\]

\[
\text{Reduction: } \omega_{H_2} = \dot{n}_{\text{red,in}} x_{H_2,O,\text{out}} = \frac{P^0 \dot{V}^0_{\text{red,in}}}{R T^0} \tag{4.4}
\]

Here, \( \omega_{O_2} \) and \( \omega_{H_2} \) are the oxidation and reduction rates (unit, mole s\(^{-1}\)), respectively. \( \dot{n}_{\text{ax,in}} \) and \( \dot{n}_{\text{red,in}} \) are the total mole fraction inflow rates of gas mixture for the oxidation and reduction. \( x_{i,\text{in}} \) and \( x_{i,\text{out}} \) are the mole fraction of species \( i \) at the inlet and exit. The ratio in eq. (4.3) utilizes the fact that the Ar molar flow remains unchanged as the mixture flows through the reactor. \( P^0, T^0 \), and \( \dot{V}^0 \) are the pressure, temperature, and the total volumetric inflow rate at standard temperature and pressure (STP). The above derivations assume a quasi-steady state and neglect the accumulation or depletion effect in the control volume. This is valid as the flow residence time is much shorter than the characteristic time of the redox conversion. The conversion of the OC, \( X \), is defined as follows:

\[
\text{Oxidation: } X_{ox}(t) = \frac{1}{N_{O_2,\text{tot}}} \int_{t=0}^{t'} -\omega_{O_2,\text{tot}} \tag{4.5}
\]

\[
\text{Reduction: } X_{\text{red}}(t) = \frac{1}{N_{H_2,\text{tot}}} \int_{t=0}^{t'} -\omega_{H_2,\text{tot}} \tag{4.6}
\]

Here \( N_{i,\text{tot}} \) is the maximum amount of O₂/H₂ consumed, calculated based on the weight of the nickel sample assuming full conversion.
Figure 4-8 Oxidation of 10μm foils at 900°C under varying flow rate. (a) O₂ concentration at inlet (solid lines), and outlet (dashed lines); (b) oxygen consumption rate; and (c) conversion of OC. O₂ flow is fixed at 10 sccm. The overall flow is varied: 150sccm, 250sccm, and 350sccm.

Figure 4-8 shows the effect of the flow residence time on the oxidation rates using 10 μm foil at 900°C. The oxygen flow is fixed at 10 sccm while the total flow is varied at 150, 250, 350 sccm. Panel (a) shows the measured O₂ concentration at the inlet and the exit of the reactor. Panel (b) shows the oxygen consumption rate, calculated from eq.(4.3), and panel (c) shows the OC conversion, from eq. (4.5). From Figure 4-8, increasing the total flow rate reduces the apparatus flow residence time and shifts the O₂ profiles to the left. For flow rates above 250 sccm,
difference in flow responses is insignificant (panel a). The O₂ consumption rate spikes as the oxygen concentration rises and drops quickly afterwards. After 1 min, the OC continues to adsorb oxygen, but reaction rates are too low to be of any practical interest. Raising the flow rates effectively decreases the O₂ concentration, leading to a reduced reactivity. The difference is small since the peak rates roughly correspond to similar O₂ concentrations (~ 2.5%, 3.0%, and 3.5%) in the flow.

Figure 4-9 shows the effect of the O₂ concentration with 2.5μm foils at 1000°C. The total flow is fixed at 250 sccm and the O₂ concentration is varied at 2.1%, 4.2%, and 8.4%. As seen in panel (a), the inlet flow rises within a similar time window, while the exit flow spikes faster with a higher O₂ feed. As expected, the profile of ωO₂ becomes taller and narrower under higher O₂ feed flow (panel b). This indicates a strong dependence of the oxidation rate on the O₂ concentration. Panel (c) compares the profiles of the OC conversion. Similarly as in Figure 4-8, higher O₂ concentration leads to a higher OC conversion.

Figure 4-10 shows the temperature effect with the measurements of 100 μm foils. The O₂ concentration is fixed at 8.4% and the temperature is varied from 800°C to 1000°C. Raising temperature only mildly increases the oxidation rate, indicating a weak temperature dependence of the oxidation rate. The peak O₂ consumption rate is increased by around 20% comparing the case at 1000°C to that at 800°C. The weak temperature dependence is mostly attributed to the nature of nickel oxidation process: the highly exothermic surface chemistry is virtually barrierless; the fast short-circuit diffusional paths as well as the direct permeation of O₂ via pores, responsible for the initial fast oxidation, is mostly determined by the surface microstructure, and
thus less sensitive to temperature comparing to the bulk phase diffusion. As a result, one can expect an insignificant activation energy barrier for the oxidation process, as showed later.

Figure 4-9 Oxidation of 2.5μm foils at 1000°C. (a) O₂ concentration at inlet (solid lines), and outlet (dashed lines); (b) oxygen consumption rate; and (c) conversion of OC. The O₂ flow rate is varied at 5 sccm, 10 sccm, and 20 sccm. The carrying gas (Ar) is varied to keep the total flow fixed at 250 sccm.
As seen in panels (b) and (c) of Figure 4-8—Figure 4-10, oxidation proceeds via three different stages, roughly divided by the dashed lines. The stage I is a fast surface process during which the surface nickel quickly consumes $O_2$ to form a rapid growing oxide scale (Figure 4-6(a,b)). The spike of the reaction rate curve coincides with the rise of the $O_2$, indicating that the process is mainly driven by the feed of $O_2$. The oxidation is less affected by the defect structure and surface morphologies; rather, the direct interaction between Ni and $O_2$ on the surface completely
determines the spike of the overall consumption rates. As the oxide scale develops, the conversion quickly moves over to a surface assisted diffusion stage (stage II, see Figure 4-6b-c), where the O₂ concentration remains constant at the set-point, but ω drops. At this stage, the scale thickens and overlaps. Thus, the direct contact between nickel core and O₂ is attenuated and the further growth of the NiO layer requires diffusional paths. The outward diffusion of Ni²⁺ via dislocations, grain-boundary as well as the direct inward permeation of O₂ through micro-channels in NiO are the major mass-transfer paths. As a result, the surface defect microstructure becomes the determining factor. As oxidation continues, the formation of the thick scale domain saturates the defects and closes the O₂ permeation channel. The reactivity slows down remarkably, and the oxidation finally moves to the bulk-diffusion stage (stage III) as characterized by the classic parabolic diffusion theory [33]. Comparing to stage III, the initial stage (I) is much faster, but only lasts for a few seconds, while stage II proceeds at a lower yet significant oxidation rate, and it spans up to several minutes. Therefore, the first two stages should be the focus for CLC applications.

Table 4-3-Table 4-5 show the conversion of OC (X₉ₒₓ) achieved during the initial two stages (I and II). Here we use t = 1 min as a characteristic time window for these two stages for the purpose of comparison. The obtained conversions are around 25%, 10%, and 1.6% for the 2.5 μm, 10 μm and 100 μm foil, roughly corresponding to the oxidation of 1 μm Ni layer on each side of a foil⁹. The results here would provide us a simple thumb rule for designing OC: nickel grains prepared in the OC with size close to 1 μm may suffice to ensure fast oxidation and a better overall utilization. As seen in Table 4-3-Table 4-5, higher O₂ concentration and higher temperature both favor the OC oxidation.

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⁹ The 2.5 μm and 10 μm foils enlarge in thickness by a factor of 3, and 2.5, respectively. See below
Table 4-3: OC conversation for 10μm foil after 1 min oxidation.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>900°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set O₂ conc.</td>
<td>3.0% 4.2% 7.0%</td>
<td>3.0% 4.2% 7.0%</td>
</tr>
<tr>
<td>Xₐₓ (t = 1min)</td>
<td>9.0% 10.2% 11.0%</td>
<td>9.1% 11.3% 11.9%</td>
</tr>
</tbody>
</table>

Table 4-4: OC conversation for 2.5μm foil after 1 min oxidation

<table>
<thead>
<tr>
<th>Temperature</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set O₂ conc.</td>
<td>2.1% 4.2% 8.4%</td>
<td>2.1% 4.2% 8.4%</td>
<td>2.1% 4.2% 8.4%</td>
</tr>
<tr>
<td>Xₐₓ (t = 1min)</td>
<td>23.1% 26.6% 28.2%</td>
<td>23.9% 27.2% 27.7%</td>
<td>23.8% 26.0% 27.8%</td>
</tr>
</tbody>
</table>

Table 4-5: OC conversation for 100 μm foil after 1 min oxidation.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set O₂ conc.</td>
<td>2.1% 4.2% 8.4%</td>
<td>2.1% 4.2% 8.4%</td>
<td>2.1% 4.2% 8.4%</td>
</tr>
<tr>
<td>Xₐₓ (t = 1min)</td>
<td>1.2% 1.4% 1.5%</td>
<td>1.4% 1.4% 1.7%</td>
<td>1.6% 1.8% 1.8%</td>
</tr>
</tbody>
</table>

Figure 4-11 shows the effect of the foil thickness on oxidation. Panel (a) compares the O₂ consumption rates per foil for the three cases. The rate of the 2.5μm foil is lowest, although most pieces of foils are used for measurements. On the other hand, the peak rate for the 100μm case is more than twice as much. The difference is attributed to the loss of surface area of the thin foils after redox treatment. As highlighted in Figure 4-2, thin foils (2.5μm and 10μm cases) shrink in diameter and enlarge in thickness resulting from the redox treatment, while the 100 μm foil remains its original structure. Because of the low specific surface area of the foil sample (<0.03 m²/g for 10 μm foil), a direct BET measurement of the surface area is difficult. Here, we qualitatively estimate the actual surface area of the 2.5μm and 10μm foils by matching their specific surface reaction rates during stage I to that of the 100 μm sample. The reason is that, as seen in Figure 4-5, the surface structures of the reduced foils are very similar, and differences are mostly related to the pore distributions. As a result, the conversion process during stage I mostly depends on the intrinsic Ni-O₂ chemistry: O₂ undergoes the same adsorption and dissociation
process to interact with Ni, regardless of the pore structure. The 2.5 μm and the 10μm foils are found to be 32% and 42% of the original (apparent) area, denoted as $\chi_{2.5\mu m} = 32\%$, and $\chi_{10\mu m} = 42\%$. Figure 4-11(b) plots the surface reaction rate after accounting for the area change. The obtained curves perfectly overlap in stage I among all the three cases. In stage II, similar $O_2$ consumption rates are obtained for the 2.5μm and 10μm cases, both of which are remarkably higher than that of 100μm. This is in accordance with the observed surface microstructures, as presented in section 4.3, that thin (2.5μm and 10μm) foils are associated with more defects and large pores distributed over the surface, while the 100μm foil is smooth and saturated by faceted grains with fewer surface defects and fractures.

![Graph](image)

**Figure 4-11** Comparison of the oxidation rates (a) per foil and (b) per unit surface area between 2.5μm, 10μm and 100μm Ni at 900 °C. The operating flow is 50sccm $O_2$ (21%) and 200 sccm sweeping Ar.
Figure 4-12 Reduction of 100μm foils at 1000°C. (a) H₂ concentration (solid lines), and H₂O concentration (dashed lines) at the exit; (b) H₂O production rate; and (c) the reduction conversion of OC. The H₂ concentration is varied at 2.1% and 8.4%. The total flow is fixed at 250 sccm.

Figure 4-12 and Figure 4-13 show the reduction rates of 100 μm foils. In each figure, panel (a) shows the measured concentration of H₂ and H₂O at the exit, panel (b) shows the reduction rate calculated using Eq.(4.4), and panel (c) shows the evolution of OC conversion based on Eq.(4.6). No induction period is observed in any cases, and the conversion monotonically rises following a non-linear growth pattern. Figure 4-12 shows the effect of H₂ concentration and Figure 4-13 shows the effect of temperature. As compared to oxidation, the reduction is much slower, and the
peak rate is only 20-30% of that in the oxidation. The release of oxygen and production of H₂O in the reduction phase is in general slow and mild, leading to a smooth and concave conversion profile spanning over 2 min, in contrast to the sharp curve during oxidation. Raising the H₂ concentration or the temperature leads to a faster reduction rate and improved conversion. As compared to oxidation, the reduction is only weakly dependent on the reactant concentration, as also reported by Manukyan et al. [30], possibly resulting from the fast adsorption and saturation of H₂ on the surface sites. Note for reduction with 2% H₂, the peak of H₂O is lower because of the limited amount of H₂ from the flow, as seen in panel a where the H₂ profile at the exit is retarded for about 9 sec.

Figure 4-13 shows that the reduction step is more temperature sensitive compared to oxidation. Raising temperature increases the peak of H₂O remarkably. However, the profiles after 0.6 min almost overlap among different temperatures. The majority of reduction occurs within 2 min, although the conversion continues even after 10 min of conversion. A direct implication to the design of the nickel-based CLC reactor is that the residence time of the OC in the reduction phase should be longer as compared to oxidation in order to sufficiently regenerate the OC and utilize the most of the oxygen carrying capacity. A comparison of the reduction kinetics among different foils is not included here, due to the difficulty in quantifying the surface area for the oxidized thinner foils. A qualitative discussion can be found in 4.8 Supplemental Information.
Figure 4-13 Reduction of 100μm foils at different temperatures. (a) H$_2$ concentration (solid lines), and H$_2$O concentration (dashed lines) at the exit; (b) H$_2$ consumption rate; and (c) conversion of OC. Feed H$_2$ is fixed at 8%. For clarity, only the H$_2$ concentrations at 900°C are plotted in panel (a); the profiles at 800°C and 1000°C are similar.

4.5 Oxidation Kinetics

Different models [24, 34] were adopted previously to describe the surface oxidation process with respect to key state variables, such as OC conversion, temperature, reactant concentrations, etc. Commonly used models include the unreacted shrinking-core model (SCM), the changing grain size model (CGSM), and nucleation and nuclei growth models.
Based on the structural evolution observed in Section 4.3, we utilize a nucleation-growth model [35] to describe the oxidation process. Figure 4-14 shows the schematic description. Key features are summarized below:

1) Oxidation starts via nucleation of the oxide grain over the nickel surface (Figure 4-14a-b); this corresponds to the fast surface reaction stage (stage I).

2) The oxide continues to grow rapidly via a linear diffusion process. Dislocations, grain boundaries and the pores enable fast-diffusional paths (Figure 4-14c), which contribute to the rapid growth of oxide during the surface assisted diffusion stage (stage II).

3) As grains overlap, the defects are annihilated and the pores are closed. The fast-diffusion paths are attenuated, and the further growth of oxide is mainly constrained by the bulk phase diffusion (Figure 4-14d).

Figure 4-14 Schematic description of the oxidation process: (a) nucleation of oxide; (b) rapid growth of grains; (c) grains overlap and cover the surface, forming grain boundaries, and fractures; (d) well-developed grains cover the entire surface, saturate the defects and close the cracks. Panel (c) also highlights the bulk phase diffusion, $J_{\text{bulk}}$, as well as some fast-diffusion paths: the grain boundary diffusion, $J_{\text{gb}}$, and the direct permeation of $O_2$, $J_{\text{gas}}$. 

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We proceed by expressing the O₂ consumption (per unit area), \( \dot{\theta}_{O_2} \), as:

\[
\dot{\theta}_{O_2} = \dot{R}_N + \dot{R}_G,
\]

(4.7)

where \( \dot{R}_N \) and \( \dot{R}_G \) are O₂ consumption from the nuleation process, and the grain growth, respectively. Assuming a first-order chemistry for reaction (4.1), we obtain:

\[
\dot{R}_N = (1 - \alpha) k_1 p_{O_2}
\]

(4.8)

Here \( k_1 \) denotes the nucleation rate constant (unit, mole m⁻² s⁻¹) for nucleation. \( p_{O_2} \) is the partial pressure of O₂ in the gas phase, defined with respect to reference value (i.e. 1 atm). \( \alpha \) is the fractional coverage of the oxide over the surface, which evolves according to:

\[
\tilde{\rho}_{NiO} L_{cr} \frac{d\alpha}{dt} = 2 \dot{R}_N
\]

(4.9)

Eq. (4.9) describes that the oxide nucleation leads to the increase of the oxide coverage and hence decrease of the nickel surface coverage, \( 1 - \alpha \). \( \tilde{\rho}_{NiO} \) is the molar density of nickel oxide. The coefficient, 2, on the right-hand side is the stoichiometric coefficient of NiO. \( L_{cr} \) is the critical thickness of the oxide formed during nucleation. During the nucleation stage, a strong electric field is established from contact potential, driving the fast transport of Ni²⁺ and quickly forming a very thin film [36]. Once the oxide reaches a critical thickness (~10 nm), the field effect is significantly attenuated, and the growth of oxide grain transits to a diffusion-limited mechanism [10, 32] (as modeled below). In this study, \( L_{cr} \) is chosen to be 10 nm, as in refs. [10, 37]. Substituting eq. (4.8) into eq. (4.9) and integrating the equation, we obtain:

\[
\alpha(t) = 1 - \exp\left( -\frac{2k_1}{\tilde{\rho}_{NiO} L_{cr}} \int_0^t p_{O_2} dt \right)
\]

(4.10)
where \( t_0 \) is the starting time of oxidation. Eq. (4.10) is essentially the first-order Avrami-Erofeev model. More detailed models describing the field-driven growth during this stage can be found in refs. [32, 36], but for the purpose of this study, the eq. (4.10) is used for simplicity.

We proceed by expressing the growth of the oxide grains following parabolic law as [33]:

\[
\frac{\partial \Delta(t,\tau)}{\partial t} = \frac{k_p}{2\Delta}
\]  

(4.11)

In eq. (4.11), \( \Delta(t,\tau) \) is the thickness at time \( t \) of the grain (Figure 4-14b). \( \tau \) is the formation time of the grain \( (t \geq \tau \geq t_0) \). \( k_p \) is the instantaneous parabolic rate constant. Eq. (4.11) describes a linear diffusion process [2, 6, 36]. The initial condition for the grain size is, \( \Delta_0 = L_{cr} \), obtained from the nucleation process. \( k_p \) varies throughout the oxidation process, and it can be expressed [2] as:

\[
k_p = (1 - f)k_{p,\text{bulk}} + fk_{p,\text{fast}}
\]

(4.12)

where \( k_{p,\text{bulk}}, k_{p,\text{fast}} \) are the parabolic growth constants for the bulk-phase diffusion, and other fast diffusion pathways. \( f \) is the volume fraction of fast-diffusion paths, written as [38, 39],

\[
f = 2d / D
\]

(4.13)

where \( d \) is the width of the fast-diffusion paths, and \( D \) is the radius of grains on the surface (see Figure 4-14b). \( D \) grows with oxidation, leading to the decrease of the diffusion flux. It has been demonstrated that the growth of \( D \) can be similarly described using the parabolic law [2, 39]:

\[
D^2 = D_0^2 + k_{p,g} (t - t_0)
\]

(4.14)

where \( D_0 \) is the initial radius, and \( k_{p,g} \) is radius growth constant (unit, \( m^2/s \)), which is a function of surface strains, grain thickness, diffusivity, etc. \( t_0 \) is the starting time of oxidation. By combining the preceding equations, when \( k_{p,\text{bulk}} \ll k_{p,\text{fast}} \), ([6, 38], see Figure 4-16 as well), we obtain,
\[ k_p = k_{p,\text{bulk}} + \frac{k_2}{\sqrt{1 + A(t-t_0)}} \]  \hspace{1cm} (4.15)

where \( k_2 = 2k_{p,\text{fau}}d / D_0 \), \( A = k_{p,g} / D_0 \) are the kinetic constants to be determined. \( k_{p,\text{bulk}} \) is adopted from the tracer measurements from ref. [32]. Integrating eq. (4.11) gives:

\[ \Delta^2(t, \tau) = L_{cr}^2 + k_{p,\text{bulk}}(t-\tau) + \frac{2k_2}{A} \left( \sqrt{1 + A(t-t_0)} - \sqrt{1 + A(\tau-t_0)} \right) \]  \hspace{1cm} (4.16)

The corresponding \( O_2 \) consumption from oxide growth is (using eq. (4.11)):

\[ \dot{\rho}_G = \frac{1}{2} \frac{\rho_{\text{NiO}}}{\Delta} = \frac{1}{4} \frac{\rho_{\text{NiO}} k_p}{\Delta} \]  \hspace{1cm} (4.17)

Combining the consumption from all the grains gives \( \dot{\rho}_G(t) \):

\[ \dot{\rho}_G(t) = \int_0^t \dot{\rho}_G(t, \tau) \rho_G(\tau) d\tau \]  \hspace{1cm} (4.18)

where \( \rho_G(\tau) \) is the fractional density of grains formed at time \( \tau \), expressed as:

\[ \rho_G(\tau) = \frac{d\alpha}{d\tau} = \frac{2k_1p_{O_2}(1-\alpha)}{\rho_{\text{NiO}}L_{cr}} \]  \hspace{1cm} (4.19)

Substitute eqs. (4.8) and (4.18) into eq. (4.7) gives:

\[ \dot{\tilde{\omega}}_{O_2} = (1-\alpha)k_{p,\tilde{\rho}_{O_2}} + \int_0^t \frac{\rho_{\text{NiO}} \rho_G k_p}{4\Delta} d\tau \]  \hspace{1cm} (4.20)

Eqs. (4.10), (4.15), (4.16), (4.19), and (4.20) form the complete description of the oxidation process. The kinetics parameters to be obtained are \( k_1 \), \( k_2 \), and \( A \). The rate constants, \( k_1 \) and \( k_2 \), are assumed to follow the Arrhenius expression, \( k_i = k_{i,0} \exp(-E_i/RT) \), with \( k_{i,0} \) being the pre-exponential factor, \( E_i \) activation energy. Note here, the equilibrium analysis [2] shows that the parabolic rate constant weakly depends on \( p_{O_2} \), i.e., \( k_p \propto (p_{O_2})^{1/n} \), with \( 4 \leq n \leq 6 \) (depending on the nature of the major defects and the diffusion mechanisms). However, this is not included in the current model, because the kinetic process during the intial stage is overwhelmingly in one
direction and local equilibrium is unlikely to be established. The dependence of \( p_{O_2} \) is hence lumped into \( k_2 \) for kinetics fitting, and cautions are necessary when comparing the obtained kinetics with the literature.

With the time-resolved profiles of \( p_{O_2} \) measured using QMS, the entire oxidation process can be predicted based on a given set of kinetics parameters. The preceding equations are calculated numerically and the predicted reactivity is compared to the experimental measurement. The kinetics parameters are then varied to minimize the difference:

\[
\text{Diff} = \sum_{\text{all tests}} \sqrt{\sum_{\text{all tests}} \left( \dot{\omega}_{\text{predicted}} - \dot{\omega}_{\text{measured}} \right)^2}
\]  

(4.21)

Here the reaction rates (\( \dot{\omega}_{\text{predicted}} \) or \( \dot{\omega}_{\text{measured}} \)) are normalized by the maximum rate in each test. The minimization is obtained numerically in MATLAB using fminsearch solver [40]. The measurements of the 100 \( \mu \)m foils are used to extract the kinetics parameters, because of the certainty in the surface area. The obtained kinetics are then applied to the 2.5 \( \mu \)m and 10 \( \mu \)m foils with \( A \) varying to account for the observed difference of the structural evolutions.

Table 4-6: Kinetic parameters for the oxidation reactions with 2.5 \( \mu \)m, 10\( \mu \)m and 100\( \mu \)m samples.

<table>
<thead>
<tr>
<th></th>
<th>2.5 ( \mu )m</th>
<th>10 ( \mu )m</th>
<th>100 ( \mu )m</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 )</td>
<td>0.0254 mole m(^{-2})s(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_2 )</td>
<td>( 1.35 \times 10^7 \exp(-22.1 \text{kJ mole}^{-1}/\text{RT}) \text{cm}^2\text{s}^{-1} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A )</td>
<td>9.1 s(^{-1})</td>
<td>9.1 s(^{-1})</td>
<td>23.8 s(^{-1})</td>
</tr>
<tr>
<td>( \chi )</td>
<td>32%</td>
<td>42%</td>
<td>100%</td>
</tr>
</tbody>
</table>

The obtained kinetics are listed in Table 4-6. The nucleation step (\( k_1 \)) is fast and barrierless and the parabolic growth rate (\( k_2 \)) has the activation barrier of 20 kJ/mol. The obtained activation energy reasonably agrees with data reported for CLC (Table 4-1). Similarly, Dueso and co-
workers [27-29] reported an activation energy of around 20 kJ/mol for nickel supported on Al₂O₃.

The obtained grain radius growth rates, A’s, are the same for 2.5 μm and 10μm foils, higher than that for 100μm. This is in accordance with the observed differences in the structural evolutions (Figure 4-3) and the oxidation rates in stage II (Figure 4-11b).

![Graphs showing oxygen rate vs time for different foils at 900°C and 1000°C.](image)

Figure 4-15 Comparison of the model predictions (lines) with the measurements (circles) for the oxidation of the three types of foils with 4% O₂ at 900°C and 1000°C.

Figure 4-15 compares the model predictions and the measurements for the 2.5μm, 10μm and 100μm cases with 4% O₂. A quantitative agreement is found for all the cases. The predictions well characterize the spike-decay behaviors of the oxidation processes. The temperature dependence is precisely represented; the subtle difference among different foils is also adequately captured. Small discrepancy appears near the spike for the case of 10μm foils, likely
due to the uncertainty in estimating the surface area. Similar agreement is observed for other oxidation measurement.

Figure 4-16 Parabolic growth rate constant obtained in this study compared with experimental values from the literature. Solid line is the calculated $k_p$ based on the bulk diffusion [32] of Ni in NiO, and the gray area encloses the range of the data that has been reported in the literature [32]. Results from refs. [6] (circles) and [31] (triangles) comparing short-term (filled symbols) and long-term oxidation (open symbols) are also included. The time to reach $1\mu$m of oxide is 17s, 13s, and 11s, for temperature of 800, 900, and 1000°C. Time to reach $5\mu$m is 52 min, 34 min, 22 min respectively.

Figure 4-16 compares the parabolic rate constant, $k_p$, calculated from eq. (4.15), with experimental values from the literature. $k_p$'s from this study are the instantaneous parabolic rates with an average oxide thickness ($\Delta_{avg}$) of $1\mu$m and $5\mu$m, which correspond to an oxidation period
of 10-20 sec, and 0.5-1hr, respectively. Since oxidation in the current experiment only lasts 10 min, the rates with 5µm oxide scale thickness are extrapolated based on the preceding model with 4% O₂ feed. The obtained $k_p$’s fit properly in the range and reasonably match the values from refs. [6] and [31] at high temperature. $k_p$ for the initial oxidation (1µm) lies along the upper bound, which is over one order-of-magnitude faster than that for 5µm. It is worth noting that the comparsion here is only qualitative, as the measurements in the literature were reported at atmospheric oxygen pressure.

As evident from Figure 4-16, a large scatter of data were previously reported within the temperature range 700 – 1100 °C, more significant at lower temperature. This scatter has been shown to depend on metal purity, pre-treatment, and crystal orientations [32, 39]. Furthermore, the parabolic rate is also reported to vary dramatically with time [6, 31, 38], resulting from the attenuation of the fast diffusion paths through oxidation. Thus, $k_p$ is significantly fast initially (filled symbols in Figure 4-16), decays throughout the course of oxidation, and eventually stabilizes after hours of oxidation (open symbols). Nevertheless, all reported values lie above the rates calculated from the bulk diffusion ($k_{p,bulk}$, solid line in Figure 4-16), indicating the significance of fast-diffusion paths. The reported kinetics within this temperature range generally exhibit a weaker temperature dependence, with the activation energy ranging from 80-100 kJ mole⁻¹ [6] as compared to ~250kJ mole⁻¹ for the lattice diffusion [32]. The reported temperature dependence from this study is even weaker, with the activation around 20kJ mole⁻¹. This is possibly resulting from the redox pre-treatment, which may enhance the coverage of the short-circuit paths (larger $f$), leading to an improved oxidation towards lower temperature. The weak temperature dependence is also commonly reported in other CLC studies, as showed in Table 4-1.
Figure 4-17 Oxidation of 100μm foils at 1000°C. (a) Comparison of predicted (symbols) and measured (lines) OC conversion with varying O₂ flow. (b) Evolution of the nickel surface coverage (1-α); O₂ concentration at exit (dashed lines) are also plotted. (c) Evolution of the parabolic rate constants, $k_p$, with time at 4.2% O₂; 2.5μm case (same as 10μm) is also included for comparison.
Figure 4-17 further illustrates the details of the oxidation process. Figure 4-17(a) shows a quantitative match of the OC oxidation conversion between the model predictions and the measurements. All three stages of conversion are adequately captured by the model. From Figure 4-17(b), the unreacted nickel on the surface, \(1-\alpha\) (eq. (4.10)), decreases quickly with the feed of the O\(_2\). Reducing the feed O\(_2\) to 2.1% slows down this process remarkably, as the limited amount of O\(_2\) retards the conversion. Figure 4-17(c) shows the rapid evolutions of the instantaneous parabolic growth rate, \(k_p\) (eq. (4.15)), during the early stage of conversion. The 2.5 \(\mu\)m and 10 \(\mu\)m foils exhibit a faster \(k_p\) throughout the conversion, as compared to the 100 \(\mu\)m foils. Similar patterns of \(k_p\) were also previously reported [6, 31].

Figure 4-18 shows the evolution of the oxide scale with conversion. The fractional density (\(\rho_G\)) of the oxide thickness (\(\Delta\)) follows a bell-shaped distribution, as showed in Figure 4-18(a). The oxide thickness initially spans over a wide range, as evident from the nonuniform surface in Figure 4-6(b). As conversion proceeds, the average thickness increases and the distribution becomes narrower, corresponding to the smooth and uniform surface observed in Figure 4-3(c). The peak density (eq. (4.19)) remains constant throughout the conversion, determined by the O\(_2\) feed and the evolution of surface nickel coverage, as in Figure 4-17(b).

Figure 4-18(b) shows the evolution of the average oxide thickness, \(\Delta_{av}\), with varying temperature. The growth undergoes several stages: a rapid jump occurs with the start of the oxidation, followed by a decrease in the growth rate limited by the available O\(_2\) in the flow; as the O\(_2\) concentration rises, the growth accelerates again with the oxide quickly covering the surface (stage I); when the surface becomes fully saturated, the rate slows down remarkably (stage II-III) and further growth
is controlled by the evolution of the $k_p$. A higher temperature enhances the conversion and shifts the growth curve up.

Figure 4-18 Evolution of the oxide scales under various conditions for the 100$\mu$m foils. (a) Comparison of the grain thickness distribution at 15s, 60s, and 120s after the start of the oxidation ($t_0$). (b) Evolution of the mean oxide thickness with time under different temperatures. (c) Comparison of $O_2$ consumption rates between nucleation and the grain growth process at 1000$^\circ$C and 800$^\circ$C. Note the scales in panel c are different between two y-axes.
Figure 4-18(c) compares the O₂ consumption rates between nucleation ($\dot{R}_n$) and grain growth ($\dot{R}_g$). The majority of O₂ consumption is from the oxide growth process. In contrast, the nucleation process determines the initiation of the oxidation. Raising the temperature accelerates the flow, leading to a slightly higher and narrower $\dot{R}_n$ profile. On the other hand, $\dot{R}_g$ is largely increased, resulting from the accelerated nucleation process as well as the enhanced $k_p$ at high temperature.

4.6 Reduction Kinetics

The reduction modeling involves the description of the adsorption/desorption process, the nucleation and the growth of the metal grains, and the diffusion mechanism by which H₂ penetrates through the formed nickel layer and consumes the residual oxygen, as showed schematically in Figure 4-19. Various models were used in the literature to describe the reduction process where one or more of these steps control. Richardson et al [41] investigated the reduction at 450-570K, and described it as a nucleation process followed by a first-order reaction. The induction period observed at the start of the reduction is associated with the formation of metallic nuclei, which accelerates the conversion as the clusters grow. The slower kinetics near completion was attributed to the decreased accessibility of residual oxygen and the inhibition effect from produced water. Jeangros et al [11] adopted the Avrami model to describe the reduction of nickel nano-particles (573 - 923K), and similarly attributed the slow residual conversion to the presence of water. Manukyan et al [30] modeled the reduction process similarly, and concluded that both nucleation and diffusion-related process control the conversion at low temperature (543-773K), while nucleation becomes less important at high
temperature (1173-1593K). A sharp interface is observed between the unreacted NiO and reduced Ni at high temperature. Similarly, Utigard and co-workers [42] observed the sharp interface and hence modeled it using the shrinking-core model. The formed nickel layer creates a large resistance for the H$_2$ diffusion and hence becomes the rate-limiting step. The shrinking-core model was also applied to the porous nickel particles with structural support at high temperature [26, 29].

In this study, we use a semi-empirical model to characterize the reduction process, with the consideration of the adsorption/desorption process, and the decreased accessibility of the residual oxygen. The nucleation and the autocatalytic effects are not included in the modeling as they have been showed to be less important under high temperature [30, 41]. The reduction rate for reaction (4.2) is expressed as:

\[
\tilde{\omega}_{H_2O} = \frac{k_3 \theta_O K_{H_2} P_{H_2}}{\left(1 + \sqrt{K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}}\right)^2}
\]

Here $\tilde{\omega}_{H_2O}$ is the reduction rate (unit, mole m$^{-2}$s$^{-1}$). $k_3$ is the rate constant. $\theta_O$ denotes the fraction coverage of oxygen available at the reaction interface (see Figure 4-19b). In eq. (4.22), Langmuir equation is used to describe the adsorption and desorption of H$_2$ and H$_2$O following:

\[
H_2 + 2s \xrightleftharpoons[K_{H_2}]{K_{H_2O}} 2H(s)
\]  

\[
H_2O(g) + s \xrightleftharpoons[K_{H_2O}]{K_{H_2}} H_2O(s)
\]

where $K_{H_2}$, and $K_{H_2O}$ are the equilibrium constant. Thus, the removal of oxygen within the oxide layer can be expressed as:

\[
\frac{dN_O}{dt} = S \tilde{\omega}_{H_2O}
\]

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Here $S$ is the total surface area of the foil. $N_O$ is the available oxygen within the oxide layer, written as, $N_O(t) = \tilde{\rho}_{\text{ox}} S \Delta_m \alpha_{\text{red}}(t)$, where $\tilde{\rho}_{\text{ox}}$ is the molar density of the nickel oxide, $\Delta_m$ is the thickness of the oxide on each side of the foil from the previous oxidation cycle (Table 4-5), and $\alpha_{\text{red}}$ is the conversion extent of the oxide layer.

Figure 4-19 Schematic description of the reduction process: (a) oxidized NiO (b) adsorption and dissociation of $H_2$, desorption of $H_2O$, and nucleation of metallic grain; (c) grain growth and clustering, penetration of the reaction interface into the oxide grains underneath the surface nickel layer, removal of residual oxygen (d) dense and smooth reduced surface with pores between grains. The red line in panel b highlights the NiO reaction interface.
With the knowledge of the dynamic evolution of $\theta_{O} = \theta_{O}(t)$, a complete description of the reduction process is obtained. According to the definition, $\theta_{O}(0) = 1$, and $\theta_{O}(\infty) = 0$. Thus, we relate $\theta_{O}$ to $1 - \alpha_{\text{red}}$, following the Sestak and Berggren (SB) approach [43], as $^{10}$:

$$\theta_{O} = (1 - \alpha_{\text{red}})^{n}$$  \hspace{1cm} (4.26)

Eq. (4.26) is an empirical relationship that characterizes the evolution of the available oxygen with the movement of the NiO reaction interface. The constant $n$ represents the possible diffusional mechanism. $n = 0$, $1/2$, or $2/3$ corresponds to the shrinking-core model, and $n = 1$ represents the Avrami model.

By substituting eqs. (4.22) and (4.26) into (4.25), and re-arranging, we obtain:

$$\frac{d\alpha_{\text{red}}}{dt} = \frac{k_{3}(1 - \alpha_{\text{red}})^{n}}{\rho_{\text{NiO}} \Delta_{\text{ox}}} \cdot \frac{p_{H_{2}}}{\left(\sqrt{p_{H_{2}}} + K_{1} + K_{2}p_{H_{2}O}\right)^{2}}$$  \hspace{1cm} (4.27)

Here $K_{1} = 1/\sqrt{K_{H_{2}}}$, $K_{2} = K_{H_{2}O}/\sqrt{K_{H_{2}}}$, $k_{3}$, and $n$ are the kinetic constants to be determined. Eq. (4.27) is integrated numerically in MATLAB and the predicted reactivity is compared to the experiments, following a similar procedure as for the oxidation. The reduction measurements of the 100 $\mu$m foils are used to extract the kinetics.

$^{10}$ Note that the complete expression of the SB model is $\theta_{O} = a^{m} \left(1 - a\right)^{n} \left(-\ln(1 - a)\right)^{p}$, where $a^{m}$ and $(-\ln(1 - a))^{p}$ are related to the nucleation and autocatalytic effects. These terms are neglected in this study for simplicity.
Figure 4-20 Comparison of the model predictions (lines) with the measurements (circles) for the reduction of 100μm foils.

Figure 4-20 compares the model predictions and the measurements for reduction. A quantitative agreement is found for all the cases. The predictions well characterize the reduction patterns. The temperature dependence is well captured. Small discrepancy appears near the spike with high H₂ feed, which may be due to the deviation from equilibrium for the adsorption step during the initial stage of reduction.

The obtained kinetics are listed in Table 4-7. The activation energy is ~ 30 kJ/mol, which is comparable to previously reported data in the literature (Table 4-1). The obtained reduction rate constant, $k_3$, is compared to the literature. As seen in Figure 4-21, the obtained $k_3$ well fits within
range of data from previous CLC measurements. Particularly, a perfect match is found with the results from ref. [17].

The adsorption constants, $K_1$ and $K_2$ are found to be close to zero (statistically insignificant), indicating a strong H$_2$ adsorption ($K_{H2}$) and eventual saturation on the surface. As a result, the reduction rate essentially becomes independent of the H$_2$ concentration. This was also reported previously in refs. [30, 44] with unsupported nickel. The effect of H$_2$O desorption on reactivity is found to be less important. The constant, $n$, is around 2.5, corresponding to a rapid decay of the accessible oxygen with the conversion and large mass-transfer resistance induced by the formed nickel layer. In contrast, the reported measurements in the literature using supported nickel particle usually have a faster diffusion, with $n = 0$ (e.g. ref. [29]), 2/3 (ref. [17]), or 1 (ref.[25]). The difference is attributed to the usage of support which enhances the dispersion and enables a better exposure of the oxide to the reacting environment, as seen in Chapter 5.

Table 4-7 Kinetic parameters for the reduction reactions with 100μm samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>100 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_3$ (mole m$^{-2}$s$^{-1}$)</td>
<td>0.053 exp(-30.5 kJ/mol/RT)</td>
</tr>
<tr>
<td>$n$</td>
<td>2.57</td>
</tr>
<tr>
<td>$K_1, K_2$</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 4-21 Reduction rate constant obtained in this study compared with experimental values from the literature. The values from the literature correspond to $p_{H_2} = 1$ atm. Note there seems to be a problem with the numbers from ref. [29]: the reported unit in table 2 is mole m$^2$s$^{-1}$ (after accounting for H$_2$), but in the context the unit for $k$ is s$^{-1}$. For comparison, we convert the values by multiplying a factor, $\tilde{p}_{H_2} r_g$, with $r_g$, grain radius, adopted from ref. [17] from the same authors.

4.7 Summary

This chapter presents a detailed redox study of nickel thin foils with emphasis on the structural evolution and the connection to the measured kinetics w.r.t CLC applications. Three types of nickel thin foils (thickness 2.5, 10, and 100 μm) are tested in a button cell with temperature range in 800 – 1000°C. The samples are alternatively exposed to synthetic air and H$_2$ for redox cycles.
The samples undergo structural and morphological changes during the initial redox treatment with the thin foils shrinking in surface area, but no further change was found after reaching cyclic equilibrium.

SEM images clarify the stages and key features of the redox conversion. The oxidation starts via the anisotropic nucleation of the oxide grains, which is then followed by a rapid growth of the grain driven by the fast diffusion via dislocations, grain boundaries, and pores. As the oxide grains overlap and saturate the surface, the defects are annihilated and the fast diffusion paths are eventually closed. Large facetted oxide grains are formed over the fully oxidized surface of thick foils. In contrast, the oxidized surface of thin foils is irregular with smaller cellular-like grains loosely packed, rich of defects which facilitate the reaction. The reduction process is initiated by the loss of oxygen atom on the outer surface, forming dense nickel clusters blocking the interior NiO. Macropores are also formed to accommodate the volume loss, and collapse to form larger voids providing the direct gas-diffusion passages. Ridges are formed along the grain boundaries during the redox process of 2.5 μm and 10 μm foil.

The reaction kinetics is determined by quantifying the flue stream composition using an on-line mass-spectrometer (MS). The oxidation rate is found to be 3-5 times faster as compared to reduction, and it is highly sensitive to O₂ concentration, but only weakly to the temperature. The conversion in oxidation undergoes three stages: (1) fast surface reaction stage; (2) surface assisted diffusion stage; and (3) slow bulk diffusion stage. The reactivity spikes during the stage I, and gradually decreases in stage II. In stage III, the reaction is mainly limited by the lattice diffusion. The first two stages complete within 1 min, roughly corresponding to the oxidation of
1 μm Ni layer. Comparing to oxidation, the reduction is more sensitive to temperature but almost independent on the H₂ concentration.

A nucleation-growth model is developed to characterize the oxidation process. The proposed model comprises a rapid nucleation process, followed by the growth of oxide grain. Kinetic parameters are extracted and excellent agreement of the model with the fitted parameters is achieved compared to the measurements. The model reveals that the growth of the oxide grain follows a parabolic law, with the rate constant decreasing remarkably during the early stage, which results from the attenuation of the fast-diffusion paths. The observed structural difference among the three foils contributes to the difference in the decay. The activation energy is found to be 20kJ/mol for the grain growth. The reduction is modeled as a one-step reaction, with the consideration of the adsorption/desorption process, and the decreased accessibility of the residual oxygen. Excellent agreement is found with the measurements. The model reveals that the surface of nickel is nearly completely covered with adsorbed hydrogen, and the reaction is less affected by H₂O. The decrease of the accessible oxygen follows a power law, indicating large mass-transfer resistance induced by the formed dense nickel layer. The activation energy is 30kJ/mol for reduction. The results establish a baseline for developing supported nickel oxygen carrier, and also provide guidance for the design and the practical application of the chemical-looping technology.

4.8 Supplemental Information
The microstructural and morphological evolutions after 10 min oxidation differ remarkably among the three types of foils, as discussed in Section 4.3 (Figure 4-3 and Figure 4-4). Figure
4-22 further highlights some of the key differences during the initial stage of reduction. Evidently, thicker foils are dense, smooth, and well-developed, while the thinner foils have highly irregular grains covered with defects, pores, and ridges. The reduction process critically relies on the surface defects [9, 11, 30]; therefore, one can expect a large difference for the kinetics among different foils. Additional complexity is associated with the change of the surface area resulting from large volumetric expansion during oxidation (~70%). Hence, a quantitative comparison of the reduction kinetics among different foils is difficult.

Here we qualitatively compare the reduction kinetics, by assuming that the surface area remains the same with that in oxidation process (Figure 4-11b): the 2.5 μm and the 10μm foils are 32% and 42% of the original (apparent) area. As seen in Figure 4-23, the reactivity increases dramatically with thinner foils. The reduction rate of 2.5 μm or 10 μm is more than twice that of the 100 μm throughout the entire conversion. The initial stage for the 2.5 μm and 10 μm samples are similar, although with the 2.5 μm, the reactivity decreases much slower. The improvement on the reduction rates with thin foils results from the abundance of the surface defect as active sites for adsorption and dissociation, and the porous structure which leads to a direct exposure of its interior to reaction. The measured reduction rates are in good accordance with the observed surface microstructures.
Figure 4-22 Comparison of the surface morphology for (a) 2.5 µm, (b) 10 µm, and (c) 100 µm foils after 15 sec reduction. Red circles are the ridges formed on the thin foils.

Figure 4-23 Comparison of the reduction rates per unit surface area among 2.5µm, 10µm and 100µm Ni at 1000 °C with 8% H₂.

4.9 Bibliography


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[28] M. Ortiz, Reformado de metano con transportadores sólidos de oxigeno. "Chemical looping reforming", in, Universidad de Zaragoza, Zaragoza, Spain, 2011.
Chapter 5

Redox Study of NiO/YSZ for Chemical-looping Combustion

This chapter explores NiO/YSZ as OC, in an attempt to achieve practical redox repeatability for the CLC applications. Nickel particles with size less than 1μm are used in this study to prepare the solid mixture, supported on fine YSZ nano-powders. The redox reactivity with NiO (45mol%)/YSZ is measured in the temperature range 500-1000°C. Samples are subjected to alternate redox cycles using synthetic air (O₂+Ar) as oxidizer, and H₂/Ar, or CO/Ar mixture as fuel, respectively. NiO/YSZ demonstrates superb cyclic regenerability starting the 2nd cycle, with the full utilization of its carrying capacity during H₂/O₂ redox cycling. The peak rates reached during the redox steps with H₂ and O₂ are 223 μmole H₂O g⁻¹s⁻¹, and 263μmole O₂ g⁻¹s⁻¹, respectively. Compared to pure nickel foils, pronounced improvement is achieved on the redox kinetics and the total oxygen utilization.

The redox reactions are modeled with the consideration of bulk-transport and surface chemistry. It is found that the use of YSZ significantly enhances the ionic transport process for both oxidation and reduction steps. Oxidation follows a shrinking-core model under the control of internal chemistry, while reduction with H₂ or CO generally follows a similar adsorption-reaction pathway, and the oxygen removal step (i.e., the formation of H₂O or CO₂ product)
remains the rate-limiting step. The presence of H$_2$O does not affect the reduction rate. Reduction with CO/CO$_2$, on the other hand, leads to lower OC utilization, resulting from the backward reaction by CO$_2$, more pronounced as OC is reduced. The obtained results on the redox kinetics can be used for the design, fabrication, and optimization of the CLC reactor system.

5.1 Introduction

Chapter 4 shows that pure nickel suffers severe reactivity degradation during the initial cycles. The degradation of the materials is accompanied by the annihilation of structure defects, which significantly slows the ionic diffusion process. Only a small portion (<1 μm in thickness) of the available oxygen carrying capacity is activated within the practical time window, rendering the direct utilization of pure nickel less interesting.

In an attempt to enhance the reactivity, carrying capacity, and the regenerability, nickel is commonly supported on a binding material. The contributions of the binder are mainly threefold:

1) Porous support with fine NiO particles enables a better dispersion of nickel core, hence maintaining the surface area.

2) The inert substrate enhances structure stability and maintains the fast diffusional paths, minimizes annihilation effect and reduces the stresses associated with the phase change.

3) Support materials may act as an oxygen conductor, thus promoting oxygen ion exchange.

Various support materials have been explored and examined for nickel-based OC [1-5], including Al$_2$O$_3$, SiO$_2$, TiO$_2$, sepiolite, YSZ, etc, and a thorough comparison can be found in refs. [6, 7]. Among them, YSZ was commonly suggested as one of the most promising option, which
perfectly provides all the three features [1, 2, 8-13]: fine YSZ powder acts as a perfect porous matrix, enabling the dispersion of nickel without formation of any irreversible spinel nickel compound; YSZ is chemically inert to redox conditions, thus it is capable of maintaining its grain structure even under harsh conditions; YSZ is known as a good ionic conductor, enabling alternative fast ionic diffusional pathways, enhancing ionic exchange and promoting the redox kinetics.

Thus, the objectives of this chapter are to explore the redox kinetics with NiO/YSZ pair under CLC-relevant conditions. The OC is prepared by mechanically mixing fine nickel particles with the YSZ nano-powder. The redox reactivity with NiO/YSZ is measured in the button cell reactor in the temperature range 500-1000°C. Samples are subjected to alternative redox cycles using synthetic air (O₂+Ar) as oxidizer, and H₂/Ar, or CO/Ar mixture as fuel, respectively. The obtained kinetics is described with semi-empirical models, and the effects of CO₂/H₂O on the reaction rates are explored. The obtained results on the redox kinetics can be used for the design, fabrication, and optimization of the CLC reactor system.

5.2 Experiment

Commercial high purity nickel powder from Sigma Aldrich and YSZ nano-powder from Inframat Advanced Materials are used for the preparation of oxygen carrier samples. Nickel powder with size less than 1μm is selected, on the basis of the conclusions from Chapter 4, to ensure a complete redox conversion within 1 minute. The size of the YSZ powder is 30-60 nm, which provides a porous substrate with high surface area. The preparation of NiO/YSZ follows a mechanical mixing method (as detailed in Chapter 2): the nickel particles and the fine YSZ nano-
powder are thoroughly mixed with ethylene glycol as a binding agent, and continuously stirred at 150°C for 1 hr; the obtained paste is then grinded and calcined at 1000°C for 8hrs. The loading of NiO in the prepared OC is 45mol%, as confirmed by the chemical reaction measurements (as shown in Section 5.3). As shown in Figure 5-1, nickel grains are well dispersed within the fine YSZ powder substrate. The size of the nickel oxide particle is less than 1 µm, optimal for CLC as concluded in Chapter 4.

Figure 5-1 SEM image of the prepared NiO/YSZ OC. The fine particles are YSZ support, and the larger particles (surrounded by YSZ) are NiO grains.

50mg of prepared OC powder is embedded in quartz wool and placed at the bottom of the outer quartz tube inside the reactor. The sample undergoes redox cycles, with argon as purging gas flowing in between. Fuel (H₂/Ar, or CO/Ar mixture) and air (synthetic, Ar balance) are alternately introduced into the reactor. The total flow rate into the reactor is maintained constant at 350 sccm (standard cm³ per min). The measurement in each redox step proceeds for 1 min, with 5 min Ar purging to clean up all residuals. Additional 2 min oxidation is performed after each oxidation step, allowing for complete re-oxidation and sufficient regeneration of the OC,
thus ensuring an identical initial state for the following reduction step. In the base case, the gaseous reactant concentration is maintained at 21% for O₂, 10% for H₂, and 5% for CO. In the case with CO as fuel, carbon deposition may occur (via the Boudouard reaction, or Pyrolysis reaction), which leads to CO₂ production in the following oxidation step. To avoid the carbon issue, 20mol% CO₂ is flown into the reactor as a carrier gas, simulating the realistic environment in the fuel reactor during CLC applications. Variations of the feed concentration are also tested.

Table 5-1 Properties of the Ni/YSZ OC

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni powder</td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>99.8%</td>
</tr>
<tr>
<td>Particle size, d</td>
<td>&lt;1 μm</td>
</tr>
<tr>
<td>density, ρNi</td>
<td>8.9 g cm⁻³</td>
</tr>
<tr>
<td>Molar density, ρNi</td>
<td>1.52 × 10⁻⁵ mol m⁻³</td>
</tr>
<tr>
<td>Surface molar density, ρNi,s</td>
<td>5.35 × 10⁻⁵ mol m⁻²</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>0.352 nm</td>
</tr>
<tr>
<td>Melting point</td>
<td>1453 °C</td>
</tr>
<tr>
<td>Oxidation energy, ΔHᵢₒ</td>
<td>-239.70 kJ/mol Ni</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3mol% Y₂O₃ stabilized ZrO₂ (YSZ)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity</td>
<td>&gt;99.9%</td>
</tr>
<tr>
<td>Particle size</td>
<td>30-60 nm</td>
</tr>
<tr>
<td>Density, ρNiO</td>
<td>6.10 g cm⁻³</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>126.30 g mol⁻¹</td>
</tr>
<tr>
<td>Molar density, ρNiO</td>
<td>4.83 × 10⁻⁴ mol m⁻³</td>
</tr>
<tr>
<td>Melting point</td>
<td>2700 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Prepared NiO/YSZ sample</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO loading (prepared), ϕNi</td>
<td>45mol%</td>
</tr>
<tr>
<td>Total sample mass</td>
<td>50 mg</td>
</tr>
<tr>
<td>Ni content</td>
<td>12.81 mg</td>
</tr>
<tr>
<td>Oxygen carrying capacity, Rₒₒ</td>
<td>4.39 × 10³ μmol O g⁻¹ OC</td>
</tr>
</tbody>
</table>

Pure nickel exhibits a significant variation of the redox reactivity during the initial 20 cycles, as shown in Figure 4-1. In contrast, NiO/YSZ demonstrates superb cyclic regenerability starting the 2nd cycle. Figure 5-2 shows the measured species concentration during the initial 10 cycles at 1000°C. Panels (a) and (b) compare the measured O₂ and H₂/H₂O concentration with varying cycles for oxidation, and reduction, respectively, while the total consumption of O₂ and yield of H₂O are compared in panel (c). After the 2nd cycle, the measured concentration profiles almost
overlap, and the difference is within the noise level. The ratio of the total O\textsubscript{2} consumption to the cumulative H\textsubscript{2}O yield is approximately 1:2, indicating precise oxygen balance between the reduction and oxidation steps. The obtained yield closely matches with the oxygen carrying capacity, \( R\textsubscript{OC} \) (see Table 4-2), suggesting a complete redox conversion during 1 min time window at 1000\textdegree C. This is not a surprise, given the observation in the last chapter that roughly 1 \( \mu \)m of the nickel foils is activated during the 1 min redox reactions.

In each set of measurement, the cyclically stabilized NiO/YSZ (pre-treated with H\textsubscript{2}) undergoes redox measurements starting from 1000\textdegree C till 500\textdegree C with a step of 100\textdegree C. Each operating condition is repeated for at least three times, and the results are averaged to minimize the noise. The reaction kinetics for O\textsubscript{2} and H\textsubscript{2} are evaluated similarly as with the previous chapter, based on eqs.(4.3)-(4.6). In the case of CO reduction, the reduction step is described as:

\[
\text{CO Reduction: } \text{NiO} + \text{CO} \rightarrow \text{Ni} + \text{CO}_2 \tag{5.1}
\]

By considering the element balance, as detailed in Chapter 2, the reduction rate is expressed as:

\[
\dot{\omega}_{\text{CO}} = \frac{\dot{n}_m \left( X_{\text{out,CO}_2} - X_{\text{in,CO}_2} \right)}{m_{\text{OC}}} \tag{5.2}
\]

Here \( \dot{n}_m \) is the flow rate, \( X_i \) is the measured species mole fraction. Reaction rates are normalized by the mass of the OC, i.e., \( m_{\text{OC}} = 50\text{mg} \). The conversion of OC during the redox reactions, \( X_{\text{OC}}(t) \), is calculated using eqs. (4.5) and (4.6), with zero being fully reduced state and unity fully oxidized.
Figure 5-2 Cyclic measurement of (a) O₂ concentration in oxidation and (b) H₂/H₂O concentration in reduction, and (c) total O₂ consumption or H₂O production for the initial 10 cycles. Initial cycling is carried out at 1000°C with 10%H₂ and 21% O₂. R_{oc} in panel (c) marks the oxygen carrying capacity based on stoichiometry.

5.3 Reduction with H₂

Reduction with H₂ is the simplest case. Figure 5-3 shows the base case results with H₂ as fuel and O₂ as oxidizer. Panels (a) and (d) show the measured species concentration at the inlet and exit of the reactor; panels (b) and (e) are calculated oxygen removal rate in reduction and O₂ consumption rate in oxidation; panels (c) and (f) are the calculated evolution of oxygen carrier conversion. The reaction rates spike with the intake of the gaseous reactant, followed by a
gradual decay. The peak rates reached during the redox steps are 223 μmole H₂O g⁻¹s⁻¹, and 263μmole O₂ g⁻¹s⁻¹, respectively; similarly as observed previously with nickel foils, reduction of OC is noticeably slower, given the fact that the consumption of 1 mole O₂ is accompanied by incorporation of two O ions into the solid. With the fast oxidation reactivity, the majority of the oxygen intake process completes roughly within 0.5 min, while reduction spans over the entire reduction step. A slower residual oxidation stage is evidently observed after t = 0.5 min, as seen in panel (f), during which the further intake of oxygen is limited by the slow solid-state diffusion through oxide scale in search for residual oxygen deficiency within the particle. The reduction step, on the other hand, proceeds more gradually (see panel c) without a clear transition between the initial and later stages. Similar redox conversion patterns were clearly observed in the previous chapter with nickel foils, e.g., Figure 4-10 and Figure 4-12, again demonstrating the similarity of the redox reactions regardless of the form factors.

Despite the similarity, distinctive features are associated with the NiO/YSZ powders, which lead to more promising behaviors. As seen in panels c and f, the support of YSZ activates full oxygen carrying capacity of NiO, with X cycling between zero (fully reduced) and unity (fully oxidized) between the redox steps. This is in stark contrast to the observation in the previous chapter that less than 30% of the available carrying capacity is utilized with 2.5 μm foils, and the number with thicker foils is even lower. With nickel foils, the reduction rate is slower with the peak rate about half that of oxidation. The normalized (on nickel mass basis) peak rates for 2.5 μm are within the same order of magnitude as compared to NiO/YSZ, i.e., 320 μmole O₂ g⁻¹s⁻¹ (Figure 4-9b), and 190.7 μmole H₂O g⁻¹s⁻¹ (Figure 4-23), suggesting similar processes during the initial conversion. The absolute values, however, are noticeably slower as compared to the normalized
rates with NiO/YSZ (i.e., 1027 μmole O\textsubscript{2} g\textsuperscript{-1}s\textsuperscript{-1}, and 870 μmole H\textsubscript{2}O g\textsuperscript{-1}s\textsuperscript{-1}, normalized by nickel content, see Table 4-2), owing to the insufficient utilization of the foils\textsuperscript{11}.

![Graphs](image)

Figure 5-3 Reduction with H\textsubscript{2} and Oxidation with O\textsubscript{2} of 50mg NiO/YSZ at 1000°C with. (a, d) Species concentration at inlet, and outlet; (b, e) reduction or oxygen consumption rate; and (c, f) conversion of OC. The total flow is fixed at 350 scem, and O\textsubscript{2} and H\textsubscript{2} are 21% and 10%, respectively.

\textsuperscript{11} If we discount the mass of foils by the actual utilized portion (27%, see Table 4-4), the peak rates with 2.5 μm foils become 1150 μmole O\textsubscript{2} g\textsuperscript{-1}s\textsuperscript{-1}, and 686 μmole H\textsubscript{2}O g\textsuperscript{-1}s\textsuperscript{-1}. 
**Effect of H\textsubscript{2} concentration**

The effect of H\textsubscript{2} is examined by varying the intake H\textsubscript{2} concentration from 5\% to 14\%, as shown in Figure 5-4. The reduction reactivity is dependent on H\textsubscript{2} concentration: at higher H\textsubscript{2} mole fraction, the rate profile spikes higher followed by a rapid decay, while at lower H\textsubscript{2} concentration, the conversion spans over a longer period. This is different from the case with the nickel foils, as seen in Figure 4-12, where the surface sites are mostly saturated with adsorbed H\textsubscript{2}, and the reduction reactivity is only weakly sensitive to H\textsubscript{2} concentration. The difference is partially attributed to the usage of support which leads to a less favored adsorption, as will be shown in Section 5.3.6. This phenomenon is also observed with in the ceria-based study, in which the addition of zirconia (see Chapter 7) leads to a less energetically favored adsorption. Additionally, the use of YSZ enhances the H\textsubscript{2}O formation step (eq. (3.35)) by improving transport of the oxygen ionic, which leads to a more rapid consumption of H(s) surface adsorbates. This in turns promotes the adsorption, leading to stronger H\textsubscript{2} dependence. Detailed derivation can be found in Appendix B of ref. [14]. The strong H\textsubscript{2} dependence was also previously reported in the literature for NiO/YSZ [9], as well as other nickel-binders OCs [15, 16] (see Table 4-1 for details).

Complete utilization of oxygen carrying capacity is achieved with H\textsubscript{2} over 10\%, as seen in Figure 5-4(c), while reduction with 5\% H\textsubscript{2} utilizes over 85\% of the overall carrying capacity. The following oxidation step (not shown) after reduction with 14\% H\textsubscript{2} or 10\% H\textsubscript{2} is essentially identical, and the reactivity is only slightly higher than the case with 5\% H\textsubscript{2}. 

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Figure 5-4 Reduction with varying H₂ concentration at 1000°C. (a) Species concentration at exit; (b) reduction rate; and (c) conversion of OC. The total flow is fixed at 350 sccm, and O₂ is fixed at 21%. H₂ is varied from 5%, 10% (base case), and 14%.

**Effect of O₂ concentration**

The effect of O₂ concentration on the oxidation step, on the other hand, is very similar as compared to the foil cases. As shown in Figure 5-5, oxidation with NiO/YSZ exhibits a strong O₂ dependence: the profile of ωO₂ (panel b) becomes taller and narrower at higher O₂ feed flow, with the OC conversion (panel c) rising more rapidly towards unity. A full recovery of the oxygen stoichiometry is achieved for all the cases within 1 min. The following reduction step is identical regardless of the O₂ concentration used in the previous oxidation step.
Figure 5-5 Oxidation with varying O₂ concentration at 1000°C. (a) Species concentration at exit; (b) reduction rate; and (c) conversion of OC. The total flow is fixed at 350 sccm, and H₂ is fixed at 10%. O₂ is varied from 5%, 10%, and 21% (base case).

**Effect of H₂O concentration**

Reduction process is accompanied by the production of H₂O, which may hinder the reactivity by either saturating the surface sites or promoting the backward reactivity [17]. To understand the effect of H₂O on the reduction reactivity, a fixed steam flow with H₂O at 2% or 4% is admitted into the reactor during the reduction step, and the obtained measurements are compared to the base case in Figure 5-6. As seen in panel (a), the feed of H₂O as well as that produced during the reaction contributes to H₂O measured at the exit. The obtained profiles of reaction rates (panel b) and the OC conversion (panel c) completely overlap among the three cases, suggesting that
reduction is not affected by the presence of H₂O in the reacting environment. This agrees with the modeling results from Chapter 4, which shows that the effect of H₂O on reduction is negligible.

Figure 5-6 Effect of H₂O carrying gas on the reduction step at 1000°C. (a) Species concentration (b) reduction rate; and (c) conversion of OC. The total flow is fixed at 350 sccm. H₂ is fixed at 10%, and O₂ is fixed at 21%. H₂O concentration is varied at 0%, 2%, and 4%. Panel (a) only plots the measurements for the 4% H₂O case for clarity.

Effect of Temperature

The effect of temperature on the redox processes is examined in Figure 5-7 and Figure 5-8. Evident temperature dependence is observed in reduction, similarly as with the nickel foils in Chapter 4. The rate profile becomes taller at elevated temperature, with the oxygen conversion profile decays more rapidly. The residual conversion rate near the end of reduction is slowest at
1000°C, in line with a full depletion of available oxygen, while the rate in the later stage at 700°C is noticeably higher. Complete utilization of OC capacity is achieved at 1000°C, as shown in panel (b).

Figure 5-7 Effect of temperature on (a) reduction rates, and (b) conversion of OC. Total flow is fixed at 350 sccm with 10% H₂ and 21% O₂.

The temperature dependence for the oxidation step is weaker, as shown in Figure 5-8. The rate profiles are analogous, and the temperature dependence is monotonic throughout the entire oxidation step. The peak rate is slightly lower at low temperature, in accordance with a higher
initial oxygen conversion as shown in panel (b). The oxidation conversion proceeds via a fast initial stage followed by a slower residual stage, and the transition takes place at \( X = 0.8-0.9 \) similar among different temperatures. These patterns are also consistent with those observed with nickel foils.

![Graph](image)

Figure 5-8 Effect of temperature on (a) oxidation rates, and (b) conversion of OC. Total flow is fixed at 350 sccm with 10% \( \text{H}_2 \) and 21% \( \text{O}_2 \).

The peak redox reaction rates and the total yield are shown in Figure 5-9. Oxidation rate is significantly faster than reduction, and it is less sensitive to temperature. The ratio between the
total consumed $O_2$ and the $H_2O$ yield is close to 1:2, as shown in panel (b). Oxygen utilization, defined as, the ratio of total $H_2O$ yield to the oxygen carrying capacity (see in Table 4-2), is also included in panel (b). A complete utilization is reached at 1000°C.

Figure 5-9 Comparison of the (a) peak rates, and (b) total yield of the redox reactions with varying temperature. The OC utilization is also included in panel (b).
Kinetics Modeling of Oxidation Step

The fast oxidation achieved with NiO/YSZ suggests a dramatic improvement of the reaction mechanism from the diffusion-pathway limited process as shown in the last chapter. To understand the new rate-limiting mechanism for the oxidation process, we formulate a modeling description of the oxidation process in this sub-section, on the basis of the framework presented in Chapter 3.

The external (interface between nickel oxide and O₂) and internal (interface between nickel core and nickel oxide) surface reactions for nickel may be expressed as (eqs. (3.18), and (3.28)):

External: \[
\frac{1}{2} O_2 \leftrightarrow O'_O + V^*_\text{Ni} + 2h^* \tag{5.3}
\]
\[
\dot{r}_\text{ex} = k_{f,\text{ex}} P_{O_2}^{1/2} - k_{b,\text{ex}} \left[ V^*_\text{Ni,ex} \right] \left[ h^* \right]_{\text{ex}}^2 \tag{5.4}
\]

Internal: \[
\text{Ni} + V^*_\text{Ni} + 2h^* \leftrightarrow \text{Ni}^*_{\text{Ni}} \tag{5.5}
\]
\[
\dot{r}_\text{int} = k_{f,\text{int}} \left[ V^*_\text{Ni,\text{int}} \right] \left[ h^* \right]_{\text{int}}^2 - k_{b,\text{int}} \tag{5.6}
\]

where \( V^*_\text{Ni} \), \( h^* \), \( O'_O \), and \( \text{Ni}^*_{\text{Ni}} \) denote nickel cation vacancy, electron hole, oxygen ion at regular anion site, and nickel ion at regular cation site. \( k_i \) is the (forward or backward) reaction rate constant (unit \( s^{-1} \)). Here the dilute limit is assumed and the normal sites are excluded from the Law of Mass Action. At equilibrium, \( r_{\text{ex}} \) and \( r_{\text{int}} \) are zero, leading to the definition of the equilibrium defect concentration:

\[
\left[ V^*_\text{Ni,ex} \right]_\text{eq} = \left( \frac{K_{\text{ex}}}{4} \right)^{1/3} P_{O_2}^{1/6} \tag{5.7}
\]
\[
\left[ V^*_\text{Ni,\text{int}} \right]_\text{eq} = \left( 4 K_{\text{int}} \right)^{-1/3} \tag{5.8}
\]
where $K_{eq}$ from ref. [18] is adopted,

$$K_{ex} = \frac{k_{f, ex}}{k_{b, ex}} = 0.0053 \exp\left(\frac{223.5 \text{kJ/mol}}{RT}\right) \quad (5.9)$$

and $K_{int}$ can be obtained based on equilibrium of the overall nickel oxidation reaction,

$$\frac{1}{2} O_2 + Ni \leftrightarrow K_{nilex} \rightarrow NiO, \text{ where } K_{nilex} = 3.3 \times 10^{-5} \exp\left(\frac{234.23 \text{kJ/mol}}{RT}\right) \quad (5.10)$$

$$K_{int} = \frac{K_{nilex}}{K_{ex}} = 0.0062 \exp\left(\frac{457.73 \text{kJ/mol}}{RT}\right) \quad (5.11)$$

In deriving eqs. (5.7) and (5.8), we use the electro-neutrality condition:

$$[V_{Ni}^*] = 2\left[h^*\right] \quad (5.12)$$

The defects between the external and internal surfaces are connected via a diffusion process, as

$$\frac{\partial [V_{Ni}^*]}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 J_{V_{Ni}^*}\right) = 0 \quad (5.13)$$

$$J_{V_{Ni}^*} = -\tilde{D} \frac{\partial C_{V_{Ni}^*}}{\partial r}, \text{ where } \tilde{D} = \frac{3D_{V_{Ni}^*}D_{h^*}}{D_{h^*} + 2D_{V_{Ni}^*}} \quad (5.14)$$

Here $D_{V_{Ni}^*}$ and $D_{h^*}$ are self-diffusivity of defects, and $\tilde{D}$ is the ambipolar diffusivity. In the case with multiple diffusional pathways (see Figure 4-14), $\tilde{D}$ is replaced by a weighted averaged among all possible diffusion mechanisms, i.e., eq. (4.12). Thus, the oxidation process is completely described by eqs. (5.4), (5.6), (5.13), and (5.14). In deriving the above formulations, we assume that the phase and the crystal structures of the oxide scale and the nickel core remain unaltered. Given the role of the YSZ in maintaining the structural matrix, one can expect phase stability during the majority of the conversion process. This is also in line with the observed cyclic repeatability even starting the very first redox cycling, as shown in Figure 5-1. This
assumption, however, becomes inaccurate with the case of pure nickel foils, for which substantial morphological and microstructural evolutions are clearly observed, as presented in the last chapter. As a result, sub-models that describe the structural evolution (see Section 4.4) must be included to close the formulations for nickel foils.

From Chapter 4, it is concluded that the surface nucleation process completes rapidly (less than a few second), and it only contributes to a very minor amount (< 2%) of the overall O₂ consumption, as seen in Figure 4-18(c). Therefore, we assume that the surface defect formation reaction is effectively maintained at equilibrium and the external defect concentration is determined by eq. (5.4). Additionally, as shown in Figure 4-17(c), the ambipolar diffusivity, $\tilde{D}$, (or equivalently the parabolic rate constant, $k_p$, in eq. (4.12)), is very fast for the grains with smaller dimensions. The decay of the diffusivity with time observed in Figure 4-17(c) was attributed to the annihilation of the fast diffusional paths, which, however, is expected to be less significant in the case of NiO/YSZ, as the irreducible YSZ effectively maintains the grain structure throughout the course of conversion. Based on the modeling results in Chapter 4, the characteristic time, $\tau$, for a diffusion-limited process from the expression, $\tau \sim d^2/4D$, (see eq. (3.58)), is estimated to be less than 0.5 sec for a particle smaller than 1 µm. This estimation indicates that the bulk diffusion through the oxide scale is fast enough that spatial variations of defect concentrations should be negligible. The defect segregation effect, as observed in the case of ceria-based studies [19, 20] (see later chapters), is expected to be less significantly, given the role of YSZ as the support and the fact that the surface nucleation process is fast.
Thus, for the oxidation process controlled by the internal reaction (see Figure 5-10), the rate expression, eq. (5.6), is simplified to:

$$r = 4k_{f, int} \left( \left( [V'_{\text{Ni}}]_{\text{eq}} \right)^3 - \left( [V''_{\text{Ni}}]_{\text{eq}} \right)^3 \right) = k_{f, int} \left( K_{\text{ex}} p_{O_2}^{1/2} - K_{\text{int}}^{-1} \right)$$  \hspace{1cm} (5.15)

Here, the reaction is essentially driven by the off-equilibrium bias established at the internal interface. Consequently, the conversion proceeds via consumption and hence contraction of the interior nickel core, with radius of $r_c$ evolving as (see Figure 5-10):

$$-\frac{d}{dt} \left( \tilde{\rho}_{\text{Ni,s}} \frac{4\pi r_c^3}{3} \right) = -4\pi r_c^2 \tilde{\rho}_{\text{Ni,s}} k_{f, int} \left( K_{\text{ex}} p_{O_2}^{1/2} - K_{\text{int}}^{-1} \right)$$  \hspace{1cm} (5.16)

where $\tilde{\rho}_{\text{Ni,s}}$ and $\tilde{\rho}_{\text{Ni}}$ are the surface (unit, mole m$^{-2}$) and volumetric molar density (unit, mole m$^{-3}$). By integrating eq. (5.16), and substituting $X = 1 - \frac{r_c^3}{R^3} + X_0$, ($R$ is the radius of particle, and $X_0$ corresponds to unused NiO from the preceding reduction step), we obtain:
\begin{equation}
\frac{t}{\tau} = 1 - (1 - X + X_0)^{1/3}, \text{ where } \tau = \frac{\tilde{\rho}_{Ni} R}{\tilde{\rho}_{Ni,s} k_{f, int} \left( K_{ex} p_{O_2}^{1/2} - K_{int}^{-1} \right)} \tag{5.17}
\end{equation}

Eq. (5.17) essentially becomes the shrinking-core model (SCM) under chemical reaction rate control [6]. The initial condition, \( X(t=0) = X_0 \), describes the amount of NiO left unconsumed in the previous reduction step. Thus, complete re-oxidation is achieved at \( t = (1 - X_0^{1/3}) \tau \) and \( r_c = RX_0^{1/3} \). The \( O_2 \) consumption rate can be calculated as:

\begin{equation}
\omega_{O_2} = \frac{1}{2MW_{OC}} \phi_{Ni} \frac{dX}{dt} = \frac{\phi_{Ni}}{2MW_{OC}} \frac{3(1 - X + X_0)^{2/3}}{\tau} \tag{5.18}
\end{equation}

where \( \phi_{Ni}, MW_{OC} \) are nickel loading, and molecular weight of the OC (see Table 4-2). With the time-resolved profiles of \( p_{O_2} \) measured using QMS, the entire oxidation process can be predicted based on eq. (5.17). The kinetics parameter, \( k_{f, int} \) can be varied to minimize the difference between the measurement and the model prediction.

Comparison of the oxygen conversion between modeling predictions (solid lines) and the measurements (circles) is shown in Figure 5-11. The kinetics modeling precisely captures the oxidation conversion during the most of the process; however, the eq. (5.18) overestimates the reaction rate as \( X \) approaches unity. This discrepancy arises from the deviation from the ideal conversion process: as the majority of nickel is oxidized (i.e., \( X \) approaches unity), the interface that delimits the nickel oxide and the unreacted nickel core becomes less defined; the ionic diffusion process essentially becomes a part of the oxidation in search for residual vacancies to fill in. Therefore, the spatial variation of the defect concentration needs to be resolved to accurately capture the slowed kinetics after the transition. However, to empirically account for the two-stage conversion without solving the detailed differential equations, a correction function, \( F(1-X) \), can be used with eq. (5.18):
\[
\omega_{O_2} = \frac{\phi_{Ni}}{2MW_{OC}} \frac{3(1 - X + X_0)^{2/3}}{\tau} F(1 - X)
\] (5.19)

Here, \( F \) is almost all zero, except when \( X \) approaches unity, thus restricting the oxidation rate as the conversion approaches completion. Many analytical expressions can be used for \( F \), including polynomials, Gauss error function, sigomodal functions, etc. For simplicity, we use a sigomodal function as below

\[
F(1 - X) = \begin{cases} 
1 & X \leq X_{cr} \\
\frac{1}{2} - \frac{1}{2} \cos \frac{1 - X}{1 - X_{cr}} \pi & X_{cr} \leq X \leq 1 \\
0 & X \geq 1 
\end{cases}
\] (5.20)

Here \( X_{cr} \) marks the transition. The modified kinetics predictions with \( X_{cr} = 0.8 \) (corresponding to the transition observed in Figure 5-8) are also included in Figure 5-11, and a perfect agreement is observed for the entire range of conversion. The measured and predicted \( O_2 \) consumption rate are also compared in Figure 5-12.

The obtained kinetic parameter is listed in Table 5-2. Given the equilibrium constant in eqs. (5.9) and (5.11), it is clear \( [V''_{Ni}] \) is over two-order-of-magnitude lower as compared to \( [V''_{Ni}]_{ex} \). As a result, the backward rate in eq. (5.15) is negligible, leading to simplification of eq. (5.18) as,

\[
\omega_{O_2} = \frac{1}{2} \frac{\phi_{Ni}}{MW_{OC}} \frac{dX}{dt} = \frac{\phi_{Ni}}{2MW_{OC}} 3k_{eff} P_{O_2}^{1/2} (1 - X + X_0)^{2/3}, \text{ where } k_{eff} = \frac{\tilde{\rho}_{Ni,k_{f,int}K_{ex}}}{\tilde{\rho}_{Ni,R}}
\] (5.21)

Here \( k_{eff} \) is the effective rate constant. Eq. (5.21) shows that the oxidation process is proportional to \( P_{O_2}^{1/2} \) with an effective activation energy is \( \sim 7kJ/mol \) (see Table 5-2). These are in reasonable agreement with the values reported in refs. [9, 21-24].
Figure 5-11 Comparison of the model predictions (lines for eq. (5.21) and dashed lines for eq. (5.22)) with the measurements (circles) for oxidation conversion.

Table 5-2 Kinetic parameters for oxidation of NiO/YSZ

<table>
<thead>
<tr>
<th></th>
<th>$k_0$</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{eff}}$</td>
<td>0.23 s$^{-1}$</td>
<td>6.8 kJ/mol</td>
</tr>
<tr>
<td>$k_{\text{f, int}}$</td>
<td>6.2$\times$10$^4$ s$^{-1}$</td>
<td>-216.7 kJ/mol</td>
</tr>
<tr>
<td>$K_{\text{ex}}$ (ref. [18])</td>
<td>0.0053</td>
<td>223.5 kJ/mol</td>
</tr>
<tr>
<td>$K_{\text{int}}$ (ref. [18])$^*$</td>
<td>0.0062</td>
<td>-457.7 kJ/mol</td>
</tr>
</tbody>
</table>

$^*$ Note, $K_{\text{int}}$ is calculated based on $K_{\text{ex}}$ via equilibrium, see eq. (5.11)
Kinetics Modeling of the Reduction Step with H₂

The reduction step is modeled following a similar approach as used with foils. Eq. (4.27) can be written for the NiO/YSZ sample as:

\[
\frac{dX}{dt} = -k_{\text{red}} X^n \frac{P_{H_2}}{\left(\sqrt{P_{H_2}} + K\right)^2} \tag{5.22}
\]

Here \( K = 1/\sqrt{K_{H_2}} \), where \( K_{H_2} \) is the equilibrium constant of H₂ adsorption reaction (eq.(4.23)). The effect of H₂O (i.e., backward reaction and the saturation on the surface sites) is excluded from the modeling, since the measurements show that H₂O concentration does not affect the reduction kinetics (see Figure 5-6 as well as Chapter 4). \( X^n \) is the empirical term used to describe the evolution of the available oxygen that is exposed to the reducing environment. The constant \( n \)
represents the possible oxygen diffusional mechanism. \( n = 0, 1/2, \) or \( 2/3 \) corresponds to the shrinking-core model (SCM), and \( n = 1 \) represents the Avrami model. The previous chapter reports \( n \) of 2.57, indicating a slow oxygen ionic diffusion and hence a dramatic drop of the available oxygen exposed to the environment. The high oxygen ionic diffusivity of YSZ as support is expected to significantly enhance the exposure, thus effectively lowering \( n \) and improving the reactivity.

Assuming \( k_{\text{red}} \) and \( K \) follow the Arrhenius expression, and \( n \) is fixed with temperature, we can obtain the kinetics parameters by minimizing the difference of the reduction rate (\( \omega_{\text{H}_2\text{O}} \)) between the measurement and the prediction. The comparison of conversion and the reactivity is shown in Figure 5-13 and Figure 5-14, respectively.

![Figure 5-13](image-url)  
**Figure 5-13** Comparison of the model predictions (lines for fixed \( n \) and dashed lines varying \( n \)) with the measurements (circles) for reduction conversion.
The modeling results with a fixed reaction order $n$ (black lines) generally describe the pattern of reduction; however, the predictions underestimate the reduction rate at high temperature while over-predict the results at low temperature. The discrepancy is related to the temperature dependence of the ionic diffusional mechanism in NiO/YSZ. The oxygen diffusivity of YSZ is highly temperature sensitive (e.g., $80 - 100$ kJ/mol for YSZ (4.5mol%Y) [25]). The fast diffusivity at high temperature enables a rapid transport process, effectively exposing the interior oxygen to the reducing environment, and hence leading to a smaller reaction order $n$. At low temperature, on the other hand, the diffusional contribution from YSZ becomes less pronounced, and the reduction pattern approaches that observed with pure nickel (hence larger $n$).

To further quantify this effect, we allow the reaction order $n$ to vary for each temperature, and the modeling results are also included in Figure 5-13 and Figure 5-14. Evident improvement of the modeling results is observed, which precisely captures the conversion patterns at varying temperature. The obtained $n$ with temperature is plotted in Figure 5-15. Interestingly, $n$ remains unchanged when temperature is below 700°C, or as temperature approaches 1000°C, with a large drop from 700°C to 800°C, which echoes the observed jump in Figure 5-7. The reaction order with NiO/YSZ is significantly lower than that of pure foils (blue lines), emphasizing the role of YSZ in reduction. At 1000°C, the reaction order is close to 2/3, suggesting a similar conversion pattern as described by the reaction-controlled shrinking-core model (SCM).

The obtained reduction kinetic parameters are summarized in Table 5-3. The obtained activation energy, $\sim 20$kJ/mole, is slightly lower than that obtained with nickel foils. $K$ becomes significant with the value in the range $0.015 \sim 0.03$, in contrast to negligible value with nickel foils.
Consequently, the adsorption equilibrium, \( K_{H_2} = (K)^2 \), is smaller with NiO/YSZ. The dependence on \( H_2 \) varies from unity at low \( p_{H_2} \) to zero at high \( p_{H_2} \). Similar kinetics is reported in refs. [16, 21, 23, 26, 27].

Figure 5-14 Comparison of the model predictions (lines for fixed \( n \) and dashed lines varying \( n \)) with the measurements (circles) for the reduction consumption rates.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( k_{red} (s^{-1}) )</th>
<th>( E (kJ/mol) )</th>
<th>( K_0 (s^{-1}) )</th>
<th>( E (kJ/mol) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model w/ fixed ( n )</td>
<td>1.14</td>
<td>0.48</td>
<td>19.5</td>
<td>0.085</td>
</tr>
<tr>
<td>Model w/ diff. ( n )</td>
<td>1.6</td>
<td>1.66</td>
<td>1.60</td>
<td>1.05</td>
</tr>
</tbody>
</table>
5.4 Reduction with CO

The reduction kinetics with CO is shown in Figure 5-16. CO is kept at 5% for reduction with 20% CO₂ as carrying gas to avoid any carbon deposition from Boudouard reaction. The oxidation process is maintained the same as with H₂. As seen in panel (a), the profile of CO₂ at exit rises with the intake of CO, and falls back to the background level asymptotically during the course of conversion. The temperature dependence of the reduction reactivity is shown in panel (b). Much weaker temperature dependence is observed here, and the increase of peak rate from 500°C to 1000°C is less than 50%. The reactivity approaches zero near the end of reduction and the conversion patterns become flattened, even though more than 40% of oxygen is still available for reduction, as seen in panel (c). This is starkly different from the case with pure H₂, in which a
complete reduction is achieved at high temperature. The difference is further examined in Figure 5-17: both the peak rate and the total yield with CO are less than half than those with H₂.

Figure 5-16 Reduction with CO. (a) Species concentration (b) reduction rate; and (c) conversion of OC. The total flow is fixed at 350 sccm. CO is fixed at 5%, with 20% CO₂ as carrying gas. Temperature is varied from 1000°C to 500°C. Panel (a) only plots the measurements at 1000°C for clarity.
Figure 5-17 Comparison of the peak rates (lines), and total yield (column) of reduction with H₂ (black) and CO (red).

Given the fast oxygen diffusion and sufficient exposure to the reducing environment observed in the H₂ case, one can expect an analogous diffusional process with CO. The slower kinetics observed here is therefore associated with the hindered surface chemistry in the CO/CO₂ environment. To understand the surface chemistry with CO, we model the reduction process similarly as H₂/H₂O as in Chapter 4 (see Section 3.3 for derivation),

\[
\frac{dX}{dt} = k_j X^n \frac{K_{CO}P_{CO}}{1 + K_{CO}P_{CO} + K_{CO₂}P_{CO₂}} - k_h (1 - X) \frac{K_{CO₂}P_{CO₂}}{1 + K_{CO}P_{CO} + K_{CO₂}P_{CO₂}}
\]  

(5.24)

where \( K_{CO} \) and \( K_{CO₂} \) are the equilibrium constant for the adsorption reactions:

\[
CO(g) + s \underset{K_{CO}}{\rightleftharpoons} CO(s)
\]  

(5.25)

\[
CO₂(g) + s \underset{K_{CO₂}}{\rightleftharpoons} CO₂(s)
\]  

(5.26)

Note that the backward rate in eq. (5.24) is assumed to linearly depend on \( 1 - X \). Compared to eq. (4.27), it is clear that the slow CO reduction rate originates from three factors: (1) a slower rate constant, \( k_j \); (2) saturation of CO₂ on the surface sites, \( K_{CO₂} \); and (3) backward reaction, \( k_h \). The flattened pattern of \( X \) observed near the end of reduction with \( X > 40\% \) (see Figure 5-17(c))
indicates that the slower rate constant, $k_6$, cannot be the sole reason. On the other hand, $p_{CO_2}$ remains relatively stable (see Figure 5-17(a)) throughout the course of reduction, suggesting that the saturation of the surface sites by CO$_2$ are unlikely to be the major reason constraining reduction during the later stage. To further illustrate the effect of the carrier gas CO$_2$, we compare the base CO case to that with 10% CO$_2$ in Figure 5-18. Compared to the base case, reduction rate is increased by less than 10%. The difference is mostly at the later stage of reduction ($t > 0.5$ min), and the initial conversion ($t < 0.4$ min) remains almost identical. The comparison indicates that CO$_2$ adsorption on the surface is negligible, and the slow residual reduction is mostly attributed to the pronounced backward reaction at low $X$.

Figure 5-18 Effect of CO$_2$ carrying gas on the reduction step at 1000°C. (a) Reduction rate; and (b) conversion of OC. The total flow is fixed at 350 sccm. CO is fixed at 5%, and O$_2$ is fixed at 21%. CO$_2$ concentration is varied at 10% and 20%.
The fitted results from eq. (5.24) are compared to the measurements in Figure 5-19 and Figure 5-20, which exhibit excellent agreement. The fitting utilizes the reaction order, $n$, derived in the H$_2$ reduction case (Table 5-3) for each temperature, indicating a similar oxygen diffusional process between H$_2$ and CO cases. Minor discrepancy is observed near the end of reduction at low temperature (Figure 5-20(d-f)), which is possibly attributed to the deviations from the linear dependence on $1 - X$ in eq.(5.24).

![Figure 5-19 Comparison of the model predictions (lines for fixed $n$ and dashed lines varying $n$) with the measurements (circles) for the reduction consumption rates.](image)

The obtained kinetic parameters are listed in Table 5-4. The obtained $K_{CO_2}$ is negligible in the denominator of eq. (5.24), with the value of 0.002 $\sim$ 0.035 at 1000°C to 500°C, respectively, thus confirming the assumption that the presence of CO$_2$ does not affect the surface sites.
Table 5-4 Kinetic parameters for CO reduction

<table>
<thead>
<tr>
<th>$k_f$ (s$^{-1}$)</th>
<th>$E$ (kJ/mol)</th>
<th>$k_o$ (s$^{-1}$)</th>
<th>$E$ (kJ/mol)</th>
<th>$K_{CO}$</th>
<th>$E$ (kJ/mol)</th>
<th>$K_{CO2}$</th>
<th>$E$ (kJ/mol)</th>
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<tbody>
<tr>
<td>$k_0$ (s$^{-1}$)</td>
<td>$E$ (kJ/mol)</td>
<td>$k_0$ (s$^{-1}$)</td>
<td>$E$ (kJ/mol)</td>
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<td>2.5×10$^1$</td>
<td>67.5</td>
<td>1.5×10$^4$</td>
<td>34.8</td>
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<td>-67.7</td>
<td>2.3×10$^{-5}$</td>
<td>-47.0</td>
</tr>
</tbody>
</table>

Figure 5-20 Comparison of the model predictions (lines) and the measurements (circles) for reduction conversion with CO.

5.6 Summary

This chapter examines the redox reactivity with NiO supported by YSZ nano-powders exposed to H$_2$ or CO as fuel. The NiO/YSZ sample is prepared by mechanically mixing nickel particles with fine YSZ nano-powder. The redox reactivity with NiO (45mol%) supported on YSZ is measured in the button cell reactor in the temperature range 500-1000°C. Samples are subjected to alternative redox cycles using synthetic air (O$_2$+Ar) as oxidizer, and H$_2$/Ar, or CO/Ar mixture as fuel, respectively. NiO/YSZ demonstrates superb cyclic regenerability starting the 2$^{nd}$ cycle, with the full utilization of its carrying capacity during H$_2$/O$_2$ redox cycling. The peak rates reached during the redox steps with H$_2$ and O$_2$ are 223 μmole H$_2$O g$^{-1}$s$^{-1}$, and 263μmole O$_2$ g$^{-1}$s$^{-1}$.
respectively. Compared to pure nickel foils, pronounced improvement is achieved on the redox kinetics and the total oxygen utilization.

Significantly temperature dependence is observed for the H₂ reduction process, while oxidation is sensitive to the O₂ concentration. Reduction with CO, on the other hand, leads to lower OC utilization, resulting from the backward reaction by CO₂. The presence of H₂O, however, does not affect the reduction rate. Kinetics modeling reveals that the use of YSZ effectively maintains the fast ionic diffusion for both oxidation and reduction steps. Oxidation follows a shrinking-core model under the control of internal chemistry. Reduction with H₂ or CO generally follows a similar adsorption-reaction pathway. The effect of YSZ on improving the transport of oxygen during reduction is more pronounced at high temperature. The obtained results on the redox kinetics can be used for the design, fabrication, and optimization of the CLC reactor system.

5.7 Bibliography

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Chapter 6

Redox Kinetics Study of Fuel Reduced Ceria for
Chemical-Looping Water Splitting

Chemical-looping water splitting is a novel and promising technology for hydrogen production with CO₂ separation. Its efficiency and performance depend critically on the reduction and oxidation (redox) properties of the oxygen carriers (OC). Ceria is recognized as one of the most promising OC candidates, because of its fast chemistry, high ionic diffusivity, and large oxygen storage capacity. The fundamental surface redox pathways, including the complex interactions of mobile ions, electrons between the bulk and the surface, along with the adsorbates and electrostatic fields remain yet unresolved. This chapter presents a detailed redox kinetics study with an emphasis on the surface ion-incorporation kinetics pathway, using time-resolved and systematic measurements in the temperature range 600-1000°C. By using fine ceria nano-powder, we observe an order of magnitude higher hydrogen production rate compared to the state-of-the-art thermo-chemical or reactive chemical-looping water splitting studies. We show that the reduction is the rate-limiting step, and it determines the total amount of hydrogen produced in the following oxidation step. The redox kinetics is modeled using a two-step surface chemistry (an H₂O adsorption/dissociation step and a charge transfer step), coupled with the bulk-to-surface transport equilibrium. Kinetics and equilibrium parameters are extracted with excellent
agreement with measurements. The model reveals that the surface defects are abundant during redox conditions, and charge transfer is the rate-determining step for \( H_2 \) production. The results establish a baseline for developing new materials, and provide guidance for the design and the practical application of water splitting technology (e.g., the design of OC characteristics, the choice of the operating temperatures, periods for redox steps, etc.). The method, combining well-controlled experiment and detailed kinetics modeling, enables a new and thorough approach for examining the defect thermodynamics in the bulk and at the surface, as well as redox reaction kinetics for alternative materials for water splitting.

6.1 Introduction

Various metal oxides candidates (see Table 1-4) have been examined for RCLWS, among which the use of ceria as an OC leads to higher \( H_2 \) production because of its fast surface kinetics, high oxygen ionic diffusivity, large oxygen carrying capacity, and robust structural stability. The bulk-phase properties of ceria-based materials have been widely studied. The physical, chemical, and electrochemical properties of pure and doped ceria at equilibrium have been examined and documented [1-3]. Recently, there is an increasing effort towards a better understanding of the surface-oriented defect chemistry of ceria, owing to the growing interests in fuel cells, electrolyzers, and water splitting [4, 5]. Density functional studies examined surface defect formation and the energy landscape of the redox process [6-8]. In-situ techniques, such as in-situ X-ray photoelectron spectroscopy (XPS), have emerged recently, and have been successfully applied to ceria [4, 9-12]. The majority of the work concentrated on the surface and intermediate species at equilibrium. Despite the recent efforts in developing analytical models for reaction kinetics [13-16], the fundamental surface redox pathway of ceria is not well understood. The
complexities involved in the interactions of mobile ions, and electrons between the bulk and the surface, along with the adsorbates and electrostatic fields remain yet unresolved. Applying ceria in RCLWS requires a good knowledge of the time-resolved reactivity under conditions relevant for its application (temperature, gaseous composition), which is still missing.

In this chapter, we investigate the ceria redox mechanism with an emphasis on the surface ion-incorporation kinetics pathway, using a detailed time-resolved measurement under conditions relevant for RCLWS. Isothermal redox cycles of CeO₂ nano-powder are carried out in a button cell reactor in the temperature range 600-1000°C. H₂ is used as a surrogate fuel in this study in order to explore the fundamentals of redox reactions on ceria. Reaction kinetics is determined by quantifying the flue stream composition using an on-line quadrupole mass-spectrometer (QMS). H₂ is produced by water splitting during the oxidation cycle as a mixture of H₂O vapor and Ar is flown over CeO₂ samples. An order-of-magnitude higher hydrogen production rate is observed as compared to the state-of-art TCWS (Table 1-3) and RCLWS (Table 1-4) methods, resulting from the utilization of fine ceria nano-powder, which also ensures a surface-reaction-limited process. Kinetic models are subsequently developed to characterize the oxygen-ion incorporation dynamics during the redox process. The model consists of a series of intermediate steps: adsorption/dissociation of gaseous reactant, charge transfer on the surface, and the bulk-to-surface transport. The model reveals the importance of the surface defect and its connection to the bulk phase. Driven by the difference of the defect formation energy, the surface is enriched with the key defects (oxygen vacancy and polarons), consistent with the in-situ observations reported in the literature [4, 11]. With the proposed kinetics, the rate-limiting step is identified, and suggestions are obtained for the development of better materials in the future.
6.2 Experiment

The schematics of the system layout are shown in Figure 2-2, and Figure 2-7. Ceria powder from Sigma Aldrich (99.95% purity) is used for the reaction study. Table 6-1 lists the properties of the sample. The BET surface area is 15.4 m$^2$/g and the average size of the particle is 50 nm. 100 mg of ceria powder is embedded in quartz wool and placed at the bottom of the outer quartz tube. Lesser amount of sample is also tested (50 mg, and 25 mg), and negligible difference is found in the obtained redox kinetics. The sample undergoes redox cycles, with argon as purging gas flowing in between. Oxidation is performed using a gas mixture of water vapor and argon. The total flow rate into the reactor during the oxidation step is maintained constant at 337 sccm (standard cm$^3$/min), and the H$_2$O mole fraction is varied between 5% and 26%. H$_2$-Ar mixture is used for the reduction, with the total flow fixed at 350 sccm and the H$_2$ mole fraction from 5% to 20%. While the ultimate technology objective is to use methane for reduction, H$_2$ is used as a surrogate to examine the process while simplifying the modeling of the redox reactions. The oxidation and reduction times are fixed at 2 min each for the base case. Before measurements, the samples are pre-treated for 100 redox cycles at 1000°C to reach periodic stationary states. Afterwards, the measurements are taken from 1000°C till 600°C with a step of 50°C. Each operating condition is repeated for at least five times, and results are averaged to reduce the noise. The measurements at 500°C are also taken as a reference, although the reactivity is too low and can hardly be distinguished from background noise. Experiments with different oxidation and reduction conditions are also carried out to evaluate the effects on the H$_2$ production reactivity.
Table 6-1 Some physical properties of the CeO₂

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, ( \rho )</td>
<td>7.22 g cm(^{-3})</td>
</tr>
<tr>
<td>Molar density, ( \tilde{\rho}_{Ce} )</td>
<td>4.19 x 10⁴ mol m(^{-3})</td>
</tr>
<tr>
<td>Lattice constant, ( a )</td>
<td>0.54112 nm</td>
</tr>
<tr>
<td>Surface molar density, ( \tilde{\rho}<em>{Ce,s} = \tilde{\rho}</em>{Ce} a )</td>
<td>2.27 x 10⁻⁵ mol m(^{-2})</td>
</tr>
<tr>
<td>Melting point</td>
<td>2750K</td>
</tr>
<tr>
<td>Relative dielectric constant (0.5-50MHz)</td>
<td>11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>fresh sample</th>
<th>Bulk density</th>
<th>0.53 g cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Purity</td>
<td>99.95%</td>
</tr>
<tr>
<td></td>
<td>Spec. surface area, ( s₀ )</td>
<td>15.4 m(^2) g(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Particle size</td>
<td>~ 50nm</td>
</tr>
<tr>
<td>cycled sample</td>
<td>Spec. surface area, ( s₁ )</td>
<td>3.99 m(^2) g(^{-1})</td>
</tr>
<tr>
<td></td>
<td>Particle size</td>
<td>~ 200nm</td>
</tr>
</tbody>
</table>

The redox process can be written as a reversible reaction:

\[
\text{H}_2\text{O}(g) + \frac{1}{\Delta \delta} \text{CeO}_2_{-\delta} \leftrightarrow \text{H}_2(g) + \frac{1}{\Delta \delta} \text{CeO}_2_{-\delta} \quad (6.1)
\]

where \( \Delta \delta = \delta_1 - \delta_2 \) is the bulk-phase non-stoichiometry change. In order to derive the \( \text{H}_2 \) production rate based on the flue stream composition, we consider a control volume as outlined in Figure 2-7. In the redox process, the production (or consumption) of one mole of \( \text{H}_2\text{O} \) leads to the consumption (or production) of one mole of \( \text{H}_2 \). Therefore, the total molar flow rate throughout the control volume remains constant, i.e., \( \dot{n}_m = \dot{n}_\text{out} \). Thus, we can express the reaction rates as:

**Oxidation:**

\[
\omega_{H_2} = \frac{X_{H_2,\text{out}} \dot{n}_{\text{ax, out}}}{m_{\text{CeO}_2}} = \frac{X_{H_2,\text{out}}}{m_{\text{CeO}_2}} \frac{P^0 \dot{V}_{\text{ax, in}}}{RT^0} \quad (6.2)
\]

**Reduction:**

\[
\omega_{H_2O} = \frac{X_{H_2O,\text{out}} \dot{n}_{\text{red, out}}}{m_{\text{CeO}_2}} = \frac{X_{H_2O,\text{out}}}{m_{\text{CeO}_2}} \frac{P^0 \dot{V}_{\text{red, in}}}{RT^0} \quad (6.3)
\]

\( X_{H_2,\text{out}} \) and \( X_{H_2O,\text{out}} \) are the measured mole fractions of the produced \( \text{H}_2 \) and \( \text{H}_2\text{O} \) at the exit. \( \dot{n}_{\text{ax, in}} \) and \( \dot{n}_{\text{red, in}} \) are the total molar inflow rates of the gas mixture for the oxidation and reduction,
respectively. $P^0$, $T^0$, and $V^0$ are the pressure, temperature, and the total volumetric inflow rate at standard temperature and pressure (STP). The reaction rates (unit, $\mu$ mole g$^{-1}$s$^{-1}$) are normalized by the total ceria sample $m_{\text{CeO}_2}$, i.e., 100mg, used in the measurement. The derivation assumes a quasi-steady state and neglects the accumulation or depletion effect in the control volume. This is valid as the flow residence time is much shorter (~0.1s) than the characteristic time of the redox conversion [17]. $\Delta\delta$ is calculated as

$$\left|\Delta\delta(t)\right| = \frac{n_o(t)}{n_{\text{CeO}_2}}$$  (6.4)

where $n_o(t) = \int_0^t \dot{n}_o dt$ is the accumulated intake of oxygen ions. $n_{\text{CeO}_2} = \frac{m_{\text{CeO}_2}}{M_{\text{CeO}_2}}$ is the moles of ceria used in the experiment. $M_{\text{CeO}_2}$ is the molecular weight.

### 6.3 Theory

To model the reaction kinetics, ceria particles at cyclic stationary state are treated as identical spheres with diameter $r_p = 100$nm (Table 6-1). The particle size is assumed to remain unchanged during the redox cycle, as CeO$_2$ is known to maintain its fluorite structure even under large non-stoichiometry at elevated temperatures [1].

The overall reaction between the bulk ceria and the external gas-phase reactants may be written as [1-3]:

$$\text{H}_2\text{O}(g) + 2\text{Ce}_{\text{Ce}}' + V_{\text{O}}^{\text{V}} \rightleftharpoons \text{H}_2(g) + \text{O}_0' + 2\text{Ce}_{\text{Ce}}'$$  (6.5)

where $V_{\text{O}}^{\text{V}}$ is a doubly-charged oxygen vacancy, $O_0'$ is an oxygen ion on a normal site. $\text{Ce}_{\text{Ce}}'$ denotes a polaron (a localized electron, Ce$^{3+}$), and $\text{Ce}_{\text{Ce}}'$ is a regular Ce$^{4+}$ cation. $\text{Ce}_{\text{Ce}}'$ and $V_{\text{O}}^{\text{V}}$ are believed to be the major defects in the bulk as well as on the surface [1-3, 11].
Figure 6-1 (a) Schematics of the water splitting pathway. The ion-incorporation surface process comprises the adsorption and dissociation of H₂O forming OH⁻ (R1); charge transfer, association and desorption of H₂ (R2). The heterogeneous chemistry is linked to bulk phase via the bulk-to-surface transport of the electron defect, e, and the oxygen vacancy defect, V_0⁻. (b) Schematics of the surface enrichment of Ce³⁺ relative to the bulk.

Eq. (6.5) merely describes the overall equilibrium between the defects in the bulk ceria and oxygen from the H₂O/H₂ environment. The electrochemical process, however, involves serial steps of important heterogeneous surface reactions, i.e., adsorption/dissociation of gaseous reactant forming adsorbates, ion/electron transfer on the surface, association and desorption of products. The surface chemistry is further connected with the bulk phase via bulk-to-surface transport driven by the electrochemical potential gradient. Bulk-phase diffusion continues to adjust the spatial defect distribution, and eventually equilibrates the sample with the environment. Figure 6-1 schematically highlights the key steps in the oxidation direction.
In the following two sub-sections, we will present the sub-models for the surface chemistry and diffusion process, respectively.

6.3.1 Surface Chemistry

The surface water splitting and oxygen incorporation reactions are modeled using a two-step mechanism (Figure 6-1a) [4-8]:

\[
R_1: \quad H_2O(g) + V_o^- (s) + O'_o (s) \xrightarrow{k_{1,1}} 2OH'_o (s)
\]

\[
R_2: \quad 2OH'_o (s) + 2Ce'_c (s) \xrightarrow{k_{2,1}} 2O'_o (s) + 2Ce'_c (s) + H_2 (g)
\]

OH'_o is a hydroxyl ion group on an oxygen anion site. The surface reactions are assumed to occur only within the first unit cell layer on the surface, and s in the parenthesis emphasizes this assumption. (R1) describes the adsorption and dissociation process: a H2O molecule is adsorbed onto an oxygen vacancy site, and dissociates into a hydroxyl ion and an extra proton, which then bonds to an adjacent oxygen to form a second OH'_o group. (R2) describes the charge transfer process, followed by the association and desorption of H2.

Using the law of mass action, we express the species reaction rates for R1 and R2 as:

\[
r_1 = k_{1,1} p_{H_2O} \left[ V_o^- \right] \left[ O'_o \right] - k_{1,1} \left[ OH'_o \right]^2
\]

\[
r_2 = k_{2,1} \left[ OH'_o \right] \left[ Ce'_c \right] - k_{2,1} \left[ O'_o \right] \left[ Ce'_c \right]^2
\]

In eqs. (6.8) and (6.9), the brackets denote the mole of species per mole of CeO2. The subscript, s, again, emphasizes that the concentrations of the reactant are taken on the surface. \( k_{1,1} \) and \( k_{1,1} \).
denote the rate coefficients (unit, s\(^{-1}\)) of the aforementioned reactions, and are assumed to follow the Arrhenius expression. Partial pressure of \(\text{H}_2\) or \(\text{H}_2\text{O}\) in the gas phase is defined with respect to reference value (i.e., 1 atm). Because of the high flow rates used in this study the gas residence time through the control volume (Figure 2-7) is much shorter (<300 ms) as compared to chemistry, and thus the reactant partial pressure on the surface is essentially identical to that in the gas phase as measured in the QMS. Therefore, the measured \(p_{\text{H}_2\text{O}}\) and \(p_{\text{H}_2}\) accurately represent the redox environment to which the ceria sample is exposed. At equilibrium, \(r_1\) and \(r_2\) are zero. This leads to the definition of the corresponding equilibrium constants \(K_1\) and \(K_2\).

Similar pathway has been discussed in the literature [4-8]. Feng et al [4] emphasized the importance of the charge transfer process, by further breaking (R2) into, \(\text{OH}_0^-' + \text{Ce}^{3+}_c \rightarrow \text{OH}_0^-' + \text{Ce}^{4+}_c\), followed by the dissociation, \(2\text{OH}_0^- = 2\text{O}_0^- + \text{H}_2\text{(g)}\). Similar steps were calculated in a theoretical study by Marrocchelli and Yildiz [6]. Hansen and Wolverton [7] calculated the minimum energy pathway during R2, and concluded that the process may happen asymmetrically: \(\text{Ce}^{3+}\) hops close to \(\text{OH}_0^-'\), weakens the O-H bond; the weakly bonded proton then moves towards the adjacent \(\text{OH}_0^-\) and forms \(\text{H}_2\) as the last \(\text{Ce}^{3+}\) is oxidized. Identifying the detailed elementary steps during (R2) is beyond the scope of this study. Here we couple the charge transfer with the \(\text{H}_2\) formation process and model it as a single step.

The governing equations for the surface species are written as:

\[
\frac{\partial \tilde{C}_i}{\partial t} = \dot{\tilde{R}}_i + \dot{J}_i, \quad i = \text{OH}_0^-, \text{V}_0^- \quad (6.10)
\]
where $\tilde{C}_i$ is the species concentration on the surface, $\tilde{R}$, the production/consumption rate of species $i$, and $\tilde{J}_i$ is the diffusion flux from the bulk phase. We proceed by coupling these species equations with the O-, and Ce-site conservation equations and the electro-neutrality condition:

**O-site:** \[ [\text{V}''_o]_s + [\text{OH}'_o]_s + [\text{O}^-]_s = 2 \] (6.11)

**Ce-site:** \[ [\text{Ce}'_{ce}]_s + [\text{Ce}^+_{ce}]_s = 1 \] (6.12)

**electro-neutrality** \[ 2[\text{V}''_o]_s + [\text{OH}'_o]_s = [\text{Ce}'_{ce}]_s \] (6.13)

It is worth noting that the electro-neutrality condition may break down in the space-charge region (SC) on the surface. The doubly-charged oxygen vacancies along with the polarons form a double layer (i.e. positive charge from $\text{V}''_o$ on one layer and negative charge from $\text{Ce}'_{ce}$ on the other), creating a large disturbance of the spatial electrostatic potential gradient near the surface. This may lead to charge enrichment and simultaneous countercharge depletion in this region. However, Chueh and co-workers reported surface enrichment for both $\text{V}''_o$ [4] and $\text{Ce}'_{ce}$ [11] in SC for Sm-doped CeO$_2$. Feng et al. [4] further quantified the contribution of the electrostatic potential gradient near the surface under redox conditions, and concluded that the charge neutrality is preserved near the surface. As such, we adopt the electro-neutrality assumption in this study for the sake of simplicity. This assumption can be relaxed and examined in depth in the future study.

With eqs. (6.11)-(6.13), the two species equations (OH'$_o$, V''$_o$) describe the surface kinetics. Since the proton conductivity is less pronounced compared to the major defects (vacancies and polarons) in the bulk, we assume that all hydroxyl ions are confined to the surface layer and...
hence neglect its diffusion. Thus, we express the species conservation equations for the surface hydroxyl group and the surface oxygen vacancy as:

\[
\frac{\partial}{\partial t} \left[ \mathrm{OH}^- \right] = \tilde{\rho}_{C_{\text{e.s}}} \left( 2r_1 - 2r_2 \right)
\]  \hspace{1cm} (6.14)

\[
\frac{d}{dt} \left[ \mathrm{V}_0^- \right] = -\tilde{\rho}_{C_{\text{e.s}}} r_1 + J_{\text{v}_0^-}
\]  \hspace{1cm} (6.15)

Here \( \tilde{\rho}_{C_{\text{e.s}}} \) is the surface molar density of the unit cell (unit, mole m\(^{-2}\)). With the knowledge of \( J_{\text{v}_0^-} \), eqs. (6.14)-(6.15) complete the description of the surface species evolution under the redox conditions.

6.3.2 Bulk-to-Surface Transport

The conservation of a defect species \( i \) can be expressed as:

\[
\frac{\partial C_i}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 J_i \right) = 0
\]  \hspace{1cm} \( i = \mathrm{V}_0^- , \mathrm{Ce}^- \)  \hspace{1cm} (6.16)

where \( C_i \) is the molar concentration, and \( J_i \) the flux of the defect species \( i \). In eq. (6.16), we assume a 1D spherically symmetric diffusion. The flux density is expressed using the Nernst-Planck equation:

\[
J_i = -\frac{C_i D_i}{RT} \frac{\partial \tilde{\mu}_i^*}{\partial r}
\]  \hspace{1cm} (6.17)

where \( D_i \) is the diffusion coefficient, \( R \) the universal gas constant, and \( T \) the temperature. \( \tilde{\mu}_i^* \) is the electro-chemical potential.

The diffusion process involves the exchange of defects between two points, \( x_1 \) and \( x_2 \) [18]:

\[221\]
By re-arranging the above equations, we obtain equivalently:

\[ V_0^\prime(x_1) + O_0^\prime(x_2) \rightleftharpoons V_0^\prime(x_2) + O_0^\prime(x_1) \]  \hspace{1cm} (6.18)

\[ Ce_{ce}^\prime(x_1) + Ce_{ce}^\prime(x_2) \rightleftharpoons Ce_{ce}^\prime(x_2) + Ce_{ce}^\prime(x_1) \]  \hspace{1cm} (6.19)

Eqs. (6.20) and (6.21) re-state the diffusion process in terms of the "defect elements", i.e., the structural defect minus the original normal site [18]. Thus, \( \bar{\mu}_i^* \) for the oxygen vacancy and polaron can be expressed as:

\[ \bar{\mu}_{V_0^\prime}^* = \bar{\mu}_{V_0} - \bar{\mu}_{O_0^\prime} \]  \hspace{1cm} (6.22)

\[ \bar{\mu}_e^* = \bar{\mu}_{Ce_{ce}^\prime} - \bar{\mu}_{Ce_{ce}^\prime} \]  \hspace{1cm} (6.23)

Here \( \bar{\mu}_i \) is the electro-chemical potential for each species. We note that the contribution of the normal sites (\( \bar{\mu}_{O_0} \) and \( \bar{\mu}_{Ce_{ce}^\prime} \)) to the diffusion process cannot be neglected here, because the redox conversion involves a large non-stoichiometry change, and the availability of the normal sites significantly influences the diffusion.

We proceed by defining the electro-chemical potential of the structural defects and the normal sites as:

\[ \bar{\mu}_j = \mu_j^0 + RT \ln a_j + z_j F \phi \quad j = V_0^\prime, O_0^\prime, Ce_{ce}^\prime, Ce_{ce}^\prime \]  \hspace{1cm} (6.24)

where \( \mu_j^0 \) is the chemical potential at the reference condition, and \( z_j \) the effective charge. \( \phi \) is the internal electrostatic potential. \( F \) is Faraday constant. \( a_j \) is the activity, defined as:
\[ a_j = \gamma_j \frac{C_j}{C_{\text{ref}}} \]  

(6.25)

where \( \gamma_j \) is the activity coefficient, and \( C_{\text{ref}} = \text{const} \) is a reference molar concentration. Assuming that \( \gamma_j \) is independent of concentration, we express the spatial derivatives of \( \tilde{\mu}_j \) as:

\[ \frac{\partial \tilde{\mu}_j}{\partial r} = \frac{\partial \mu_j^0}{\partial r} + RT \frac{\partial \ln C_j}{\partial r} + z_j F \frac{\partial \phi}{\partial r} \]  

(6.26)

Substituting eqs. (6.22)-(6.26) into eqs. (6.16) yields:

\[ \frac{\partial \left[ V_0^{**} \right]}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \left[ V_0^{**} \right] \frac{D_{v_0}}{RT} \left[ \frac{\partial \left( \mu_{v_0}^0 - \mu_{v_0}^0 \right)}{\partial r} + RT \frac{\partial \ln \left[ V_0^{**} \right]}{\partial r} \right] + 2F \frac{\partial \phi}{\partial r} \right\} \]  

(6.27)

\[ \frac{\partial \left[ Ce_{ce}^e \right]}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \left[ Ce_{ce}^e \right] \frac{D_{Ce_{ce}}}{RT} \left[ \frac{\partial \left( \mu_{Ce_{ce}}^0 - \mu_{Ce_{ce}}^0 \right)}{\partial r} + RT \frac{\partial \ln \left[ Ce_{ce}^e \right]}{\partial r} \right] - F \frac{\partial \phi}{\partial r} \right\} \]  

(6.28)

Coupling with the Ce-, and O- site conservation equations and the electro-neutrality condition:

O-site:  \[ \left[ V_0^{**} \right] + \left[ O_0 \right] = 2 \]  

(6.29)

Ce-site:  \[ \left[ Ce_{ce}^e \right] + \left[ Ce_{ce}^e \right] = 1 \]  

(6.30)

electro-neutrality  \[ 2\left[ V_0^{**} \right] = \left[ Ce_{ce}^e \right] \]  

(6.31)

Eqs. (6.27)-(6.31) formulate a complete description of the bulk diffusion process.

The characteristics and the properties of ceria sample allow us to significant simplify these equations. The electronic and ionic diffusivities \( D_{Ce_{ce}} \) and \( D_{v_0} \) of ceria are very high, and bring the bulk defects to dynamic equilibrium during the redox process. Using the diffusivity data
reported in ref. [19], the characteristic time, \( t \), for a diffusion-limited process from the expression 
\[ t \sim R^2/4D, \]
is estimated to be less than 200 ms, which is significantly faster compared to the surface chemistry. A more rigorous calculation that takes into account the temporal and spatial variation of the defect concentration is included in Section 6.7, which shows that the concentration variation caused by the mass transfer resistance is less than 4%. This estimation indicates that the bulk diffusion within ceria macro particle is fast enough that any spatial variations of \( \tilde{\mu}_{V_0}^* \) and \( \tilde{\mu}_{Ce^{\prime} \text{Cs}}^* \) will be readily removed via diffusion. As such, the conversion process is essentially surface-reaction-limited. Thus, \( \tilde{\mu}_{V_0}^* \) and \( \tilde{\mu}_{Ce^{\prime} \text{Cs}}^* \) remain uniform throughout the particle while responding dynamically to the changing environment. Eqs. (6.27) and (6.28) can be simplified as:
\[
\tilde{\mu}_{V_0}^* = \text{const} : \quad \frac{\partial}{\partial r} \left( \mu_{V_0}^0 - \mu_{O_0}^0 \right) + RT \frac{\partial}{\partial r} \ln \left[ \frac{V_0^{\text{**}}}{O_0} \right] + 2F \frac{\partial \phi}{\partial r} = 0 \tag{6.32}
\]
\[
\tilde{\mu}_{Ce^{\prime} \text{Cs}}^* = \text{const} : \quad \frac{\partial}{\partial r} \left( \mu_{Ce^{\prime} \text{Cs}}^0 - \mu_{Ce^{\prime} \text{Cs}}^0 \right) + RT \frac{\partial}{\partial r} \ln \left[ \frac{Ce^{\prime} \text{Cs}}{Ce^{\prime} \text{Cs}} \right] - F \frac{\partial \phi}{\partial r} = 0 \tag{6.33}
\]
However, the uniformity of the \( \tilde{\mu}_{V_0}^* \) and \( \tilde{\mu}_{Ce^{\prime} \text{Cs}}^* \) does not necessarily means the same value of the defect concentration, \( V_0^{\text{**}} \) and \( Ce^{\prime} \text{Cs} \), in the bulk and at the surface. In fact, owing to the difference of the standard chemical potentials (\( \mu_{V_0}^0 - \mu_{O_0}^0 \), and \( \mu_{Ce^{\prime} \text{Cs}}^0 - \mu_{Ce^{\prime} \text{Cs}}^0 \)) between the bulk and the surface, a pronounced surface defect segregation phenomenon (see schematics in Figure 6-1b) has been observed in several studies [4, 10, 11]. Chueh et al [11] reported a two-order-of-magnitude surface-to-bulk \( Ce^{\prime} \text{Cs} \) enrichment for Sm-doped ceria at 466°C. Similar results were observed for the oxygen vacancies by Feng et al. [4]. To model the surface effect, we assume
that \( \mu^0_T \) varies from the bulk \( (r < r_p) \) to the surface \( (r = r_p) \) according to a step-function, as depicted in Figure 6-2. Thus, the defect concentration in the bulk phase is uniform, and it connects dynamically to the kinetic process on the surface via diffusion. Eliminating \( \phi \) in eqs. (6.32)-(6.33) and integrating from the bulk to the surface yields:

\[
\frac{\left[ V^{\infty}_0 \right] \left[ Ce^0_{ce} \right]}{\left[ O^0_0 \right] \left[ Ce^0_{ce} \right]} = \exp \left( -\frac{\Delta \mu^0_R}{RT} \right) = K_T
\]

(6.34)

where

\[
\Delta \mu^0_r = \left( \mu^0_{O_0} - \mu^0_{O^0_0} + 2 \mu^0_{Ce_{ce}} - 2 \mu^0_{Ce^0_{ce}} \right)_{surface} - \left( \mu^0_{O_0} - \mu^0_{O^0_0} + 2 \mu^0_{Ce_{ce}} - 2 \mu^0_{Ce^0_{ce}} \right)_{bulk}
\]

(6.35)

Eq. (6.34) essentially describes the transport equilibrium between the bulk and the surface, by combining reactions (6.20) and (6.21), as:

\[
V^{\infty}_0 (b) - O^0_0 (b) + 2 Ce^0_{ce} (b) - 2 Ce^0_{ce} (b) \rightleftharpoons V^{\infty}_0 (s) - O^0_0 (s) + 2 Ce^0_{ce} (s) - 2 Ce^0_{ce} (s)
\]

(6.36)

If we add \( \frac{1}{2} O_2 \) to both sides of eq. (6.36), we arrive at the defect formation reaction [1-3]:

\[
O^0_0 (b) + 2 Ce^0_{ce} (b) \rightleftharpoons V^{\infty}_0 (b) + 2 Ce^0_{ce} (b) + \frac{1}{2} O_2
\]

(6.37)

\[
O^0_0 (s) + 2 Ce^0_{ce} (s) \rightleftharpoons V^{\infty}_0 (s) + 2 Ce^0_{ce} (s) + \frac{1}{2} O_2
\]

(6.38)

for the bulk and the surface, respectively. Therefore, \( \Delta \mu^0_r \) is the difference in the formation energy of the defect between the surface (eq. (6.38)) and the bulk phase (eq.(6.37)), \( \Delta \mu^0_r = \Delta \mu^0_{R,s} - \Delta \mu^0_{R,b} \), where \( \Delta \mu^0_{R,b} \) and \( \Delta \mu^0_{R,s} \) are the Gibbs free energy of reaction for eqs. (6.37) and (6.38), respectively. \( \Delta \mu^0_r \) can be further related to \( \Delta h^0_r \), and \( \Delta s^0_r \), as:

\[
\Delta \mu^0_r = \Delta h^0_r - T \Delta s^0_T
\]

(6.39)
Creation of one defect involves breaking up 4 Ce-O bonds in the bulk, but fewer on the surface. Thus, defects are more energetically favored on the surface. On the other hand, the defect formation causes the relaxation of the adjacent atoms with reduced vibrational frequency and increased amplitude, leading to increased entropy [18]. The entropy increase is higher in the bulk, because more adjacent atoms are relaxed, and the relaxation from its dense-packed crystal is more dramatic. Thus, both \( \Delta h_f^0 \) and \( \Delta s_f^0 \) are negative. Based on the measurements by Chueh et al. [11], we obtain \( \Delta h_f^0 = -113.7 \text{ kJ mol}^{-1} \), and \( \Delta s_f^0 = -50.2 \text{ J mol}^{-1} \text{ K}^{-1} \) for the Sm-doped ceria (see Section 6.8 for calculation).

Figure 6-2 Schematics of (a) the bulk-to-surface transport model, (b) the difference of the defect formation energy. \( b \), and \( s \) in parentheses denote the defects in the bulk phase and on the surface, respectively.

6.3.3 Numerical Simulation

With the assumption of a uniform bulk defect concentration, and eq. (6.34) to connect bulk to surface, we can simplify eq. (6.15) by considering the conservation of the overall oxygen vacancy within the particle:
\[
\frac{\partial}{\partial t} \left( \tilde{\rho}_{Ce} V R \left[ V_{O^*}^{0} \right] \right) = -S_R \tilde{\rho}_{Ce, i} \tag{6.40}
\]

where \( V_R \) and \( S_R \) are the volume and the surface area of the particle, and \( \tilde{\rho}_{Ce} \) is the molar density of the unit cell in the bulk. Eq. (6.40) describes the fact that the surface splitting reaction leads to the consumption of oxygen vacancy. We note here that the moles of the oxygen vacancy on surface is negligible compared to the bulk, and thus it is neglected from the left-hand side of eq. (6.40).

Eqs. (6.14), (6.34) and (6.40) form the complete description of the redox process. The unknown (not all kinetic) parameters are \( k_{i,6}, K_i \) (\( i = 1, 2 \)), \( \Delta h_i^0 \) and \( \Delta s_i^0 \). With the time-resolved profiles of [H\(_2\)O] and [H\(_2\)] measured using the QMS, the entire conversion process can be predicted. These equations are integrated numerically, and the predicted reactivity is compared to the experimental measurement. The unknown parameters are then varied to minimize the difference:

\[
f = \sum_{\text{all tests}} \sum_{0 \leq t \leq t^*} \left( \hat{\omega}_{\text{predicted}} - \hat{\omega}_{\text{measure}} \right)^2 \tag{6.41}
\]

Here the reaction rates (\( \hat{\omega}_{\text{predicted}} \) or \( \hat{\omega}_{\text{measure}} \)) are normalized by the maximum rate in each test. The minimization is performed numerically in MATLAB using fminsearch solver [20]. The redox measurements at 600\(^\circ\)C, 700\(^\circ\)C, 800\(^\circ\)C, 900\(^\circ\)C, and 1000\(^\circ\)C are used to extract the unknown parameters. \( \Delta h_i^0 \) and \( \Delta s_i^0 \) for Sm-doped ceria calculated in Section 6.8 are taken as the initial guess, but variations are allowed to account for the difference between Sm-doped and un-doped ceria. To ensure a global minimum, the intial guess is randomly sampled over a wide range of values (ln\( k_0 \) from -20 to 20, \( E \) from 0 to 200) for 200 tests, and the results with minimum \( f \) are chosen.
6.4 Results

6.4.1 CeO$_2$ morphology evolution and cyclic repeatability

Figure 3-9 shows the SEM images of the fresh (panel a) and aged (panel b) ceria powder. It is found that the fresh sample contains particles of size $\sim$50nm, clumping together into a mushroom-like structure. During pre-treatment, the surface area is reduced and the particles sinter into an inter-connected structure with a size of $\sim$ 200nm (based on the BET measurement). This structural relaxation is caused by sintering during the initial redox treatment (first 100 cycles). Samples after additional 20 redox cycles are also examined, and the same micro-structure and redox rates are obtained, indicating that a periodic and reversible stationary equilibrium is reached.

Figure 6-3 shows the profiles of H$_2$ and H$_2$O for three redox cycles at 1000 °C. Reduction proceeds for 2 min with 14% H$_2$ at 350 sccm, while oxidation with 26% H$_2$O for 2 min. 2 min Ar purging is used in between to remove residuals. H$_2$ spikes with the rise of H$_2$O, with the peak H$_2$ over 7%, roughly a quarter of the feed H$_2$O. After the peak, H$_2$ drops quickly, and diminishes after 0.5 min. The H$_2$ near the end of the oxidation phase is essentially zero. After oxidation, the ceria sample is also tested with 1% O$_2$ (Ar balance), and no further consumption of O$_2$ is observed. This indicates a complete re-oxidation of ceria with H$_2$O. Similarly, the produced H$_2$O during reduction spikes at the beginning of each reduction cycle. The peak H$_2$O reaches around 3%, approximately 1/5 of the feed H$_2$ during reduction. H$_2$O decays slower as compared to H$_2$ during oxidation, and approaches zero after 2 min, indicating a slower reactivity compared to oxidation. The cycles are repeatable with no noticeable difference. Figure 6-4 compares the total...
cumulative H₂ and H₂O production during the oxidation and reduction steps, respectively, for 8 cycles measured at 1000°C. The total H₂ production closely matches with the H₂O production, indicating cyclic regenerability. The total produced H₂ is about 1250 μmole/gram ceria, corresponding to a Δδ of 0.215.

Figure 6-3 3 redox cycles at 1000°C with 26% H₂O for oxidation and 13.7% H₂ for reduction. The redox step takes 2 min each, and the purging section takes 2 min in between. Total CeO₂ is 100 mg.
Figure 6-4 Total $\text{H}_2$ and $\text{H}_2\text{O}$ production during the oxidation and reduction, respectively, for 8 cycles at 1000°C.

6.4.2 Effect of Temperature

Figure 6-5 compares $\omega_{\text{H}_2}$ and $\omega_{\text{H}_2\text{O}}$ as a function of temperature from 500°C to 1000°C. In each plot, the reaction rate exhibits a fast initial stage, followed by a quick decrease. During oxidation, the fast initial rise of $\text{H}_2$ corresponds to the rapid ion-incorporation process with the enriched surface oxygen vacancies, as showed in Section 6.5. The reactant concentration on the surface plays a significant role in determining the maximum rate. For temperatures lower than 700°C, $\text{H}_2$ production is limited, owing to the slow oxygen removal kinetics and hence limited oxygen vacancy created in the previous reduction step. Increasing the temperature till 850°C leads to a significant jump and the peak rate doubles almost every 50°C. Further increase in the temperature, however, only mildly improves $\text{H}_2$ production rates during the initial stage. As will be discussed in Section 6.5, the nonlinear temperature dependence is caused by the surface defect segregation.
Following the peak, H₂ production sharply decays, and approaches zero after 0.5 min, exhibiting linear dependence on temperature, as it is mainly controlled by the available oxygen vacancy in the bulk phase.

Figure 6-5 (a) H₂ production rate (μmole g⁻¹ s⁻¹) during the oxidation step, and (b) H₂O production rate (μmole g⁻¹ s⁻¹) during the reduction step. Temperature is varied from 1000°C to 500 °C. 26% H₂O at 337 sccm is used for oxidation, and 14.3% H₂ at 350 sccm is used for reduction. The uncertainties of the rate measurements are ±0.5 μmole g⁻¹ s⁻¹ for H₂ production, and ±0.75 μmole g⁻¹ s⁻¹ for H₂O production.
Compared with oxidation, the reduction step is slower, and more sensitive to temperature. A fast initial spike is again observed, followed by a slower decay. The peak occurs around 0.08 min similar to that shown in Figure 6-5(a), while the decay continues even after 1 min (see Figure 6-3). During the initial stage, the rise of $\rho_{H_2O}$ depends almost linearly on the temperature throughout the entire range, indicating a large activation energy barrier. However, $\rho_{H_2O}$ profiles start to overlap during the decay stage for temperature above 850°C, as the removal of oxygen essentially brings the surface closer to the beginning of the oxidation phase, where the segregation effect reduces the difference among different temperatures.

![Graph showing peak H2 and H2O production rates as a function of temperature during the oxidation and the reduction cycles.](image)

Figure 6-6 Peak H2 and H2O production rates as a function of temperature during the oxidation and the reduction cycles.

Figure 6-6 emphasizes the observed behavior of the peak rates at varying temperature. The peak H2 rate exhibits a sigmoidal profile with a rapid increase around a threshold temperature of 700 °C, while the peak H2O rate continuously increases with temperature. The total H2/H2O production during the 2 min oxidation/reduction process is illustrated in Figure 6-7. In all the cases, a close match is found between the H2 and H2O production. Governed by the temperature
sensitive reduction step, the overall \( \text{H}_2 \) production rises continuously with temperature. Figure 6-8 compares the difference in the profiles of the non-stoichiometry \( \Delta \delta \), as calculated in eq. (6.4), during oxidation and reduction. The initial stage of oxidation ends within 15 sec, but accounts for more than 80\% of the overall change, and the residual oxidation only leads to a minor increase. Raising the temperature enlarges the overall oxygen carrying capacity, but the conversion follows a similar pattern. In comparison, reduction proceeds more gradually, and it is more temperature sensitive. The transition between the initial and residual stages is less obvious, and both stages equally contribute to the overall non-stoichiometry change. The reduction continues after 2 min although the rate is too slow to be of practical interests.

![Graph](image)

Figure 6-7 Total \( \text{H}_2 \) and \( \text{H}_2\text{O} \) production as a function of temperature during the oxidation and the reduction steps.
Figure 6-8 Non-stoichiometry change $\Delta \delta$ during (a) the oxidation step and (b) the reduction step as a function of temperature.

The measured peak $\text{H}_2$ rate is $\approx 160 \, \mu\text{mole g}^{-1}\text{s}^{-1}$ at $1000^\circ\text{C}$ and $60 \, \mu\text{mole g}^{-1}\text{s}^{-1}$ at $700^\circ\text{C}$ (also included in Table 1-4 for comparison). The fast $\text{H}_2$ production rate is because of the fine particles, and hence large surface area, used in the measurements. Comparing to TCWS, the utilization of
fuel in the reduction step creates many oxygen vacancies, and hence leads to an enhanced H\textsubscript{2} production. The oxygen removal in reduction is the limiting step and is more temperature sensitive. 700°C is the threshold temperature to achieve a large oxygen non-stoichiometry, and hence enables a transition to a fast H\textsubscript{2} production rate in the following oxidation step. Therefore, 700°C (or above) along with a longer residence time in reduction is beneficial.

6.4.3 Effect of H\textsubscript{2}O/H\textsubscript{2} Concentration

Figure 6-9 and Figure 6-10 show the effect of H\textsubscript{2}O and H\textsubscript{2} concentration, respectively. The measured rates are plotted in panel a, while the peak rate and the total production are highlighted in panel b. \( \omega_{h_2} \) becomes taller and narrower at higher H\textsubscript{2}O concentration. The peak rate linearly depends on the H\textsubscript{2}O concentration, while the total production remains the same. In contrast, a stronger reducing environment shifts the entire \( \omega_{h_2,o} \) curve outwardly, and hence enlarges the overall oxygen carrying capacity. The peak rate also linearly depends on the H\textsubscript{2} concentration.

Figure 6-9 (a) Oxidation rate at different H\textsubscript{2}O concentration. (b) Peak rate and total production as a function of H\textsubscript{2}O concentration. The temperature is fixed at 1000°C. The H\textsubscript{2} concentration is fixed at 13.7% during reduction.
Figure 6-10 (a) Reduction rate at different H₂ concentration. (b) Peak rate and total production as a function of H₂ concentration. The temperature is fixed at 1000°C. The H₂O concentration is fixed at 26% during oxidation.

H₂O concentration is adjusted by changing the Ar flow rate through the water flask. Thus, at low H₂O concentration with low flow rate through the flask, it takes much longer time for steam to flow through the steam feeding line. For comparison, 26% H₂O is achieved with 100 sccm Ar flowing through the water flask, while 5% H₂O only corresponds to 20 sccm. Therefore, the ramping period with 5% H₂O can be 5 times longer. The slow ramping-up of the H₂O is also shown in the Figure 6-11(a) below. This results in the delay of the oxidation rate (see Figure 6-9(a)), as expected based on eq. (6.8). To further demonstrate the effect of H₂O concentration, we include the H₂O splitting rate v.s. conversion plot (panel b), as well as the normalized rate vs. conversion plot (panel c) below. In panel c, the oxidation rate is normalized by the measured H₂O concentration, thus excluding the effect of the H₂O partial pressure. Panel b demonstrates the linear dependence of the reaction rates on the H₂O mole fraction. The peak oxidation rate results from a combined effect from the concentration of H₂O and the concentration of defects.
The normalized rates in panel (c) almost overlap among different H2O cases, again confirming the proposed kinetics model. By eliminating the contribution from H2O, as seen in panel (c), the peak of the normalized rates occurs at the very beginning of the conversion. The less smooth H2 production curve with 5% H2O results from the rapid consumption of H2O, thus a much lower signal-to-noise ratio of the measurements. This, however, does not affect the validity of the kinetics modeling, as the measurements in QMS still well represent the H2O/H2 environment in the control volume, since the total gas flow is maintained at 350 sccm. Nevertheless, only the results with 26% H2O concentration were used to extract the kinetics parameters for better accuracy.

![Figure 6-11 Effect of H2O concentration on oxidation. (a) Evolution of H2O, (b) H2 production rates as a function of the non-stoichiometry; and (c) normalized production rates, i.e., rates divided by H2O molar fraction, as a function of the non-stoichiometry.](image)

6.4.4 Effect of Reduction Time

The effect of reduction time was examined, and the results are shown in Figure 6-12 below. Here the reduction time is varied from 15s to 2 min, while the oxidation time is fixed at 2 min. As seen in panel (b), a longer reduction time leads to a faster H2O splitting rate in the following oxidation step, as well as a larger total evolved H2 amount. Increasing the reduction time from 15s to 30 s shifts the curve upward significantly, while a further increase to 2 min leads to a very minor
improvement, due to the slower reduction kinetics after 1 min. As seen in panel (a), the reduction step follows the exact same profile, except that the curve stops earlier with a shorter reduction period.

![Graph showing H₂O production rate vs. time for different reduction times.](a)

![Graph showing H₂ production rate vs. time for different reduction times.](b)

Figure 6-12 Effect of reduction time on (a) reduction and (b) oxidation. The reduction time is varied from 15 s to 2 min. Oxidation is fixed at 2 min, and temperature is 1000°C.

6.5 Discussion

The kinetics and the defect equilibrium parameters derived in this study for un-doped ceria are summarized in Table 6-2 and Table 6-3. The values of Δₜₜ and Δₜ₀ are close to those obtained for Sm-doped ceria (see Section 6.8). The bulk equilibrium for reaction (6.37) is also calculated by combining eqs. (6.6), (6.7), and (6.36) along with the water splitting reaction, \( \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) \), as:

\[
K_b = \exp\left( -\frac{\Delta h^0_b - T \Delta s^0_b}{RT} \right) = \frac{p_{O_2}^{1/2} [V_{O_{2}}]^b [Ce_{Ce}]^2}{[O_{2}]_b [Ce_{Ce}]^2} = (K_1 K_2 K_T K_W)^{-1} \tag{6.42}
\]

Here \( K_1, K_2, K_T, \) and \( K_W \) are the equilibrium constants for the surface reactions R1 and R2, the bulk-to-surface transport, and the water splitting reaction, respectively. The calculated bulk
phase equilibrium ($\Delta h^0_n$ and $\Delta s^0_n$) is in a close match with the literature [2, 3], as shown in Table 6-3. Figure 6-13 depicts the isothermal bulk oxygen vacancy concentration as a function of the equivalent $p_{O2}$, compared with the measurements reported by Panlener et al.[2] and Tuller and Nowick [3]. Quantitative agreement is found at large non-stoichiometry, although discrepancy is seen when $p_{O2}$ is high, resulting from a slightly larger $\Delta s^a$. Both ref. [3] and the current study report a dependence of $-1/6$ near stoichiometry, while Panlener et al.[2] reported a dependence close to $-1/5$, possibly due to the existence of impurities [1].

![Figure 6-13](image)

Figure 6-13 Isothermal oxygen non-stoichiometry as a function of $p_{O2}$ for CeO$_2$ from 800-1000°C (solid lines). Dashed lines are based on the conductivity measurements by Tuller and Nowick [3]. Symbols are from Panlener et al.[2]. Gray lines are for guiding the eyes.
Table 6-2 Fitted kinetic parameters for both the forward and backward reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$ ($s^{-1}$)</th>
<th>$k$ ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward</td>
<td>$1.3 \times 10^2 \exp(-7.0 \pm 7 \text{ kJ mol}^{-1} \text{ / RT})$</td>
<td>$1.5 \times 10^{14} \exp(-190 \pm 50 \text{ kJ mol}^{-1} \text{ / RT})$</td>
</tr>
<tr>
<td>Backward</td>
<td>$8.2 \times 10^{14} \exp(-210 \pm 50 \text{ kJ mol}^{-1} \text{ / RT})$</td>
<td>$4.4 \times 10^{14} \exp(-97 \pm 5 \text{ kJ mol}^{-1} \text{ / RT})$</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$1.6 \times 10^{-3} \exp(203 \pm 50 \text{ kJ mol}^{-1} \text{ / RT})$</td>
<td>$3.4 \times 10^{-9} \exp(-93 \pm 50 \text{ kJ mol}^{-1} \text{ / RT})$</td>
</tr>
</tbody>
</table>

Table 6-3 Parameters for the transport and bulk defect equilibria

<table>
<thead>
<tr>
<th></th>
<th>This work CeO$_2$</th>
<th>Ref. [2] CeO$_2$ $^a$</th>
<th>Ref. [3] CeO$_2$</th>
<th>Ref. [11] Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{1.9}$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta h^0$ (kJ mol$^{-1}$)</td>
<td>$-107.6 \pm 16.8$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-95.7$</td>
</tr>
<tr>
<td>$\Delta s^0$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>$-54.0 \pm 11.9$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-26.5$</td>
</tr>
<tr>
<td>$\Delta h^0$ (kJ mol$^{-1}$)</td>
<td>$467.4 \pm 8.9$</td>
<td>$455.2$</td>
<td>$450.2$</td>
<td>$373.2$</td>
</tr>
<tr>
<td>$\Delta s^0$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>$172.9 \pm 6.4$</td>
<td>$144.3$</td>
<td>$131.8$</td>
<td>$101.5$</td>
</tr>
</tbody>
</table>

$^a$ Note ref. [2] reports varying enthalpy and entropy with $\delta$; the values are averaged for $\delta = 0 \sim 0.05$.

$^b$ The values are calculated based on the chemical potential of atom oxygen as reported in ref. [11]. See Section 6.8 for calculations.

Figure 6-14 Comparison between the model predictions (lines) and the measurements (circles) for both oxidation (upper panels) and reduction (lower panels). The scales in y-axis are different at lower temperature for clarity.
Figure 6-14 shows a comparison between the measured reactivity and model predictions for both oxidation and reduction. An excellent match is found for all the cases. The predictions well characterize the spike-decay behaviors of both redox steps. The temperature dependence is precisely represented; the subtle difference between the reduction and oxidation steps is also adequately captured.

Figure 6-15 shows the calculated energy landscape (black lines) for the surface chemistry (see Table 6-2). The energy levels for the intermediate species on the surface as well as the transition states are plotted in reference to the perfect crystal as the ground state. RI is highly exothermic with a minor barrier. The second step is highly endothermic, and requires a significant energy to break up the O-H bond. The intermediate species, OH\textsuperscript{-}, lies in a deep valley, and hence one may expect high surface coverage at low temperature. The overall H\textsubscript{2} production process (eq. (6.5)) is exothermic with the enthalpy of reaction around −120 kJ mol\textsuperscript{-1}. The theoretical calculations by Hansen and Wolverton [7] (red lines) and Marrochelli and Yildiz [6] (blue lines) are also included in this plot for comparison. Both obtained similar reaction energy for the first step, although they split it and simulated the adsorption and the dissociation processes separately. Similarly, no substantial activation barriers were found for RI in either work. Marrochelli and Yildiz [6] modeled the breaking up of the O-H bond as a symmetric process, and reported a significant barrier around 400 kJ/mol for H\textsubscript{2} formation. In contrast, Hansen and Wolverton [7] identified an asymmetric pathway with a much lowered barrier (281 kJ/mol). The current study reported a barrier around 200 kJ mol\textsuperscript{-1}. The lower barrier may result from alternative fast desorption pathways, especially at large non-stoichiometry when the surface defect vacancy
concentrations are high. Marrocchelli and Yildiz [6] reported a similar overall energy of reaction ($\Delta h^0$ for eq. (6.38)) as in this study, while Hansen and Wolverton [7] reported a slightly lower value. The bulk phase defect formation energy, $\Delta h_b^0$, is also included in Figure 6-15, and the difference between the bulk and the surface is $\Delta h_f^0$.

Figure 6-15 Energy landscape for the reaction pathway (black), and comparison with the theoretical calculations by Hansen and Wolverton [7] (red) and Marrocchelli and Yildiz [6] (blue). The dashed black line on the left side denotes the bulk phase defect. $\Delta h_b^0$, and $\Delta h_s^0$ denotes the defect formation energy for bulk (eq. (6.37)) and surface (eq.(6.38)), respectively, and $\Delta h_f^0$ denotes the difference. Unit is kJ mole$^{-1}$.

Figure 6-16 plots the species concentration in the bulk and on the surface. The reduction reaction starts from stoichiometry (complete oxidation from previous step), while oxidation begins with the defects determined from the previous reduction step. During the oxidation step, all species
undergo a quick decay, leading to a rapid H₂ production during the initial stage as observed in Figure 6-5. The initial stage is followed by a much slower decay as the conversion transits to the second stage where the species concentrations are mainly affected by the equilibrium with the H₂O/H₂ environment. Hydroxyl is quickly formed as the reaction starts, and remains in a quasi-steady state during the rest of the process. Low temperature favors the formation of hydroxyl ions, owing to the large energy barriers as seen in Figure 6-15. The bulk defect concentrations are highly sensitive to temperature, as evident from the large ΔH° shown in Table 6-3, leading to a significant difference between the high and the low temperature cases. On the other hand, the surface defect is less dependent on the temperature. In all cases, the concentrations on the surface are observed to be much higher than the bulk. The surface segregation effect is more significant at low temperature, causing over an order of magnitude improvement compared to the bulk phase. Similar behavior is observed during the reduction step, where the segregation effect is more pronounced near the end of conversion.

To further examine the surface segregation effect, Figure 6-17(a) shows the calculated equilibrium concentration of Ce'Ce in the bulk and on the surface as a function of the effective pO₂. Each line corresponds to the same range of H₂O:H₂ ratio, from 10⁻³ (reducing) to 10³ (oxidizing). Under all conditions, the surface [Ce'Ce] value is significantly greater than the bulk, indicating that the surface is more reduced. The ratio between surface and bulk, as shown in Figure 6-17(b), ranges from 1.5 to 15, favoring the low temperature. Apart from the difference in the absolute values, the temperature and oxygen dependence also differs remarkably between bulk and surface. [Ce'Ce] on the surface is only weakly sensitive to temperature, and becomes almost the same above 800°C (with H₂O:H₂), causing the overlap of the measured reaction rates.
during the first stage of oxidation (Figure 6-5a) and the second stage of reduction (Figure 6-5b). [Ce'_{Ce}] in the bulk generally exhibits – 1/6 dependence on the p_{O2}, as expected from eq. (6.42). On the other hand, the p_{O2} dependence for surface [Ce'_{Ce}] flattens from – 1/6 with decreasing p_{O2}, and eventually goes to zero as the surface becomes fully reduced. This nonlinearity results from the reduced concentration of the normal sites (O_{O}, Ce'_{Ce} in eq. (6.42)) on the surface. As a result, the ratio in panel b exhibits a nonlinear pattern with p_{O2}.

Figure 6-16 Concentrations of the bulk and surface species for oxidation (panels a, b) and reduction (panels c, d) at 1000°C and 700°C.
Figure 6-17 (a) Ce\textsuperscript{3+} concentration at equilibrium on the surface (solid) and in the bulk (dashed). Value of 1 corresponds to a complete reduction to the reduced 3+ state. (b) Ratio of the surface to bulk Ce\textsuperscript{3+} concentration.

Figure 6-18 shows the forward and the backward reaction rates for the redox processes. At all temperatures, the H\textsubscript{2}O adsorption and dissociation step (R1) during oxidation is much faster; equilibrium is quickly established and maintained throughout the rest of the conversion. In contrast, the ion/electron transfer process (R2) is slower and its backward reaction rate is close to...
zero. This indicates that the reaction is limited by the charge transfer process (R2), as also observed by Feng et al [4]. Compared to oxidation, the reduction rate is much slower. The forward and backward rates for both steps are at similar magnitude, and equilibria are established during most of the conversion process. The low rates for R1 are mainly attributed to the low H$_2$O produced during reduction. A more reducing environment (e.g., higher H$_2$ concentration) effectively shifts the equilibrium backwards, leading to more reduced ceria, as observed in Figure 6-10.

Figure 6-18 Surface reaction rates for both steps in oxidation (panels a, b) and reduction (panel c, d). The forward reaction rates are plotted as positive values, and the backward rates are negative. Note different scales are used in panels (c) and (d) for clarity.
The surface segregation effect along with the plausible rate-limiting step observed in this study suggests directions for improving the water splitting activity of ceria and potentially other oxygen incorporation materials. The reduction step is in general much slower, and it limits the redox capability at low temperature (≤700°C). Therefore, promoting the reduction step is essential to the low temperature water splitting process. On the other hand, the surface is nearly enriched with the defects at high temperature (>700°C), and the overall H₂ production is constrained by the charge-transfer step. Thus, efforts should concentrate on accelerating the charge transfer step at high temperature.

6.6 Summary

This chapter presents a detailed redox study with an emphasis on identifying surface ion-incorporation kinetics pathway. Time-resolved kinetics is measured for ceria nano-powder in a button cell reactor for 600-1000°C at atmospheric pressure. The ceria sample is alternatively exposed to water vapor in the oxidation cycle to produce H₂, and H₂/Ar mixture in the reduction cycle to remove the lattice oxygen. The ceria sample undergoes structural and morphological changes during the initial redox treatment before reaching cyclic equilibrium.

We find over one order of magnitude higher H₂ production rate compared to the state-of-art thermo-chemical water splitting and reactive chemical-looping water splitting studies. The high redox rates are attributed to the fine particles and hence large surface areas used in the study, which ensure a surface-limited-process. The peak rates measured are 160 μmole g⁻¹s⁻¹ at 1000°C and 60 μmole g⁻¹s⁻¹ at 700°C. The maximum non-stoichiometry change (Δδ) achieved is 0.215 at
1000 °C. It is found that the H₂ production rate depends weakly on temperature in the range 800-1000°C, while the reduction process critically depends on the reaction temperature. Overall, reduction is the limiting step especially at low temperature, and it determines the total amount of the hydrogen produced in the following oxidation step.

The redox kinetics is modeled using a two-step surface chemistry while considering bulk-to-surface transport equilibrium. The proposed surface chemistry comprises an H₂O adsorption/dissociation step and a charge transfer step. Kinetics and equilibrium parameters are extracted and excellent agreement is achieved between the model predictions and the measurements. Driven by the difference in the free energy of formation, the surface defect concentration is found to be an order-of-magnitude higher than the bulk. The model reveals that the surface defects are abundant during the redox conditions, and the charge transfer process is the rate-determining step for H₂ production. The kinetic model along with the surface-controlled experiments provides a new approach to examine the redox pathways and defect equilibrium for alternative materials. The kinetics study also provides guidance for the design and the practical application of the chemical-looping water splitting technology: 1) finer particles are preferred to enable faster kinetics; 2) the operating temperature is recommended to be higher than the threshold 700°C to ensure fast redox conversion; 3) an oxidation period less than 30 s suffices to regenerate the oxygen vacancy while a slightly longer residence time in reduction is beneficial.
6.7 Appendix A

The diffusion flux for $V_o^-$ and $Ce'_c$, can be expressed as

$$-rac{J_{V_O^-}}{\rho_c v^- D_{V_O^-}} = \frac{\partial [V_O^-]}{\partial r} \left( \frac{1}{[V_O^-]} + \frac{1}{2-[V_O^-]} \right) + \frac{2F}{RT} \frac{\partial \phi}{\partial r}$$

(6.43)

$$-rac{J_{Ce'_c}}{\rho_c v^- D_{Ce'_c}} = \frac{\partial [Ce'_c]}{\partial r} \left[ \frac{1}{[Ce'_c]} + \frac{1}{1-[Ce'_c]} \right] - \frac{F}{RT} \frac{\partial \phi}{\partial r}$$

(6.44)

Here we consider region sufficiently away from the surface, such that the defect segregation effect is not important (i.e., $\mu_j^0$ is constant)

Eliminating the electrostatic potential, we have

$$-rac{J_{V_O^-}}{\rho_c v^- D_{V_O^-}} - \frac{2J_{Ce'_c}}{\rho_c v^- D_{Ce'_c}}$$

$$= \frac{\partial [V_O^-]}{\partial r} \left( \frac{1}{[V_O^-]} + \frac{1}{2-[V_O^-]} \right) + 2\frac{\partial [Ce'_c]}{\partial r} \left[ \frac{1}{[Ce'_c]} + \frac{1}{1-[Ce'_c]} \right]$$

(6.45)

The electro-neutrality assumption in the bulk phase requires that:

Charge neutral: $2[V_O^-] = [Ce'_c]$  

(6.46)

Zero net current: $2J_{V_O^-} = J_{Ce'_c}$  

(6.47)

Substitute eqs (6.46) and (6.47) into (6.45), we have:

$$J_{V_O^-} = -\tilde{D} \frac{\partial [V_O^-]}{\partial r}, \text{ where } \tilde{D} = \frac{3D_{V_O^-} D_{Ce'_c}}{D_{Ce'_c} + 2D_{V_O^-}} \left( 1 + \frac{[V_O^-]}{6-[V_O^-]} + \frac{4[V_O^-]}{3-[V_O^-]} \right)$$

(6.48)

$\tilde{D}$ is the chemical (or ambipolar) diffusion coefficient, which critically depends on the operating condition, as well as the dopant/impurity concentrations. A range of values have been reported in
the literature. To evaluate the contribution of the solid-phase diffusion to the overall redox process, we use the chemical diffusivity reported by Stan et al. [19], which is in the lower range of the available data in the literature (see ref. [13] for comparison), and hence leads to an estimation of the upper bound for the diffusional resistance.

The governing equations for \( V_o^* \) in the bulk phase can be expressed as:

\[
\frac{\partial C_{V_o}}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 J_{V_o} \right) = 0
\]  
(6.49)

Substitute (6.48) into eq. (6.49), we have,

\[
\frac{\partial C_{V_o}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \tilde{D} \frac{\partial C_{V_o}}{\partial r} \right)
\]  
(6.50)

with initial condition

\[
C_{V_o} (t = 0) = C_{V_o,0}
\]  
(6.51)

and the boundary conditions:

\[
s \tilde{D} \frac{\partial C_{V_o}}{\partial r} \bigg|_{r=R} = \omega
\]  
(6.52)

\[
\frac{\partial C_{V_o}}{\partial r} \bigg|_{r=0} = 0
\]  
(6.53)

In eq. (6.52), \( s \) is the surface area, as listed in Table 6-1. \( \omega \) is the surface H\(_2\) (or H\(_2\)O) production rate (unit mole s\(^{-1}\)). Eqs.(6.50)-(6.53) are solved for the oxidation reaction of the particle with \( R = 100 \) nm. The peak H\(_2\) production rate at each temperature is used to represent \( \omega \), and the \( \Delta \delta \) is

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used as the initial condition. Calculation shows an upper bound for the diffusional contribution.

Figure A1 plots the normalized difference of $C_{\nu_0}$ between the center and the surface:

$$
\Delta = \frac{C_{\nu_0}(r = 0) - C_{\nu_0}(r = R)}{C_{\nu_0}(r = R)} \quad \text{when} \quad C_{\nu_0}(r = R) = \frac{1}{2} C_{\nu_0,0}
$$

(6.54)

From Figure 6-19, the maximum difference is found to be less than 4% at 600°C, and reduces to less than 0.001% at 1000°C. Calculation here indicates that the bulk diffusion is unlikely to be rate-limiting in the redox process.

![Figure 6-19](image.png)

Figure 6-19 The relative difference of the oxygen vacancy concentration between the center and the surface. Line is for guiding the eyes.

### 6.8 Appendix B

Chueh et al. [11] measured both the bulk and the surface concentration Ce$^{3+}$ (or Ce$^{4+}$) for Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ under equilibrium for the temperature at 466°C, 521°C, 586°C and 650°C. The authors compared the chemical potential of atomic oxygen for the surface and bulk, and
attributed the higher concentration of surface Ce\(^{3+}\) to the higher entropy the surface oxygen. Here, we take into account the difference of the defect formation energy as well as the entropy, and present a detailed analysis following a similar approach as detailed in the section 3 (see Figure 6-2).

The site conservation and electro-neutrality conditions are:

\[
\left[ V_{O}^{\prime} \right] + \left[ O_{0} \right] = 1.9 \quad (6.55)
\]

\[
\left[ Ce_{Ce}^{\prime} \right] + \left[ Ce_{Ce}^{\prime} \right] + \left[ Sm_{Ce}^{\prime} \right] = 1 \quad (6.56)
\]

\[
2\left[ V_{O}^{\prime} \right] = \left[ Sm_{Ce}^{\prime} \right] + \left[ Ce_{Ce}^{\prime} \right] \quad (6.57)
\]

In the bulk phase, \( \left[ Sm_{Ce}^{\prime} \right]_{b} = 0.2 \). By substituting eqs. (6.55)-(6.57) into eq.(6.42), and fitting with respect to the measurements of the bulk \( [Ce_{Ce}^{\prime}] \) and \( \rho_{O_{i}}^{1/2} \), we obtain the equilibrium constant for the bulk-phase defects, \( K_{b} \):

\[
K_{b} = \exp \left( \frac{379.5 \text{ kJ/mol} - 97.1 \text{ J/molK}}{RT} \right) \quad (6.58)
\]

The bulk-to-surface transport equilibrium is described by eq.(6.34). The dopant concentration on the surface, \( \left[ Sm_{Ce}^{\prime} \right]_{s} \), is in the range between 0.26 and 0.35, slightly greater than the bulk. For simplicity, we use \( \left[ Sm_{Ce}^{\prime} \right]_{s} = 0.3 \). Note here the RHS of (6.55) becomes 1.85 for the surface \( (Sm_{0.3}Ce_{0.7}O_{1.85}) \).
By substituting eqs. (6.55)-(6.57) into eq. (6.34), and comparing with the measurements of the surface [Ce_e^\text{Ce}] at given temperature and oxygen partial pressure, we obtain the equilibrium constant for the transport, $\Delta\mu_T^0$:

$$\Delta\mu_T^0 = \left( -113.7 \frac{\text{kJ}}{\text{mol}} \right) - \left( -50.2 \frac{\text{J}}{\text{molK}} \right) T$$ (6.59)

The model predictions are plotted in Figure 6-20 along with the measurements, and an excellent agreement is found for both the surface and the bulk defect concentrations.

It is interesting to note that compared to the bulk, the surface has 30% less defect formation enthalpy, and over 50% less defect formation entropy. The ratio of the surface to bulk Ce$^{3+}$ is highest at low temperature, and drops dramatically as the temperature is raised. Cross-over, $\Delta\mu_T^0 = 0$, is reached when $T = 2265 \, K$, approaching the melting point.

Chueh et al [11] reported the chemical potential of atomic oxygen for the surface and bulk, defined as:

$$\mu_o = \frac{1}{2} \mu_{O_2} = \frac{1}{2} \left( \mu_{O_2}^0 + RT \ln p_{O_2} \right)$$ (6.60)

where $\mu_{O_2}^0$ is the standard potential at 1 atm. $\mu_O$ can further be related to the partial molar enthalpy ($H_O$) and entropy ($S_O$) from: $\mu_O = H_O - TS_O$. The reported $H_O$, and $S_O$ are $-373.2 \, \text{kJ mole}^{-1}$, and $-86.1 \, \text{J mole}^{-1} \text{K}^{-1}$ for [Ce$^{3+}$]$_{\text{bulk}} = 0.0071$, and $-277.5 \pm 28.7 \, \text{kJ mole}^{-1}$, and $28.7 \pm 28.7 \, \text{J mole}^{-1} \text{K}^{-1}$ for [Ce$^{3+}$]$_{\text{surf}} = 0.36$. 

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Figure 6-20 (a) Comparison of the surface (closed) and bulk Ce\(^{3+}\) (open) concentration between the measurements (symbols) by Chueh et al [11] and the model predictions (lines). (b) Ratio of the surface to bulk Ce\(^{3+}\) concentrations. Symbols are from ref. [11], and lines are from the modeling.

To relate the partial molar free energy of the oxygen atom to the defect formation free energy, we consider the defect formation reaction, eqs. (6.37) and (6.38), at equilibrium. The Gibbs free energy is zero: \( \Delta G = 0 = \mu_{\text{v}_0} + 2\mu_{\text{v}_s} + \frac{1}{2} \mu_{\text{h}_s} - \mu_{\text{c}_0} - 2\mu_{\text{c}_s} \). Substitute eqs. (6.24) and (6.60), we obtain:
\[ \mu_i = H_i - TS_i = \]

\[ -\left( \mu_{V_o}^0 + RT \ln \left[ \dfrac{V_o^0}{V_e^0} \right] + 2\mu_{Ce}^0 + 2RT \ln \left[ Ce'_0 \right] - \mu_{O_0}^0 - 2RT \ln \left[ O_0 \right] - 2\mu_{Ce}^0 - 2RT \ln \left[ Ce'_0 \right] \right) \]

\[ = -\left( h_{V_o}^0 + 2h_{Ce}^0 - h_{O_0}^0 - 2h_{Ce}^0 - T \left( s_{V_o}' + 2s_{Ce}' - s_{O_0}' - 2s_{Ce}' \right) + RT \ln \left[ \dfrac{V_o^0}{V_e^0} \left[ Ce'_0 \right]^2 \right] \right) \]

(6.61)

Therefore,

\[ H_i = -\left( \Delta h_i^0 - \dfrac{1}{2} h_{O_2}^0 \right) \quad (6.62) \]

\[ S_i = -\left( \Delta s_i^0 - RT \ln \left[ \dfrac{V_o^0}{V_e^0} \left[ Ce'_0 \right]^2 \right] - 0.5s_{O_2}^0 \right) \quad (6.63) \]

where \( \Delta h_i^0 \) and \( \Delta s_i^0 \) are the defect formation energy and entropy. Based on the reported values for \( H_i \), and \( S_i \), we obtain \( \Delta h_i^0 = 373.2 \text{ kJ mole}^{-1} \) and \( \Delta s_i^0 = 101.5 \text{ J mole}^{-1} \text{ K}^{-1} \) for \([Ce^{3+}]_{\text{bulk}} = 0.0071\), and \( \Delta h_i^0 = 277.5 \pm 28.7 \text{ kJ mole}^{-1} \) and \( \Delta s_i^0 = 75.0 \pm 28.7 \text{ J mole}^{-1} \text{ K}^{-1} \) for \([Ce^{3+}]_{\text{surf}} = 0.36\).

Therefore, the differences between the surface and the bulk are, \( \Delta h_i^0 = -95.7 \pm 28.7 \text{ kJ mole}^{-1} \) and \( \Delta s_i^0 = -26.5 \pm 28.7 \text{ J mole}^{-1} \text{ K}^{-1} \).

The results here are in reasonable agreement with the fitted value using the defect model. The difference in \( \Delta h_i^0 \) and \( \Delta s_i^0 \) may be attributed to the fact that ref. [11] used \([Ce^{3+}]_{\text{bulk}} = 0.0071\) and for \([Ce^{3+}]_{\text{surf}} = 0.36\) for the calculation, while the results from our model are based on the entire dataset. Nevertheless, the difference is within the error bar.

6.9 Bibliography

Chapter 7

Kinetics Study and Non-Stoichiometry Characterization of Ceria Zirconia Solid Solution

This chapter work presents a detailed kinetics study and non-stoichiometry characterization of Ce$_{0.5}$Zr$_{0.5}$O$_{2-\delta}$ (CZO) with an emphasis on the surface ion-incorporation kinetics pathway using time-resolved and systematic measurements in the temperature range 500-900°C. Compared to un-doped ceria, we find 60% improvement in the kinetic rates and over twice the total H$_2$ yield at 700°C, resulting from the improved reducibility of ceria with the addition of Zr. The peak H$_2$ production rate is 95 μmole g$^{-1}$s$^{-1}$ at 700°C and the total production is 750 μmole g$^{-1}$. A threshold temperature of 650°C is required to achieve significant H$_2$ production at fast rates. Oxidation (water splitting) kinetics is slower than reduction. The redox kinetics is modeled using two-step surface chemistry with bulk-to-surface transport equilibrium. Kinetics and equilibrium parameters are extracted and the model predictions show good agreement with the measurements. The enthalpy of bulk defect formation for CZO is found to be 262 kJ/mol, over 40% lower than that of un-doped ceria. As oxygen vacancy is gradually filled up, the surface H$_2$O splitting chemistry undergoes a transition from exothermic to endothermic, with the cross-over around $\delta = 0.04 \sim 0.05$, which constrains the further ion incorporation process. Our kinetics study reveals that the H$_2$O splitting process with CZO is kinetics limited at low temperature and transitions to
partial-equilibrium with significantly enhanced backward reaction at high temperature. The charge-transfer step is found to be the rate-limiting step for H₂O splitting. The detailed kinetics and non-stoichiometric equilibria should be helpful in guiding the design and optimization of CZO as a catalyst, oxygen storage material, as well as oxygen carrier for water splitting applications.

7.1 Introduction

Ceria (CeO₂) is commonly considered as a viable candidate for TCWS and RCLWS because of its fast surface kinetics, high ionic diffusivity, large non-stoichiometric capacity, and robust structural stability. Chapter 6 reported remarkable water splitting rates of ceria nano-particles above a threshold temperature 750°C. At lower temperature, however, the slow reduction step significantly limits oxygen non-stoichiometry, leading to a much lower H₂ production capacity. In an attempt to improve low temperature redox kinetics, zirconia is often suggested as a dopant to promote reducibility [1]. Zr⁴⁺ cation remains isovalent and redox inactive [2], and therefore its addition does not involve the creation of any charge compensating defects [3]. Instead, the undersized Zr⁴⁺ cation induces structural distortion [4], leading to lower defect formation energy [5] and enhanced oxygen mobility [6]. The relaxation in the bond energy facilitates the reduction of Ce⁴⁺ to the larger Ce³⁺ ion [7]. The long-term structural stability is also improved with the addition of Zr [8, 9]. These merits have led to wide applications of the ceria-zirconia oxide system (CZO) in other areas [1, 4, 10, 11], including three-way catalysis, water-gas shift, solid oxide fuel cells, methane reforming, etc.
With the increase of Zr content, the ceria-zirconia solid solution undergoes a phase transition from the cubic to tetragonal fluorite, and eventually forming the monoclinic phase at high Zr concentration \([4, 12, 13]\). The phase change with Zr content is accompanied by changes in the lattice structure, bond energy, electrical properties, and hence reducibility. It was observed that with the increase of Zr content in \(\text{Ce}_1.5\text{Zr}_0.5\text{O}_2\), the oxygen non-stoichiometry capacity shows an increase and then decrease, with the optimum occurring at \(x = 0.2\sim0.5\) \([4, 14-17]\). While a number of studies have examined the electrical and redox properties of the CZO system \([14-16, 18-22]\), more complete data for the thermodynamics of the defect formation are lacking \([14]\). The exact nature of the phase diagram or the transformation dynamics is still a matter of debate \([4]\), resulting mostly from the difference in the preparation method and the testing conditions \([1, 13]\), leading to discrepancy in the reported non-stoichiometry properties. In addition, previous work concentrated on the bulk-phase equilibrium. Applying CZO in the water-splitting application requires a good knowledge of the time-resolved reactivity under relevant conditions, which is still missing. The surface redox kinetics, including the complex interactions of mobile ions, defect transfer between the bulk and the surface, along with the adsorbates and electrostatic fields are yet to be explored.

In this chapter, we investigate the defect formation and the redox mechanism of \(\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_{2-\delta}\) using a detailed time-resolved measurement under conditions relevant for water splitting. Isothermal redox cycles of CZO nano-particles are carried out in a button cell reactor in the temperature range 500-900°C. \(\text{H}_2\) is used as a surrogate fuel for reduction. A significant improvement of \(\text{H}_2\) production is observed at low temperature as compared to pure ceria. Previously developed kinetics model for pure ceria is successfully applied to describe the
oxygen-ion incorporation dynamics for CZO. The model consists of a two-step surface chemistry and the bulk-to-surface transport sub-models. Based on the kinetics models, the thermodynamics of the defect formation and the non-stoichiometric equilibrium are also extracted. Similarity of the H$_2$O splitting process between pure and doped ceria is demonstrated and the effect of the improved reducibility is examined in details. The results in this work demonstrated the applicability of the modeling framework to various ceria-based OC systems for kinetics and thermodynamics study.

7.2 Theory

Here we briefly describe the modeling framework, which generally follows the same derivation in Chapter 6. The model involves description of the defect equilibrium, surface chemistry, and diffusion processes.

7.2.1 Bulk-phase Defect Equilibrium

Since Zr$^{4+}$ remains isovalent [14], the defect formation reaction and the equilibrium mass-action relation may be written similarly as with pure ceria [23]:

\[
O^-_O (b) + 2Ce'^-_{Ce} (b) \rightleftharpoons V^0_o (b) + 2Ce'_{Ce} (b) + \frac{1}{2}O_2 (g)
\]  

(7.1)

\[
K_b = \exp \left( -\frac{H_b - TS_b}{RT} \right) = \frac{P_{O_2}^{1/2} [V^0_o]_{b} [Ce'_{Ce}]^2}{[O^-_O]_{b} [Ce'^-_{Ce}]} \]  

(7.2)

Here the major defects are the doubly-charged oxygen vacancy, $V^0_o$, and the localized electrons, $Ce'^-_{Ce}$, (small polarons) [24, 25]. $K_b$, $H_b$, and $S_b$ are the equilibrium constant, enthalpy and entropy of the defect formation reaction. The brackets denote the mole of species per mole of
Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}. The subscript, $b$, emphasizes the bulk-phase equilibrium. By definition, $[V'_{o}^\text{b}] = \delta$, as in Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2.5}.

With the large change of the non-stoichiometry ($0 \leq \delta \leq 0.25$) during the redox reaction, one may expect a varying defect formation enthalpy ($H_b$), as previously reported with the CZO system [14, 15, 26] as well as other ceria-based materials [27-29]. The formed vacancies result in a chemical expansion of the crystalline lattice with a consequent reduction in $H_b$ [28, 29]. Alternatively, the effects of defect interactions and ordering become more prominent at high non-stoichiometry, leading to deviations from the ideal behavior [30]. The $\delta$-dependence of the defect formation enthalpy is modeled following a linear expression [26, 28]:

$$H_b = H_b^0 + f \delta$$

(7.3)

where $H_b^0$ is the defect formation enthalpy for the fully oxidized CZO. The effect of $\delta$ on the entropy is less important and hence not included for modeling. A detailed discussion on the $\delta$-dependence of enthalpy and entropy is included in Section 7.7.

7.2.2 Surface Redox Reactions

The surface water splitting and oxygen incorporation reactions are modeled as a two-step mechanism (Figure 7-1) [23, 31-35], with the corresponding mass action rate expressions as:

R1: \[ H_2O(g) + V'_o(s) + O'_o(s) \xrightarrow{k_{1,b}} 2OH'_o(s) \]  \hspace{1cm} (7.4)

$$r_1 = k_{1,b}P_{H_2O}[V'_o]^s[O'_o]^s - k_{1,b}[OH'_o]^2$$

(7.5)

R2: \[ 2OH'_o(s) + 2Ce'_Ce(s) \xrightarrow{k_{2,b}} 2O'_o(s) + 2Ce'_Ce(s) + H_2(g) \]  \hspace{1cm} (7.6)
OH\textsubscript{O} is a hydroxyl ion group on an oxygen anion site. \( k_{1,2} \), \( k_{i,b} \), denote the rate coefficients (unit, \( \text{s}^{-1} \)), following the Arrhenius expression, \( k = k^0 \exp(-E/RT) \) where \( k^0 \). The surface reactions are assumed to be confined within the first unit cell layer on the surface, and \( s \) in the parenthesis emphasizes this assumption. \( \text{R1} \) describes the adsorption and dissociation, while \( \text{R2} \) describes the charge transfer process, followed by association and desorption of \( \text{H}_2 \). Previous studies on ceria (pure or doped) concluded that the formation of hydroxyls via \( \text{R1} \) is energetically favored on reduced ceria with a barrierless forward reaction [23, 32, 34, 35], while \( \text{R2} \) is endothermic with large barriers for both forward and backward reactions, hence limits the overall \( \text{H}_2\text{O} \) splitting process [23, 31].

\[
\begin{equation}
    r_z = k_{2,f} \left[ \text{OH}_O^- \right]^2 \left[ \text{Ce}^{4+} \right]^2 - k_{2,b} P_{\text{H}_2} \left[ \text{O}_O^- \right]^2 \left[ \text{Ce}^{4+} \right]^2
\end{equation}
\]  

(7.7)

Figure 7-1 Schematics of the water splitting pathway. The ion incorporation surface process comprises the adsorption and dissociation of \( \text{H}_2\text{O} \) forming \( \text{OH}^- \) (\( \text{R1} \)); charge transfer, association and desorption of \( \text{H}_2 \) (\( \text{R2} \)). The heterogeneous chemistry is linked to bulk phase via the bulk-to-surface transport of the electron defect, \( e \), and the oxygen vacancy defect, \( \text{V}_O^{\alpha} \).
At equilibrium, \( r_1 \) and \( r_2 \) are zero. This leads to the definition of the corresponding equilibrium constants \( K_1 \) and \( K_2 \):

\[
K_1 = \frac{k_{1,f}}{k_{1,b}} = \exp \left( -\frac{H_1 - TS_1}{RT} \right) = \frac{[\text{OH}_0^\ast]^2}{p_{\text{H}_2\text{O}} [\text{V}_0^\ast]_s [\text{O}_0^\ast]_s} \tag{7.8}
\]

\[
K_2 = \frac{k_{2,f}}{k_{2,b}} = \exp \left( -\frac{H_2 - TS_2}{RT} \right) = \frac{p_{\text{H}_2} [\text{O}_0^\ast]^2 [\text{Ce}^\ast_{\text{Ce}}]^2}{[\text{OH}_0^\ast]^2 [\text{Ce}^\ast_{\text{Ce}}]^2} \tag{7.9}
\]

where \( H_i \) and \( T_i \) are the enthalpies and entropies of the reactions (R1) and (R2). Combining R1 and R2 gives the overall surface equilibrium as:

\[
\text{V}_0^\ast (s) + 2\text{Ce}^\ast_{\text{Ce}} (s) + \text{H}_2\text{O} (g) \rightleftharpoons \text{O}_0^\ast (s) + 2\text{Ce}^\ast_{\text{Ce}} (s) + \text{H}_2 (g) \tag{7.10}
\]

\[
K_{s,w} = \exp \left( -\frac{H_{s,w} - TS_{s,w}}{RT} \right) = \frac{p_{\text{H}_2} [\text{O}_0^\ast]_s [\text{Ce}^\ast_{\text{Ce}}]^2}{p_{\text{H}_2\text{O}} [\text{V}_0^\ast]_s [\text{Ce}^\ast_{\text{Ce}}]^2} \tag{7.11}
\]

where \( K_{s,w} \), \( H_{s,w} \), and \( T_{s,w} \) are the equilibrium constant, enthalpy and entropy. The equilibrium states at the surface (reaction (7.10)) and in the bulk (reaction (7.1)) are related via [23, 36]:

\[
\text{V}_0^\ast (b) - \text{O}_0^\ast (b) + 2\text{Ce}^\ast_{\text{Ce}} (b) - 2\text{Ce}^\ast_{\text{Ce}} (b) \rightleftharpoons \text{V}_0^\ast (s) - \text{O}_0^\ast (s) + 2\text{Ce}^\ast_{\text{Ce}} (s) - 2\text{Ce}^\ast_{\text{Ce}} (s) \tag{7.12}
\]

\[
K_T = \exp \left( -\frac{\Delta H_T^0 - T\Delta S_T^0}{RT} \right) = \frac{[\text{V}_0^\ast]_s [\text{Ce}^\ast_{\text{Ce}}]^2}{[\text{O}_0^\ast]_s [\text{Ce}^\ast_{\text{Ce}}]^2} / \frac{[\text{V}_0^\ast]_b [\text{Ce}^\ast_{\text{Ce}}]^2}{[\text{O}_0^\ast]_b [\text{Ce}^\ast_{\text{Ce}}]^2} \tag{7.13}
\]

where \( \Delta H_T^0 \) and \( \Delta S_T^0 \) denote the difference of the defect formation enthalpy and entropy, respectively, between the surface and the bulk phase. Reaction (7.12) describes the transport equilibrium of the defects between the bulk and the surface [23]. The defect formation is found to be more favored on the surface (\( \Delta H_T^0 < 0 \)) [23, 32], resulting from fewer chemical bonds.
between oxygen and cations. The entropy generation with the defect is higher in the bulk \( \Delta S^0_r < 0 \) [23, 24], owing to the stronger relaxation as compared to the surface.

From eq. (7.13), the surface equilibrium constant is related to bulk as, \( K_{s,w} = (K_b K_T K_w)^{-1} \), where \( K_w \) is the equilibrium constant of \( \text{H}_2\text{O} \) formation reaction, \( \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) \). Assuming equilibrium, we calculate the equilibrium \( p_{02} \) in the \( \text{H}_2\text{O}/\text{H}_2 \) environment as,

\[
\rho_{02} = \frac{p_{\text{H}_2\text{O}}^2}{(K_w p_{\text{H}_2})^2} \tag{7.14}
\]

where \( p_{\text{H}_2\text{O}} \) and \( p_{\text{H}_2} \) are the partial pressure of \( \text{H}_2\text{O} \) and \( \text{H}_2 \), respectively. It is worth noting that the gas-phase equilibrium is not established under a kinetics-controlled conversion, resulting from the fast gas flow and the short flow residence time used in this study. \( p_{02} \) in the reactor may deviate from the equilibrium value, especially at low temperature (Section 7.5.1).

Given the variation of \( H_b \) with \( \delta \) from eq. (7.3), it comes as no surprise to find \( \delta \) dependence in the two-step surface reactions. On one hand, the vacancy-induced chemical expansion and the defect interactions directly affect the defect formation process (R1), as discussed in Section 7.2.1. On the other hand, the spill-over of protons and the formation of the surface adsorbates, \( \text{OH}_0^* \), are also influenced by the defect-induced surface charge distribution[37]. For simplicity, we assume that the effect is mostly associated with the oxygen removal step \( (k_{1,b} \) for backward R1). Thus, \( E_{1,b} = E_{1,b}^0 + f \delta \), where \( f \) corresponds to eq. (7.3).

7.2.3 Transport and Governing equations
The transport of defects within the bulk-phase of a CZO particle is described by the Nernst-Planck equation:

$$\frac{\partial C_i}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 J_i \right) = 0, \quad i = V_{O''}, Ce'$$  \hspace{1cm} (7.15)

$$J_i = -\frac{C_i D_i \rho_i}{RT} \frac{\partial \mu_i}{\partial r}, \quad \text{where} \quad \mu_i = \mu_i^0 + RT \ln \frac{C_i}{C_{ref}} + z_i F \phi$$  \hspace{1cm} (7.16)

where $C_i, J_i, \mu_i, D_i$ are the defect concentration, diffusion flux, electro-chemical potential, self-diffusion coefficient. $\mu_i^0, \gamma_i, z_i$ are the chemical potential at reference conditions, activity coefficient, and effective charge. $\phi, T, F$ are the electrostatic potential, temperature, and Faraday constant. By assuming electro-neutrality in the bulk, and that $\mu_i^0, \gamma_i$ are constant, we obtain[23, 38],

$$J_{i,\sigma} = -\tilde{D} \frac{\partial C_i}{\partial r}$$  \hspace{1cm} (7.17)

where $\tilde{D}$ is the ambi-polar diffusion coefficient, which is found to be around $7.6 \times 10^{-9}$ cm$^2$s$^{-1}$ at 773K, and $4.5 \times 10^{-6}$ cm$^2$s$^{-1}$ at 1173K (calculated from the electrical conductivity measurements[4, 20, 26] using the Nernst-Einstein relation). The characteristic time, $\tau$, for a diffusion-limited process from the expression, $\tau \sim l^2/4D$, is estimated to be less than 0.6 ms for a particle size of 40 nm (average particle size based on BET). This estimation indicates that the bulk diffusion within the CZO nano-particle is fast enough that any spatial variations of defect concentrations within the bulk phase will be readily smoothed out. Ref. [23] presented a more rigorous calculation for un-doped ceria with larger particles (hence longer $\tau$), and a similar conclusion was achieved.
However, the defect concentrations on the surface are higher than in the bulk, owing to the difference in the formation energy, $\mu_i^0$. The fast diffusion leads to a dynamic equilibrium between the surface and the bulk, and the electro-chemical potential, $\bar{\mu}_i$, of defects are constant throughout the particle. This leads to a transport equilibrium, as depicted in eq. (7.12), with

$$\Delta \mu_i = \Delta H_i^0 - T \Delta S_i^0 = \left( \mu_{V_0}^0 + 2 \mu_{Ce}^0 \right)_{\text{surface}} - \left( \mu_{V_0}^0 + 2 \mu_{Ce}^0 \right)_{\text{bulk}}$$

(7.18)

The overall governing equations for the evolutions of the surface species $OH_0^*$ and the bulk-phase $V_0^*$ are[23]:

$$\bar{\rho}_s \frac{d[OH_0^*]}{dt} = \bar{\rho}_s (2r_f - 2r_s)$$

(7.19)

$$\frac{d}{dt} \left( \bar{\rho}V_R \left[ V_0^* \right]_{\text{b}} \right) = -S_R \bar{\rho}_{Ce,s} r_i$$

(7.20)

Here $\bar{\rho}_s$, $\bar{\rho}$ are the surface and the bulk molar density of the unit cell. $V_R$, and $S_R$ are the volume and the surface area of the particle, calculated from the BET surface area. The conservation equations for the surface become:

O-site: $\quad [V_0^*]_s + [OH_0^*]_s + [O_0^*]_s = 2$

(7.21)

Ce-site: $\quad [Ce'_{Ce}]_s + [Ce'_{Ce}]_s = 0.5$

(7.22)

electro-neutrality $\quad 2[V_0^*]_s + [OH_0^*]_s = [Ce'_{Ce}]_s$

(7.23)

The surface electro-neutrality is assumed based on the conclusions from previous work on ceria [23, 31] as well as other materials [39].
7.3 Experiment

The redox kinetics is measured in a button-cell fixed-bed reactor, which consists of a gas delivery system, a control unit, a central quartz reactor tube, and a real time flue gas analysis system using an on-line quadrupole mass-spectrometer (QMS). A detailed description can be found in Chapter 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, $\rho$</td>
<td>6.62 g cm$^{-3}$</td>
</tr>
<tr>
<td>Molar density, $\bar{\rho}_{Ce}$</td>
<td>$4.50 \times 10^4$ mol m$^{-3}$</td>
</tr>
<tr>
<td>Molar weight, MW</td>
<td>147.66 g mol$^{-1}$</td>
</tr>
<tr>
<td>Surface molar density, $\bar{\rho}<em>{Ce,a} = \bar{\rho}</em>{Ce} a$</td>
<td>$2.4 \times 10^5$ mol m$^{-2}$</td>
</tr>
</tbody>
</table>

Ceria-zirconia nano-powder from Sigma Aldrich (99.0% purity) is used for the reaction study. Table 7-1 lists the properties of the sample. The morphology and the average particle size of the CZO powders before and after the redox treatment are characterized with a JEOL 6700 scanning electron microscopy (SEM) system. The powders obtained are confirmed as single phase CZO solid solutions by XRD analysis (Cu Ka, 45 kV and 40 mA, PANalytical X’Pert Pro Multipurpose Diffractometer, Almelo, The Netherlands) performed at room temperature in air. The BET surface area is measured using a surface area and porosity analyzer (ASAP 2020 from Micrometritics). The BET surface area is $37.48$ m$^2$ g$^{-1}$ and the average size of the particle is about 25 nm (Figure 7-2a). After 50 cycles, the particle enlarges to 40 nm (based on the BET measurement) and becomes more dispersed (Figure 7-2b). Compared to un-doped ceria, the
structural change and the size enlargement are less significant, indicating an enhanced structural stability with the addition of Zr. No obvious difference is found for the redox kinetics during the initial several redox cycles. This indicates that the morphological relaxation most likely results from the sintering effect during the heating-up of the sample. No change is found in the XRD patterns between the fresh and tested samples.

![Figure 7-2 SEM images of the CZO powder (a) before redox cycles and (b) after 50 redox cycles.](image)

During the kinetics study, 50mg of the CZO powder undergoes redox cycles with argon as purging gas flowing in between. The oxidation is performed using a gas mixture of water vapor and argon with the total flow rate into at 337 sccm, and 26mol% H₂O. H₂ is used as the reducing gas (14.3%) in reduction with the total flow maintained constant at 350 sccm. The oxidation and reduction times are fixed at 2 min each for the base case with 5 min Ar purging in between. As shown in Section 7.4.1, CZO cannot be fully oxidized by H₂O at high temperature. Thus, a supplemental 2 min oxidation with 0.5% O₂ (Ar balance) is used after the H₂O splitting step to ensure a sufficient re-oxidation [14, 15]. Longer oxidation with higher pO₂ is also tested, and no
observable difference of the redox kinetics is obtained. Tests without the O₂ oxidation step are also performed to validate the kinetics modeling, as discussed below.

Defect and redox modeling is performed numerically using MATLAB. The kinetic parameters to be obtained are $k_{1,f}$, $k_{2,f}$, $K_1$, $K_b$, $K_T$, and $f$, with the other kinetic parameters obtained via equilibrium relations. With the time-resolved profiles of feed [H₂O] for oxidation and [H₂] for reduction measured using the QMS, the entire conversion process can be predicted based on a given set of kinetic parameters. Equations (7.19) and (7.20) are integrated numerically, and the predicted reactivity is compared to the measurements. The kinetics parameters are varied to minimize the residual:

$$\text{Fitting Residual} = \sum_{\text{all tests}} \left[ \frac{1}{N} \sum_{i \in \text{tests}} \left( \hat{\omega}_{\text{predicted}} - \hat{\omega}_{\text{measure}} \right)^2 \right]$$

(7.24)

Here the reaction rates (\hat{\omega}_{\text{predicted}} or \hat{\omega}_{\text{measure}}) are normalized by the maximum rate, and $N$ is the number of measurement points in each test. The minimization is obtained numerically in MATLAB using fminsearch solver [40]. The redox measurements (with the supplemental O₂ oxidation) at 600°C, 700°C, 800°C, 900°C are used to extract the kinetic parameters. The parameters from the previous work for un-doped ceria [23] are used as initial estimations. To ensure a global minimum, the initial guess is varied randomly, and the result with the minimum residual is chosen.

### 7.4 Results

The measured H₂O splitting kinetics and the temperature dependence will be presented in this section. The modeling results will be discussed in Section 7.5.
7.4.1 H₂O Splitting Kinetics and Bulk Oxidation States

Figure 7-3 and Figure 7-4 show the H₂ and H₂O production rates at 900 °C during the oxidation and reduction steps, respectively. Panel (a) shows the measured H₂O and H₂ mole fraction in the gas phase. Panel (b) shows the evolution of the bulk defect, \([V_0^-]\) and \([\text{Ce'}_{\text{Ce}}]\), calculated by integrating the H₂ and H₂O production rates, as shown in panel (c). For oxidation, the fast initial rise of the H₂ production rate overlaps with the feed of the H₂O, leading to rapid incorporation of oxygen ion into the vacancy. The concentration of the reactants (feed H₂O and \(V_0^-\)) thus plays an important role in determining the maximum rate during this stage. As oxygen vacancy is gradually filled up, the H₂O splitting rate slows down quickly and eventually reaches zero, as evident in eq. (7.5). The majority of the conversion is completed within a time window of 0.5 min, although the oxygen incorporation process continues towards the end. Interestingly, oxidation with H₂O only regenerates the OC up to \(\delta = 0.05\), in contrast to the study with undoped ceria [23] where a complete re-oxidation is achieved with H₂O. The rate-limiting mechanism along with the temperature dependence will be discussed in Section 7.5 based on the derived kinetics mechanism.

The regeneration of oxygen deficiency during the reduction step follows a similar spike-decay pattern. The reaction starts with the feed of H₂, and continues throughout the entire course of reduction. The fraction of the oxygen vacancy increases as the produced H₂O is purged, indicating that a stronger reducing environment (lower \(p_{O_2}\), eq. (7.14)) enhances the oxygen carrying capacity. The kinetics is slower near the end of reduction, in accordance with the saturation of the defect, Ce⁴⁺ and V₀⁻, as shown in Figure 7-4(b), which hinders the charge transfer (backward R2, eq. (7.7)).
Figure 7-3 H₂ production during the oxidation step at 900°C. (a) Evolution of species mole fraction of H₂ (red) and H₂O (black); (b) evolution of the bulk defect fraction of Ce³⁺ and V⁰⁻; and (c) the H₂ production rate. H₂O flow is switched on at t = 0.2 min, and terminated at t = 2.2 min. The ramp-up of H₂O takes ~ 0.1 min. The feed H₂O (dashed line), equal to summation of exit H₂ and H₂O, is also included in panel (a). The initial defect fraction is adopted from the end of the reduction step. δ_red and δ_ox mark the non-stoichiometry reached before and after oxidation, also shown in Figure 7-6.
Figure 7-4 H$_2$O production during the reduction step at 900$^\circ$C. (a) Evolution of species mole fraction of H$_2$ (red) and H$_2$O (black); (b) evolution of the bulk defect fraction of Ce$^{3+}$ and V$_{\delta}^{-}$; and (c) the H$_2$O production rate. H$_2$ flow is switched on at t = 0.2 min, and terminated at t = 2.2 min. The feed H$_2$ (dashed line) is also included in panel (a). The initial defect fraction is zero, resulting from a complete re-oxidation with O$_2$ (see Section 7.8). $\delta_{\text{red}}$ mark the non-stoichiometry reached after reduction.

The most interesting feature comparing the redox steps is the significantly faster reduction kinetics as compared to oxidation, in contrast to the case with un-doped ceria where the reduction step is rate-limiting. The oxygen non-stoichiometry after 2 min reduction is above 0.20, accounting for over 80% of the overall oxygen carrying capacity ($\left[V_{\delta}^{-}\right]_{\text{max}} = 0.25$), while less
than 40% of the capacity is utilized with un-doped ceria under the same condition. This comparison highlights the significantly improved reducibility with the addition of Zr.

7.4.2 Effect of Temperature

Figure 7-5 compares the profiles of H₂ and H₂O rates during oxidation and reduction, respectively, as a function of temperature from 500°C to 900°C. Solid lines are predictions from the kinetic modeling, as detailed in Section 7.5. Both steps exhibit strong temperature dependence: the oxygen removal rate is significantly accelerated at high temperature with the H₂O profile being taller and narrower; the enhanced oxygen non-stoichiometry then leads to improved H₂ production rates in the following H₂O splitting step. The strong temperature dependence indicates large activation barriers for both steps; thus one can expect a kinetics-limited redox conversion at low temperature, as shown Section 7.5.

Despite the similar profiles during both redox steps, subtle differences need to be carefully examined. During reduction, the peak rates depend almost linearly on the temperature without an obvious threshold, suggesting a kinetics-limited mechanism during the initial stage of reduction. The later stage (after t = 0.5 min in Figure 7-5b), however, exhibits an inverse temperature dependence above 700°C, indicating a different controlling mechanism at high temperature. Consequently, the oxygen non-stoichiometry, δ_red, achieved after 2 min reduction varies nonlinearly and becomes flattened at high temperature (Figure 7-6a). Therefore, the following oxidation step, starting with δ established from reduction, exhibits a non-linear improvement with temperature (Figure 7-5a): the H₂O splitting rate undergoes a large jump from 600 to 800°C, but only mildly improves from 800 to 900°C. The nonlinearity of the H₂O splitting kinetics was
observed previously with un-doped ceria[23], which originates from the saturation of defects on the surface above 800°C. The oxygen non-stoichiometry established after the H_2O oxidation step (Figure 7-6b) decreases with increasing temperature, resulting from faster oxidation kinetics which leads to a higher extent of re-oxidation with H_2O. The non-monotonous behavior at 500°C is caused by slow reduction step which limits the oxygen non-stoichiometry achieved before oxidation, as seen in Figure 7-6a.

![Figure 7-5 (a) H_2 production rate during the oxidation step, and (b) H_2O production rate during the reduction step. Temperature is varied from 900°C to 500 °C for the measurements. 26% H_2O at 337 sccm is used for oxidation, and 14.3% H_2 at 350 sccm is used for reduction. Lines are from model predictions. Different scales are used for clarity.](image)
Figure 7-6 Fraction of bulk Ce\(^{3+}\) (red) and \(V_O\) (black) obtained at the end of (a) the reduction step and (b) the oxidation step at various temperatures. Lines are for guiding the eyes. Error is based on the s.d. of redox rates multiplying the reaction time.

Model predictions are included in Figure 7-5 for comparison. A good match is found between predictions and measurements for all the cases. The predictions precisely simulate the spike-decay behaviors of both redox reaction steps, and the temperature dependence is precisely captured. The subtle difference between the reduction and the oxidation is also adequately represented.
Figure 7-7 (a) Comparison of the total H\(_2\) rate between CZO and un-doped ceria from ref. [23].
(b) Peak H\(_2\) or H\(_2\)O production rate during oxidation or reduction. Error is based on the s.d. of triplicate measurements.

Comparisons of the H\(_2\) production rate as well as the total H\(_2\) production capacity with un-doped ceria are shown in Figure 7-7. As seen in panel a, the total H\(_2\) production of CZO is significantly higher, and improved over twice as much compared to un-doped ceria at low temperature. This is interesting, considering the fact that only the CeO\(_2\) portion in Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) (less than 60% in weight) contributes to oxygen transfer. A critical temperature around 650 \(\degree\)C is found for CZO, as
compared to 750°C for un-doped ceria, above which H₂ production capacity is significantly enhanced. This again demonstrates the improved reducibility at low temperature with the addition of Zr. Panel (b) compares the peak redox rates. Similar oxidation rates are observed at higher temperature, while more evident improvement is found towards the low temperature with over 60% increase at 700°C. The reduction rate with CZO is significantly faster, with an almost order-of-magnitude improvement over un-doped ceria. Compared to oxidation, the reduction rate is faster throughout the entire temperature range. This is in contrast to un-doped ceria, in which reduction is the overall rate-limiting step.

The peak H₂ rate is 175 µmole g⁻¹ s⁻¹ at 900°C, and 95 µmole g⁻¹ s⁻¹ at 700°C. The faster H₂ production rate as compared to un-doped ceria is attributed to the enhanced reducibility with Zr, as well as the finer particle structures maintained under cyclic equilibrium. The oxidation step is the limiting step for the overall splitting process. The total production is 1130 µmole g⁻¹ s⁻¹ at 900°C, and 750 µmole g⁻¹ s⁻¹ at 700°C, corresponding to Δδ of 0.167 and 0.11, respectively. Table 7-2 compares the measured H₂O splitting rate with the previous studies. The total evolved H₂ amounts fit well within in the range, while the obtained peak rates are faster, resulting from the utilization of fine particles and well-controlled experiments which ensure a surface-limited-process.
### Table 7-2 Reported total and peak H₂ production rates using CZO as OC for TCCS or RCLCS

<table>
<thead>
<tr>
<th>Temp °C (Red/Ox)</th>
<th>Tot. H₂ b (μmole/g)</th>
<th>Peak rate b (μmole/g/s)</th>
<th>Feed H₂O (%)</th>
<th>Reducer</th>
<th>Oxygen Carrier (OC)</th>
<th>OC surface area (m²/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400/1050</td>
<td>338</td>
<td>-</td>
<td>5.8</td>
<td>thermal</td>
<td>CeO₂(25%Zr 1%Gd)</td>
<td>-</td>
<td>[41]</td>
</tr>
<tr>
<td>1300/800</td>
<td>109</td>
<td>-</td>
<td>30</td>
<td>thermal</td>
<td>Ce₁₁₋₅Zr₀₅O₂</td>
<td>1.0</td>
<td>[42]</td>
</tr>
<tr>
<td>1400/1050</td>
<td>468</td>
<td>-</td>
<td>38.3</td>
<td>thermal</td>
<td>CeO₂(50% Zr)</td>
<td>0.12</td>
<td>[43, 44]</td>
</tr>
<tr>
<td>800/500</td>
<td>840</td>
<td>0.29</td>
<td>2.4</td>
<td>CH₄</td>
<td>Ce₀₈Zr₀₂O₂</td>
<td>-</td>
<td>[45]</td>
</tr>
<tr>
<td>850/700</td>
<td>1580</td>
<td>1.3</td>
<td>83</td>
<td>CH₄</td>
<td>Ce₀₇Zr₀₂O₂</td>
<td>40 a</td>
<td>[46]</td>
</tr>
<tr>
<td>800/800</td>
<td>2167</td>
<td>24</td>
<td>70</td>
<td>CH₄</td>
<td>Ce₀₈Zr₀₂O₂</td>
<td>-</td>
<td>[47]</td>
</tr>
<tr>
<td>800/800</td>
<td>1954</td>
<td>18.6</td>
<td>73</td>
<td>CH₄</td>
<td>Ce₀₈Zr₀₂O₂</td>
<td>28</td>
<td>[48]</td>
</tr>
<tr>
<td>800/800</td>
<td>326</td>
<td>0.65</td>
<td>27</td>
<td>CH₄</td>
<td>10wt% CeO₂/ZrO₂</td>
<td>9 a</td>
<td>[49]</td>
</tr>
<tr>
<td>900/900</td>
<td>1130</td>
<td>175</td>
<td>26</td>
<td>H₂</td>
<td>Ce₀₅Zr₀₅O₂</td>
<td>22.6</td>
<td>This study</td>
</tr>
<tr>
<td>700/700</td>
<td>750</td>
<td>95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The surface area was for the fresh sample; the value for the aged sample was not reported.  
* Note some studies tested various material compositions for repeated cycles. The highest values are chosen and listed here for comparison. The conversion of H₂ production unit from mL/g to μmole/g utilizes ideal-gas law at standard temperature and pressure (25°C 1 atm).

### 7.5 Discussion

#### 7.5.1 Non-stoichiometric Equilibria

The defect equilibrium and kinetics parameters derived in this study for Ce₀.₅Zr₀.₅O₂₋δ are summarized in Table 7-3 and Table 7-4. Other relevant values from the literature are also included in Table 7-4 for comparison. The enthalpy of reduction is in good agreement with values obtained using TGA [14], O₂ titration [15] and impedance spectroscopy [26]. Comparing Ce₀.₅Zr₀.₅O₂₋δ to Ce₀.₈Zr₀.₂O₂ [22, 26], we find that with Zr content increasing from 0.2 to 0.5, the defect formation enthalpy is only slightly decreased, in contrast to the remarkable change from un-doped ceria. Similar trend was observed previously in ref. [14]. The entropy derived from this study is slightly higher than the values in refs. [14] and [15]. Nevertheless, both studies observed an increase of Sₘ with non-stoichiometry. However, the effect of δ on entropy is found to be less important, as shown in Section 7.7, and hence it is not included in the modeling. Compared to un-doped ceria, the addition of Zr is found to remarkably decrease the bulk defect formation energy (by 40%) and entropy (by 50%) at stoichiometry. The weakened bond along with the irreducible Zr sites as the structural support leads to a smaller difference in the defect formation...
enthalpy ($\Delta H^0_T$) and entropy ($\Delta S^0_T$) between the bulk and the surface, as compared to un-doped ceria.

Table 7-3 Fitted kinetic parameters for both the forward and backward reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forward</td>
<td>$1.2 \times 10^7 \exp(-5 \pm 5$ kJ mol$^{-1}$/RT)</td>
</tr>
<tr>
<td>Backward</td>
<td>$5.0 \times 10^{11} \exp(-92 \pm 42$ kJ mol$^{-1}$/RT)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$2.5 \times 10^{11} \exp(87 \pm 42$ kJ mol$^{-1}$/RT)</td>
</tr>
</tbody>
</table>

Note: Error corresponds to 5% increment of the fitting residual.

Table 7-4 Parameters for the transport and bulk defect equilibria

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</td>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$</td>
<td>Ce$<em>{0.8}$Zr$</em>{0.2}$O$_2$</td>
<td>CeO$_2$</td>
</tr>
<tr>
<td>$H^0$ (kJ mol$^{-1}$)</td>
<td>261.7 ± 5.8</td>
<td>250.6</td>
<td>249.3$^a$</td>
<td>283$^e$</td>
<td>276</td>
<td>467.4</td>
</tr>
<tr>
<td>$S^0$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>80.1 ± 4.2</td>
<td>38$^c$</td>
<td>29$^a$</td>
<td>65$^e$</td>
<td>76.1</td>
<td>172.9</td>
</tr>
<tr>
<td>$\Delta H^0_T$ (kJ mol$^{-1}$)</td>
<td>$-30.0 \pm 6.8$</td>
<td>$-,$</td>
<td>$-,$</td>
<td>$-,$</td>
<td>$-,$</td>
<td>$-107.6$</td>
</tr>
<tr>
<td>$\Delta S^0_T$ (J mol$^{-1}$ K$^{-1}$)</td>
<td>$-9.6 \pm 4.8$</td>
<td>$-,$</td>
<td>$-,$</td>
<td>$-,$</td>
<td>$-,$</td>
<td>$-54.0$</td>
</tr>
<tr>
<td>$f$ (kJ)</td>
<td>$368.1 \pm 8.1$</td>
<td>$1040^d$</td>
<td>$510^b$</td>
<td>$530^f$</td>
<td>$60$</td>
<td>$-,$</td>
</tr>
</tbody>
</table>

$^a$ calculated from the partial molar enthalpy and entropy of oxygen, the values are averaged for $\delta = 0.15 - 0.2$; $^b$ estimated from $\delta = 0.15$ and 0.2; $^c$ calculated based on the model predictions from ref. [14]; $^d$ estimated from $\delta = 0.04$ and 0.13; $^e$ calculated from the partial molar enthalpy and entropy of oxygen, the values are taken for $\delta = 0.01$; $^f$ estimated from $\delta = 0.01$ and 0.19;

Figure 7-8 depicts the isothermal non-stoichiometric equilibria as a function of $p_{O_2}$, calculated from eq. (7.2), and compares with the measurements by Kuhn et al. [14] and Zhou et al. [15]. At intermediate to high $p_{O_2}$, an approximate $-1/6$ slope is observed, as expected from eq. (7.2). At lower $p_{O_2}$, the profile deviates from $-1/6$ and the non-stoichiometry becomes $p_{O_2}$ insensitive. This nonlinearity results from the reduced concentration and hence larger influences of the normal sites ($O'_O$ and $Ce'_Ce$ in eq. (7.2)). The slope eventually goes to zero as $\delta$ reaches 0.25, indicating a complete reduction of Ce$^{4+}$ to Ce$^{3+}$. Raising the temperature leads to a remarkable
increase in the non-stoichiometry at intermediate to high $p_{O2}$. The temperature dependence, on the other hand, is weaker in a reducing environment. The obtained isotherms fit well within the reported values in the literature. Good agreement is found with ref. [14] at 900°C as well as other temperatures with high $p_{O2}$. Discrepancy is found between refs. [14] and [15] at large $\delta$, where results from our study fall in between. It is worth noting that Kuhn et al.[14] observed a substantial increase in the reducibility (larger $\delta$) under the same conditions after repeated oxidation. The authors attributed this to the defect ordering and the phase segregation. Nevertheless, no difference is observed in our study between adjacent redox cycles in all cases.

![Graph showing non-stoichiometric equilibria comparison](image)

**Figure 7-8** Comparison of bulk-phase non-stoichiometric equilibria with literature. Lines are from this study. Results from Kuhn et al.[14] (circles) and Zhou et al.[15] (triangles) are also included for comparison.

Figure 7-9 maps the range of the redox operations and outlines the evolution of the oxygen non-stoichiometry along the equilibrium isotherms during the redox cycles. The $y$-axis is plotted in a
linear scale for clarity. The non-stoichiometry established during reduction (dash-dot line) and oxidation (dashed line) are included, in accordance with the obtained defect concentration in Figure 7-6. The isotherms in between (gray area) correspond to the ranges of δ utilized for H₂ production. \( p_{\text{O}_2} \) along established after reduction (dash-dot line) is in the range of \( 10^{-25} \sim 10^{-21} \), while that in oxidation (dashed line) varies significantly with temperature, ranging from \( 10^{-25} \) to \( 10^{-10} \). The equilibrium \( p_{\text{O}_2} \) calculated from eq. (7.14) is also included (shaded blue areas), which outlines the minimum or maximum oxygen activity during reduction and oxidation, respectively. Large deviations of \( p_{\text{O}_2} \) (dashed, or dash-dot lines) are found from equilibrium (shaded blue areas) at 500 – 600°C, which suggests a kinetics-limited process in the low temperature regime. This is expected, given the strong temperature dependence of the splitting kinetics observed in Figure 7-5. As a result, the incomplete re-oxidation with H₂O (Figure 7-6b) is largely attributed to the slow kinetics at low temperature. In comparison, the non-stoichiometry (dashed, dash-dot lines) at 800°C or 900°C is in much closer match with those at equilibrium \( p_{\text{O}_2} \) (blue area), indicating that the redox conversion is partially equilibrated at high temperature. Consequently, the reactivity in the later stage at high temperature is adversely affected by the residual product formed during the conversion. The transition of the controlling mechanism with temperature, from kinetics-limited to equilibrium-constrained, explains the nonlinearity observed in the bulk defect fraction in Figure 7-6.

From Figure 7-9, the non-stoichiometry boundaries (dash-dot and dashed lines) intersect around 550°C, corresponding to the minimum temperature practical for H₂ production with CZO. At 500°C, very limited amount of H₂ is produced during oxidation, as seen in Figure 7-7. The significant jump in the H₂O production around 650°C is in accordance with the large expansion
of the gray area in this region. The dotted area underneath the oxidation $p_{O_2}$ curve (dashed line) corresponds to the saturation of oxygen vacancy during the supplemental $O_2$ oxidation phase (see Section 7.8 for details).

Figure 7-9 Mapping of the operating non-stoichiometry throughout the redox cycles. Red, black, blue, pink, and green correspond to equilibrium values at 900°C, 800°C, 700°C, 600°C, and 500°C. The dashed line is the oxygen non-stoichiometry after oxidation, and the dash-dot line is the oxygen non-stoichiometry after reduction. Gray area and the dotted area enclose the range of the oxygen non-stoichiometry for the $H_2O$ splitting and the supplemental $O_2$ oxidation steps, respectively. The upper and lower blue areas correspond to the equilibrium $p_{O_2}$ achieved at the end of the reduction and oxidation steps, calculated from eq. (7.14) based on the s.d. of triplicate measurements. The non-stoichiometry, $\delta_{\text{red}}$, or $\delta_{\text{ox}}$, reached during redox reactions at 900°C is marked, in accordance with Figure 7-3 and Figure 7-4.

The concentration of defects on the surface, however, differs from that in the bulk phase, owing to the lower defect formation free energy, as characterized by eq. (7.13). Figure 7-10(a) compares the calculated equilibrium concentration of $Ce^{3+}$ in the bulk and on the surface within
the range of non-stoichiometry achieved during redox reactions (Figure 7-9). Under all conditions, the surface Ce$^{3+}$ value is significantly higher, indicating that the surface is more reduced. The ratio between surface and bulk, as shown in Figure 7-10(b), ranges from 1.2 to 2.5, favoring the low temperature. In contrast to the remarkable difference of the defect concentrations in the bulk phase, the surface defect concentrations are similar and less temperature sensitive above 700°C. Compared to un-doped ceria, the defect enrichment effect at the surface is less pronounced, as evident in the smaller $\Delta H_f^0$ and $\Delta S_f^0$ as listed in Table 7-4.

![Figure 7-10](image)

Figure 7-10 (a) Ce$^{3+}$ concentration at equilibrium on the surface (solid) and in the bulk (dashed). Value of 0.5 corresponds to a complete reduction of Ce$^{4+}$ to Ce$^{3+}$. (b) Ratio of surface to bulk Ce$^{3+}$ concentration. Each line corresponds to the range of oxygen non-stoichiometry established during redox steps at each temperature.
Figure 7-11 Energy landscape for the water splitting pathways for stoichiometric CZO (black) as well as reduced CZO (red) with $\delta = 0.2$. The pathway for un-doped ceria is also included for comparison. The dashed black lines on the left side denote the bulk phase defect formation. $\Delta H_f^0$ corresponds to the difference of the defect formation energy between the surface and the bulk, eq. (7.18). Unit is kJ mole$^{-1}$. TS1 and TS2 are transition states for the two reactions.

7.5.2 Kinetics and Energy Landscape

Figure 7-11 shows the calculated energy landscape for the water splitting pathway. The energy levels for the intermediate species on the surface as well as the transition states (TS1 and TS2) are included with reference to the perfect crystal as the ground state. R1 is exothermic and barrierless, and R2 is endothermic, with large activation barriers for both forward and backward reactions. The intermediate species, $\text{OH}_o^-$, lies in the valley, and its concentration is expected to increase at lower temperature. The reduction enthalpy increases with $\delta$ according to eq.(7.3), leading to a higher energy level for R1 and hence a larger activation barrier for backward R1.
The overall surface water splitting reaction (eq. (7.10)) undergoes a transition from an exothermic process at $\delta = 0.2$, to an endothermic process at $\delta = 0$, with the cross-over occurring at $\delta = 0.04 - 0.05$, which roughly corresponds to the minimum non-stoichiometry reached during $H_2O$ oxidation step, as evident in Figure 7-9. The bulk-phase equilibrium, combining eqs. (7.10) and (7.12)

$$V''(b) + 2Ce'_c(b) + H_2O(g) \rightleftharpoons O'_o(b) + 2Ce'_c(b) + H_2(g)$$ (7.25)

remains mildly exothermic due to the larger defect formation energy (i.e., $262 \sim 336$ kJ mole$^{-1}$ > 249 kJ mole$^{-1}$ for water dissociation reaction, see Figure 7-11). The difference between the surface and the bulk corresponds to $\Delta H^0_f$.

The oxidation process starts with a more favored $H_2O$ dissociation step (R1, red line), leading to the quick formation of hydroxyl radicals on the surface, facilitating the subsequent charge-transfer and $H_2$ production (R2). As the conversion proceeds, the defect energy level decreases ($\delta$ dependence), and the R1 backward reaction becomes more prevailed, which slows down the overall $H_2$ production rate by consuming of the formed $OH^-$. The reduction process, on the other hand, follows a reversed sequence: the formation of defects via $H_2$ reduction on the surface is energetically favored during the early stages; as defects start to saturate, a further removal of surface oxygen becomes more difficult. The effect of $\delta$ on the water splitting energy landscape is assumed to be confined to the defect formation step (R1 backward), consistent with the observed $\delta$-dependence of the bulk defect formation enthalpy[14, 15]. This, however, does not rule out the possible variations of the charge transfer step (R2) with $\delta$. A recent theoretical study by Kumar and Deshpande [37] compared the formation energy of the $OH^-$ complex via $H_2$ adsorption (R2 backward) on ceria-based materials, and concluded that the oxidized surface favors the hydroxyl
formation compared to the reduced surface, resulting from the repulsive interactions between the protons and the oxygen vacancies. As a result, the energy level of the OH\textsuperscript- complex (as well as the transition state, TS2) may also increase with δ. Nevertheless, quantifying the effect of δ on R2 during the water splitting process is beyond the scope of this work, and requires further study in the future.

The landscape for un-doped ceria from ref. [23] is also included for comparison. The energy roadmap for R2 of ceria is analogous to that of CZO, indicating a similar charge-transfer process and proton recombination energetics. This similarity is further examined by comparing the pre-exponential rate constant, $k^0$, of R2 between CZO ($k_{2,f}^0 = 7.1 \times 10^{14}$ s\textsuperscript{-1}, $k_{2,b}^0 = 1.0 \times 10^5$ s\textsuperscript{-1}) and undoped ceria [23] ($k_{2,f}^0 = 1.5 \times 10^{14}$ s\textsuperscript{-1}, $k_{2,b}^0 = 4.4 \times 10^4$ s\textsuperscript{-1}), which are within the same order of magnitude. By using the transition state theory [50], we can estimate the rate of the charge-transfer step (R2 forward) in the form of an attempt frequency multiplied by a Boltzmann factor [35], as: $k_{2,f} = v_0 \exp(-E_a/k_BT)$, where $k_B$ is the Boltzmann constant, and $v_0$ is the attempt frequency. Since the transition state of R2 involves breaking up the O-H bond, we take the vibrational frequency of the OH\textsuperscript- complex, $v_0 = 1.1 \times 10^{14}$ s\textsuperscript{-1}, as a simple approximation [51, 52]. The estimated attempt frequency is in good match with the obtained $k_{2,f}^0$ from kinetics fitting.

The similarity of the reaction rates of R2 between CZO and un-doped ceria comes as no surprise, given the fact that the charge-transfer step mostly depends on the migration of adsorbed protons and the interaction with the anions, and less affected by the structural relaxation effect.
In contrast, the H₂O adsorption and dissociation step (R1) differs starkly between CZO ($k_{1,f}^0 = 12$ s⁻¹, $k_{1,h}^0 = 5.0 \times 10^{11}$ s⁻¹) and un-doped ceria ($k_{1,f}^0 = 130$ s⁻¹, $k_{1,h}^0 = 8.2 \times 10^{14}$ s⁻¹), as the more compact crystal structure with stronger bond energy leads to larger defect formation barrier with higher vibrational frequency for R1 backward reaction. The difference in $k_{1,f}^0$ may be attributed to the difference in the preferable H₂O adsorption sites. Given the fact that Zr⁴⁺ remains inert during H₂O splitting, it is not surprising to find a lower $k_{1,f}^0$ for CZO. The obtained $k_{1,h}^0$'s are within the range of values reported for oxides [35, 52, 53].

7.5.3 Rate-limiting Mechanism

To examine the transition of the rate-limiting mechanism from low to high temperatures, Figure 7-12 and Figure 7-13 show the calculated evolution of the surface species (solid lines) along with the forward and the backward reaction rates for oxidation and reduction, respectively. The evolution of the surface species under equilibrium (both R1 and R2) with the H₂O/H₂ environment is also included (dashed lines) in panels (a) and (b) for comparison. For oxidation at high temperature, all surface species undergo a quick decay as H₂O is admitted into the reactor, leading to a rapid H₂ production, as observed in Figure 7-3. The conversion then transitions to a slow decay period where the species concentrations remain relatively stable and vary gradually, responding to the H₂O/H₂ environment. Hydroxyl groups are quickly produced, and then decay slowly throughout the rest of the conversion. The profiles of the surface species match closely with those at equilibrium (dashed lines), suggesting an equilibrium-constrained oxidation at high temperature. In contrast, oxidation proceeds more mildly at low temperature and the species concentration remains almost unchanged during the conversion. Low temperature favors the
formation of hydroxyl ions, as expected from the large energy barriers shown in Figure 7-11. Large differences are observed as compared to the equilibrium case, indicating a kinetics-limited H₂O splitting process at 600°C. Similar behavior is observed in the reduction step.

Figure 7-12 Concentrations of the surface species and the surface reaction rates for oxidation at (a, c) 900 °C and (b, d) 600 °C. The evolution of the surface species under equilibrium with the H₂O/H₂ environment is also included (dashed lines) in panels (a) and (b) for comparison.
Figure 7-13 Concentrations of the surface species and the surface reaction rates for reduction at (a,c) 900 °C and (b,d) 600 °C. Different scales are used in panels (c) and (d) for clarity. The evolution of the surface species under equilibrium with the H₂O/H₂ environment is also included (dashed lines) in panels (a) and (b) for comparison.

The evolution profile of the intermediate hydroxyl complex reveals the dynamics between the two steps, with one creating OH and the other consuming it to form product. Given the role as a buffer linking H₂O and H₂, [OH] is expected to follow a rise-decay pattern during the redox steps,
as observed in Figure 7-12(a,b) and Figure 7-13(a) as well as all the equilibrium cases. Exception is reduction at low temperature, in which [OH] continues to increase with conversion. Nevertheless, [OH] on the surface is minor as compared to other major species in all cases, as observed by Chueh et al [24].

To further clarify the limiting step, we compare the forward and backward redox rates for the redox processes in panels (c,d). During oxidation, H$_2$O dissociation (R1) is much faster in all cases, and equilibrium is quickly established and maintained throughout the conversion. The charge transfer step (R2) is slower, especially at low temperature, and the backward reaction is close to zero, showing that the charge transfer process is the rate-limiting step for H$_2$ production, similarly as observed for un-doped ceria [23] and Sm-doped ceria [31]. Sensitivity analysis is performed to quantify the effect of each step on H$_2$ production; results can be found in Section 7.9.

Compared to oxidation at 900°C, the forward and backward reaction rates of R1 are slightly faster during oxidation at 600°C. This finding is at first surprising, given the significant activation barrier for the backward R1 reaction, which favors high temperature. Instead, this behavior is again attributed to the high concentration and slow consumption of the surface species (V$_o^-$ and OH') via the charge-transfer process. At 900°C, the rapid consumption of the surface defects slows down the further H$_2$O adsorption process, while the defect consumption is much slower at 600°C and the concentrations on the surface exceed those at high temperature soon after the initiation of oxidation, leading to a faster forward R1. The OH' concentration is over an order-of-magnitude higher at 600°C, resulting in a faster backward R1 reaction as
compared to 900°C. As seen in Figure 7-12(c), backward R1 lags slightly (~5 sec) behind the forward reaction, originating from the larger activation barrier associated with large δ (see Figure 7-11). Therefore, a spike of H₂ is observed during the initial oxidation stages at high temperature. The lag is less obvious at 600°C.

Compared to oxidation, the reduction rates are all accelerated at high temperature. The backward reaction rates exceed the forward rates, and a similar magnitude is found between R1 and R2. Equilibria are quickly established at 900°C and the rates mildly vary in response to the H₂O/H₂ environment. In contrast, the forward rates at 600°C are negligible as compared to the backward rates, and equilibrium is not reached during the entire reduction step. This leads to the rising profile of OH⁺ as observed in Figure 7-13(b).

7.6 Summary

We present a detailed kinetics study and non-stoichiometry characterization of Ce₀.₅Zr₀.₅O₂. The time-resolved kinetics are measured for CZO nano-powder in a button cell reactor in the temperature range 500-900°C at atmospheric pressure. The CZO sample is alternatively exposed to H₂/Ar mixture in the reduction step to remove the lattice oxygen, and water vapor in the oxidation step to produce H₂.

Compared to un-doped ceria, we find over twice the improvement of the total H₂ with 60% improvement in the kinetic rate at 600-700°C. The significant enhanced H₂O splitting process is attributed to the improved reducibility with the addition of Zr and the finer particle structures under cyclic equilibrium. The measured peak rates are 175 μmole g⁻¹s⁻¹ at 900°C and 95 μmole
g⁻¹s⁻¹ at 700°C with the total H₂ yield of 1130 µmole g⁻¹ and 750 µmole g⁻¹, respectively. A threshold temperature of 650°C is required to achieve significant H₂ production at fast rates. Oxidation is found to be much slower than reduction, and hence it is the rate-limiting step for the H₂ production process. The minimum temperature for water splitting by CZO is around 550°C.

Previously developed kinetics model for pure ceria is successfully applied to describe the oxygen-ion incorporation dynamics during the redox cycle. The model consists of a two-step surface chemistry and the bulk-to-surface transport sub-models. Kinetics and equilibrium parameters are extracted and excellent agreement is achieved. The enthalpy of defect formation for CZO is over 40% lower, indicating an enhanced reducibility compared to un-doped ceria. The reduction enthalpy is found to increase with the non-stoichiometry, δ, leading to a transition of the surface water splitting reaction from an exothermic process to endothermic, with the cross-over around 0.04 ~ 0.05. The low temperature H₂O splitting process is kinetics-controlled, while the conversion is close to equilibrium at high temperature. The charge-transfer step is found to be the overall rate-limiting step. Similarity of the H₂O splitting process between pure and doped ceria is also shown. The results in this work demonstrated the applicability of the modeling framework to various ceria-based OC systems for kinetics and thermodynamics study. The obtained redox kinetics and non-stoichiometric equilibria can provide important guidance in optimizing CZO as a catalyst, oxygen storage material, and water splitting candidate.

7.7 Appendix: Comparison of defect chemistry sub-models

Three defect models are considered to describe the defect equilibrium:
A. Ideal model: ideal reduction of Ce, constant enthalpy, $H_b = H_b^0$, and entropy, $S_b = S_b^0$, and random distribution of defects.

B. $\delta$-linear model: linear dependence of the reduction enthalpy, $H_b = H_b^0 + f_H \delta$, constant entropy $S_b = S_b^0$, and random distribution of defects.

C. Generalized $\delta$-linear model: linear dependence of the reduction enthalpy, $H_b = H_b^0 + f_H \delta$, and entropy, $S_b = S_b^0 + f_S \delta$.

Two sets of mechanisms are considered to model the surface chemistry:

1. One-step mechanism (eq.(7.10))

   \[
   \text{R1: } V'_0 (s) + 2Ce'_c (s) + H_2O(g) \rightleftharpoons O'_0 (s) + 2Ce'^c (s) + H_2 (g)
   \]

2. Two-step mechanism (eqs. (6.6) and (6.7))

   \[
   \text{R1: } H_2O(g) + V'_{0} (s) + O'_{0} (s) \rightleftharpoons 2OH'_{0} (s)
   \]
   \[
   \text{R2: } 2OH'_{0} (s) + 2Ce'_{c} (s) \rightleftharpoons 2O'_{0} (s) + 2Ce'^{c} (s) + H_2 (g)
   \]

By combining the defect model (A, B, or C) and the surface chemistry (1 or 2), we consider in total 6 sets of kinetic models (labeled as A1 – C2) to analyze the experimental data (Table 7-5). B2 is the model adopted in the main context. The non-ideal $\delta$ dependence is assumed to be associated with the oxygen removal step (backward R1). The bulk-to-surface transport constants, $\Delta H_f^0, \Delta S_f^0$ in eq.(7.18), are included in all models. The kinetic parameters are obtained following the same fitting procedure as detailed in Section 7.3, with the residual (eq.(7.24)) minimized. The obtained parameters are listed in Table 7-6.
Table 7-5 Kinetic models categorized based on defect model and surface chemistry

<table>
<thead>
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<th>Defect model</th>
<th>Surface chemistry</th>
<th>1-step mechanism</th>
<th>2-step mechanism</th>
</tr>
</thead>
<tbody>
<tr>
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<td>(H₀, S₀, ΔHᵣ, ΔSᵣ)</td>
<td>Model A1</td>
<td>Model A2</td>
</tr>
<tr>
<td>δ-linear model</td>
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<td>Model B1</td>
<td>Model B2</td>
</tr>
<tr>
<td>generalized δ-linear model</td>
<td>(H₀, S₀, ΔHᵣ, ΔSᵣ, φₗₗ, φₗₗₛ)</td>
<td>Model C1</td>
<td>Model C2</td>
</tr>
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</table>

Comparing the obtained kinetics parameters as listed in Table 7-6, it is interesting to notice the similarities among models with different levels of fidelity. The obtained enthalpy and entropy of defect formation, H₀ and S₀, are similar among all six models. The H₂ adsorption reaction (k₆ or k₂₆₆) is also similar, and the obtained pre-exponential factors and the activation barriers are within a close range among different models.

The H₂ production rates of CZO measured using the QMS between 600 and 900 °C are shown in Figure 7-14(a)-(d), along with the predictions from each model. Predictions from ideal models (A1 or A2) or assuming one-step mechanism (A1-C1) deviate significantly from the measured reaction rates near the peak area as well as in the decay stage. A magnification of this stage is also included in panels (a) and (b), where the inaccuracy of these models can be clearly observed.

The deviations between the measurement and the model predictions decrease with increasing temperature, as evident in panel (c). Comparing the six models, only B2 and C2 produce accurate predictions throughout the entire temperature range, with the fitting residual less than 4%. The generalized δ-linear model with the δ-dependence of entropy (C1 or C2) only leads to minor improvement over the δ-linear model, as their predictions practically coincide with the results of
B1 or B2. Based on the comparison, it is clear that B2 is the model with minimum fitting parameters to accurately characterize the H₂O splitting kinetics.

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>B1</th>
<th>C1</th>
<th>A2</th>
<th>B2*</th>
<th>C2</th>
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<td>86.0</td>
<td>103.2</td>
<td>91.7</td>
<td>86.2</td>
</tr>
</tbody>
</table>

* B2 is the model used in the context.
Figure 7-14 Fit of the various kinetic models to the H\textsubscript{2} production rate of CZO at (a) 900°C, (b) 800°C, (c) 700°C, (d) 600°C and (e) comparison of the fitting residual (eq. (7.24)) obtained from each model as a function of temperature. Insets are magnified comparison near the peak.
7.8 Appendix: Supplemental O\textsubscript{2} oxidation

Complete oxidation is achieved by a supplemental 2 min oxidation with 0.5% O\textsubscript{2} (Ar balance). A longer period of O\textsubscript{2} oxidation is also tested, but no difference is observed for the following reduction cycle. Figure 7-15 compares the change of non-stoichiometry during reduction and oxidation. The non-stoichiometric change in the reduction step (δ\textsubscript{red}) is evidently higher than that in the following H\textsubscript{2}O splitting process (δ\textsubscript{ox}). Raising temperature leads to an almost linear increase in the reduction δ\textsubscript{red}, different from δ\textsubscript{ox} for oxidation which exhibits a jump around 650°C. The difference, δ\textsubscript{red} - δ\textsubscript{ox}, corresponds to the supplemental O\textsubscript{2} phase, as plotted in Figure 7-6. δ\textsubscript{red} - δ\textsubscript{ox} exhibits a non-linear behavior, resulting from the transition of the rate-limiting mechanism with varying temperature, as discussed in Section 7.5.

![Figure 7-15](image)

**Figure 7-15** The non-stoichiometric change at different temperature. The results from the cases without supplemental O\textsubscript{2} oxidation are included for comparison.

The supplemental O\textsubscript{2} oxidation with an additional oxygen source leads to a substantial increase in the amount of oxygen adsorbed and carried to the reduction step. As a result, more fuel can be partially oxidized to generate synthesis gas. To further examine this effect, we compare the total non-stoichiometric variations (Figure 7-15) as well as the redox rates (Figure 7-16) with and
without the supplemental O₂ step. As seen in Figure 7-15, a close match is found among the H₂ and H₂O production for the case without the supplemental O₂, demonstrating a precise oxygen balance during the periodic cycling. The non-stoichiometric changes (without O₂) are found to be very close to, although slightly higher than, that of the H₂ production from the base case (with O₂). The difference is attributed to the less produced H₂O, which results in a lower effective pO₂ (thus more reducing environment), and hence a larger non-stoichiometry that can be achieved during the reduction step for the case without the supplemental O₂, as evident in Figure 7-16(b).

The model predictions for the case without O₂ oxidation are also included in Figure 7-16, and a perfect match is found with the measurements. The exact same equilibrium and kinetic parameters from the main context are used for the prediction, and the oxygen non-stoichiometry after oxidation in the base case is used as the initial condition for the fitting. Similar agreement is obtained for other temperatures as well (not shown).

Figure 7-16 Comparison of (a) reduction rates and (d) oxidation rates (with H₂O) at 900°C, with and without the supplemental O₂ oxidation. Lines are model prediction.
7.9 Appendix: Sensitivity study on redox kinetics

Sensitivity analysis is performed to quantify the effect of the forward and the backward reactions of the two-step mechanism on the \(\text{H}_2\text{O}\) splitting process. The sensitivity \(\left( S_{x \to y} \right)\) of an output \((y)\) to an input \((x)\) is defined as:

\[
S_{x \to y} = \frac{\partial \ln y}{\partial \ln x} \approx \frac{x \Delta y}{y \Delta x}
\]  

(7.26)

The sensitivities of the total \(\text{H}_2\) production and the peak production rate are calculated and shown in Figure 7-17, with temperature at 900\(^\circ\text{C}\) and 600\(^\circ\text{C}\) for comparison. Input parameters, the pre-exponential rate constant \((k_{1,f}^0, k_{1,b}^0, k_{2,f}^0, k_{2,b}^0)\), are varied between \(-10\%\) and \(+10\%\) from its base value. To deconvolute the kinetics effect from the equilibrium constraint, two more tests are also included, in which the rate constants are varied without changing the equilibrium. This is achieved by varying the \(k_{i,f}\) and \(k_{i,b}\) \((i = 1, 2)\) simultaneously while fixing the ratio, i.e., \(K_i = k_{i,f}/k_{i,b}\).

As shown in panel (a), the sensitivity of the total \(\text{H}_2\) production on \(k_{1,f}^0\) and \(k_{1,b}^0\) is the same in the magnitude, and opposite in sign, suggesting a thermodynamic limitation of R1. A higher \(k_{1,f}^0\) (or equivalently a lower \(k_{1,b}^0\)) shifts the equilibrium of R1 to the right, leading to the formation of more surface OH complex, which favors the charge-transfer step (R2). Raising \(k_{1,f}^0\) and \(k_{1,b}^0\) simultaneously without changing \(K_1\), on the other hand, negligibly affects the total \(\text{H}_2\) production. In comparison, the \(\text{H}_2\text{O}\) splitting process is more sensitivity to R2 forward, but only mildly affected by R2 backward. Raising \(k_{2,f}^0\) and \(k_{2,b}^0\) proportionally leads to significant improvement of the total \(\text{H}_2\) production, suggesting that the charge-transfer kinetics is the rate-limiting step.
Comparing 900°C and 600, the sensitivities at high temperature are generally lower, again confirming the observed transition of the controlling mechanism, from kinetics-limited at low temperature to equilibrium-constrained at high temperature.

Figure 7-17 Sensitivity of (a) total H₂ production and (b) peak rate on rate constants.
The dependence of the peak H\textsubscript{2} production rate generally follows a similar pattern, as shown in panel (b). One noticeable difference is that the sensitivity on $k'_{1,f}$ is stronger than that on $k'_{1,b}$. As a result, a higher $k'_{1,f}$ raises the peak rate, leading to a more rapid splitting process, although the total H\textsubscript{2} production remains unchanged (with $K_1$ fixed). This is in accordance with Figure 7-12, which show that the backward reaction lags slightly during the initial stage, and the forward reactions (R1 and R2) determines the peak reaction rate at 900°C.

7.10 Appendix: CH\textsubscript{4} Conversion Improvement with Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}

The endothermicity of the surface oxidation (eq. (7.10)) with stoichiometric CZO may suggest a potential improvement of the fuel conversion equilibrium for the CH\textsubscript{4} reforming reaction. The direct steam methane reforming (SMR) reaction is written as:

$$\text{SMR: } \text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2, \Delta H_{\text{SMR}} = 224 \text{kJ/mol, and } \Delta S_{\text{SMR}} = 251 \text{J/K mol} \quad (7.27)$$

where $\Delta H_{\text{SMR}}$ and $\Delta S_{\text{SMR}}$ are the enthalpy and entropy of reaction. The use of Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} as OC effectively splits the above reaction into:

**Oxidation:**

$$\text{H}_2\text{O} + V'_o(s) + 2\text{Ce}_e^+(s) = \text{H}_2 + O'_o(s) + 2\text{Ce}_e^+(s) \quad (7.28)$$

**Reduction:**

$$\text{CH}_4 + O'_o(s) + 2\text{Ce}_e^+(s) = \text{CO} + 2\text{H}_2 + V'_o(s) + 2\text{Ce}_e^+(s) \quad (7.29)$$

For a stoichiometric surface, the energetics of oxidation are $\Delta H_{\text{ox}} = 17.3 \text{kJ/mol}$ and $\Delta S_{\text{ox}} = -14.1 \text{J/K mol}$ (see Table 7-4). Thus, the energetics of reduction are calculated as: $\Delta H_{\text{red}} = \Delta H_{\text{SMR}} - \Delta H_{\text{ox}} = 206.7 \text{kJ/mol}$, and $\Delta S_{\text{red}} = \Delta S_{\text{SMR}} - \Delta S_{\text{ox}} = 265.1 \text{J/K mol}$. The equilibrium constant for the above three reactions are plotted as a function of temperature in Figure 7-18. As expected, the equilibrium constant for fuel reduction with CZO is over one order of magnitude higher than direct SMR. The reason for this enhancement is that the overall highly endothermic SMR
reaction is now split into two endothermic surface reactions: the enthalpy of fuel conversion reaction becomes smaller, and the entropy of reaction is increased. As a result, CL reforming is capable of achieving same fuel conversion at lower temperature. The improvement in the fuel conversion at lower temperature highlights the advantages of CLR/H₂O splitting as compared to the conventional SMR process. Similar conclusions can be drawn for the CO₂ splitting process.

![Equilibrium Constant vs Temperature](image)

Figure 7-18 Comparison of the equilibrium constant for methane reforming reaction (or reduction reaction). The equilibrium constant for H₂O splitting is also included.

The Law of Mass Action for SMR and reduction can be written as

\[ K_{SMR} = \frac{p_{CO}p_{H_2}^3}{p_{CH_4}p_{H_2O}} \]

\[ K_{red} = \frac{p_{CO}p_{H_2}^2 \left[ V_0 \right] \left[ Ce^{\prime}_{ce} \right]^2}{p_{CH_4} \left[ O_2 \right] \left[ Ce^{\prime\prime}_{ce} \right]} \]
Interestingly, given the low concentration for defects, \( [\nu_{o}^{**}] \ll [O_{o}^{\ast}] \) and \( [Ce_{Ce'}^{\ast}] \ll [Ce_{Ce'}^{\ast}] \), one may expect even higher \( CH_4 \) conversion by comparing the equilibrium relationship in the above equations.

7.11 Bibliography


[42] A. Pappacena, M. Boaro, L. Armelao, J. Llorca, A. Trovarelli, Water splitting reaction on Ce0.15Zr0.85O2 driven by surface heterogeneity, Catalysis Science & Technology, 6 (2016) 399-403.


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Chapter 8

CO₂ Splitting Using Non-Stoichiometric Ceria and Ceria-Zirconia: A Kinetics Study

CO₂ splitting via thermo-chemical or reactive chemical-looping approaches has emerged as a novel and promising carbon-neutral energy solution. Its performance depends critically on the properties of the oxygen carriers (OC). Ceria is recognized as one of the most promising OC candidates, because of its fast chemistry, high ionic diffusivity, and large oxygen storage capacity. The fundamental surface ion-incorporation pathways, along with role of surface defects and the adsorbates remain largely unknown. This chapter presents a detailed kinetics study of CO₂ splitting with CeO₂ and Ce₀.₅Zr₀.₅O₂ using time-resolved and systematic measurements in the temperature range 600-900°C. We observed evidently higher splitting kinetics compared to literature, resulting from the utilization of fine particles and well-controlled experiments which ensure a surface-limited-process. The peak rates with CZO are 85.9 μmole g⁻¹s⁻¹ at 900°C and 61.2 μmole g⁻¹s⁻¹ at 700°C, and those of CeO₂ are 70.6 μmole g⁻¹s⁻¹ and 28.9 μmole g⁻¹s⁻¹. Kinetics models are developed to describe the ion incorporation dynamics, with the consideration of the CO₂ activation and the charge transfer reactions. The CO₂ activation energy is found to be – 120 kJ mole⁻¹ for CZO, half of that with CeO₂, while the CO desorption energetics is analogous among the two samples with the value of ~160 kJ mole⁻¹. The charge-
transfer process is found to be the rate-limiting step for CO₂ splitting. Using the derived kinetics, the evolution of CO₃²⁻ with surface Ce³⁺ is examined. We show that the concentration of CO₃²⁻ varies with Ce³⁺ in a linear-flat-decay pattern, resulting from mismatch of the kinetic rates of the two reactions. The kinetics study here provides new insights in the significant role of the surface defects and adsorbents in determining the splitting kinetics.

8.1 Introduction

CO₂ emission from fossil fuel combustion is a major contributor to global warming. One of the currently proposed approaches to reduce anthropogenic CO₂ emissions is carbon capture and sequestration (CCS), in which CO₂ is separated from flue gases, liquefied, and injected in geological formations. Significant challenges remain with CCS, mostly in the process economics, safety, and long-term stability. Developing alternative approaches, such as CO₂ splitting technologies, is thus motivated by energy needs and environmental concerns. Among various options, thermo-chemical CO₂ splitting has attracted significant interests, inspired by thermo-chemical H₂O splitting [1-3]. Using of oxygen-deficient metal oxide (commonly referred to as oxygen carrier, OC), CO₂ is catalytically dissociated into CO according to:

\[ \text{Oxidation:} \quad \text{CO}_2(g) + \text{V}_0^- + 2e' \rightleftharpoons \text{CO}(g) + \text{O}_0^\cdot \] (8.1)

where \( \text{V}_0^- \) denotes surface oxygen vacancy and \( \text{O}_0^\cdot \) is an oxygen ion on a normal site. The surface defect acts as oxygen sink, enabling CO₂ dissociation at low temperature (<1000°C, in contrast to the direct thermolysis reaction). Oxidation is then followed by a reduction step, where the defects are regenerated from the healed surface according to one of the following reactions:

\[ \text{Thermal reduction:} \quad \text{O}_0^\cdot \rightleftharpoons \frac{1}{2} \text{O}_2(g) + \text{V}_0^- + 2e' \] (8.2)
Fuel reduction: \[ \text{O}_2^- + \text{CH}_4 (g) \rightleftharpoons \text{CO(g)} + 2\text{H}_2 (g) + \text{V}_0^- + 2e^- \] (8.3)

Here the oxygen removal step is achieved by either heating the metal oxides using e.g., concentrated solar irradiation, eq. (8.2) \textit{thermo-chemical CO}_2 \textit{splitting}, or reducing the OC with fuel, eq. (8.3) \textit{reactive chemical-looping CO}_2 \textit{splitting}. The net reaction combining the reduction and oxidation (redox) steps becomes CO_2 \textit{thermolysis}, i.e., \text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2, or the dry reforming reaction, i.e., \text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2, respectively. The OC remains intact as it catalyzes and facilitates the dissociation of CO_2 through this two-step process. The transfer of oxygen between the redox steps exploits the oxygen non-stoichiometric capacity of the metal oxide by mediating the oxygen fugacity in the reactive environment, by either heating or a fuel, which drives the two-way ionic exchange between the gas and the solid. Promising results have been demonstrated on the efficient production of CO/syn-gas [2, 4-6], which are the key precursors to the synthesis of liquid fuel and commodity chemicals.

Among various OC options for CO_2 splitting, ceria has emerged as one of the most promising candidate, owing to its fast surface chemistry and high ionic conductivity [2, 7, 8]. The large non-stoichiometric capacity achieved at elevated temperature allows it to effectively exchange oxygen while adjusting to the redox environment [9, 10]. A variety of experiments have demonstrated the feasibility of CO_2 splitting using ceria and ceria-based materials [2-4, 7, 11-19], and a brief comparison is shown in Table 1-5. Extensive efforts have been made lately to extend the redox properties of ceria towards lower temperature with improved system efficiency [15, 20, 21]. The addition of undersized dopant, such as Zr^{4+}, induces structural distortion [22], leading to enhanced oxygen mobility [23] and lower defect formation energy [24] with improved long-term structural stability [25, 26]. A recent kinetics study [27] demonstrates that doping with 50mol%
Zr in ceria reduces reduction of the defect formation enthalpy by over 40%, resulting in dramatic improvement of the redox kinetics at 600 °C. These redox properties of ceria and ceria-zirconia have been widely exploited in the thermo-chemical water splitting studies [27, 28], as well as many other applications [7, 8, 20, 22, 28-31], including three-way catalyst, water-gas shift, solid oxide fuel cells, electrolyzers, methane reforming, etc.

CO oxidation on ceria has been extensively investigated over the past few decades, with focuses on oxygen storage capacity [23, 32], adsorbates [33, 34], and spillover pathways between ceria and supported metal catalysts [35, 36]. CO$_2$ reactivity, however, is not well understood, and it is usually treated as the “reverse” of the CO oxidation reaction [37]. There has been an increasing effort towards a better understanding of CO$_2$ activation and the catalytic role of the surface defects [38-42], owing to the rising interests in fuel cells, electrolyzers, and thermo-chemical CO$_2$ splitting. Advanced in-situ techniques, such as X-ray adsorption spectroscopy (XAS) [43], and X-ray photoemission spectroscopy (XPS) [44, 45], have been applied to probe the structural dynamics and the adsorbate-vacancy interactions under a CO$_2$/CO environment. Density functional studies examined the preferable sites and surface orientations for CO$_2$ activation and evaluated the importance of surface vacancies on the formation of chemisorbed carbonates, CO$_3^{2-}$ [37, 40, 46-48]. Most recently, few studies have examined the redox kinetics following an equilibrium approach [49] or empirical models [14, 15, 17], and a general consensus has been reached regarding the critical role of the surface chemistry on CO$_2$ splitting [17]. Despite the efforts and promising proof-of-principles in lab-scale prototypes, investigation on the fundamental surface redox pathways requires more attention [7, 35]. The details involved in the interactions of mobile ions, and electrons between the bulk and the surface, along with the
gaseous reactants, adsorbates and electrostatic fields are complex; a thorough understanding of these mechanisms is technologically important for the design and optimization of the CO₂ splitting process.

In this work, we investigate the CO₂ splitting mechanism on CeO₂ and Ce₀.₅Zr₀.₅O₂ (CZO) over a wide range of operating conditions, with an emphasis on the surface ion-incorporation kinetics pathway. Isothermal redox cycles of CeO₂ and CZO nano-powder are carried out in a button cell reactor in the temperature range 600-900°C. H₂ is used as a surrogate fuel in the reduction step to construct the oxygen non-stoichiometry. Kinetics and the oxygen-ion incorporation pathway for CO₂ splitting are probed on the basis of the previously derived defect equilibria and mechanism framework from H₂O splitting studies [27, 28]. The mechanism consists of a series of intermediate steps: adsorption/dissociation of gaseous reactant, charge transfer on the surface, and the bulk-to-surface transport. Based on the kinetics models, rate-limiting steps are identified, and insights are gained on the role of surface defects and interactions with adsorbates.

8.2 Experimental Setup and Theoretical Methods

8.2.1 Sample characterization

Ceria and ceria-zirconia nanopowder similarly as in Chapter 6 and Chapter 7 are used here for CO₂ splitting study. Table 8-1 again summarizes the properties of the sample. Figure 8-1 compares the SEM images of fresh and redox cycled samples. The fresh samples of CeO₂ and CZO contain very fine particles with a size less than 50nm. The CeO₂ particle is slightly coarser with lower specific surface area (Table 8-1), and the particles clump together into a mushroom like structure with dimension of ~ 200 nm. After redox treatment, the boundaries within the
clumped grain disappear: the particles sinter into larger grains forming an inter-connected structure with decreased surface area. Compared to CeO$_2$, the structural change and the size enlargement for CZO are less significant, resulting from the enhanced structural stability with the addition of Zr. Interestingly, the variations in the measured kinetics of CeO$_2$ and CZO are rather small except a few initial (<5) cycles, indicating that morphological relaxation most likely results from the sintering effect during the heating and initial redox cycling. Samples after additional 20 redox cycles are also examined, and the same micro-structure and redox rates are obtained, indicating that a periodic and reversible stationary equilibrium is established. Similar morphological evolutions were reported previously with H$_2$O splitting studies [27, 28]. The material was confirmed to remain in single phase by XRD analysis (Cu Ka, 45 kV and 40 mA, PANalytical X'Pert Pro Multipurpose Diffractometer, Almelo, The Netherlands) performed at room temperature in air. No change is found in the XRD patterns between the fresh and tested samples.

Table 8-1 Some physical properties of the CeO$_2$ and Ce$_{0.5}$Zr$_{0.5}$O$_2$

<table>
<thead>
<tr>
<th>Property</th>
<th>CeO$_2$</th>
<th>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample mass, $m$</td>
<td>100 mg</td>
<td>50 mg</td>
</tr>
<tr>
<td>Density, $\rho$</td>
<td>7.22 g cm$^{-3}$</td>
<td>6.62 g cm$^{-3}$</td>
</tr>
<tr>
<td>Molar density, $\rho_{\text{Ce}}$</td>
<td>4.19 x10$^4$ mol m$^{-3}$</td>
<td>4.50 x10$^4$ mol m$^{-3}$</td>
</tr>
<tr>
<td>Molar weight, MW</td>
<td>172.11 g mol$^{-1}$</td>
<td>147.66 g mol$^{-1}$</td>
</tr>
<tr>
<td>Surface molar density, $\rho_{\text{Ce,s}} = \rho_{\text{Ce}} a$</td>
<td>2.27 x10$^{-5}$ mol m$^{-2}$</td>
<td>2.4 x10$^{-5}$ mol m$^{-2}$</td>
</tr>
<tr>
<td>fresh sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purity</td>
<td>99.95%</td>
<td>99.0%</td>
</tr>
<tr>
<td>Spec. surface area, $s_0$</td>
<td>15.4 m$^2$ g$^{-1}$</td>
<td>38.74 m$^2$ g$^{-1}$</td>
</tr>
<tr>
<td>Adsorption average pore width</td>
<td>11.2 nm</td>
<td>7.7 nm</td>
</tr>
<tr>
<td>Particle size</td>
<td>~ 50nm</td>
<td>~ 24 nm</td>
</tr>
<tr>
<td>cycled sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spec. surface area, $s_1$</td>
<td>4.07 m$^2$ g$^{-1}$</td>
<td>22.96 m$^2$ g$^{-1}$</td>
</tr>
<tr>
<td>Adsorption average pore width</td>
<td>8.6 nm</td>
<td>6.7 nm</td>
</tr>
<tr>
<td>Particle size</td>
<td>~ 200nm</td>
<td>~ 40nm</td>
</tr>
</tbody>
</table>
8.2.2 Redox kinetics measurement

During the kinetics study, a minute amount of CeO$_2$ (100 mg) or CZO (50 mg) powder is embedded in quartz wool and placed at the bottom of the outer quartz tube. The sample undergoes redox cycles with argon used as a purging gas flowing in between. The total flow rate into the reactor is fixed at 350 scm, corresponding to a gas residence time of less 300 ms through the dispersed sample. Oxidation is performed using a gas mixture of carbon dioxide (14.3 mol%) and argon. H$_2$ is used as the reducing gas instead of CH$_4$ or CO to rule out coke formation and its subsequent contribution towards H$_2$ generation through steam-carbon reaction. The total flow for
reduction is maintained constant at 350 sccm with the H\textsubscript{2} mole fraction of 14.3 mol\% (Ar balance). The oxidation and reduction times are fixed at 2 min each with 5 min Ar purging in between. A supplemental 2 min oxidation with 0.5\% O\textsubscript{2} (Ar balance) is used after the CO\textsubscript{2} splitting step to ensure a complete regeneration of stoichiometry. Both samples are pre-treated at 1000°C to reach periodic stationary states. Afterwards, the measurements are taken from 900°C till 600°C with a step of 100°C. Each operating condition is repeated for at least three times, and results are averaged to reduce the noise. The measurements for CeO\textsubscript{2} at 1000°C and those for CZO at 500°C are also taken for comparison with H\textsubscript{2}O splitting studies [27, 28]. The flue stream composition is analyzed in real-time using the QMS. The instantaneous reaction rates can be obtained as:

\[
\text{CO}_2 \text{ splitting: } \omega = \frac{X_{\text{CO}_2, \text{out}} \dot{\dot{n}}_{\text{ox, out}}}{m} = \frac{X_{\text{CO}_2, \text{out}} P^0 \dot{V}^0}{m RT^0} \tag{8.4}
\]

\(X_{\text{CO}_2, \text{out}}\) is the measured mole fractions of the produced CO in the exit. \(\dot{n}_{\text{ox, in}}\) is the total molar inflow rates of the gas mixture. \(P^0\), \(T^0\), and \(V^0\) are the pressure, temperature, and the total volumetric inflow rate at standard temperature and pressure (STP). The reaction rates (unit, \(\mu\)mole g\textsuperscript{-1}s\textsuperscript{-1}) are normalized by the total ceria sample \(m\), i.e., 100mg for CeO\textsubscript{2}, and 50mg for CZO, used in the measurement.

8.2.3 Non-stoichiometric defect equilibrium

Here we briefly describe the non-stoichiometric defect chemistry in the bulk phase and at the surface, following a similar approach as detailed in previous chapters. The defect formation reaction and the equilibrium mass-action relation may be written as:

\[
\text{O}_0^* + 2\text{Ce}_{\text{Ce}}^* \xrightleftharpoons[K_1]{\kappa} V_0^* + 2\text{Ce}_{\text{Ce}}^* + \frac{1}{2} \text{O}_2 (g) \tag{8.5}
\]
Here the major defects are the doubly-charged oxygen vacancy, $V_0^{**}$, and the localized electrons, $Ce'_Ce$, (small polarons) [8, 38]. $K_b$, $H_b$, and $S_b$ are the equilibrium constant, enthalpy and entropy of the defect formation reaction. The brackets denote the mole of species per mole of $CeO_2$ or $Ce_0.5Zr0.5O_2$. By definition, $[V_0^{**}] = \delta$, as in $CeO_2-\delta$ or $Ce_0.5Zr0.5O_2-\delta$. Variations of $K_b$ with large change of $\delta$ are expected, resulting from the chemical expansion of the crystalline lattice [50, 51] as well as the defect interactions and ordering [10], leading to deviations from the ideal behavior. This effect was reported to be significant for the CZO system [52-54], which is described following a linear expression [27, 50, 52]:

$$H_b(\delta) = H^0_b(\delta = 0) + f\delta$$  \hspace{1cm} (8.7)$$

where $H^0_b$ is the defect formation enthalpy for the fully oxidized CZO, and $f$ is the $\delta$-linear coefficient.

The transport process between the bulk and the surface enables the participation of bulk oxygen in the surface reaction. The bulk phase acts as the oxygen sink in the $CO_2$ splitting process or the oxygen source in the reduction step. The two-way oxygen exchange is generally governed by the defect diffusion process, described by the Nernst-Planck equation:

$$\frac{\partial C_i}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 J_i \right) = 0 \quad i = V_0^{**}, Ce'_Ce$$ \hspace{1cm} (8.8)$$

$$J_i = -\frac{C_i D_i}{RT} \frac{\partial \tilde{\mu}_i}{\partial r}, \text{ where } \tilde{\mu}_i = \mu^0_i + RT \ln \frac{C_i}{C_{ref}} + z_i e \phi$$ \hspace{1cm} (8.9)$$
where \( C_i, J_i, \mu_i, D_i \) are the defect concentration, diffusion flux, electro-chemical potential, self-diffusion coefficient. \( \mu_i^0, \gamma_i, z_i \) are the chemical potential at reference conditions, activity coefficient, and effective charge. \( \phi, T, F \) are the electrostatic potential, temperature, and Faraday constant. The fine nano-powder used in the kinetics study along with the fast electronic and ionic conductivities of ceria-based OCs allows for a homogeneous distribution of defect concentration within the bulk-phase of each nano-particle. The characteristic time \( (\tau) \) for diffusion from the expression \( \tau \sim l^2/4D \) was estimated to be \(< 200 \) ms for CeO\(_2\) [28] and \(< 1 \) ms for CZO [27], significantly faster than the surface chemistry. However, the defects are more stable on the surface as compared to the bulk phase (see Figure 8-2c), owing to the lower defect formation free energy [28, 38, 55]. The defect transport equilibrium between the surface and the bulk is described as [28, 56]:

\[
V_o^\prime (b) - O_o^\prime (b) + 2Ce_c^\prime (b) \rightarrow 2Ce_c^\prime (s) + 2Ce_c^\prime (s) - O_o^\prime (s) + 2Ce_c^\prime (s) \quad (8.10)
\]

\[
K_T = \frac{[V_o^\prime]_s [Ce_c^\prime]_s^2}{[O_o^\prime]_s [Ce_c^\prime]_s^2} \frac{[V_o^\prime]_b [Ce_c^\prime]_b^2}{[O_o^\prime]_b [Ce_c^\prime]_b^2} \quad (8.11)
\]

The transport equilibrium constant, \( K_T \), is expressed as, \( K_T = \exp(-\Delta \mu_T / RT) \), where

\[
\Delta \mu_T = \Delta H_T^0 - T \Delta S_T^0 = \left( \mu_{V_o}^0 + 2\mu_{Ce_c}^0 \right)_s - \left( \mu_{V_o}^0 + 2\mu_{Ce_c}^0 \right)_b \quad (8.12)
\]

Here \( \Delta H_T^0 \) and \( \Delta S_T^0 \) denote the difference of the defect formation enthalpy and entropy, respectively, between the surface and the bulk phase. A detailed derivation can be found in previous chapters. The transport and defect equilibrium constant for CeO\(_2\) and CZO are listed in Table 6-3 and Table 7-4.
Figure 8-2 (a) Schematics of the CO₂ splitting pathway. The ion-incorporation surface process comprises the adsorption and activation of CO₂ forming carbonates, CO₃²⁻ (R1); charge transfer, association and desorption of CO (R2). The heterogeneous chemistry is linked to bulk phase via the bulk-to-surface transport of the electron defect, e, and the oxygen vacancy defect, V₀⁻. (b) Side view of CO₃²⁻ on the O-bridge site of the (110) surface. (c) Schematics of the surface enrichment of Ce³⁺ relative to bulk.

8.2.4 CO₂ Surface chemistry

The CO₂ splitting reaction on the surface is modeled using a two-step mechanism (Figure 8-2) [46, 47, 57-60], with the corresponding mass action rate expressions as:

\[
\text{R1: } \text{CO}_2 (g) + V_0^- (s) + O_o (s) \xrightarrow{\frac{k_{f}}{k_{b}}} (\text{CO}_3)_o^- (s)
\]  

(8.13)
\[ r_i = k_{i,f} P_{CO_2} \left[ V_{O}^{\cdot} \right] \left[ O_2^+ \right] - k_{i,b} \left[ (CO_3)_O^{2-} \right] \]  

\text{(8.14)}

\[ R2: \quad (CO_3)_O^{2-} (s) + 2Ce_{Ce}^{\cdot} (s) \stackrel{k_{i,b}}{\longrightarrow} CO (g) + 2Ce_{Ce}^{\cdot} (s) + 2O_2^+ (s) \]  

\text{(8.15)}

\[ r_2 = k_{2,f} \left[ (CO_3)_O^{2-} \right] \left[ Ce_{Ce}^{\cdot} \right]^2 - k_{2,b} P_{CO} \left[ O_2^+ \right] \left[ Ce_{Ce}^{\cdot} \right]^2 \]  

\text{(8.16)}

\((CO_3)_O^{2-}\) (or equivalently \(CO_3^{2-}\)) is a surface carbonate group formed near the vacancy. \(k_{i,f}, k_{i,b}\), denotes the rate coefficients (unit, \(s^{-1}\)), following the Arrhenius expression, \(k = k_0 \exp(-E/RT)\).

The surface reactions are assumed to occur only within the first unit cell layer on the surface, and \(s\) in the parenthesis emphasizes this assumption. \(R1\) describes the chemisorption and activation process of \(CO_2\), which is then followed by the charge transfer and desorption step (\(R2\)). \(R1\) is energetically favored on the oxygen-deficient surface [40, 57], while \(R2\) is an endothermic process, hence most likely limiting the overall \(CO_2\) splitting process [44]. This has also been shown for \(H_2O\) splitting, both experimentally [28, 61] and computationally [28, 40, 62, 63].

It is generally agreed that the adsorption and activation of \(CO_2/CO\) over ceria favors the more active surfaces, e.g., (110), (100), etc., as opposed to (111) for \(H_2O\) splitting [40]. Density functional studies [46, 47, 57] identified the O-bridge on (110) surface near the vacancy (see Figure 8-2b) as one of the most preferred sites for the \(CO_2/CO\) activation process: upon adsorption, a carbonate \(CO_3^{2-}\) is formed, likely bent and tilted, with two electrons localized in the nearest neighbor (or next nearest neighbor) cation sites and the two surface O ions slightly pulled away from the surface. The exact shape of the adsorbate and the elementary pathway leading to its formation, however, still remain a matter of debate. Other chemisorbates, such as \(CO_2, CO_2^-,\) etc., are also possible [40], and their formation depends on the types of vacancies [37], surface orientation [57, 58], sites and dopant [47, 64], coverage [44, 48], and the sequence of the charge
transfer [37, 44], etc. The addition of Zr$^{4+}$ does not alter the electronic structure, thus maintaining an analogous splitting pathway as with CeO$_2$; however, subtle differences exist on the electron localization patterns resulting from fewer available Ce$^{4+}$ in CZO [47]. Identifying the detailed elementary steps and precisely quantifying contribution from each factor are beyond the scope of this study. Here we model the CO$_2$ splitting kinetics following the two-step mechanism (eqs. (8.13) – (8.16)) via the formation of the surface carbonate intermediate, as commonly suggested in the literature.

At equilibrium, $r_1$ and $r_2$ are zero. This leads to the definition of the corresponding equilibrium constants $K_1$ and $K_2$. Combining R1 and R2 gives the overall surface equilibrium as:

$$V_0^\cdot (s) + 2\text{Ce}_{\text{ce}}^\cdot (s) + \text{CO}_2 (g) \xrightleftharpoons{K_s} \text{O}_0^\cdot (s) + 2\text{Ce}_{\text{ce}}^\cdot (s) + \text{CO} (g)$$  (8.17)

which is related to the bulk-phase equilibrium, eq. (7.1), and the transport equilibrium, eq. (8.10), via $K_s = (K_b K_{\text{CO}_2} K_T)^{-1}$. Here, $K_{\text{CO}_2}$ is the equilibrium constant of CO$_2$ formation reaction, CO(g) + ½ O$_2$(g) = CO$_2$(g), from which the equilibrium oxygen fugacity in the CO$_2$/CO environment can be defined, as

$$p_{O_2} = p_{\text{CO}_2}^2 / \left( K_{\text{CO}_2} p_{\text{CO}} \right)^2$$  (8.18)

8.2.5 Simulation and Fitting Process

The overall governing equations for the evolutions of the surface adsorbate $(\text{CO}_3)_0^\cdot$ and the bulk-phase $V_0^\cdot$ are [28]:

$$\tilde{\rho}_s \frac{d[ (\text{CO}_3)_0^\cdot ]}{dt} = \tilde{\rho}_s (r_1 - r_2)$$  (8.19)
where $\rho_s$, $\rho$ are the surface and the bulk molar density of the unit cell. $V_R$, and $S_R$ are the volume and the surface area of the particle. The conservation equations for the surface are:

\[
\text{O-site:} \quad \left[ V_O^{\text{m}} \right]_s + 2 \left[ (\text{CO}_3)_O^{\text{m}} \right]_s + \left[ O_0^{\text{m}} \right]_s = 2 \tag{8.21}
\]

\[
\text{Ce-site:} \quad \left[ \text{Ce}_c^{\text{e}} \right]_s + \left[ \text{Ce}_c^{\text{e}} \right]_s = 1 \text{ (for CeO}_2\text{) or 0.5 (for CZO)} \tag{8.22}
\]

\[
\text{electro-neutrality} \quad 2 \left[ V_O^{\text{m}} \right]_s + 2 \left[ (\text{CO}_3)_O^{\text{m}} \right]_s = \left[ \text{Ce}_c^{\text{e}} \right]_s \tag{8.23}
\]

The surface electro-neutrality is assumed based on the conclusions from previous work on ceria [27, 28, 61] as well as other materials [65].

The governing equations are numerically integrated in MATLAB. The kinetic and equilibrium parameters to be obtained are $k_{1,b}$, $k_{2,b}$, $K_2$, with the other kinetic parameters obtained via equilibrium relations. The variation of $H_b$ with $\delta$ from eq. (8.7) for CZO is assumed to be associated with the oxygen removal step ($k_{1,b}$ for backward R1) [27]. Thus, $E_{1,b} = E_{1,b}^0 + f \delta$, where $f$ corresponds to eq. (8.7). With the time-resolved profiles of $[\text{CO}_2]$ using the QMS, the entire conversion process can be predicted based on a given set of kinetic parameters. The predicted CO production profile is then compared to the measurements, and the kinetics parameters are varied to minimize the difference:

\[
\text{Diff} = \sum_{all \, tests} \sqrt{\frac{1}{N} \sum_{\phi \in \Omega^*} (\Phi_{\text{model}} - \Phi_{\text{measure}})^2} \tag{8.24}
\]
Here the reaction rates (\(\hat{o}_{\text{model}}\) or \(\hat{o}_{\text{measure}}\)) are normalized by the maximum rate, and \(N\) is the number of measurement points in each test. The minimization is obtained numerically in MATLAB using fminsearch solver [66].

### 8.3 Results & Discussion

Figure 8-3 compares the CO\(_2\) splitting kinetics between CeO\(_2\) (solid lines) and CZO (dashed) at 900 °C. Panel (a) shows the measured CO\(_2\) and CO mole fraction in the gas phase. Panel (b) shows the evolution of the bulk defect, \([V_0^-]\) and \([\text{Ce'}_e]\), calculated by integrating eq. (8.4). Panel (c) shows the splitting kinetics. The CO\(_2\) splitting process for both samples follows a similar pattern: the reactivity spikes with the feed of CO\(_2\), and transits to a slow residual conversion, which eventually ceases near the end of oxidation. The fast conversion at the initial stage is accompanied by a rapid incorporation of O ions into the lattice, as seen in panel (b). As oxygen vacancy is gradually filled up, the splitting rate slows down quickly and eventually reaches zero. The maximum rate is thus a combined effect from the intake of gaseous reactant and the consumption of defects. The majority of the conversion is completed within 0.5 min, although the oxygen incorporation process continues towards the end.

Despite the significant difference in the stoichiometric composition and the particle geometry, similarities between CeO\(_2\) and CZO are found in the initial defect concentration and the splitting kinetics. The analogous oxygen vacancy concentration, determined in the preceding reduction step, is attributed to the oxygen carrying capacity and the utilization efficiency: on one hand, CeO\(_2\) possesses twice the available oxygen as compared to Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\), since only the CeO\(_2\) portion contributes to oxygen transfer; on the other hand, the addition of Zr\(^{4+}\) results in an 40%
reduction of the defect formation enthalpy, leading to an enhanced activation of lattice oxygen and hence a better utilization (~72%) of its carrying capacity as compared to CeO₂ (~35%).

Figure 8-3 CO₂ splitting during the oxidation step at 900°C for 100 mg CeO₂ (solid lines) and 50 mg CZO (dashed lines). (a) Species mole fraction of CO, CO₂; (b) evolution of the bulk defect fraction; (c) the CO₂ splitting rate. The initial defect concentration in panel (b) is taken from the previous reduction cycle.

Given the similarity in the initial oxygen deficiency in both samples but the difference in the surface area (Table 8-1), one may expect a much faster CO₂ splitting kinetics for CZO, as opposed to the overlapping rate kinetics observed during the initial stage in Figure 8-3(a). The similarity in the splitting kinetics originates from the much enhanced charge-transfer rate for CeO₂ at high temperature, resulting from the more pronounced defect segregation and hence
higher defect concentration at the surface. As shown in Figure 4, Ce$^{3+}$ concentration on the surface of CeO$_2$ is almost twice that of CZO, accounting for over 75% of all available Ce sites on the surface. The highly reduced surface thus leads to a much higher concentration of the activated carbonate in CeO$_2$ (see the modeling results in Figure 8-9), which facilitates the charge-transfer reaction (R2).

![Graph comparing CeO$_2$ and CZO polaron concentration over time](image)

Figure 8-4 Comparison of the polaron concentration in the bulk and on the surface for oxidation at 900°C. The surface polaron concentration is calculated from eq. (8.11), with the bulk concentration from Figure 8-3. The total Ce sites for CeO$_2$ and CZO are also included for reference. The calculation here assumes [CO$_3^{2-}$] = 0 on the surface.

Following the rapid initial stage, CeO$_2$ oxidation continues and the CO$_2$ splitting kinetics slows down gradually. A complete regeneration of stoichiometry is established at the end of oxidation. This is in contrast to CZO, where the rate decays more rapidly, and the conversion ceases around $\delta = 0.05$, where equilibrium is established between oxygen non-stoichiometry and the CO$_2$/CO environment [27].
Figure 8-5 Comparison of the temperature dependence for CO₂ splitting rate (top) and the oxygen vacancy (bottom) between (a, b) CeO₂ and (c, d) Ce₀.₅Zr₀.₅O₂. 14.3 mol% CO₂ at 350 sccm is used for oxidation. Reduction occurs at 14.3 mol% H₂ for 2 min at the temperature in accordance with the oxidation step. The data at 1000°C for CeO₂ and 500°C for CZO are also included. The maximum oxygen vacancy is 0.5 for CeO₂ and 0.25 for Ce₀.₅Zr₀.₅O₂.

Figure 8-5 compares the profiles of CO₂ splitting rates as a function of temperature between CeO₂ and CZO. Both exhibit strong temperature dependence with the rate profile becoming taller and wider at higher temperature, indicating a large activation barrier associated with the splitting process. The peak rate varies nonlinearly with temperature: a large jump takes place as temperature is raised over 700°C for CeO₂ and 600°C for CZO, but minor improvement is observed at higher temperature. The non-linearity is in good accordance with the variation of the initial defect concentrations at the surface, as seen in panels (b) and (d), which rises and flattens.
at high temperature. Comparing to the bulk phase, the vacancy on the surface is significantly higher, and the surface enrichment effect is more pronounced in the case of CeO$_2$.

![Graph of peak CO$_2$/H$_2$O splitting rate vs. temperature](image)

**Figure 8-6** Comparison of (a) peak splitting rates and (b) total CO production. H$_2$O splitting results are adopted from refs. [27, 28]. Note the H$_2$O splitting rates in panel (a) are converted from 26mol% H$_2$O to 14.3mol% H$_2$O using a linear dependence, as confirmed in ref. [28]. Error for the peak rate is based on the s.d. of triplicate peak measurements. Error for total CO production is estimated by multiplying the averaged s.d. of CO measurement by the total oxidation time, which gives an upper bound.

The peak rates and the total CO production are compared in Figure 8-6. Comparable CO$_2$ splitting rates are observed at higher temperature, while more evident improvement is found for CZO at low temperature with twice as fast kinetics at 700°C, resulting from the enhanced
reducibility with Zr and the finer particle structures maintained throughout the redox cycling. The peak rates with CZO are 85.9 μmole g⁻¹s⁻¹ at 900°C and 61.2 μmole g⁻¹s⁻¹ at 700°C, and those of CeO₂ are 70.6 μmole g⁻¹s⁻¹ and 28.9 μmole g⁻¹s⁻¹, respectively. Panel (a) also includes the peak rates from the H₂O splitting experiments [27, 28]. At high temperature, the rate of H₂O splitting is higher for both cases, while an opposite trend is observed at low temperature with CZO where the CO₂ and H₂O splitting curves cross around 700~800°C. Compared to H₂O splitting, the CO₂ curve for CZO exhibits weaker temperature dependence, suggesting a lower activation barrier.

Panel (b) compares the overall CO and H₂ yield during the 2 min oxidation step. H₂O and CO₂ splitting yields match closely for CeO₂: both oxidation processes completely restore the oxygen stoichiometry; therefore the total evolved H₂ or CO is determined by the non-stoichiometry created during the reduction steps, as shown in Figure 8-5(b). On the other hand, discrepancy is observed for CZO, where H₂O oxidation prevails at high temperature with the opposite at low temperature. Previous study [27] attributed insufficient OC regeneration of CZO to the combined effects of equilibrium constraints and slow charge-transfer kinetics, with the former more dominating at high temperature and the latter at low temperature. Given the fact that CO₂/CO environment has a higher equilibrium $p_{O₂}$ (eq. (8.18)) above 800°C as compared to H₂O/H₂, which becomes lower $p_{O₂}$ at lower temperature (i.e., $K_{CO₂}(900°C) = 1.1×10^8 < K_{H₂O}(900°C) = 1.43×10^8$, $K_{CO₂}(700°C) = 4.2×10^{10} > K_{H₂O}(900°C) = 2.7×10^{10}$), one may expect an opposite trend to what is shown in Figure 8-6(b). The reason is again due to the weaker barrier in CO₂ splitting, as will be shown in Figure 8-8 and Figure 8-10, where the splitting rate becomes faster with CO₂ at low temperature. Compared to CZO, the splitting yield of H₂ or CO with CeO₂ is generally
less over most of the temperature range, with an exception at 900°C, where the CO yield with CZO is lower, as is also evident from Figure 8-3(c). The total CO yield for CeO$_2$ is 1014 µmole g$^{-1}$s$^{-1}$ at 900°C, and 186 µmole g$^{-1}$s$^{-1}$ at 700°C, corresponding to Δδ of 0.175 and 0.03, respectively, while that for CZO is 827 µmole g$^{-1}$s$^{-1}$ (Δδ = 0.12), and 555 µmole g$^{-1}$s$^{-1}$ (Δδ = 0.082), at 900°C and 700°C, respectively. Comparing the measured peak CO$_2$ splitting rate and the CO yield with the previous studies (Table 1-5), we find that the total evolved CO are within the range of reported values, while the peak rates are faster, resulting from the utilization of fine particles and well-controlled experiments which ensure a surface-limited-process.

Model predictions for CO$_2$ splitting rates at various temperatures are shown in Figure 8-7 for CeO$_2$ and Ce$_{0.5}$Zr$_{0.5}$O$_2$. A good match is found between model predictions and measurements for all the cases. The models precisely capture the spike-decay behaviors of oxidation, and the non-linear temperature dependence. The kinetic parameters derived in this study for CeO$_2$ and Ce$_{0.5}$Zr$_{0.5}$O$_2$ are summarized in Table 6-2.

Figure 8-8 shows the calculated energy landscape for the surface chemistry pathways. R1 is exothermic and barrierless, and R2 is endothermic with large activation barriers, indicating that the charge-transfer step (R2) is the rate-limiting step [28, 44]. The deep valley connecting the two reaction steps suggests an inverse dependence of CO$_2^-$ concentration on temperature. The CO$_2$ adsorption/activation energy is found to be $-120$ kJ mole$^{-1}$ for CZO, half of that with CeO$_2$, in accordance with the reduced defect formation energy. The following CO desorption energetics, on the other hand, is analogous among the two samples with the value of $\sim160$ kJ mole$^{-1}$, although the activation barrier for CZO is noticeably smaller.
Figure 8-7 CO₂ splitting rate for (a) CeO₂ and (b) Ce₀.₅Zr₀.₅O₂ as a function of temperature. Solid lines represent the defect model. The data sets have been separated to clearly show the comparison.

Table 8-2 Fitted kinetic parameters for both the forward and backward reactions.

<table>
<thead>
<tr>
<th></th>
<th>CeO₂ (CO₂)</th>
<th>CZO (CO₂)</th>
<th>CeO₂ (H₂O) [28]</th>
<th>CZO (H₂O) [27]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Adsorption (R1)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k₁₁ (1/s)</td>
<td>1.3×10²</td>
<td>6.4</td>
<td>1.3×10⁴</td>
<td>12</td>
</tr>
<tr>
<td>E₁₁ (kJ/mol)</td>
<td>12±10</td>
<td>0±4</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>k₁₂ (1/s)</td>
<td>9.4×10¹⁴</td>
<td>8.4×10¹¹</td>
<td>8.2×10¹⁴</td>
<td>5.0×10¹¹</td>
</tr>
<tr>
<td>E₁₂ (kJ/mol)</td>
<td>251.1±30</td>
<td>120±40</td>
<td>210</td>
<td>92</td>
</tr>
<tr>
<td><strong>Charge transfer (R2)</strong></td>
<td>(CO₃)⁺ + 2Ce⁺ + 2H⁺</td>
<td>(CO₂)⁻ + 2Ce⁺ + 2H₂O⁻</td>
<td>2OH⁻ + 2Ce⁺ + 2O⁺ + 2H₂O⁻ + H₂</td>
<td></td>
</tr>
<tr>
<td>k₂₁ (1/s)</td>
<td>1.4×10¹³</td>
<td>1.4×10¹³</td>
<td>1.5×10¹⁴</td>
<td>7.1×10¹⁴</td>
</tr>
<tr>
<td>E₂₁ (kJ/mol)</td>
<td>299±40</td>
<td>175±45</td>
<td>190</td>
<td>186</td>
</tr>
<tr>
<td>k₂₂ (1/s)</td>
<td>98</td>
<td>16</td>
<td>4.4×10⁴</td>
<td>1.0×10⁵</td>
</tr>
<tr>
<td>E₂₂ (kJ/mol)</td>
<td>49±4</td>
<td>5±5</td>
<td>97</td>
<td>82</td>
</tr>
</tbody>
</table>

Note: Error corresponds to 5% increment of the fitting residual.
Figure 8-8 Energy landscape for the surface reaction pathways for CeO$_2$ (black) and CZO (red, at stoichiometry). The pathways for H$_2$O splitting are also included (gray and light red) for comparison. Unit is kJ mole$^{-1}$. The increase of defect formation enthalpy with non-stoichiometry for CZO, expressed in eq. (8.7), is also included.

Similar energetics were reported previously based on density functional theory (DFT). Huang and Fabris [46] investigated CO adsorption, (i.e., R2 backward), on an O-bridge site over a stoichiometric ceria (110) surface, and reported −212 kJ mole$^{-1}$ for the adsorption energy, which matches the experimental enthalpy of CO adsorption (−219 kJ mole$^{-1}$) measured by microcalorimetry at 300°C [67]. Similar values were also reported by Yang et al. [57] (−189 kJ mole$^{-1}$), Herschend et al. [68] (−205 kJ mole$^{-1}$) and Nolan et al. [69] (−188 kJ mole$^{-1}$). The current study of CO$_2$ splitting with CeO$_2$ reports a slightly lower CO desorption energy (−160 kJ mole$^{-1}$), likely resulting from a modified structure or energy level of the adsorbed species in the "reverse" (CO$_2$ oxidation) process, as argued by Cheng et al. [37]. Their DFT calculations obtained a CO desorption enthalpy of 182 kJ mole$^{-1}$, although the overall splitting process was found to be endothermic because of the lower predicted O-defect formation enthalpy. Yang et al.
[47] examined the CO₂ desorption process (i.e., R1 backward) following CO adsorption step using CeO₂ or Ce₀.₇₅Zr₀.₂₅O₂ as the OC, and identified a desorption enthalpy of 245 kJ mole⁻¹, and 162 kJ mole⁻¹, respectively. These values are in good agreement with those derived in this study. The formation of CO₃²⁻ via CO adsorption was also found to be slightly more favored with CZO, as observed in Figure 8-8, which was believed to originate from the more separated excess electrons and hence weaker coulomb repulsion [47]. Nevertheless, the effect is considered to be minor: ~40 kJ mole⁻¹ from ref. [47], and ~ 10 kJ mole⁻¹ in this study. The addition of Zr was also found to reduce the CO adsorption barrier [64], in line with the our observation.

The landscape for H₂O splitting is also included for comparison. The energetics of these two processes are generally similar, and subtle differences are on the formation of surface adsorbates as well as the charge-transfer step. This similarity can be further examined by comparing the pre-exponential factors, as listed in Table 8-2. For each material, \( k_{1,f} \) and \( k_{1,b} \) are almost identical between the H₂O and CO₂ splitting cases, suggesting that the adsorption (R1 forward) or the defect formation (R1 backward) process is highly structure-oriented, and the attempt frequency is mostly controlled by the surface defects, less sensitive to the specific molecular structure of the gaseous oxidizer. R1 differs starkly between CeO₂ and CZO, as the more compact crystal structure with stronger bonding energy leads to larger defect formation barrier at higher vibrational frequency for R1 backward reaction [27]. The higher \( k_{1,f} \) for CeO₂ may be related to the higher defect concentrations (see Figure 8-4) and more favorable adsorption sites. \( k_{1,b} \)'s are within the range of vibrational frequencies reported for oxides [62, 70, 71].
On the other hand, the charge-transfer process (R2) is highly analogous between CeO$_2$ and CZO with the same oxidizer. This is expected, given the fact that the charge-transfer step mostly depends on the evolution of the surface adsorbates and the interactions with the lattice oxygen, and less affected by the structural relaxation effect from Zr. $k_{2,f}$ can be estimated based on the vibrational frequency of the adsorbates [28, 62], i.e., $v_0$ (CO$_3^{2-}$) = $1.5 \times 10^{13}$~$5 \times 10^{13}$ [47, 69, 71, 72], and $v_0$ (OH$^-$) = $1 \times 10^{14}$ s$^{-1}$ [71, 73]. The estimated attempt frequency is in good match with the $k_{2,f}$ derived from kinetics fitting. The much higher $k_{2,b}$ in the H$_2$O cases may be attributed to the much faster collision frequency of H$_2$ with more preferable adsorption sites and orientations as compared to CO.

To further understand the rate-limiting mechanism, the calculated forward and the backward reaction rates and the evolution of the surface carbonate concentration are shown in Figure 8-9. The CO$_2$ activation step (R1) is faster in all cases, and the equilibrium is rapidly established between the surface carbonates and the gaseous CO$_2$. The charge transfer step (R2) is slower, especially at low temperature, and the backward reaction is close to zero, showing that the charge transfer process is the rate-limiting step, as observed for CO$_2$ splitting with Sm-doped ceria [44] as well as in the H$_2$O splitting processes [27, 28, 61]. The calculated activation barriers (i.e. 209 kJ mole$^{-1}$ for CeO$_2$ and 175 kJ mole$^{-1}$ for CZO) for the rate-limiting step correspond to the range of the apparent activation energy, 120~200 kJ mole$^{-1}$, reported in ref. [17]. Compared to CZO, the rates of R1 at 900°C with CeO$_2$ are faster initially followed by a rapid decay, in accordance with the evolution of the surface defects, as shown in Figure 8-4. In contrast, the rates with CZO at 700°C are consistently higher, owing to the higher surface area and the larger oxygen non-stoichiometry established after reduction. The rates of the forward R1 with CZO are
almost the same between 900°C and 700°C, resulting from negligible $E_{1,f}$ and the similar surface defect concentration (see Figure 8-5d). The similarity of the backward R1 rates between 900°C and 700°C is a combined effect from $E_{1,b}$ and the reverse temperature dependence of CO$_3^{2-}$, as shown in panels (b) and (d). CO$_3^{2-}$ concentration with CeO$_2$ is higher and more temperature sensitive in line with the deeper valley in Figure 8-8.

Figure 8-9 Comparison of the surface reaction rates (top) and surface carbonate concentrations (bottom) at 900°C and 700°C for CeO$_2$ (solid lines) and CZO (dashed lines). Backward reactions are plotted as negative values for clarity.

The surface absorbates act as a buffer to mediate the differences in the reaction rate kinetics of adsorption and the following charge-transfer step, and their formation and evolution critically rely on the surface defect structure. To understand the correlation between the surface defects
and the adsorbates, and their roles in CO₂/H₂O splitting, we examine the off-equilibrium dynamics of Ce³⁺ and CO₃²⁻ in response to the ion-incorporation flux, J, by equating eqs. (8.14) and (8.16) as:

\[
J = k_{1,f} P_{CO} \left[ V_0^+ \right] \left[ O_0^- \right] - k_{1,b} \left[ CO_3^{2-} \right] \\
= k_{2,f} \left[ CO_3^{2-} \right] \left[ Ce_0^{3+} \right]^2 - k_{1,b} P_{CO} \left[ O_0^- \right]^2 \left[ Ce_0^{3+} \right] \left[ Ce_0^{3+} \right] \tag{8.25}
\]

Eq. (8.25) essentially represents the majority of the conversion process where \( d[CO_3^{2-}] / dt \approx 0 \) (eq. (8.19)), as seen in Figure 8-9, with the only exception at the onset of oxidizer flow. J is positive during oxidation and negative during reduction. By re-arranging eq. (8.25), J and \([CO_3^{2-}]\) are expressed as:

\[
J = \frac{k_{1,f} k_{2,f} P_{CO} \left[ V_0^+ \right] \left[ O_0^- \right] \left[ Ce_0^{3+} \right]^2 - k_{1,b} k_{2,b} P_{CO} \left[ O_0^- \right]^2 \left[ Ce_0^{3+} \right]^2}{k_{2,f} \left[ Ce_0^{3+} \right]^2 + k_{1,b}} \tag{8.26}
\]

\[
\left[ CO_3^{2-} \right] = \frac{k_{1,f} P_{CO} \left[ V_0^+ \right] \left[ O_0^- \right] + k_{2,b} P_{CO} \left[ O_0^- \right]^2 \left[ Ce_0^{3+} \right]^2}{k_{2,f} \left[ Ce_0^{3+} \right]^2 + k_{1,b}} \tag{8.27}
\]

The numerator in eq. (8.26) is the off-equilibrium (i.e., biasing) potential, and the denominator describes the resistances to the generation of fluxes from both redox directions (i.e., \( k_{2,f} \left[ Ce_0^{3+} \right]^2 \) is the charge transfer resistance for the oxidation step, and \( k_{1,b} \) is defect formation resistance for reduction). Therefore, eq.(8.25) essentially describes the electro-chemical processes in a solid-oxide electrode cells for CO₂ splitting, in which the ion flux controlled by over-potential and J represents the current density, as in refs. [44, 61]. Coupled with eqs. (8.21)-(8.23), the concentrations of Ce³⁺ and CO₃²⁻ are evaluated for different J, and the correlations at a typical oxidizing environment (CO₂ = 0.14 bar, and CO = 0.02 bar) are shown in Figure 8-10.
Figure 8-10 Calculated evolutions of the concentration of surface adsorbates (panels a, c), and ion-incorporation flux (panels b, d) as a function of the surface Ce$^{3+}$ concentration at 900°C (black) and 700°C (red). The results with H$_2$O splitting (dashed lines, OH$^-$ as adsorbate) are also included with surface chemistry from refs. [27, 28] and kinetic parameters are summarized in Table 6-2. CO$_2$ or H$_2$O is fixed at 0.14 bar, and CO or H$_2$ is 0.02 bar, which represents a typical environment in oxidation. Filled areas in panel b, or d correspond to oxidation, i.e., a positive flux, and reduction, i.e., a negative flux. Panels a, b are for CeO$_2$, and panels c, d are for CZO.

As seen in panel (a), in the case of CeO$_2$, CO$_3^{2-}$ concentrations rises linearly with Ce$^{3+}$ initially, flattens when half of the surface is reduced, and eventually starts to decrease as the surface is near completely reduced. This behavior originates from the mismatch of the kinetic rates between R1 and R2. At low [Ce$^{3+}$], charge-transfer reaction (R2) is slow, and CO$_3^{2-}$ concentration is solely determined by R1: eq. (8.27) becomes \([\text{CO}_3^{2-}] \approx K_{1,CO_2} [V_0^+][O_0^-] \), thus
exhibiting a linear dependence. With the increase of [Ce\(^{3+}\)], R2 becomes more pronounced following a parabolic dependence. The rapid consumption via R2 slows down the accumulation of CO\(_3^{2-}\) via R1, leading to the observed transition. During this stage, the dependence of CO\(_3^{2-}\) can be approximated as $[\text{CO}_3^{2-}] \sim \frac{[\text{Ce}^{3+}]}{[1 + A_0[\text{Ce}^{3+}]^2]}$. Similar phenomena was reported by Chueh and co-workers [44] when the surface of Sm\(_{0.2}\)Ce\(_{0.8}\)Ce\(_{1.9}\) electrode was examined using ambient pressure X-ray photoelectron spectroscopy in a CO\(_2\) oxidizing environment at 500°C. They attributed this observation to the carbonate coverage effect, and argued that the adsorbate-adsorbate interaction modifies the adsorption and charge transfer electrochemistry, hence leading to the varying dependence. Our analysis here shows that this phenomenon can simply be explained in terms of the mismatch in the kinetic rates of R1 and R2. The surface carbonate coverage reaches a maximum of \(~3\%\) at 700°C, but is significantly lower (\(~0.03\%\)) at 900°C, in line with the deep valley in energy roadmap (Figure 8-8). [CO\(_3^{2-}\)] at 500°C is calculated to be around 10\% ~ 30\%, in reasonable agreement with the estimation (\(~20\%\)) from ref. [44].

The evolution of OH\(^-\) during the H\(_2\)O splitting process is also included in panel (a) for comparison. In contrast to the pattern of CO\(_3^{2-}\), the [OH\(^-\)] curve is concave and increases mildly with Ce\(^{3+}\) without a linear initial stage. Similar pattern was also identified by Chueh and co-workers [61]. This behavior is related to the fact that two OH\(^-\) adsorbates are involved in R1 or R2 (see Table 6-2). Consequently, $[\text{OH}^-] \sim \sqrt{[\text{Ce}^{3+}]}$ at the early stage, and then transits to $[\text{OH}^-] \sim \sqrt{[\text{Ce}^{3+}]} \times \sqrt{[1 + A_0[\text{Ce}^{3+}]^2]}$. The temperature dependence is weaker, because of the slightly higher energy level associated with OH\(^-\) as shown in Figure 8-8.
The correlation between the ion-incorporation flux, $J$, and the surface Ce$^{3+}$ concentration is shown in panel (b). Under an oxidizing environment, i.e., CO$_2$ = 0.14 bar, and CO = 0.02 bar, the ion flux is mostly positive, except at very low Ce$^{3+}$ where the removal of surface oxygen via R2 backward becomes prominent. Interestingly, the flux curve exhibits very weak temperature dependence, because of roughly the same temperature dependence for the numerator and the denominator in eq. (8.26). Despite the observed similarity in the ion-incorporation fluxes, the surface defects created in the preceding reduction step critically depends on temperature, which results in the observed dependence of the splitting kinetics on temperature. Consequently, the splitting peak rate increases significantly around 700°C, but varies mildly at further elevated temperature (see Figure 8-5), consistent with a similar trend of Ce$^{3+}$ at the surface. It is worth noting that a further decrease in temperature, however, leads to a much reduced flux, (e.g. blue line in panel b), because the carbonate saturates on the surface, hence reduces the concentration of $V_0^-$ and $O_0^-$. Compared to CO$_2$ splitting, H$_2$O oxidation with CeO$_2$ is noticeably faster, as also evident in Figure 8-6(a).

Compared to CeO$_2$, the concentration of CO$_3^{2-}$ on CZO surface is much lower and its evolution starts with an exponential rise, followed by a slight decrease when all available Ce$^{4+}$ is reduced to Ce$^{3+}$, as seen in panel (c). This is related to the $\delta$ dependence of $E_{1,b}$ as stated in eq. (8.7). Consequently, $k_{1,b}$ in the denominator of eq. (8.27) decays with the creation of oxygen vacancy, thus leading to the observed exponential increase of CO$_3^{2-}$ with Ce$^{3+}$. This effect becomes less prominent at high concentration of Ce$^{3+}$ when the first term in the denominator, $k_{2,f}[\text{Ce}']^2$, becomes comparable with $k_{1,b}$. OH$^-$ concentration is conceivably higher compared to CO$_3^{2-}$ at all temperatures, again echoing the deeper valley as seen in Figure 8-8. As shown in panel (d), the
ion-incorporation flux exhibits different patterns as compared to CeO$_2$. The range of reduction with negative $J$ is significantly expanded, resulting from the much improved reducibility of CZO. As a result, oxygen removal is favored when the concentration of Ce$^{3+}$ is below 25%, even under highly oxidizing environment.

Compared to CO$_2$ splitting, oxidation with H$_2$O is noticeably faster at 900$^\circ$C, but becomes slower at 700$^\circ$C although the difference is minor. The comparison of the flux here is in good accordance with the observation in Figure 8-6(a). The surface Ce$^{3+}$ concentration at equilibrium, i.e., $J=0$, is in fact very similar in both cases, although H$_2$O splitting equilibrates at slightly higher Ce$^{3+}$ (thus with a higher equilibrium $p_{O_2}$) compared to CO$_2$ splitting at 900$^\circ$C, and it becomes slightly lower at 700$^\circ$C. This comparison supports the speculation that the observed difference in the CO/H$_2$ yield in Figure 8-6(b) is kinetics-related, originating from the weaker temperature dependence of CO$_2$ splitting kinetics.

8.4 Summary

This work presents a detailed kinetics study of CO$_2$ splitting using CeO$_2$ and Ce$_{0.5}$Zr$_{0.5}$O$_2$ nanopowder. The time-resolved kinetics are measured in a button cell reactor in the temperature range 600-900$^\circ$C at atmospheric pressure. The ceria-based sample is alternatively exposed to H$_2$/Ar mixture in the reduction cycle, and CO$_2$ in the oxidation cycle. Evident improvement is found for CZO at low temperature with twice the kinetics rate at 700$^\circ$C, resulting from the enhanced reducibility with Zr and the finer particle structures maintained throughout the redox cycling.
The peak rates with CZO are 85.9 \( \mu \text{mole g}^{-1}\text{s}^{-1} \) at 900°C and 61.2 \( \mu \text{mole g}^{-1}\text{s}^{-1} \) at 700°C, and those of CeO₂ are 70.6 \( \mu \text{mole g}^{-1}\text{s}^{-1} \) and 28.9 \( \mu \text{mole g}^{-1}\text{s}^{-1} \).

Kinetics models are developed to describe the ion incorporation dynamics, using a two-step chemistry model: \( \text{CO}_2 \) activation over surface defects followed by the charge transfer process. Using the fitted parameters, excellent agreement is achieved compared to the measurements. The \( \text{CO}_2 \) activation energy is found to be \(-120 \text{ kJ mole}^{-1}\) for CZO, half of that with CeO₂, while the following CO desorption energetics is analogous among the two samples with the value of \(~160 \text{ kJ mole}^{-1}\), with a weaker activation barrier for CZO. The reaction pathway and energetics are analogous to that of \( \text{H}_2\text{O} \) splitting, with the difference mostly on the formation of surface adsorbates and the following charge-transfer process. The \( \text{CO}_2 \) activation process differs starkly between CeO₂ and CZO, due to the different defect formation thermodynamics.

The charge-transfer process is found to be the rate-limiting step for \( \text{CO}_2 \) splitting. The evolution of the adsorbates with surface \( \text{Ce}^{3+} \) is examined using the kinetics model, and a linear-flattened-decay pattern is observed for CeO₂, resulting from mismatch of the kinetics rate of the two reactions. The formation of carbonate is found to be strongly temperature dependent, reaching 3% at 700°C. Compared to CeO₂, the concentration of \( \text{CO}_3^{2-} \) on CZO surface is much lower and it evolves more non-linearly with surface \( \text{Ce}^{3+} \). The kinetics study here unveils the significant role of the surface defects and their interactions with adsorbates in determining the splitting kinetics.

8.5 Bibliography
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Chapter 9

H₂O and CO₂ Splitting with Praseodymia-Doped Ceria:

Promoting the Splitting Kinetics with Dopant Induced Oxygen Vacancy

This chapter examines Pr-doped ceria as another option to promote the low temperature splitting kinetics. Pr remains inactive under the redox conditions relevant for H₂O or CO₂ splitting; therefore, it acts as an electron-acceptor, freezing a portion of oxygen vacancy, regardless of the temperature. The high oxygen vacancy concentration facilitates the formation of surface adsorbates, and hence promotes the following charge-transfer step. The detailed time-resolved reaction kinetics with Pr₀.₂Ce₀.₈O₂ nano-powder is measured with H₂O and CO₂ as oxidizer while H₂ as fuel. Evident improvement is found for both H₂O and CO₂ as compared to pure ceria, while the reactivity at high temperature is lower along with a reduced oxygen carrying capacity. The peak H₂O splitting rate is 44 μmole H₂ g⁻¹ s⁻¹ at 600°C, reaching twice that of CZO and about ten times faster than CeO₂. The peak rate with CO₂ at 600°C is 28.9 μmole g⁻¹ s⁻¹. The two-step kinetics model is used to describe the redox process with H₂O and CO₂ and excellent agreement is found between the model prediction and the measurements. The charge transfer step is found to be analogous to CeO₂ or CZO, and it is the rate-limiting step. The defect formation enthalpy
for PCO is comparable to that of CeO$_2$ within the range $\delta = 0.1 - 0.2$. The modeling results clarify the role of Pr$^{3+}$ in creating oxygen vacancy at low temperature, and hence promoting the splitting kinetics. This feature of PCO, along with (strain-related) structural relaxation of CZO, suggests potential directions for improving and optimizing ceria-based OCs for H$_2$O and CO$_2$ splitting.

9.1 Introduction

Modified ceria-based solid solutions offer many interesting properties, such as enhanced ionic mobility [1], ferromagnetism [2], selective oxidation [3], and mixed ionic and electronic conductivity (MIEC) [4], the effects of which critically depend on the oxygen vacancy ($V^+_o$) formed in the solid. Praseodymium-doped ceria is one of the most interesting options, in which Pr exhibits a mixed valence state (Pr$^{4+}$ and Pr$^{3+}$). As the neighbor rare earth element of Ce, Pr has many similar physical and electrochemical properties (see Table 9-1), which enable the formation of a praseodymia-ceria (PCO) solid solution at high miscibility [3, 5]. On the other hand, the much higher reducibility and faster oxygen exchange activity of praseodymia (Pr$_6$O$_{11}$) facilitates the vacancy formation as well as the ionic conductivity in PCO, enabling it as an interesting option for low temperature oxygen storage [6, 7].

In PCO system, there exist three distinctive regimes: (1) MIEC at low $p_{O2}$, (2) ionic conductivity at intermediate $p_{O2}$, and (3) MIEC again at high $p_{O2}$. The corresponding variation of O-deficiency, i.e., $\delta$ in Pr$_x$Ce$_{1-x}$O$_{2-\delta}$, exhibits a three-stage pattern with $p_{O2}$: decrease, plateau, and decrease [8]. Reduction of Pr$^{4+}$ to Pr$^{3+}$ initiates at a much higher $p_{O2}$, i.e., 1 to $\sim 10^{-6}$ atm [4], producing small polarons (localized electrons) hopping between different Pr sites, thus
contributing to electrical conductivity. Reduction of Pr$^{4+}$ is charge-compensated by the release of oxygen and hence the formation of O vacancy, which facilitates the ionic diffusion (under sufficient dopant loading, $x$ in Pr$_x$Ce$_{1-x}$O$_2$). Once all Pr is fully reduced to Pr$^{3+}$, PCO becomes a pure ionic conductor with diminished electrical conductivity, similarly as with a trivalent dopant. A further decrease of $p_{O2}$ below $10^{-12}$ atm [4, 8] leads to the transition to the Ce reduction regime, in which the low oxygen activity activates the reduction of Ce$^{4+}$ to Ce$^{3+}$, similarly as in pure ceria. The hopping of polarons between Ce$^{4+}$ and Ce$^{3+}$ along with the high oxygen vacancy concentration (resulting from trivalent Pr) constitutes the mixed conductivity of the PCO system.

<table>
<thead>
<tr>
<th>Table 9-1 Physical properties of Ce, Pr, and Zr elements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular weight</strong></td>
</tr>
<tr>
<td><strong>Valence state</strong></td>
</tr>
<tr>
<td><strong>Ionic radius (pm)</strong></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Note, subscript in ionic radius denote the coordination number. Ionic radius is taken from ref. [9].

The electrochemical properties of PCO solid solutions have been examined and documented. Both the electronic ($\sigma_e$) and ionic ($\sigma_i$) conductivities were found to increase rapidly with the addition of Pr, with the maximum total conductivity ($\sigma = \sigma_e + \sigma_i$) established at around 30% Pr, although the ionic transference number (i.e., $t_i = \sigma_i/\sigma$) continuously decreases with Pr loading [10, 11]. The thermal expansion of PCO crystal lattice is found to be higher as compared to undoped ceria, and the difference becomes more pronounced at higher temperature [12]. The changes in microstructures of the solid solutions with regards to different atmosphere were investigated using in-situ X-ray diffraction (XRD) [13] and in-situ Raman spectroscopy [14], and differences were observed between the bulk shell and the surface region. Non-stoichiometry and defect chemistry of PCO system were measured in a few studies using coulometric titration [7, 8, 345]
15], thermo-gravimetric analysis [4, 8], impedance spectroscopy [16, 17], and chemical capacitance [18, 19], and the different regimes were clearly identified. The $p_{O2}$ dependence of the O-deficiency and conductivity were evaluated based on defect chemistry, and the creation of extra electronic levels within the energy gap of ceria was found to cause the dramatic variation of conductivity and defect non-stoichiometry throughout different $p_{O2}$ regimes. The thermodynamic equilibria at different stages were extracted, and an evident $\delta$-dependence for the defect formation enthalpy was observed, resulting from chemical expansion, in the case of Pr$_{0.1}$Ce$_{0.9}$O$_{2-\delta}$ [4] and Pr$_{0.2}$Ce$_{0.8}$O$_{2-\delta}$ [8], although the origin of the dependence is associated with Ce reduction (at low $p_{O2}$) [4] and Pr reduction (at high $p_{O2}$) [8], respectively. The effects of additives, e.g., Co, Mn, or Pd, on the electric conductivities and surface exchange rates in a PCO system were also examined [20-22].

More recently, interests have more concentrated on PCO-based nanostructures with more desirable redox properties [23], and it was found that the defect formation energy with thin film is conceivably lower [19] than its bulk-phase value [4]. Despite the increasing efforts on understanding the defect equilibria, there seems to be a lack of understanding on the surface kinetics under redox conditions. Previous chapters concluded that the existence of oxygen vacancy on the surface plays a paramount role in determining the kinetic process; therefore one can expect very interesting H$_2$O/CO$_2$ splitting behaviors of PCO system especially at low temperature. The differences in defect formation thermodynamics between the bulk and the surface remain unclear, and an application of the previously developed defect modeling to the PCO system will provide important information.
In this chapter, we investigate the H₂O/CO₂ splitting mechanism on Pr₀.₂Ce₀.₈O₂₋₆, with a focus on exploring the role of Pr on the splitting kinetics. Isothermal redox cycles are carried out in a button cell reactor in the temperature range 600-900°C, using H₂ as a surrogate fuel during reduction to construct the oxygen non-stoichiometry. The kinetics and the oxygen-ion incorporation pathway for the splitting processes are quantified using the developed defect equilibria and mechanism framework, taking into account of two-step surface chemistry (adsorption/dissociation of gaseous reactant, charge transfer on the surface) and the bulk-to-surface transport equilibrium. Based on the kinetics models, insights are gained on the effect of surface vacancies on the redox kinetics.

9.2 Experimental Setup and Theoretical Methods

9.2.1 Sample characterization

Commercial Pr₀.₂Ce₀.₈O₂ nano-powder from Sigma Aldrich is used for the kinetics study. Table 9-1 lists the properties of the fresh and aged PCO sample. Figure 9-1 compares the SEM images of fresh and redox cycled samples. The fresh sample contains very fine particles with the size less than 50nm. After redox treatment, the particles sinter into larger grains forming an interconnected structure, similarly as with pure ceria. Compared to CeO₂ (Figure 3-9), the structure is similar, although the size enlargement seems slightly less significant, consistent with the lower sintering temperature (900°C as opposed to 1000°C for ceria). Similarly as CeO₂ or CZO, minor variations are observed on the redox kinetics during the pretreatment except a few initial (<5) cycles, suggesting that the agglomeration likely results from the sintering effect during heating and the initial redox cycling. Comparing H₂O and CO₂ cases, the structures of the aged samples are similar, and the particles in CO₂ are slightly larger, although the difference is insignificant.
Samples after additional 20 redox cycles are also examined, and the same redox rates are obtained, indicating a periodic stationary state.

Table 9-2 Some physical properties of the Pr$_{0.2}$Ce$_{0.8}$O$_2$

<table>
<thead>
<tr>
<th>Property</th>
<th>Pr$<em>{0.2}$Ce$</em>{0.8}$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample mass, m</td>
<td>100 mg</td>
</tr>
<tr>
<td>Molar density, $\tilde{\rho}_{PCO}$</td>
<td>$4.2 \times 10^4$ mol m$^{-3}$</td>
</tr>
<tr>
<td>Molar weight, MW</td>
<td>172.11 g mol$^{-1}$</td>
</tr>
<tr>
<td>Surface molar density, $\tilde{\rho}_{PCO,a}$</td>
<td>$2.3 \times 10^{-4}$ mol m$^{-2}$</td>
</tr>
<tr>
<td>Particle Size*</td>
<td></td>
</tr>
<tr>
<td>Fresh</td>
<td>~40 nm</td>
</tr>
<tr>
<td>H$_2$O cycled</td>
<td>~160 nm</td>
</tr>
<tr>
<td>CO$_2$ cycle</td>
<td>~180 nm</td>
</tr>
</tbody>
</table>

* Note the particle size is estimated by averaging the diameter of 50 grains within the SEM image.

Figure 9-1 SEM images of the PCO (a) fresh sample, (b) aged sample after 20 H$_2$O cycles, and (c) aged sample after 20 CO$_2$ cycles.

9.2.2 Redox kinetics measurement

100mg of PCO powder is embedded in quartz wool and placed at the bottom of the outer quartz tube. The sample undergoes redox cycles with argon as a purging gas in between. The total flow rate is fixed at 350 scm, corresponding to a gas residence time less 300 ms through the dispersed sample. Oxidation with H$_2$O is performed using a gas mixture of H$_2$O with total flow rate of 337 sccm. The concentration of feed oxidizer for H$_2$O and CO$_2$ in the base case is maintained at 26% and 25.7%, respectively, while reduction is carried out with 14.3mol% H$_2$. The oxidation and
reduction times are fixed at 2 min each with 5 min Ar purging in between. In either H₂O or CO₂ splitting test, fresh sample is first pre-treated at 900°C for 20 cycles to reach periodic stationary states. The redox measurements start from 900°C and ramp down to 500°C with a step of 100°C. Each operating condition is repeated for at least three times, and results are averaged to reduce the noise. The instantaneous reaction rates for oxidation with H₂O and CO₂, as well as reduction with H₂ are calculated similarly as in previous chapters.

An accurate quantification of the evolution of the oxygen non-stoichiometry is a critical component in extracting the redox kinetics. However, praseodymium in a PCO system maintains its reduced form even under highly oxidizing environment (i.e., pO₂ = 0.21 bar), thus creating a major challenge to accurately quantify the initial O-deficiency in PCO system. Interestingly, the effective oxygen activity established in the H₂O environment within the fixed bed reactor fails properly within the O-deficiency plateau stage of Pr₀.₂Ce₀.₈O₂, at which all Pr is fully reduced while Ce remains at its oxidized state. To demonstrate this point, we re-draw the range of effective oxygen activity in Figure 9-2 along with the non-stoichiometry isotherms for Pr₀.₂Ce₀.₈O₂ reported by Chatzichristodoulou and Hendriksen [8]. Here the range of pO₂ corresponds to Figure 7-9 with the lower bound being the pO₂ along the CZO isotherms (dashed line in Figure 7-9) and the upper bound being the values reached under equilibrium (lower blue area in Figure 7-9). As seen in Figure 9-2, pO₂ falls within the plateau (regime 2) along the isotherms. Consequently, the oxygen deficiency established after oxidation with H₂O can be assumed to be δ = 0.1. In the case with CO₂ splitting, a supplemental 1 min H₂O oxidation is applied to ensure sufficient regeneration of oxygen non-stoichiometry to 0.1.
Therefore, the redox conversions with PCO only utilizes the oxygen carrying capacity associated with Ce, and the trivalent Pr\(^{3+}\) in the solid solution acts as an electron acceptor inducing the charge-compensated oxygen vacancy at 0.1.

9.2.3 Non-stoichiometric defect chemistry
The defect chemistry for PCO can be modeled similarly as pure ceria [24, 25]. The defect formation reaction in the bulk, surface reactions, and the bulk-to-surface transport equilibrium are written as:

**Bulk defect equilibrium:**

\[
O_\text{o}^-(b) + 2Ce^\text{ce'}_c(b) \xrightleftharpoons{K_b} V_\text{o}^-(b) + 2Ce^\text{ce'}_c(b) + \frac{1}{2} O_2(g)
\]  
(9.1)

\[
K_b = \exp\left(\frac{-H_b - TS_b}{RT}\right) = \frac{P_{O_2}^{1/2}\left[V_\text{o}^{**}\right]\left[Ce^\text{ce'}_c\right]^2}{\left[O_\text{o}^-\right]\left[Ce^\text{ce'}_c\right]^2}
\]  
(9.2)

**Transport equilibrium:**

\[
V_\text{o}^- (b) - O_\text{o}^- (b) + 2Ce^\text{ce'}_c(b) - 2Ce^\text{ce'}_c(b) \xrightleftharpoons{K_T} V_\text{o}^- (s) - O_\text{o}^- (s) + 2Ce^\text{ce'}_c(s) - 2Ce^\text{ce'}_c(s)
\]  
(9.3)

\[
K_T = \exp\left(\frac{-\Delta H^0_T - T\Delta S^0_T}{RT}\right) = \frac{\left[V_\text{o}^-\right]\left[Ce^\text{ce'}_c\right]^2}{\left[O_\text{o}^-\right]\left[Ce^\text{ce'}_c\right]^2} / \frac{\left[V_\text{o}^-\right]\left[Ce^\text{ce'}_c\right]^2}{\left[O_\text{o}^-\right]\left[Ce^\text{ce'}_c\right]^2}
\]  
(9.4)

**H\textsubscript{2}O surface reactions:**

**R1:** \( \text{H}_2\text{O}(g) + V_\text{o}^- (s) + O_\text{o}^- (s) \xrightarrow{k_{1,f}} 2\text{OH}^- (s) \)  
(9.5)

\[
r_1 = k_{1,f} p_{H\text{O}} \left[V_\text{o}^-\right]\left[O_\text{o}^-\right] - k_{1,b} \left[\text{OH}^-\right]^2
\]  
(9.6)

**R2:** \( 2\text{OH}^- (s) + 2Ce^\text{ce'}_c (s) \xrightarrow{k_{2,f}} 2O_\text{o}^- (s) + 2Ce^\text{ce'}_c (s) + \text{H}_2 (g) \)  
(9.7)

\[
r_2 = k_{2,f} \left[\text{OH}^-\right]^2 \left[Ce^\text{ce'}_c\right]^2 - k_{2,b} p_{H\text{O}} \left[O_\text{o}^-\right]^2 \left[Ce^\text{ce'}_c\right]^2
\]  
(9.8)

**CO\textsubscript{2} surface reactions:**

**R1:** \( \text{CO}_2 (g) + V_\text{o}^- (s) + O_\text{o}^- (s) \xrightarrow{k_{1,f}} (\text{CO}_3)_\text{o}^- (s) \)  
(9.9)

\[
r_1 = k_{1,f} p_{\text{CO}_2} \left[V_\text{o}^-\right]\left[O_\text{o}^-\right] - k_{1,b} \left[(\text{CO}_3)_\text{o}^-\right]
\]  
(9.10)
Here the major defects are the doubly-charged oxygen vacancy, $V_0^{**}$, and the localized electrons, $Ce'^e$, (small polarons) [1, 26]. $K_b$, $H_b$, and $S_b$ are the equilibrium constant, enthalpy and entropy of the defect formation reaction. The brackets denote the mole of species per mole of CeO$_2$ or Pr$_{0.2}$Ce$_{0.8}$O$_2$. $K_T$, $\Delta H^0_T$, and $\Delta S^0_T$ denote the transport equilibrium constant, the difference of the defect formation enthalpy and entropy, respectively, between the surface and the bulk phase. OH" , and (CO$_3$)$_2^-$ (or equivalently OH-, and CO$_3$$^2-$) are surface hydroxyl and carbonate ion group on an oxygen anion site. $k_{i,b}$, $k_{i,b}$, denotes the rate coefficients (unit, s$^{-1}$), following the Arrhenius expression, $k = k_0 \exp(-E/RT)$. At equilibrium, $r_1$ and $r_2$ equal zero, yielding the definition of $K_1$ and $K_2$, i.e., $K_i = k_{i,b}/k_{i,b}$.

The bulk diffusion process within the PCO particle is negligible, given the fact that the addition of Pr dramatically improves the ionic and electronic conductivity [10, 11], and that the particle size of aged PCO is smaller than that of pure ceria. The characteristic time ($\tau$) for diffusion from the expression $\tau \sim \bar{r}^2/4D$ was estimated to be $< 0.1$ ms for PCO [11], significantly faster than the surface chemistry.

The reduction of Pr can be similarly described as,

$$O_2^-(b) + 2Pr^+(b) \rightarrow k_{r_1} V_0^{**} (b) + 2Pr'^e (b) + \frac{1}{2} O_2 (g)$$  \hspace{1cm} (9.13)
Combining eqs. (9.13) and (9.1) yields:

\[ \text{Pr}_c^\text{Ce} + \text{Ce}_c^\text{Ce} \xrightleftharpoons[K_{Pr}]{K_{Pr}} \text{Pr}_c^\text{Ce} + \text{Ce}_c^\text{Ce} \]  

(9.15)

\[
K_{Pr} = \sqrt{\frac{K_{b,Pr}}{K_{b}}} = \exp\left( \frac{-\Delta H_{Pr} - T\Delta S_{Pr}}{RT} \right) = \frac{[\text{Pr}_c^\text{Ce}][\text{Ce}_c^\text{Ce}]}{[\text{Pr}_c^\text{Ce}][\text{Ce}_c^\text{Ce}]} 
\]

(9.16)

Eq. (9.15) describes the de-ionization of an electron from conduction band to Pr-induced impurity band [4]. Under the redox conditions relevant for H2O and CO2 splitting, Pr remains completely at +3 state, [Pr_c^Ce] = 0.2, resulting from the large impurity band gap (\(\Delta H_{Pr} = -1.2 \text{ eV} [8]\)). Thus the conservation equations for the bulk and the surface are expressed as:

**Bulk phase:**

O-site: \[ [V_{O}^\text{g}]_b + [O^\text{g}]_b = 2 \]  

(9.17)

Ce-site: \[ [\text{Ce}_c^\text{Ce}]_b + [\text{Ce}_c^\text{Ce}]_b = 0.8 \]  

(9.18)

electro-neutrality \[ 2[V_{O}^\text{g}]_b = [\text{Ce}_c^\text{Ce}]_b + 0.2 \]  

(9.19)

**Surface:**

O-site: \[ [V_{O}^\text{s}]_s + [O^\text{s}]_s + [\text{OH}^\text{s}]_s \text{ (or } 2[(\text{CO}_3)_{O}^\text{s}]_s \text{)} = 2 \]  

(9.20)

Ce-site: \[ [\text{Ce}_c^\text{Ce}]_s + [\text{Ce}_c^\text{Ce}]_s = 0.8 \]  

(9.21)

electro-neutrality: \[ 2[V_{O}^\text{s}]_s + [\text{OH}^\text{s}]_s \text{ (or } 2[(\text{CO}_3)_{O}^\text{s}]_s \text{)} = [\text{Ce}_c^\text{Ce}]_s + 0.2 \]  

(9.22)

The dopant concentration ([Pr_c^]) on the surface may be higher than the bulk value [26], resulting from the elastic contribution as mentioned in Section 3.5. Given the similarity in the physical
properties of Pr and Ce, this effect is expected to be less significant and hence it is neglected here for simplicity.

Similarly as in previous chapters, the surface reactions for the H₂O and CO₂ splitting processes are connected via eqs. (9.1) and (9.3) as:

\[
K_{\text{H}_2\text{O}} \left( \frac{k_{1,f}}{k_{1,b}} \frac{k_{2,f}}{k_{2,b}} \right)_{\text{H}_2\text{O}} = K_{\text{CO}_2} \left( \frac{k_{1,f}}{k_{1,b}} \frac{k_{2,f}}{k_{2,b}} \right)_{\text{CO}_2} = \left( K_b K_T \right)^{-1}
\]  

(9.23)

Here, \( K_{\text{H}_2\text{O}} \) and \( K_{\text{CO}_2} \) are the equilibrium constant of H₂O and CO₂ formation reaction, \( \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) \), \( \text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) \), from which the equilibrium oxygen activity can be defined (see eq.(8.18)).

**9.2.4 Simulation and Fitting Process**

The overall governing equations for the evolutions of the surface adsorbate (eq. (7.19) or (8.19)) and the bulk-phase \( V_{\text{O}^-} \) (eq. (7.20)) are numerically integrated in MATLAB. The measurements of the reduction and oxidation rates in the H₂O case are used to extract the thermodynamic \((K_b, K_1)\). The kinetic and equilibrium parameters to be extract are \( k_{1,b}, k_{2,b} \) and \( K_2 \) for each case. The variation of \( H_b \) with \( \delta \) in the case of CZO is not included in the modeling, since the ideal defect model, i.e., \( H_b \) remains constant, suffices to quantitatively represent the defect equilibria in regime 1, as will be shown in Section 9.3.

**9.3 Results & Discussion**

Figure 9-3 shows the evolution of species concentration for H₂O oxidation, CO₂ oxidation, and H₂ reduction at 900°C. Top panel shows the gaseous species, and bottom panels show the oxygen
non-stoichiometry, calculated by integrating the reaction rates with time (eqs. (6.2), (6.3), and (8.4)). The reduction step showed here is from the H_2O measurements, and the results are identical to those measured in the reduction step during the CO_2 splitting study. The evolutions of species follow a similar pattern as illustrated in previous chapters: the reactivity spikes with the intake of gaseous reactant, transitions to a slow residual conversion with the depletion (or saturation) of defects, and eventually ceases near the end of oxidation. The oxidation rate with H_2O is slightly faster than that in the CO_2 case, and hence the oxygen deficiency in bottom panel decays more rapidly. The maximum conversion (lowest δ) established after the oxidation steps is at δ = 0.1, consistent with a complete re-oxidation of all Ce^{3+}. The reactivity of the reduction step is slowest, and the oxygen removal continues towards the end of conversion.

Figure 9-3 Evolution of species (top) and oxygen non-stoichiometry (bottom) at 900°C for 100 mg PCO during (a) H_2O oxidation, (b) CO_2 oxidation, and (c) H_2 reduction. Dashed lines in top panels are the feed species at the inlet, and solid lines are measured at exit. Feed of reactant starts at t = 0.1 min, and stops at t = 2.1 min.
9.3.1 Effect of Temperature

Figure 8-5 shows the effect of temperature on the reaction kinetics. Each plot exhibits strong temperature dependence, suggesting large activation energy barriers, as expected based on previous chapters. H₂O splitting rate is consistently faster as compared to CO₂, similarly as with pure ceria (Figure 8-6). The non-linear temperature dependence of the peak splitting rates, i.e., large jump at intermediate temperature and relatively unchanged at high temperature as illustrated in Figure 6-5, however, is not observed for PCO. Reduction rates are slowest, consistent with the measurements for pure ceria (see Figure 6-6), and their decay with time is milder and spans over a longer time window. The threshold temperature to reach significant splitting kinetics is around 600°C, dramatically lower than that for pure ceria (700°C) or CZO (650°C).

Figure 9-4 Comparison of the temperature dependence for reactivity for (a) H₂O splitting, (b) CO₂ splitting, and (c) H₂ reduction.

To understand the effect of Pr on the splitting kinetics, we plot the comparison of the peak rates for H₂O and CO₂ splitting in Figure 9-5. The H₂O splitting rate is significantly faster at low temperature as compared to CeO₂ or CZO: the peak rate at 600°C is 44 μmole H₂ g⁻¹ s⁻¹, twice
that of CZO and about ten times faster than CeO₂. On the other hand, the rate at high temperature is slower than the other two: the peak rate with PCO at 900°C is 133 μmole H₂ g⁻¹s⁻¹, 20% and 25% lower than that of CeO₂ and CZO, respectively. Overall, the variation of the rates with temperature exhibits a rather linear dependence, in contrast to the sigmoidal shape with CeO₂ or CZO. The peak rates for CO₂ splitting follow a similar trend, although the rate with CZO at low temperature exceeds either CeO₂ or PCO, consistent with the lowered charge-transfer barrier with CZO as shown in Figure 8-8. The peak CO₂ splitting rates at 900°C and 600°C are 84, and 27 μmole CO g⁻¹s⁻¹, respectively.

Figure 9-5 Comparison of (a) peak H₂O splitting rates and (b) peak CO₂ splitting rates among CeO₂, CZO, and PCO. Note the CO₂ splitting rates in panel (b) are converted from 14.3mol% CO₂ to 25.7mol% CO₂ using a linear dependence. Error for the peak rate is based on the s.d. of triplicate peak measurements.
Figure 9-6 Comparison of total H\textsubscript{2}/CO production. Error bar is estimated by multiplying the averaged s.d. of CO measurement by the total oxidation time, which gives an upper bound.

Figure 9-6 compares the total H\textsubscript{2} and CO yield during the 2 min oxidation step. The CO yield is slightly less than that of H\textsubscript{2}, consistent with the slower oxidation kinetics with CO\textsubscript{2}, although the difference is generally within the error bar. The H\textsubscript{2} or CO yield is lower at high temperature as compared to CeO\textsubscript{2}, because of the lower oxygen carrying capacity. On the other hand, the yield at 600–700°C is noticeably higher than CeO\textsubscript{2}, consistent with the faster kinetics as shown in Figure 9-5.

Figure 9-7 compares the oxygen non-stoichiometry and the peak rate during reduction. As seen in panel (a), PCO possesses largest O deficiency at low temperature, roughly 0.1 higher than that of CeO\textsubscript{2}. δ with CZO at 500-600°C falls in the between, resulting from the significantly improved reducibility. Above 700°C, however, the non-stoichiometry of PCO and CZO almost overlaps, and the value of CeO\textsubscript{2} gets closer with temperature. The maximum non-stoichiometry
reached is around 0.23~0.24 for all three OCs, likely determined by the limit of the fluorite-related structure (α phase of pure ceria has range δ<0.286 [3]). The comparison of the reduction kinetics, however, shows a different pattern: the reduction rates of PCO and pure ceria are very similar, although the value with PCO slightly prevails at high temperature. The similarity of the reduction rate between PCO and CeO₂ comes as no surprise, given the fact that the Ce portion within the OC solely contributes to the oxygen removal kinetics. The rate with CZO, on the other hand, is dramatically higher, because of the enhanced reducibility as discussed in Chapter 7.

![Figure 9-7](image)

Figure 9-7 (a) Non-stoichiometry reached after reduction, (b) peak reduction rate.

The comparison in Figure 9-5, Figure 9-6 and Figure 9-7 outlines the role of Pr in the ceria-based OC on the redox processes: Pr presents as an inactive “spectator”; however, the trivalent Pr³⁺ is an electron acceptor, freezing a portion of oxygen vacancy regardless of the redox environment (before oxidation of Pr³⁺ takes place). This leads to a reduced oxygen carrying capacity, i.e., the non-stoichiometry that can be reached during cycling is effectively lowered by 40-50%. On the other hand, the presence of a large amount of oxygen vacancy at low temperature under relatively oxidizing environment directly facilitates the adsorption and activation of adsorbates,
hence promoting the following charge-transfer step. This leads to the remarkable improvement of the splitting kinetics at low temperature, as observed in Figure 9-6. This feature of PCO, along with (strain-related) structural relaxation of CZO, suggests potential directions for improving and optimizing ceria-based OCs for H₂O and CO₂ technologies.

9.3.2 Kinetics and Defect equilibria

Model predictions for the H₂O/CO₂ splitting rates as well as the H₂ reduction step at various temperatures are shown in Figure 9-8. A good match is found between predictions and measurements for all the cases. The predictions precisely capture the spike-decay behaviors of oxidation, and the non-linear temperature dependence is precisely captured. The obtained kinetic and equilibrium parameters are summarized in Table 9-3 and Table 9-4.

As shown in Figure 9-9, the calculated energy landscape for the surface chemistry pathways with PCO follows a very similar pattern as with CeO₂ and CZO: R1 is exothermic and barrierless, and R2 is endothermic with large activation barriers, suggesting the rate-limiting mechanism being the charge-transfer step (R2) [24, 27, 28]. The energy levels of the transition states and the surface adsorbates for CeO₂ and CZO outline the upper and lower bounds, while the values with PCO fall in between.
Figure 9-8 Comparison of model predictions to the measurements: (a) H₂O splitting rates, (b) CO₂ splitting rates, and (c) reduction rates. Solid lines represent the defect model. The data sets have been separated with different scales to clearly show the comparison.

The second half of the splitting process, i.e., the charge transfer step, for the three OCs is similar. This is more evident by comparing the pre-exponential rate constant, \( k_{2,f} \) and \( k_{2,b} \), and the activation energy barriers, \( E_{2,f} \), and \( E_{2,b} \), as listed in Table 9-3. This observation here again confirms the conclusion in the previous chapters that the charge-transfer step mostly depends on the evolution of the surface adsorbates and the interactions with the lattice oxygen, and less affected by the influence from dopant. \( k_{2,f} \) obtained for H₂O or CO₂ is in good accordance with the estimated vibrational frequency of adsorbates [24, 29], i.e., \( v_0 (CO_3^{2-}) = 1.5 \times 10^{13} \sim 5 \times 10^{13} [30-33] \), and \( v_0 (OH^-) = 1 \times 10^{14} \text{ s}^{-1} [30, 34] \). On the other hand, \( k_{1,f} \) and \( k_{1,b} \) are similar between the H₂O and CO₂ splitting cases for each OC material, supporting the finding that the adsorption (forward R1) or the defect formation (backward R1) process is structure-oriented, and less sensitive to the specific molecular structure of the gaseous oxidizer, as pointed out in previous
chapters. R1 differs significantly among different OCs, in line with the observed differences in the defect thermodynamics ($H_b$ and $S_b$): the more compact crystal structure with stronger bond energy leads to larger defect formation barrier at higher vibrational frequency for R1 backward reaction [25, 29, 30, 35].

Table 9-3 Fitted kinetic parameters for both the forward and backward reactions. Results for CeO$_2$ and CZO are from Chapter 6-Chapter 8.

<table>
<thead>
<tr>
<th>Adsorption (R1)</th>
<th>H$_2$O splitting</th>
<th>CO$_2$ splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{f1}$(1/s)</td>
<td>1.1x10$^7$</td>
<td>1.3x10$^7$</td>
</tr>
<tr>
<td>$E_{f1}$(kJ/mol)</td>
<td>12</td>
<td>7</td>
</tr>
<tr>
<td>$k_{b1}$(1/s)</td>
<td>1.2x10$^{11}$</td>
<td>8.2x10$^{14}$</td>
</tr>
<tr>
<td>$E_{b1}$(kJ/mol)</td>
<td>145±33</td>
<td>210</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Charge transfer (R2)</th>
<th>CO$_2$ splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{f2}$(1/s)</td>
<td>3.5x10$^{14}$</td>
</tr>
<tr>
<td>$E_{f2}$(kJ/mol)</td>
<td>191±29</td>
</tr>
<tr>
<td>$k_{b2}$(1/s)</td>
<td>4.7x10$^4$</td>
</tr>
<tr>
<td>$E_{b2}$(kJ/mol)</td>
<td>84±2</td>
</tr>
</tbody>
</table>

Note: Error corresponds to 5% increment of the fitting residual.

Table 9-4 Fitted Parameters for the transport and bulk defect equilibria

<table>
<thead>
<tr>
<th></th>
<th>Pr$<em>{0.2}$CeO$</em>{0.8}$O$_2$ (this chapter)</th>
<th>Pr$<em>{0.2}$CeO$</em>{0.8}$O$_2$ (ref. [8])</th>
<th>Pr$<em>{0.1}$CeO$</em>{0.9}$O$_2$ (ref. [4])</th>
<th>CeO$_2$ (ch. 6)</th>
<th>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$ (ch. 7)</th>
<th>CeO$_2$ (ref. [36])</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_b^0$(kJ mol$^{-1}$)</td>
<td>372.7±2</td>
<td>340</td>
<td>414.6</td>
<td>467.4</td>
<td>298.5</td>
<td>399.4</td>
</tr>
<tr>
<td>$S_b$(J mol$^{-1}$ K$^{-1}$)</td>
<td>99.8±2</td>
<td>90.66</td>
<td>147.5</td>
<td>172.9</td>
<td>80.1</td>
<td>119.7</td>
</tr>
<tr>
<td>$\Delta H_f^0$(kJ mol$^{-1}$)</td>
<td>-97.7±5</td>
<td>-</td>
<td>-</td>
<td>-107.6</td>
<td>-30.0</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta S_f^0$(J mol$^{-1}$ K$^{-1}$)</td>
<td>-59.2±3</td>
<td>-</td>
<td>-</td>
<td>-54.0</td>
<td>-9.6</td>
<td>-</td>
</tr>
<tr>
<td>$f$(kJ)</td>
<td>0</td>
<td>-</td>
<td>-446.7</td>
<td>0</td>
<td>368.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: Error corresponds to 5% increment of the fitting residual. The values here correspond to $\delta = 0.1$
Figure 9-9 Energy landscape for the surface reaction pathways for (a) H$_2$O splitting and (b) CO$_2$ splitting with PCO (black lines). The pathways for H$_2$O splitting with CeO$_2$ (blue) and CZO (red) are also included. Unit is kJ mole$^{-1}$.
Figure 9-10 Comparison of (a) defect formation enthalpy, $H_b$ and (b) entropy, $S_b$.

The obtained enthalpy and entropy of defect formation are listed in Table 9-4, and values reported in the literature for similar OCs are also included for comparison. Our calculated bulk defect thermodynamics for $Pr_{0.2}Ce_{0.9}O_2$ are in reasonable agreement with ref. [8]. Comparing it
to Pr$_{0.1}$Ce$_{0.9}$O$_2$ from ref. [4], we find that with Pr content increasing from 0.1 to 0.2, the defect formation enthalpy is reduced by 10%, while entropy is lowered by over 30%.

It is interesting to notice the similarities of the defect thermodynamics between PCO and undoped ceria (with corresponding δ as determined by Pr$^{3+}$). To further illustrate this analogy, we plot the δ dependence of defect thermodynamics in Figure 9-10. The reported defect formation thermodynamics generally varies with the oxygen non-stoichiometry, as pointed out in Chapter 7 for CZO, resulting from vacancy-induced chemical expansion of the crystalline lattice [4, 8] and defect interactions and ordering [37]. This effect is shown clearly by the values with pure ceria (red line, ref.[36]), which exhibit a convex pattern with a flattened minimum at δ = 0.1 – 0.2. Interestingly, the reported $H_b$ and $S_b$ for CeO$_2$ within this range match closely with those for Pr$_{0.2}$Ce$_{0.8}$O$_2$ from the current study. The slightly lower values with PCO are likely attributed to the smaller ionic radius of Pr, as shown in Table 9-1, which may lead to minor structural distortion as in CZO. This similarity can be further examined in the case of Pr$_{0.1}$Ce$_{0.9}$O$_2$ (blue lines), for which the reported linear trend is in a perfect match with that of CeO$_2$ within the range δ = 0.05 – 0.1. The observed similarity in thermodynamics between PCO and CeO$_2$ again provides supporting evidence to the conclusion that the contribution of the “spectator” Pr$^{3+}$ to the redox properties mostly resides in the high concentration oxygen vacancy, hence effectively shifting the range the non-stoichiometry for reactions along the equilibrium isotherms. The similarity between PCO and CeO$_2$ is further extended to the surface, with the analogous $\Delta H_f^0$ and $\Delta S_f^0$ (Table 9-4), as well as the similar values for $k_{1,f}$ (Table 6-2). The much higher $H_b$ reported in Chapter 6 for CeO$_2$ is consistent with near stoichiometry defect formation enthalpy as
reported in ref. [36]. The lower value of $H_b$ for PCO, as compared to that of stoichiometric ceria, also explains the lower attempt frequency, $k_{1,b}$, than that of CeO$_2$ (Table 9-3).

9.3.2 Surface species evolution and reaction rates

To further illustrate the effect of Pr on splitting kinetics, we show the calculated surface species evolution and the forward and the backward reaction rates in Figure 9-11 and Figure 9-12, respectively. The concentration of the surface hydroxyls for PCO is consistently higher than that for CeO$_2$, consistent with the higher oxygen surface vacancy maintained mostly throughout the conversion.

The lower initial surface Ce$^{3+}$ concentration at 900°C is expected for PCO, given the charge-compensating role of Pr$^{3+}$ for the oxygen vacancy formation, and thus relatively lesser Ce$^{3+}$ in bulk PCO (eq. (9.22)). The initial oxygen vacancy on the surface is slightly lower in PCO, which results from the slightly lower defect segregation effect (i.e., $\Delta H_f^0$ 97.7 kJ/mol for PCO v.s., 107.6 kJ/mol for CeO$_2$, see Table 9-4). The higher initial surface defect concentration in the case of CeO$_2$ contributes to much higher initial spikes of the reaction rates for the forward and backward R1 reactions, as observed in Figure 9-12 (a). Shortly after the initiation of reaction, the surface defects for PCO drops rapidly, with Ce$^{3+}$ quickly reaching zero and oxygen vacancy maintained at 10%. This is in contrast to CeO$_2$ in which the surface defects are consumed more mildly, and the conversion spans over a longer window, leading to slower reaction rates in the later stage as seen in Figure 9-12 (a).
At 600°C, on the other hand, the defect concentrations of PCO are significantly higher than the values of CeO$_2$ over the entire course of conversion, resulting from the “frozen” oxygen vacancy maintained with Pr$^{3+}$. The enhanced surface defects accelerate the adsorption process, as seen in Figure 9-12(b), leading to a quick saturation of OH$^-$ formation on the surface and the decay of the oxygen vacancy concentration below 10%. The enhanced adsorbate concentration on the surface further promotes the following charge transfer reaction, improving the splitting kinetics, as seen in Figure 9-12 (b). Similar observations are found for CO$_2$ splitting.

![Figure 9-11 Comparison of calculated surface species evolution at 900°C and 600°C for PCO (solid lines) and CeO$_2$ (dashed lines). Top panels show the evolution of OH$^-$.](image-url)
Comparison in Figure 9-11 and Figure 9-12 again highlights the influence of Pr dopant on the splitting processes: the trivalent Pr\(^{3+}\) maintains a large portion of oxygen vacancy regardless of temperature; it promotes the low temperature splitting performance at the cost of a lower oxygen carrying capacity at high temperature.

9.4 Summary

This chapter examines another option for promoting the splitting processes using ceria-based OCs. Here, the time-resolved reaction kinetics with Pr\(_{0.2}\)Ce\(_{0.8}\)O\(_2\) nanopowder is measured with either H\(_2\)O or CO\(_2\) as oxidizer and H\(_2\) as fuel, and the corresponding reaction mechanism is derived. Evident improvement is found for both H\(_2\)O and CO\(_2\) splitting as compared to pure ceria, in line with the high oxygen vacancy concentration maintained at low temperature. This improvement, however, comes at a price of a lowered oxygen carrying capacity, more significant.
at high temperature. The peak H₂O splitting rate is 44 μmole H₂ g⁻¹s⁻¹ at 600°C, twice that of CZO and about ten times faster than CeO₂. The peak rate with CO₂ at 600°C is 28.9 μmole g⁻¹s⁻¹.

The two-step kinetics model along the defect equilibrium is used to describe the redox process with H₂O or CO₂. Excellent agreement is found between the model predictions and the measurements. The charge transfer step is found to be analogous to CeO₂ or CZO, and it is the overall rate-limiting step. The adsorption step on the other hand is similar between H₂O and CO₂ cases. The defect formation enthalpy for PCO is comparable to that of CeO₂ within the range δ = 0.1 – 0.2. The modeling results demonstrate the effect of Pr dopant on the splitting processes: the trivalent Pr³⁺ maintains a large portion of oxygen vacancy regardless of temperature; it promotes the low temperature splitting performance but limits the oxygen carrying capacity at high temperature. This feature of PCO, along with (strain-related) structural relaxation of CZO, suggests potential directions for improving and optimizing ceria-based OCs for H₂O and CO₂ technologies.

9.5 Bibliography


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Chapter 10

Hydrogen and Syngas Co-Production with Ceria, Ceria Zirconia, and Praseodymium-doped ceria: Kinetics, Stability, and Carbon Formation

This chapter examines CH$_4$-fueled H$_2$O splitting for co-producing hydrogen and syngas. Three ceria-based OCs are tested, i.e., pure ceria (CeO$_2$), praseodymium-doped ceria (Pr$_{0.2}$Ce$_{0.8}$O$_2$) and ceria zirconia (Ce$_{0.5}$Zr$_{0.5}$O$_2$). Isothermal redox cycles are carried out in the temperature range 700-900°C following a two-step sequence: (1) the fresh sample is measured as temperature is ramped up from 700°C to 900°C with a step of 100°C, (2) after the measurements at 900 °C, the sample is cooled down to 700 °C with measurements repeated every 100 °C. We observe two major stages during reduction: the formation of the complete products, CO$_2$/H$_2$O, at the early stage of reduction on oxidized surface, and the formation of syngas species, CO/H$_2$, in the later stage on reduced surface with the onset of carbon deposition. Comparing the three OCs, we find that CZO produces the highest amount of H$_2$ with the best structural robustness, although it suffers from a lower syngas yield, an unfavorable syngas composition, and a higher carbon formation risk. PCO prevails in the syngas quality with less significant carbon formation; however the large oxygen vacancy renders it more prone to degradation. CeO$_2$ is highly resistant
to carbon formation, but it is less reactive with lower carrying capacity at low temperature. Compared to oxidation, reduction with CH₄ is kinetics-limited, and it constrains the oxygen non-stoichiometry for the splitting step.

The equilibrium, kinetics and the oxygen-ion incorporation mechanism developed in the previous chapters for the H₂O/CO₂ splitting processes are applied to characterize the redox reactivity. The H₂O splitting kinetics during both ramping-up and cooling-down steps is perfectly characterized based on the previously developed kinetics model. Particle enlargement is clearly observed, more evident at higher temperature with PCO or CeO₂. Based on the reduction characteristics, a reduction mechanism is proposed, which consists of two major reaction pathways characterized by the adsorption and activation sites: 1) Ce site on the oxidized surface, and 2) O-vacancy site on the reduced surface. Fitted results based on a set of simplified equations show qualitative agreement with the measurements for all the three OCs, although additional work is needed to examine the details within the reduction mechanism. From this chapter, we conclude that efforts in the OC design and optimization should focus on promoting the reduction kinetics with CH₄, mostly on accelerating the fuel cracking reactions.

10.1 Introduction

Previous chapters examined H₂O splitting kinetics using ceria-based OCs. The use of H₂ in the reduction step provides a simple and carbon-free reducing environment, and enables a quantitatively accurate characterization of defect equilibria. However, the application of CL H₂O splitting technology requires the use of hydrocarbon fuel, e.g., natural gas,

\[ \text{Reduction step with fuel: } \text{Me}_x\text{O}_y + \text{CH}_4 \rightarrow \text{Me}_x\text{O}_{y-1} + \text{CO} + 2\text{H}_2 \]  \hspace{1cm} (10.1)
Therefore, the overall process, combining reduction and oxidation, becomes methane reforming reaction. In the case of natural gas, the produced syngas stream with a $\text{H}_2:\text{CO}$ close to 2:1 is ideal for the production of $\text{H}_2$ (after shift), methanol, or liquid fuel via Fischer-Tropsch process with $\text{CO}_2$ separation. With the abundance and low price of natural gas, $\text{CH}_4$-reduced $\text{CL H}_2\text{O}$ splitting attracts great interests as a carbon-neutral hydrogen/syngas co-generation solution.

In this chapter, we examine the hydrogen and syngas co-production process using pure ceria ($\text{CeO}_2$), praseodymium-doped ceria ($\text{Pr}_{0.2}\text{Ce}_{0.8}\text{O}_2$) and ceria zirconia ($\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$). Isothermal redox cycles are carried out in a button cell reactor in the temperature range 700-900°C, with $\text{CH}_4$ (Ar balance) as a fuel. The equilibrium, kinetics and the oxygen-ion incorporation roadmap developed in the previous chapters for the $\text{H}_2\text{O}/\text{CO}_2$ splitting processes are applied to characterize the redox reactivity. The cyclic material stability and the carbon deposition issue are examined. Based on the kinetics, insights are gained on the design and optimization of OCs for $\text{CH}_4$-fueled $\text{CL H}_2\text{O}$ splitting.

10.2 Experimental Setup and Theoretical Methods

10.2.1 Sample characterization

Ceria, ceria-zirconia, and praseodymium-doped ceria nanopowders same as in Chapter 6-Chapter 9 are used here for the $\text{CH}_4$-fueled study. Table 10-1 summarizes key properties of the sample. Figure 10-1 compares the SEM images of fresh and redox cycled samples. Particle enlargement is observed for $\text{CeO}_2$ and $\text{Pr}_{0.2}\text{Ce}_{0.8}\text{O}_2$, with the former being more significant. In contrast, cycled $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ sample remains almost unchanged. The observations are analogous to those with $\text{H}_2$ as fuel in the previous chapters.
Table 10-1 Key physical properties of CeO$_2$, Ce$_{0.5}$Zr$_{0.5}$O$_2$, and Pr$_{0.2}$Ce$_{0.8}$O$_2$

<table>
<thead>
<tr>
<th>Property</th>
<th>CeO$_2$</th>
<th>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_2$</th>
<th>Pr$<em>{0.2}$Ce$</em>{0.8}$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample mass, $m$</td>
<td>100 mg</td>
<td>100 mg</td>
<td>100 mg</td>
</tr>
<tr>
<td>Density, $\rho$</td>
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<td>6.62 g cm$^{-3}$</td>
<td>7.22 g cm$^{-3}$</td>
</tr>
<tr>
<td>Molar density, $\tilde{\rho}_{i,v}$</td>
<td>$4.19 \times 10^4$ mol m$^{-3}$</td>
<td>$4.50 \times 10^4$ mol m$^{-3}$</td>
<td>$4.2 \times 10^4$ mol m$^{-3}$</td>
</tr>
<tr>
<td>Molar weight, MW</td>
<td>172.11 g mol$^{-1}$</td>
<td>147.66 g mol$^{-1}$</td>
<td>172.11 g mol$^{-1}$</td>
</tr>
<tr>
<td>Surface molar density, $\tilde{\rho}_{i,v,s}$</td>
<td>$2.3 \times 10^5$ mol m$^{-2}$</td>
<td>$2.4 \times 10^5$ mol m$^{-2}$</td>
<td>$2.3 \times 10^5$ mol m$^{-2}$</td>
</tr>
<tr>
<td>Particle size (fresh)</td>
<td>~50 nm</td>
<td>~24 nm</td>
<td>~40 nm</td>
</tr>
<tr>
<td>Particle size (tested)</td>
<td>~150 nm</td>
<td>~40 nm</td>
<td>~130 nm</td>
</tr>
</tbody>
</table>

* Note the particle size is estimated by averaging the diameter of 50 grains within the SEM image.

10.2.2 Redox kinetics measurement

100 mg of each sample is embedded in quartz wool and placed at the bottom of the outer quartz tube. The sample undergoes redox cycles with argon as purging gas flowing in between. 14% CH$_4$ (Ar balance) is used in reduction with the total flow rate at 350 sccm. Oxidation is carried out with 14.6% H$_2$O flowing at 363 sccm. The oxidation and reduction times are fixed at 3 min, and 4 min, respectively, with 5 min Ar purging in between. Fresh sample is heated to 700°C under H$_2$O environment. A two-step sequence is followed: (1) the fresh sample is measured as temperature is ramped up from 700°C to 900°C with a step of 100°C, (2) after the measurements at 900°C, the sample is then cooled down to 700°C with measurements repeated every 100°C. Each operating condition is repeated for six times, and the redox reactivity from the last three cycles is recorded and averaged to reduce noise.
Figure 10-1 SEM images of (a, b) CeO$_2$, (c, d) CZO, and (e, f) PCO. Left panels are the fresh samples, and right panels are the sample after (total 30) redox cycles.
The experimental protocol applied in this chapter does not require a cyclic regenerability at each temperature. Instead, we focus on the comparison of the reactivity during the ramping-up and cooling-down phases, thus probing the evolution of the particle dimension and its impact on the reactivity throughout the redox cycling. Given the higher defect concentrations and faster the ionic transport at high temperature, one can expect more dramatic sintering effects as temperature is raised. The largest degradation of the surface area is thus expected to occur during the six redox cycles at 900°C, and the further change during the cooling step is less significant. The size of particle listed in Table 10-1 thus corresponds to the states maintained during the cooling-down phase. Given the much fewer redox cycles applied in this study, the particle enlargement is less significant, as evident by comparing Table 10-1 to Table 6-1 and Table 9-2. The oxygen deficiency established after H$_2$O oxidation, determined by the defect equilibria as obtained in the previous chapters, is close to zero for pure CeO$_2$, at 0.1 for Pr$_{0.2}$Ce$_{0.8}$O$_2$. The oxygen deficiency for CZO after oxidation is estimated based on the equilibrium isotherms in Figure 7-9.

The reduction (oxygen removal) and oxidation (oxygen incorporation) rates during the redox steps are calculated by considering the element conservation as (see Chapter 2 for details),

$$\dot{\omega}_{\text{red}} = \frac{\dot{n}_m}{m_{oc}} \left( X_{out,CO} + 2X_{out,CO_2} + X_{out,H_2O} \right)$$

$$\dot{\omega}_{\text{ox}} = \frac{\dot{n}_m}{m_{oc}} \left( X_{out,H_2} - X_{out,CO} - 2X_{out,CO_2} \right)$$

where $\dot{n}_m$ is the intake molar flow rate, $\dot{\omega}_{\text{red}}$ and $\dot{\omega}_{\text{ox}}$ the reaction rates normalized by the sample mass, $m_{oc} = 100$mg. $X_i$ denotes the species mole fraction. Carbon formation is possible with the
feed of CH\textsubscript{4}. The terms, \(X_{\text{out,CO}}\) and \(X_{\text{out,CO}_2}\) for oxidation thus correspond to H\textsubscript{2} production originating from carbon gasification.

The carbon formation and gasification rates during the reduction and oxidation steps can be calculated as:

\[
\dot{N}_{C,\text{red}} = \frac{\dot{n}_{\text{in}}}{m_{\text{oc}}} \left( \frac{1}{2} X_{\text{H}_2,\text{out}} + \frac{1}{2} X_{\text{H}_2O,\text{out}} - X_{\text{CO,\text{out}}} - X_{\text{CO}_2,\text{out}} \right) \tag{10.4}
\]

\[
\dot{N}_{C,\text{ox}} = \frac{\dot{n}_{\text{in}}}{m_{\text{oc}}} (X_{\text{CO,\text{out}}} + X_{\text{CO}_2,\text{out}}) \tag{10.5}
\]

The production rate of syngas species, or CO\textsubscript{2}/H\textsubscript{2}O, is calculated as:

\[
\dot{\omega}_i = \frac{\dot{n}_{\text{in}}}{m_{\text{oc}}} X_{\text{out},i}, \ i = \text{CO, H}_2, \text{CO}_2, \text{H}_2O \tag{10.6}
\]

10.3 Experimental Results

10.3.1 Redox measurements with CeO\textsubscript{2}

Figure 10-2 shows the measurement with CeO\textsubscript{2} at 900\textdegree C. The profiles of oxidation are similar to the measurements shown in Chapter 6. Reduction, on the other hand, is noticeably slower. The peak rate with CH\textsubscript{4} is less than 15 \(\mu\text{mole} \ g^{-1} \ s^{-1}\), as seen in panel (e), in comparison to over 50 \(\mu\text{mole} \ g^{-1} \ s^{-1}\) reached in the H\textsubscript{2}-reduced study. The overall oxygen deficiency created after the 4 min reduction period reaches over 0.323, which, however, almost doubles that established in the H\textsubscript{2} case (i.e., \(\delta = 0.179\)). This comparison clearly demonstrates that reduction with CH\textsubscript{4} is kinetics constrained even at 900\textdegree C.
Figure 10-2 Redox measurements for CeO$_2$ at 900°C. (a, d) measured species, (b, e) reaction rates, and (c, f) evolution of oxygen nonstoichiometry. Left panels show the oxidation results, while right panels are for reduction. For clarity, CH$_4$ concentration (14%) in panel (d) is not shown. Carbon production/removal rates are also included in the middle panels. The initial nonstoichiometry in oxidation is from the end of the reduction step.

The species evolution plotted in panel (d) illustrates several interesting features. Complete products, i.e., CO$_2$ and H$_2$O, are produced only at the very beginning part of the step, and decay rapidly. The production of syngas, i.e., H$_2$ and CO, however, rises very slowly, and continues towards the end of reduction. As a result, the profile of oxygen nonstoichiometry in panel (f) shows almost a linear, although slightly accelerating, pattern with time. The formation of complete products during the initial stage contributes to the small peak of the reduction rate in panel (e), while the slow increase of the rate in the later stage is attributed to continuous syngas production. The ratio between formed H$_2$ and CO is 2:1 throughout the entire range; hence the
carbon formation is negligible based on eq. (10.4), as evident in panel (e). Consequently, no CO or CO₂ is observed in the following oxidation step, demonstrating the perfect carbon resisting characteristics of the un-doped ceria.

Figure 10-3 Effect of reduction time. (a) Measured species concentration, (b) reaction rates, and (c) evolution of oxygen nonstoichiometry.

Given the continuously rising rate profiles in the reduction step, it is interesting to examine the reduction kinetics after the 4 min mark. Figure 10-3 plots a separate measurement with a 6 min reduction (starting with fresh samples following the same measurement protocol). The measurements completely overlap with the base case during the initial 4 min, indicating a reversible process with the additional 2 min reduction. After 4 min, both H₂ and CO
concentration decreases, leading to the decay of the reduction rate in panel (b). The observed rise-decay pattern of the syngas production rates suggests that the kinetics pathways involve coupled interactions with oxygen vacancy as well as the available lattice oxygen ions. Carbon formation is clearly observed during the decay stage ($t > 4\text{min}$). Thus, for $\text{H}_2$ production purpose, a 4 min reduction is preferred to avoid any carbon deposition.

Based on the kinetics limitation observed in the reduction step at 900°C, one can expect significant temperature dependence on the splitting kinetics, and hence a much lower reactivity and yield at low temperature, as seen in Figure 10-4. The peak $\text{H}_2\text{O}$ splitting rate at 900°C is 178 $\mu$mole g$^{-1}$s$^{-1}$, significantly higher as compared to the case with $\text{H}_2$ as fuel (cf. Figure 6-5), resulting from the large oxygen non-stoichiometry. At 800°C, however, the rate becomes much lower, due to the insufficient oxygen deficiency created in the reduction step. As seen in panel (b), the reduction step, on the other hand, is consistently slower with $\text{CH}_4$ than that with $\text{H}_2$. As seen in panel (c), the evolved $\text{H}_2$/CO has a ratio close to 2:1, ideal for liquid fuel production via Fischer-Tropsch process. The produced $\text{H}_2\text{O}/\text{CO}_2$ consumes some of lattice oxygen, leading to a slightly lower syngas production amount as compared to the value determined from the oxygen intake amount during oxidation.

Comparison with $\text{H}_2$-fueled $\text{H}_2\text{O}$ splitting is further shown in Figure 10-5. The trend of the peak rate with temperature agrees well with the non-stoichiometry created during reduction, indicating the important role of the initial oxygen deficiency on the splitting kinetics. The non-stoichiometry created with $\text{CH}_4$ reduction at 900°C reaches over 0.3, exceeding the maximum value reached with $\text{H}_2$, as illustrated in Chapter 9 (see Figure 9-7). The value is even higher than
the phase range of the fluorite-related structure (α phase of pure ceria has range δ<0.286 [1]), indicating possible phase change near the later stage of the reduction process. Despite the large variation of the non-stoichiometry, oxygen is precisely balanced between the fuel reduction step and the oxidation step, demonstrating the reversibility in the oxygen exchange process. Fewer cycles are measured in this chapter, as compared to H₂-fueled measurements, leading to a less significant size enlargement, as shown in Table 10-1. This is also expected to contribute to the enhanced H₂ rate at high temperature, as will be addressed in kinetics modeling in Section 10.4.

Figure 10-4 Effect of temperature on H₂/syn-gas production with CeO₂. (a) H₂ production during oxidation, (b) H₂ production during reduction, and (c) comparison of total yield. The measurements here correspond to the cooling-down step.
Figure 10-5 Comparison between H₂-reduced and CH₄-reduced H₂O splitting for CeO₂. Panel (a) compares the peak rates, and panel (b) shows the oxygen non-stoichiometry after reduction. Note the H₂O splitting rates in panel (a) are converted from 26mol% H₂O to 14.6mol% H₂O using a linear dependence, as validated in Chapter 6. The measurements here correspond to the cooling-down step.

To illustrate the effect of redox cycling on kinetics, we compare the measured redox reactivities between the ramping-up and the cooling-down steps in Figure 10-6. As showed in panel (a), the H₂O splitting rate is significantly slower during the cooling-down period as compared to the heating-up step. The difference is partially attributed to the larger particle size with lower surface area after being exposed to redox treatment at 900°C. The slow reduction rate, on the other hand, constrains the oxygen non-stoichiometry, which further limits the H₂O splitting kinetics. The effects of these two factors, i.e., surface area and the oxygen deficiency, are taken into account in the kinetics modeling in the next section.
10.3.2 Redox measurements with Pr$_{0.2}$Ce$_{0.8}$O$_2$

From the last chapter, it was concluded that the effect of Pr as dopant is mostly charge-related: Pr$^{3+}$ maintains a large portion of oxygen vacancy within the range of CL condition, hence promoting the adsorption and activation of gaseous reactants. Its effect on the CH$_4$ reduction step is examined in this section.
Figure 10-7 Redox measurements for PCO at 900°C. (a, d) measured species, (b, e) reaction rates, and (c, f) evolution of oxygen nonstoichiometry. Left panels show the oxidation results, while right panels are for reduction. For clarity, CH₄ concentration (14%) in panel (d) is not shown. Carbon production/removal rates are also included in the middle panels. The initial non-stoichiometry in oxidation is taken from the end of the reduction step.

Figure 10-7 shows the measurements at 900°C. The most distinctive feature as compared to Figure 10-2 is that the syngas production kinetics is significantly enhanced with the peak reached at \( t = 0.5 \) min. Therefore, the reduction rate (panel (e)) exhibits a single peak at the beginning, in contrast to the two peaks observed in Figure 10-2(e). The conversion pattern in panel (f) follows a concave shape, in contrast to the linear increase seen in Figure 10-2(f). More significant carbon formation is observed with PCO, which is then removed in the later stage of oxidation. Despite a
few differences, comparison with CeO$_2$ reveals many more similarities. Both redox steps follow similar trends: oxidation peaks with the intake of H$_2$O and decays rapidly with the consumption of vacancies; reduction starts with the minor formation of CO$_2$ and H$_2$O, followed by the rise of syngas. The peak of the syngas production roughly corresponds to an oxygen deficiency around 0.25 in both cases. As a result, the high deficiency maintained initially with PCO effectively expedites the reduction process. Carbon formation initiates with $\delta$ approximately at 0.3, similarly as shown in Figure 10-3. Interestingly, these critical values for oxygen deficiency are close to the beginning of phase change from the cubic fluorite structure, $\delta$~0.286 [1]. The maximum oxygen non-stoichiometry reached with PCO is around 0.45, well above the phase transition threshold, although a complete re-oxidation (to $\delta$ = 0.1) is achieved within 1 min.

The redox reactivity at different temperature is shown in Figure 10-8. Similarly as with CeO$_2$, a significant drop in the H$_2$O splitting kinetics is observed as temperature decreases from 900°C to 800°C. The measurements at 850°C are also included to clarify the transition. Compared to 900°C, the reduction step at 850°C or lower temperature is much slower with the peak delayed. Comparison between the ramping-up and cooling-down steps is shown in Figure 10-9. The difference is significant at 800°C, with the peak H$_2$ rate during the ramping-up step almost the same as that at 900°C, doubling the value from the ramping-down step.
Figure 10-8 Effect of temperature on H₂/syn-gas production for PCO. (a) H₂ production during oxidation, (b) H₂ production during reduction, and (c) comparison of total yield. The measurements here correspond to the cooling-down step.
10.3.3 Redox measurements with Ce$_{0.5}$Zr$_{0.5}$O$_2$

The addition of Zr leads to significant reduction of the defect formation enthalpy, hence promoting the reduction kinetics. On the other hand, the substitution of Ce by Zr deactivates oxygen and constrains the non-stoichiometric capability. The redox reactions with Ce$_{0.5}$Zr$_{0.5}$O$_2$ for CH$_4$-fueled CL H$_2$O splitting are examined in this sub-section.

Figure 10-10 shows the redox measurements with CZO at 900°C. Compared to CeO$_2$ or PCO, the use of CZO significantly promotes the production of complete products during reduction, CO$_2$/H$_2$O, consistent with the much improved reducibility and hence H$_2$O/CO$_2$ formation energetics, as seen in Figure 9-9. As a result, a spike of the oxygen removal rate is seen with the
intake of CH$_4$ during reduction. The onset of syngas production is similar as with other two OCs
with the initial peak around $\delta \sim 0.12$, corresponds to 25% oxygen deficiency in the CeO$_2$ portion,
similarly as in the case of CeO$_2$ or Ce$_{0.5}$Zr$_{0.5}$O$_2$. However, significant carbon formation is
observed starting at 1 min. As a result, a significant portion of carbon from CH$_4$ is deposited on
the OC, leading to a much higher H$_2$:CO ratio. The initiation of carbon formation occurs as $\delta$
exceeds 0.15, accounting for a deficiency of 0.3 in CeO$_2$ portion, similarly as with the PCO case.
The formed carbon is then gasified in the later stage of the oxidation step to form CO$_2$ and
additional H$_2$, i.e., C + H$_2$O $\rightarrow$ H$_2$ + CO$_2$. A minor amount of CO is also observed during this
stage. During the redox steps, the OC cycles with the oxygen deficiency ranging from about
0.035 after oxidation to an almost complete reduction, i.e., 0.25, after reduction. The non-
stoichiometry reached after oxidation agrees with the defect equilibria isotherms obtained in
Chapter 7.

To further understand the carbon formation and its looping within the redox steps, we plot the
carbon evolution as a function of the oxygen deficiency in Figure 10-11. Evidently, carbon
formation initiates at large non-stoichiometry and ceases at complete reduction. This observation
here highlights the two critical prerequisites for carbon formation on ceria-based OCs: the
presence of vacancy, V$_{\text{O}}^-$ and depletion of available oxygen, O$_{\text{O}}^\circ$. Reduction with CeO$_2$ shows a
minimum carbon formation, owing to the least oxygen vacancy ($\delta$<0.33), and hence highest
availability of regular oxygen. The higher vacancy concentration in PCO results in a minor
carbon deposition issue in the later stage of reduction. In comparison, CZO exhibits the most
severe carbon issue, consistent with its exceptional reducibility. The carbon gasification in the
oxidation step does not occur until the most of the vacancy is refilled with oxygen ions, likely
suggesting that the formed carbon may occupy the oxygen vacancy and hence the gasification kinetics lags behind in the re-oxidation step. Nevertheless, the oxidation kinetics in the presence of deposited carbon can be well characterized by the previous developed kinetics model, as will be shown in the next section. The gasification reaction is less favored as compared to the ion-incorporation reaction, and hence it becomes important only near the end of oxidation.

Figure 10-10 Redox measurements for CZO at 900°C. (a, d) measured species, (b, e) reaction rates, and (c, f) evolution of oxygen nonstoichiometry. Left panels show the oxidation results, while right panels are for reduction. For clarity, CH\textsubscript{4} concentration (14%) in panel (d) is not shown. Carbon production/removal rates are also included in the middle panels. The initial non-stoichiometry in oxidation is from the end of the reduction step. The initial state in reduction is estimated from the defect equilibria isotherm in Chapter 7.
Figure 10-11 Evolution of carbon during the reduction and oxidation steps. Solid line (positive) is the production rate of carbon during reduction, and dashed line (negative) is the consumption rate of carbon during oxidation.

The effect of temperature is examined in Figure 10-12. The different H₂ production curves at 900°C result from the carbon formation effect. As seen in panel (c), carbon formation is negligible at 800°C or lower temperature. Thus, the H₂ production rate in redox steps at lower temperature is analogous to the cases of PCO or CeO₂. The syngas composition obtained at 900°C deviates from 2:1. The produced H₂ from oxidation step exceeds that from reduction, because of the formation of significant amount of CO₂ and CO. Figure 10-13 further illustrates the H₂:CO ratio and the syngas yield as a function of oxygen deficiency. The syngas yield for H₂ or CO is defined as:

\[
\text{H}_2 \text{ yield} = \frac{\text{H}_2}{(\text{H}_2 + \text{H}_2\text{O})}, \quad \text{CO yield} = \frac{\text{CO}}{(\text{CO} + \text{CO}_2)}
\]  

(10.7)

From Figure 10-13, it is observed that reduction at low δ suffers from a low syngas yield, while high δ leads to unfavorable syngas composition with carbon formation. An optimal range that
ensures the yield and composition is around $\delta \sim 0.15$ for CZO, which however constrains the overall oxygen carrying capacity.

Figure 10-12 Effect of temperature on $\text{H}_2$/syn-gas production for CZO. (a) $\text{H}_2$ production during oxidation, (b) $\text{H}_2$ production during reduction, and (c) comparison of total yield. Carbon formation is also included in panel (c).

The use of Zr is proven to enhance the cyclic repeatability with minimum structural changes. This is again confirmed by comparing the redox rates during the ramping-up and cooling-down steps, as shown in Figure 10-14. The measurements almost overlap, although slight degradation is observed, consistent with the minor enlargement of the particle after redox cycling.
Figure 10-13 (a) Syngas composition and (b) H₂, CO yield with CZO at 900°C and 800°C for CZO

Figure 10-14 Effect of redox cycling on reactivity for CZO. Comparison of (a, b) H₂ production rates, (c) peak rate, and (d) change of oxygen deficiency, between ramping-up and cooling-down steps. Note, the scales between panels (a) and (b) are different for clarity.

10.3.4 Comparison of redox kinetics among different OCs
An overall summary of the key measurements for the three ceria-based OCs is listed in Table 10-2. The peak $\text{H}_2$ production rates during the reduction and oxidation steps are compared in Figure 10-15. From the comparison, we observe that CZO produces the highest amount of $\text{H}_2$ with the most robust resistance to redox cycling, although it suffers from a lower syngas yield, an unfavorable syngas composition, and higher carbon formation risk. PCO prevails in the syngas quality with less significant carbon formation; however the large oxygen vacancy renders it more prone to degradation. $\text{CeO}_2$ is highly resistant to carbon formation, but it is less reactive with lower carrying capacity at low temperature.

Compared to $\text{H}_2$ cases (cf. Figure 9-7), $\text{CH}_4$-fueled reduction reaches a larger oxygen non-stoichiometry. However, the reduction kinetics is significantly slower, and it is the rate-limiting step for the overall $\text{H}_2\text{O}$ splitting kinetics. Promoting the reduction kinetics with $\text{CH}_4$ will be the focus for the future study (next chapter briefly discusses various options).

### Table 10-2 Summary of redox results with ceria-based materials

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<tr>
<th></th>
<th>$\text{H}_2$ (ox)</th>
<th>$\text{H}_2$ (red)</th>
<th>carbon prod.</th>
<th>$\text{H}_2$/CO</th>
<th>$\text{H}_2$ yield</th>
<th>$\text{CO}$ yield</th>
<th>$\Delta \delta$</th>
<th>Repeatability</th>
</tr>
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<tr>
<td></td>
<td>unit: μmole/gram sample</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CeO}_2$</td>
<td>700°C 162 216 trace</td>
<td>trace</td>
<td>5.0</td>
<td>80%</td>
<td>89%</td>
<td>0.015</td>
<td>-57%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800°C 405 528 trace</td>
<td>trace</td>
<td>2.25</td>
<td>88%</td>
<td>97%</td>
<td>0.058</td>
<td>-34%</td>
<td></td>
</tr>
<tr>
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<td>95%</td>
<td>98%</td>
<td>0.323</td>
<td>-</td>
<td></td>
</tr>
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<td>$\text{PCO}$</td>
<td>700°C 141 135 trace</td>
<td>trace</td>
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<td>63%</td>
<td>77%</td>
<td>0.019</td>
<td>-17%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800°C 629 916 trace</td>
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<td>91%</td>
<td>0.099</td>
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<td></td>
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<tr>
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<td>900°C 2342 4058 154</td>
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<td>98%</td>
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<td>-</td>
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</tr>
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<td>$\text{CZO}$</td>
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<td>trace</td>
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<td>32%</td>
<td>0.066</td>
<td>-21%</td>
<td></td>
</tr>
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<td></td>
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<td>trace</td>
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<td>0.162</td>
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<td></td>
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<td>97%</td>
<td>92%</td>
<td>0.215</td>
<td>-</td>
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</table>

* Results during cooling-down period; trace value correspond to production less than 100 μmole/gram OC. The $\text{H}_2$/CO ratio at 700°C is less certain, because of lower signal-to-noise ratio; repeatability is calculated by comparing the peak $\text{H}_2$ rate from $\text{H}_2\text{O}$ splitting during the ramping-up and cooling-down steps.
Figure 10-15 Comparison of the peak reduction (eq. (10.2)) or oxidation rate (eq. (10.3)). Dashed lines are reduction, and solid lines are oxidation.

The redox measurements with the three OCs share some common features, while each of them processes some unique characteristics. By comparing these features and combining the conclusions from the previous chapters, we attempt to probe the reduction mechanism with CH₄ as a fuel. The key points from this section are summarized below:

1) Reduction using ceria-based OCs initiates with formation of complete products, the amount of which is related to the reducibility of the OCs. Pure CeO₂ is most difficult to reduce, thus it provides a better yield of syngas, as compared to CZO.

2) The production of syngas in reduction slightly lags behind. Its kinetics rises and decays, in line with the creation of oxygen deficiency and the depletion of the available oxygen. The peak roughly corresponds to δ ~ 0.25, analogous among the three OCs. The higher
defect concentration in the case of CZO or PCO thus advances the occurrence of the peak of syngas production rates.

3) The carbon formation follows the syngas production, and it occurs as the majority of the lattice oxygen is removed. The formed carbon can be completely gasified in the later stage of oxidation.

4) The effects of the redox cycling are mainly two-fold: i) larger particle with smaller surface area hinders the surface chemistry; ii) the slower reduction kinetics constrains the non-stoichiometry created after reduction, which further slows the splitting kinetics.

10.4 Kinetics Modeling

10.4.1 Oxidation

Modeling of the oxidation kinetics follows the exact same method as detailed in the previous chapters (see Chapter 9, eqs. (9.1) – (9.12)), with the kinetic and defect equilibrium parameters directly applied. The particle size during the cooling-down step is assumed to remain unchanged, as determined from the SEM images in Figure 10-1 (see Table 10-1). The oxygen deficiency after the reduction step is taken as the initial value for oxidation. The predicted oxidation rates (eq. (10.3)) are shown in Figure 10-16, Figure 10-17, and Figure 10-18, for CeO$_2$, PCO, and CZO, respectively. The model predictions perfectly agree with the measurements for all the three OCs, demonstrating the validity of the modeling framework developed in this thesis. The agreement here also suggests that despite the much larger non-stoichiometry established at 900°C in the cases of CeO$_2$ and PCO, the oxidation process is well-characterized by the same defect chemistry. The results with CZO also indicate that the oxygen incorporation kinetics is independent of the formed carbon on the OC surface from the reduction step.
Figure 10-16 Comparison between modeling results (lines) and measurements (circles) for oxidation with CeO₂

Figure 10-17 Comparison between modeling results (lines) and measurements (circles) for oxidation with PCO
During the ramping-up step, the particle size enlarges, resulting from the thermal sintering and chemical stresses. As pointed out in the last section, the effects on the kinetics are related to the differences in the surface area and the non-stoichiometry created during the reduction step. Thus, to model the oxidation kinetics during the ramping-up step, we allow the particle size to vary. The modeling results are shown in Figure 10-19, and quantitative agreement is again achieved. The obtained evolution of particle sizes is listed in Table 10-3. The particle size enlarges through redox cycling. For CeO$_2$ or PCO, the enlargement is more significantly at higher temperature, and the magnitude of change is comparable. In contrast, CZO mostly maintains its original dimension, although slightly size enlargement is seen around 800°C.

<table>
<thead>
<tr>
<th></th>
<th>Fresh</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>50 nm</td>
<td>80 nm</td>
<td>100 nm</td>
<td>150 nm</td>
</tr>
<tr>
<td>Pr$<em>{0.2}$ Ce$</em>{0.8}$ O$_2$</td>
<td>40 nm</td>
<td>50 nm</td>
<td>80 nm</td>
<td>130 nm</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$ Zr$</em>{0.5}$ O$_2$</td>
<td>24 nm</td>
<td>25 nm</td>
<td>35 nm</td>
<td>40 nm</td>
</tr>
</tbody>
</table>
Figure 10-19 Comparison of oxidation kinetics during the ramping-up step between modeling predictions (lines) and measurements (circles) for CeO$_2$ (upper panels), PCO (middle panels), and CZO (bottom panels).
10.4.2 Reduction with CH₄

Reduction with CH₄ is highly complicated with many more steps involved. Identification of each elementary step and mapping out the entire reaction roadmap require much more efforts in elucidating the contribution from each individual reaction pathway. This sub-section makes an attempt to explore the most important reduction pathways based on the observations from the last section. Instead of expressing the reaction pathway as a collection of true elementary steps, I present here simplified electrochemical reactions, focusing on the evolutoinal trace of products, i.e., CO₂/H₂O, CO/H₂, and carbon. The division of the reaction steps is arbitrary to some extent, which does not necessarily represent the most stable forms of the minority species.

The observation from the last section clearly identifies the two major stages along the reduction conversion: (1) the formation of the complete products, CO₂/H₂O, at the early stage of reduction on oxidized surface; and (2) the formation of syngas species, CO/H₂, in the later stage on reduced surface with the onset of carbon formation. Therefore, we propose that there exist at least two major pathways, the importance of which relies on the oxidation state of the surface and the sites of adsorption [2]: 1) Ce site on the oxidized surface, and 2) O-vacancy site on the reduced surface. Comparing among the three OCs, it is obvious that the role of surface defects is critical in determining the length or the strength of each stage. Figure 10-20 and Figure 10-21 schematically illustrate the two pathways.
Reduction on oxidized surface

On the oxidized surface, CH$_4$ plays an analogous role as H$_2$ in the H$_2$-fueled reduction case. The adsorption and activation of CH$_4$ is analogous to R2 backward (eq. (6.7)) (see top panels in Figure 10-20):

R3, fuel cracking:

$$\text{CH}_4 (g) + 4\text{Ce}^+_\text{Ce} + 4\text{O}^-_\text{O} \rightarrow \text{C} + 4\text{OH}^-_\text{O} + 4\text{Ce}^+_\text{Ce} \quad (10.8)$$

R3 involves breaking up 4 C-H bonds. The dissociated protons attach oxygen anions forming hydroxyls. The process is accompanied by the transfer of electrons from CH$_4$ to Ce$^{4+}$ cations forming polarons, Ce$^{3+}$. The produced hydroxyls, OH$^-_\text{O}$, then proceed via R1 backward (see eq. (6.6)) to form H$_2$O as (see bottom panels in Figure 10-20):

R1 backward:

$$2\text{OH}^-_\text{O}(s) \rightarrow \text{H}_2\text{O}(g) + \text{V}^+_\text{V}(s) + \text{O}^-_\text{O}(s) \quad (10.9)$$

On the other hand, hydroxyls may also recombine to produce H$_2$ via R2 forward reaction (eq. (6.7)), as seen in the middle panels in Figure 10-20,

R2:

$$2\text{OH}^-_\text{O}(s) + 2\text{Ce}^+_\text{Ce}(s) \xrightleftharpoons[k_{-2}]{k_{+2}} 2\text{O}^-_\text{O}(s) + 2\text{Ce}^+_\text{Ce}(s) + \text{H}_2(g) \quad (10.10)$$

Dissociated carbon forms bond with oxygen, thus producing CO, via:

R4:

$$\text{C} + \text{O}^-_\text{O} + 2\text{Ce}^+_\text{Ce} \rightarrow \text{CO}(g) + \text{V}^+_\text{V} + 2\text{Ce}^+_\text{Ce} \quad (10.11)$$

The formed CO can further adsorb on the oxygen site, following the backward reactions as in the CO$_2$ splitting mechanism, i.e., eqs. (8.13) and (8.15), to produce CO$_2$.

The schematic drawing of this pathway is shown in Figure 10-20. It is evident that the fuel cracking reaction, R3, is the prerequisite for the subsequent CO$_2$/H$_2$O production. As compared to H$_2$-fueled cases, the slower reduction kinetics observed in the Section 10.3 indicates that the fuel cracking reaction, R3, is the rate limiting step during CH$_4$-fueled reduction. The formation
of hydroxyls via R3 requires 4 $O_0$ and 4 $Ce_c^{\circ}$; therefore the reaction rate of R3 is only significant at the very beginning of reduction, then significantly attenuated with the creation of surface defects. This is consistent with the observations in Figure 10-2, Figure 10-7, and Figure 10-10.

![Schematic of CH₄ reduction pathway over the oxidized surface.](image)

Figure 10-20 Schematics of the CH₄ reduction pathway over the oxidized surface. R1 backward is denoted as R1'.

**Reduction on reduced surface**

As the surface becomes more reduced with less available lattice oxygen, the further break-down of CH₄ molecules into hydroxyls via R3 (which requires 4 $O_0$ and 4 $Ce_c^{\circ}$) becomes limited. Reduction then transitions to a second stage, in which CH₄ adsorbs and activates over vacancies, similarly as H₂O during the oxidation step (see Figure 10-21):  

$$R5: CH_4 + V_o^{\bullet\bullet} + O_0^* = (CH_3)_o + OH_0^* \quad (10.12)$$
R5 describes the adsorption of CH$_4$ on a surface vacancy with the formation of one hydroxyl.

The H$_2$ formation process starts with the protons breaking up from the (CH$_3$)$_o^*$ and OH$_o^*$ radicals, recombining into H$_2$ with the transfer of two electrons, as:

\[
R6: \ (CH_3)_o^* + OH_o^* + 2Ce_{ce}^* = (CH_2)_o^* + 2Ce_{ce}^* + O_o^* + H_2 \tag{10.13}
\]

R6 frees the oxygen anion utilized in R5, hence leading to the formation of a second hydroxyl:

\[
R7: \ (CH_2)_o + O_o^* = (CH)_o + OH_o^* \tag{10.14}
\]

R7 is then followed by a second proton recombination reaction, as:

\[
R8: \ (CH)_o + OH_o^* + 2Ce_{ce}^* = CO^* + 2Ce_{ce}^* + O_o^* + H_2 \tag{10.15}
\]

After R5-R8, two H$_2$ are formed with carbon left on the vacancy. The formed carbon is then bound onto the oxygen anion to form CO, as:

\[
R9: \ CO^* + O_o^* + 6Ce_{ce}^* = CO + 2V_{O}^{***} + 6Ce_{ce}^* \tag{10.16}
\]

Unlike the first pathway, breaking-up of C-H bonds over the reduced surface only requires one oxygen anion: it remains as a catalytic site for R5-R8, and its consumption only occurs as CO is formed through R9. However, the presence of defects during this process is critical: adsorption of CH$_4$ occupies one oxygen vacancy, and the following charge transfer steps consume 4 electrons. Therefore the reduction rate via R5-R8 is slow initially on the oxidized surface, and accelerates significantly as more surface defects are created. This is consistent with the observations in the last section. The slowly accelerating reduction kinetics during the second stage also suggests that breaking-up CH$_4$ is most likely the rate-limiting process as well.
The removal of carbon via R9 consumes 6 regular Ce\(^{4+}\) sites, 4 of which are produced from the charge-transfer process during R6 and R8. Thus, R9 eventually ceases as all Ce\(^{4+}\) is reduced to Ce\(^{3+}\), leaving carbon saturating a significant portion of the surface vacancies. The depletion of lattice oxygen constrains the further adsorption and activation of CH\(_4\), eventually leading to the termination of the second reduction pathway.

The formed carbon on the vacancy sites is then oxidized in the later stage of the oxidation step, as observed in Section 10.3.

![Figure 10-21 Schematics of the CH\(_4\) reduction pathway over the reduced surface](image)

**Simplification and modeling framework**

Modeling the reduction process with the three pathways requires the knowledge of each elementary step, which is yet unavailable. In an attempt to qualitatively characterize the reduction process without fitting nearly 30 unknown parameters (i.e., \(k_i, E_i\) for each reaction), we simplify the description of the two reduction pathways based on the following assumptions:

1) Reactions are assumed to be irreversible with only the forward reaction being considered; the rate is assumed to follow the law of mass action;
2) The minority hydrocarbon radicals, i.e., \((CH_n)_{O}^\prime\) in R5-R8, remain a quasi-steady state;

3) The formed carbon via R3 is directly converted to CO through R4, while R9 is the major mechanism for the carbon deposition in the later stage of reduction;

4) Other possible reduction pathways (i.e., variations of charge transfer sequences, simultaneous C-H breaking-up, etc.) are not included;

5) Kinetics derived for the H_2O or CO_2 splitting cases from the previous chapters are included and the parameters are kept constant.

With assumption 3), the reaction rates of R3 and R4 via the first pathway are equal, and they are expressed as:

\[
\begin{align*}
  r_3 &= r_4 = k_3 p_{CH_4} [Ce_{ce}^*] [O_0^*]^4 \\
  &= r_4 = k_3 p_{CH_4} [V_0^{**}] [O_0^*] \tag{10.17}
\end{align*}
\]

Similarly, with assumption 2), the reaction rates of R5, R6, R7, and R8 are identical:

\[
\begin{align*}
  r_5 &= r_6 = r_7 = r_8 = k_5 p_{CH_4} [V_0^{**}] [O_0^*] \tag{10.18}
\end{align*}
\]

The reaction rate for R9 is:

\[
\begin{align*}
  r_9 &= k_9 [C_{O}^*] [O_0^*] [Ce_{ce}^*] \tag{10.19}
\end{align*}
\]

Therefore, the governing equations for key species are:

**Bulk vacancy:**

\[
\frac{d}{dt} \left( \rho V_r \left[ V_0^{**} \right] \right) = S_r \rho_r \left( -r_{1, H_2O} - r_{1, CO_2} + r_4 - r_5 + 2r_9 \right) \tag{10.20}
\]

**Hydroxyls:**

\[
\frac{d}{dt} \left[ OH_0^* \right] = \rho_s \left( 2r_{1, H_2O} - 2r_{2, H_2O} + 4r_3 \right) \tag{10.21}
\]

**Carbonates:**

\[
\frac{d}{dt} \left[ (CO_3)_O^* \right] = \rho_s \left( r_{1, CO_2} - r_{2, CO_3} \right) \tag{10.22}
\]

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Deposition carbon, $C'_0$

$$\tilde{\rho}_s \frac{d[C'_0]}{dt} = \tilde{\rho}_s (r_8 - r_9) \quad (10.23)$$

In eqs. (10.20)-(10.22), $\tilde{\rho}_s$, $\tilde{\rho}_s$, $S_R$, and $V_R$ are the molar density, surface molar density, surface area, and particle volume. $r_{i,\text{H}_2\text{O}}$ and $r_{i,\text{CO}_2}$ are the reaction rate for the H$_2$O or CO$_2$ splitting steps, as expressed in eqs. (6.8), (6.9), (8.14), and (8.16). The above equations are further coupled with the bulk-to-surface transport equilibrium, as described by eqs. (6.34) and (6.35). The rest of the species can be calculated based on the conservation equations:

O-site:

$$[V'_{O \cdot}]_s + [OH'_{O \cdot}]_s + [O'_{O \cdot}]_s + 2\left[CO^{2-}_{\cdot}\right] + [C'_O]_s = 2 \quad (10.24)$$

Ce-site:

$$[\text{Ce'}_s]_s + [\text{Ce}_{\cdot s}]_s = 1 \text{ (CeO}_2), \ 0.8 \text{ (PCO), or 0.5 (CZO)} \quad (10.25)$$

Electroneutrality:

$$2[V'_{O \cdot}]_s + [OH'_{O \cdot}]_s + 2\left[CO^{2-}_{\cdot}\right] = [\text{Ce'}_s]_s + 2[C'_O]_s + [Pr'_{\cdot}]_s \quad (10.26)$$

Therefore, eqs. (10.20)-(10.26) complete the description of the reduction processes. Kinetic parameters to be fitted are $k_3,0$, $E_3$, $k_5,0$, $E_5$, $k_9,0$, and $E_9$. With the measured CH$_4$ partial pressure in QMS, the entire conversion can be simulated. The partial pressure of other species, i.e., CO$_2$, CO, H$_2$, H$_2$O, is calculated by considering the mass-balance within the reaction zone (control volume in Figure 2-7(a)), as, $\dot{\omega}_j = \dot{s}\tilde{\rho}_s \sum v_{i,j} r_i = p_{CO} \dot{n}_{red} / m_{(\text{cell})}$, where $\dot{s}$ and $v_{i,j}$ are the specific surface area, and the stoichiometry coefficient for the species $j$ in reaction $i$. The kinetic parameters for each OC are obtained by minimizing the difference between the model predictions and the measurements, following a similar numerical procedure as detailed in Chapter 6.
**Reduction modeling results**

The kinetic parameters are summarized in Table 10-4. Comparison between the model predictions and the measurements are shown in Figure 10-22-Figure 10-24. Qualitative agreement is obtained for all the product species, i.e., CO₂, H₂O, CO, and H₂, indicating that the proposed reduction mechanism captures the critical steps of the reduction processes. Nevertheless, evident discrepancy is observed on the H₂ evolution during the beginning stage of CeO₂ reduction at 900°C, which is likely attributed to possible direct interactions between CHₙ radicals during the first pathway (on oxidized surface). The rise-decay curves of H₂ in Figure 10-23 and Figure 10-24 also show some deviation from measurements, indicating that additional modeling details may be considered to more accurately represent the carbon formation dynamics during the second pathway.

![Graphs showing reduction modeling results](image-url)

Figure 10-22 Comparison of model predictions (lines) and measurements (cycles) for CeO₂
Figure 10-23 Comparison of model predictions (lines) and measurements (cycles) for PCO

Figure 10-24 Comparison of model predictions (lines) and measurements (cycles) for CZO
Table 10-4 Kinetic parameters for reduction with CH₄

<table>
<thead>
<tr>
<th></th>
<th>R3</th>
<th>R5</th>
<th>R9</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>k₃₀</td>
<td>E₃</td>
<td>k₅₀</td>
</tr>
<tr>
<td>CeO₂</td>
<td>7.9×10²</td>
<td>104</td>
<td>3.5×10⁶</td>
</tr>
<tr>
<td>PCO</td>
<td>0.03</td>
<td>0</td>
<td>4.2×10¹¹</td>
</tr>
<tr>
<td>CZO</td>
<td>7.0</td>
<td>17</td>
<td>2.0×10⁶</td>
</tr>
</tbody>
</table>

10.5 Summary

This chapter examines the hydrogen and syngas co-production process using pure ceria (CeO₂), praseodymium-doped ceria (Pr₀.₂Ce₀.₈O₂) and ceria zirconia (Ce₀.₅Zr₀.₅O₂). Isothermal redox cycles are carried out in a button cell reactor in the temperature range 700-900°C, with CH₄ (Ar balance) as a fuel. A two-step sequence is followed: (1) the fresh sample is measured as temperature is ramped up from 700°C to 900°C with a step of 100°C, (2) after the measurements at 900 °C, the sample is then cooled down to 700 °C with measurements repeated every 100 °C.

Two major stages along the reduction conversion are evident: (1) the formation of the complete products, CO₂/H₂O, at the early stage of reduction on oxidized surface; and (2) the formation of syngas species, CO/H₂, in the later stage on reduced surface, with the onset of carbon formation.

We find that CZO produces the highest amount of H₂ with the robust resistance to particle enlargement, although it suffers from a lower syngas yield, an unfavorable syngas composition, and higher carbon formation risk. PCO prevails in the syngas quality with less carbon formation; however the large oxygen vacancy renders it more prone to degradation. CeO₂ is highly resistant to carbon formation, but it is less reactive with lower carrying capacity at low temperature. Reduction with CH₄ is kinetics-limited, and it constrains the oxygen deficiency created for the following splitting step.
The equilibrium, kinetics and the oxygen-ion incorporation roadmap developed in the previous chapters for the $\text{H}_2\text{O}/\text{CO}_2$ splitting are applied to characterize the redox reactivity. The $\text{H}_2\text{O}$ splitting kinetics during both ramping-up and cooling-down steps is perfectly characterized based on the previously developed kinetics model. Particle enlargement is clearly observed, more evident at higher temperature with PCO or CeO$_2$. Based on the reduction characteristics, a reduction mechanism is proposed, which consists of two major reaction pathways characterized by the adsorption and activation sites: 1) Ce site on the oxidized surface, and 2) O-vacancy site on the reduced surface. Fitted results based on a set of simplified equations show a qualitative agreement with the measurements for all the three OCs, although future work is needed to examine the additional details within the reduction mechanism. The results obtained here suggest that efforts in the OC design and optimization should focus on promoting the reduction kinetics with CH$_4$, mostly on accelerating the fuel cracking reactions.

10.6 Bibliography

Chapter 11

Improved Chemical-looping Water Splitting Activity
Using Perovskite-based OCs: a Comparative Study

This chapter presents a comparative material study using LSCF-based OCs for CH\textsubscript{4}-fueled water splitting. Specifically, we assess LSCF, Hf-modified LSCF, and the mixed LSCF-Ni as OCs for CL H\textsubscript{2}O splitting. As compared to the ceria-based OCs examined in the previous chapters, LSCF-based OCs demonstrate superb water splitting properties at 800°C or higher temperature. Among tested perovskites, LSCF produces the highest amount of H\textsubscript{2} with the fastest kinetics. However, the use of LSCF suffers from material degradation. In an attempt to mitigate the structural evolution, Hf-coated LSCF is tested, which exhibits an activation process and the H\textsubscript{2} yield increases significantly after initial redox cycles.

Despite the promising results obtained at 800°C, the use of LSCF-based OCs at 700°C or lower is limited by the slow CH\textsubscript{4} reduction step, which constrains the amount of oxygen vacancies for the following splitting process. The addition of nickel to LSCF effectively catalyzes reduction at low temperature, leading to an order of magnitude improvement of the H\textsubscript{2} production rate at 700°C as compared to LSCF as well as all ceria-based materials reported in this thesis. The redox kinetics
with various nickel content is tested, and 60%LSCF-40%Ni shows the best performance for CL H₂O splitting. The results from this chapter provide important guidance on the search of alternative materials as well as the design and optimization of OCs towards low temperature CL H₂O splitting.

11.1 Introduction

Previous chapters examined ceria-based OCs for CL H₂O/CO₂ splitting. It was concluded that charge-transfer remains the rate-limiting step for the splitting kinetics, while reduction, especially with CH₄, constrains the oxygen non-stoichiometry. In an attempt to explore alternative material options, I present a preliminary material study based on perovskite oxides in this chapter, aiming at exploring potential material options and design strategies for low temperature water splitting.

Perovskite oxides with structural formula ABO₃ are promising options for CL H₂O splitting, because of their high reducibility at lower temperature with enhanced surface exchange rates [1-3] as compared to CeO₂. Doping on the A- and B- sites is widely used for improving the kinetic and thermodynamic properties. The ability to tune their properties by doping has led to their popularity in various applications, such as catalysts [4], memristive devices [5, 6], batteries [4], and fuel cells [4, 7, 8]. Several perovskite systems, including La₁₋ₓSrₓMn₁₋ₓAlₓO₃ [2], La₀.⁶Sr₀.⁴Cr₁₋ₓCoₓO₃ [1], and La₀.⁶Sr₀.⁴Ti₁₋ₓFeₓO₃ [3] have recently been examined as promising thermochemical water splitting OCs. These studies demonstrate the better performance as compared to ceria-based OCs for low temperature water splitting (<1000 °C) [1, 2].
In this chapter, we test the redox kinetics using \((\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3\) (LSCF) as our model OC. LSCF is well known for its fast oxygen exchange kinetics and large oxygen carrying capacity [9]. However, LSCF suffers from surface instability and phase decomposition at temperatures above 400 °C, similarly as in \(\text{La}_{1-x}\text{Sr}_x\text{CoO}_3\) or \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-y}\text{Fe}_y\text{O}_3\) [10-15]. The segregation of the aliovalent dopant cations, i.e., Sr and Ba blocks the active surface sites, leading to degradation of reactivities [10-13, 15]. The extensive surface exposure to harsh redox conditions leads to structural transition into a Ruddlesden-Popper (RP) phase, i.e., \(\text{A}_2\text{B}_0\text{O}_4\), with the exsolution of B-site cation [16, 17]. In an attempt to mitigate the material degradation, hafnia-modified LSCF, (LSCF-Hf), is also tested. With the addition of less reducible cations, e.g., Ti, Zr and Hf, the surface segregation effect is mitigated and a fast kinetics can be maintained for long-term operation [13, 18].

As shown in the last chapter, the use of \(\text{CH}_4\) in reduction step is kinetics-limited even at 900°C. The slow reduction process is constrained by the fuel cracking reaction, which hinders the subsequent oxygen removal process, leading to insufficient generation of oxygen vacancies for the following oxidation step. The addition of precious metal, e.g., Ni, Rh, Pt, Pd, etc, is well-known to dramatically catalyze \(\text{CH}_4\) pyrolysis reactions, hence leading to orders of magnitude improvement of the reduction kinetics [19]. The CLC measurements with nickel presented in Chapter 4 and Chapter 5 show that the reduction kinetics with nickel is generally fast, and it is less dependent on temperature. Therefore, we expect a dramatic improvement of the \(\text{CH}_4\)-fueled \(\text{CL H}_2\text{O}\) splitting using the LSCF-Ni mixed OC system.
This chapter presents a comparative material study with the focus on LSCF-based OCs for CH₄-fueled water splitting. Specifically, we assess LSCF, Hf-modified LSCF, and the mixed LSCF-Ni as OCs for CL H₂O splitting, in comparison to the ceria-based OCs examined in the previous chapters. Two additional perovskite-based OCs are also included for comparison, i.e., Pr₀.₄Sr₀.₆Co₀.₂Fe₀.₇Nb₀.₁O₃ (PSCFN), and La₀.₆Sr₀.₄Cr₀.₈Co₀.₂O₃ (LSCC). Isothermal redox cycles are carried out in a button cell reactor in the temperature range 700-900°C, with CH₄ (Ar balance) as a fuel. Lower temperatures (i.e., 600°C-700°C) are tested in the case of the mixed LSCF-Ni OCs. The redox kinetics, cyclic stability, and carbon formation for each material are examined. The comparative study from this chapter will provide insights towards the design and optimization of alternative materials for low temperature CL H₂O splitting.

11.2 Experiment

11.2.1 Sample characterization

The A-site deficient LSCF powder is obtained from Fuel Cell Materials. The Hf-coated LSCF is prepared with use of 1 g LSCF powder in the 40 ml of 0.1 mM aqueous solution of HfCl₄. The formed solution is thoroughly mixed, stirred at 70 °C, followed by filtration and rinsing. The filtered powder is dried at 150 °C for 20 min. XPS measurements show that the Hf/(La+Sr+Co+Fe+Hf) cation ratio is around 0.2.

The LSCF-Ni mixed OC is prepared following a mechanical mixing method, similarly as in the case of NiO/YSZ detailed in Chapter 5. Commercial nickel particles (size <1μm) are mixed with LSCF powder, with organic additives (e.g., ethylene glycol) as binding agents. The formed mixture is thoroughly mixed, stirred at 150°C for 1 hr till all sample is completely dried. The
obtained sample is then grinded, and then calcined at 500°C for 3 hrs. The nickel loading within the mixed OC system is varied at 20mol%, 40mol%, 60mol%, and 80mol%. Pure nickel is also included for comparison.

Solid solutions of PSCFN, LSCC are synthesized as powders via the Pechini method: stoichiometric quantities of the metal nitrates were mixed under continuous stirring at room temperature; an excess of citric acid is used to ensure complexation of the metal cations; ethylene glycol is added, and the solution is heated to form powder, followed by calcination.

Table 11-1 summarizes key properties of the sample. Figure 11-1 compares the SEM images of fresh and redox cycled samples for LSCF-based OCs. The morphology of the fresh sample is analogous, although the particle size is slightly larger for modified LSCF, resulting from the sintering effect during calcination. Particle enlargement is evident for all the OCs. Enlargement is most pronounced with LSCF, forming interconnected macro-structures. Cycled LSCF-Hf is similar as compared to LSCF, although the size of particles is noticeably smaller. Secondary fine grains are seen, attaching to the surface of the sintered particles. The aged sample for LSCF-Ni mixture is distinctive: the LSCF grains are much smaller as compared to the other two OCs; the larger nickel particles are well dispersed and embedded within the LSCF grains.
Figure 11-1 SEM images of (left panels) fresh samples and (right panels) cycled samples for LSCF-based OCs.
Figure 11-2 SEM images of (left panels) fresh samples and (right panels) cycled samples for PSCFN and LSCC. Note different scales are used for PSCFN and LSCC for clarity.

The SEM images for PSCFN and LSCC are shown in Figure 11-2. PSCFN exhibits layered structure with large pores. Individual grains are clearly observed and the boundaries are well defined in the fresh PSCFN. After redox treatment, however, grains sinter and the boundaries disappear. LSCC mostly remains its particle morphology throughout the redox cycling, although slight enlargement is observed.
11.2.2 Redox kinetics measurement

100mg of each sample is embedded in quartz wool and placed at the bottom of the outer quartz tube. The sample undergoes redox cycles with argon as a purging gas in between. 14% CH₄ (Ar balance) is used in reduction with the total flow rate at 350 sccm. Oxidation is carried out with 14.6% H₂O at 363 sccm. The oxidation and reduction times are fixed at 3 min, and 4 min, respectively, with 2 min Ar purging in between. Fresh sample is heated to 700°C under H₂O environment. The measurements are carried out from 700°C to 900°C with a step of 100°C. Each operating condition is repeated for six times, and the redox reactivity from the last three cycles is recorded and averaged to reduce noise. An additional cooling-down step is taken for LSCF, LSCF-Hf, PSCFN, and LSCC to examine the cyclic stability. The cooling-down step starts from 900°C till 700°C with measurements repeated every 100°C. The addition of nickel results in dramatic improvement of the redox kinetics and H₂ yield even at 700°C. On the other hand, CH₄ reduction in presence of nickel is accompanied by significant carbon deposition, more pronounced at higher temperature. Thus, to explore the optimal loading for low temperature water splitting, the redox measurements for the mixed LSCF-Ni OCs are carried out at 600°C, and 700°C, only. The reduction (oxygen removal) and oxidation (oxygen incorporation) rates during the redox steps are calculated similarly as in Chapter 10 (see eqs. (10.2)-(10.6)).
11.3 Results

11.3.1 Redox measurements with LSCF

Figure 11-3 shows three redox cycles using LSCF at 900°C. The averaged results of the three cycles are shown in Figure 11-4. The profiles of the species concentration during reduction are similar as with ceria-based cases: minor amount CO₂/H₂O is released with the intake of CH₄, followed by a quick rise and decay of syngas production rates. The reduction rate with LSCF is noticeably faster, and the peak rate is over 50 µmole g⁻¹s⁻¹, comparable to the case with CZO (as the fastest ceria-based OC). The fast reduction kinetics spans over the entire reduction window, and the oxygen non-stoichiometry after reduction reaches 1.3. Despite the large non-stoichiometry created during reduction, a sufficient regeneration is obtained in the following oxidation step. The redox repeatability is also evident by comparing the evolution of species concentrations within the three successive redox cycles in Figure 11-3. Significant carbon deposition is observed during reduction starting at t = 1min. Gasification of the deposited carbon occurs simultaneously with the production of H₂ starting from the very beginning of the oxidation step, which is different from the case with ceria where carbon gasification takes place only after the majority of oxygen vacancies are filled. Gasification of carbon leads to formation of CO with a minor amount of CO₂. This is also different from the ceria-base case, in which most of the carbon is gasified to form CO₂.
Figure 11-3 Species evolution for three redox cycles with LSCF at 900°C

Figure 11-4 Redox measurements for LSCF at 900°C. (a, d) measured species, (b, e) reaction rates, and (c, f) change of oxygen nonstoichiometry. Left panels show the oxidation results, while right panels are for reduction. For clarity, CH₄ concentration (14%) in panel (d) is not shown.

Carbon production/removal rates are also included in the middle panels.

The production and gasification of carbon during the redox steps is further examined in Figure 11-5. The onset of carbon deposition during reduction occurs roughly after Δδ exceeds 0.3, and
continues till the end of reduction. The removal of carbon during oxidation accompanies the re-oxidation process, and spans over the entire range of non-stoichiometry. Strong temperature dependence is obvious: the carbon deposition or gasification kinetics is reduced by half at 800°C. Thus, to avoid possible carbon formation, the non-stoichiometry of LSCF should be limited below 0.3.

![Graph showing carbon evolution during reduction and oxidation steps](image)

**Figure 11-5** Evolution of carbon during the reduction and oxidation steps. Solid line (positive) is the production rate of carbon during reduction, and dashed line (negative) is the consumption rate of carbon during oxidation. The results at 900°C (blue) and 800°C (red) are included.

The effects of temperature and redox cycling on the redox kinetics are shown in Figure 11-6 and Figure 11-7, respectively. H₂ production kinetics at 800°C significantly exceeds ceria-based OCs, reaching over 178 μmole g⁻¹s⁻¹. Nevertheless, carbon deposition is also evident at 800°C. A further decrease of temperature to 700°C leads to much lower splitting kinetics. The reduction
step at low temperature exhibits a long induction period, which is likely attributed to an insufficient oxygen vacancy created via the first pathway (i.e., the formation of CO₂/H₂O as presented in Chapter 10). The insufficient oxygen deficiency created during the 4 min reduction at 700°C leads to a dramatic drop of the H₂O splitting kinetics, as seen in panel (a). Noticeable difference is observed between ramping-up and cooling-down stages, as shown in Figure 11-7. Specifically, the oxidation rate at 700°C during the ramping period reaches 62 μmole/g s⁻¹, but the 2nd measurement during cooling phase is only 7.4 μmole/g s⁻¹. Clearly, the lower reduction rate along with larger grain particles leads to the lower kinetics after high temperature redox treatment. On the other hand, possible phase decomposition and Sr segregation on LSCF surfaces may also lead to the dramatic degradation of the splitting kinetics.

Figure 11-6 Effect of temperature on H₂/syn-gas production for CZO. (a) H₂ production during oxidation, (b) H₂ production during reduction, and (c) comparison of total yield. Carbon formation is also included in panel (c).
Figure 11-7 Effect of redox cycling on reactivity for LSCF. Comparison of (a, b) $\text{H}_2$ production rates, (c) peak rate, and (d) change of oxygen deficiency, between ramping-up and cooling-down steps. Note, the scales between panels (a) and (b) are different for clarity.

11.3.2 Redox measurements with LSCF-Hf

The addition of Hf on LSCF is to suppress the possible phase decomposition, and improve the structural stability under harsh redox conditions. The performances of Hf-modified LSCF are examined in this sub-section.

As shown in Figure 11-8, the most interesting feature of LSCF-Hf is that the kinetics is significantly activated after a few redox cycles at 900°C. Here, LSCF-Hf sample is measured for 20 successive cycles at 900°C. Interestingly, the $\text{H}_2\text{O}$ splitting kinetics activates with, leading to twice the $\text{H}_2$ yield than the first cycle, as seen in panel (b). After 10 cycles, the changes in the kinetics become minor, and the total evolved $\text{H}_2$ remains mostly stable.
Figure 11-8 Redox cycling at 900°C with LSCF-Hf for 20 cycles. Panel (a) is the measured H₂ production rate during oxidation, and panel (b) is the evolution of total yield throughout the cycling.

Activation of the splitting kinetics is also evident by comparing the reactivity during the ramping-up and cooling-down steps, as shown in Figure 11-9. Unlike LSCF or ceria-based OCs, reactivity of LSCF-Hf is promoted after redox cycling at high temperature, leading to faster kinetics during the cooling-down stage. The largest difference is observed at 800°C with the peak H₂ rates 3 times faster during the cooling stage.

This activation behavior of LSCF-Hf may result from the evolution of the Hf surface coating during the initial cycling. The hafnia coating remains irreducible throughout the conversion,
which reduces the exposure of OCs to the reacting environment, therefore mitigates the
degradation effect. On the other hand, oxygen exchange and ionic migration during the initial
cycling may lead to re-distribution of the grain structure, leading to a direct exposure of LSCF
hence the activation of the redox kinetics. Future work is needed to further understand the
activation mechanism as well as the role of Hf in the kinetics and structural evolutions of LSCF.

![Graphs showing oxidation and reduction with respect to temperature and time.](image)

Figure 11-9 Effect of redox cycling on reactivity for LSCF. Comparison of (a, b) \( \text{H}_2 \) production rates, (c) peak rate, and (d) change of oxygen deficiency, between ramping-up and cooling-down steps. Note, the scales between panels (a) and (b) are different for clarity. The value at 900°C in panels (c) and (d) correspond to the 1^{st} cycle and the 20^{th} cycle, respectively.
11.3.4 Redox measurements with PSCFN and LSCC

Redox tests with PSCFN and LSCC at 900°C are shown in Figure 11-10 and Figure 11-11. The conversion of both perovskite oxides undergoes similar patterns as in the case of LSCF. Carbon formation is less significant with either OC. The use of LSCC has a much lower oxygen carrying capacity as compared to the other two OCs.

Figure 11-10 Redox measurements for PSCFN at 900°C. (a, d) measured species, (b, e) reaction rates, and (c, f) change of oxygen nonstoichiometry. Left panels show the oxidation results, while right panels are for reduction. For clarity, CH₄ concentration (14%) in panel (d) is not shown. Carbon production/removal rates are also included in the middle panels.
Figure 11-11 Redox measurements for LSCC at 900°C. (a, d) measured species, (b, e) reaction rates, and (c, f) change of oxygen nonstoichiometry. Left panels show the oxidation results, while right panels are for reduction. For clarity, CH₄ concentration (14%) in panel (d) is not shown.

Carbon production/removal rates are also included in the middle panels.

An overall summary of the key measurements for the four perovskites oxides is listed in Table 11-2. The H₂O splitting kinetics at 800°C is compared to the ceria-based OCs in Figure 11-12, and the peak H₂ production rates and total yield as a function of temperature are shown in Figure 11-13 and Figure 11-14, respectively. The comparison clearly demonstrates the superb water splitting properties with perovskite oxides. Among them, LSCF produces the highest amount of H₂ with the fastest kinetics, although it suffers from cyclic instability and high risk of carbon deposition. The Hf coated LSCF undergoes an activation process after redox cycling, although the kinetics is conceivably slower. PSCFN offers potential carbon-free solution at 800°C with
significant redox kinetics and oxygen carrying capacity, but it also exhibits minor activation of
the reactivity. LSCC, on the other hand, is significantly slower with limited oxygen carrying
capacity.

![Graph showing oxidation kinetics at 800°C](image)

Figure 11-12 Comparison of H₂O splitting kinetics during oxidation at 800°C.

![Graph showing peak H₂ production rate during oxidation](image)

Figure 11-13 Comparison of peak H₂ production rate in oxidation. Filled symbols correspond to
perovskite oxides, and open symbols are ceria-based OCs.
Figure 11-14 Comparison of total H$_2$ yield in oxidation.

Table 11-2 Summary of redox results with perovskite oxides

<table>
<thead>
<tr>
<th></th>
<th>H$_2$ (ox)</th>
<th>H$_2$ (red)</th>
<th>carbon prod. unit: μmole/gram sample</th>
<th>H$_2$/CO</th>
<th>H$_2$ yield</th>
<th>CO yield</th>
<th>Δδ</th>
<th>Repeatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF</td>
<td>700°C 605</td>
<td>391 trace</td>
<td>1.99 1.99 63.5% 56.3% 0.13 -88.2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800°C 5194</td>
<td>8926 211 2.42 97.6% 95.8% 0.99 -5.3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900°C 9509</td>
<td>15875 2220 2.92 98.8% 97.6% 1.34 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSCF-Hf</td>
<td>700°C 409</td>
<td>271 trace</td>
<td>3.21 60.5% 41.8% 0.09 +363%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800°C 4153</td>
<td>7198 315 2.54 96.5% 94.8% 0.78 +284%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900°C 7144</td>
<td>12749 1615 2.93 98.5% 97% 1.069 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSCFN</td>
<td>700°C 288.5</td>
<td>178 trace</td>
<td>1.72 56.5% 55.0% 0.073 +11%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800°C 3157</td>
<td>5458 trace</td>
<td>2.29 96.0% 93.5% 0.65 +6.3%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900°C 6461</td>
<td>10972 590 2.33 97.9% 97.2% 1.18 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSCC</td>
<td>700°C 165</td>
<td>126 trace</td>
<td>1.77 92% 92% 0.03 +30.5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800°C 1207</td>
<td>1797 196 4.32 94.5% 91.8% 0.15 +23.7%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>900°C 1748</td>
<td>2523 275 4.32 95.5% 95.1% 0.21 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Results during cooling-down period; trace value correspond to production less than 100 μmole/gram OC. The H$_2$/CO ratio at 700°C is less certain, because of lower signal-to-noise ratio; repeatability is calculated by comparing the peak H$_2$ rate from H$_2$O splitting during the ramping-up and cooling-down steps.
11.3.5 Redox measurements with LSCF-Ni mixed OCs

In an attempt to further lower the water splitting threshold temperature, we test the LSCF-Ni mixture for redox reactions at 600°C and 700°C. The loading of Ni in the mixed OC is varied from 20% to 80%. The measurements are summarized in Table 11-3. The significantly improved H$_2$O splitting kinetics with the addition of nickel is highlighted in Figure 11-15. Addition of 40% nickel leads to an order of magnitude improvement of the splitting kinetics as compared to LSCF or ceria-based OCs. The dramatic enhancement is attributed to the much faster CH$_4$ reduction kinetics catalyzed by metallic nickel, which results in a larger oxygen non-stoichiometry, as seen in Table 11-3.

![Oxidation at 700°C](image1)

(a)

![Reduction at 700°C](image2)

(b)

Figure 11-15 Comparison of (a) H$_2$ production rate during oxidation, and (b) reduction rate at 700°C.

Figure 11-16 compares the peak H$_2$ rate and total H$_2$ yield among the different Ni content. The mixed OC exhibits faster splitting kinetics and higher total yield as compared to either pure...
LSCF or pure Ni. The optimal composition corresponds to 40mol% Ni loading. The increase of nickel content, on the other hand, leads to carbon formation, as seen in Table 11-3.

![Graph](image)

Figure 11-16 Comparison of H₂ production in oxidation among different Ni content. Panel (a) compares the peak H₂ rate, and panel (b) compares the total yield.
Table 11-3 Summary of redox results with LSCF-Ni mixed OCs

<table>
<thead>
<tr>
<th>Temperature</th>
<th>H₂ (ox) yield</th>
<th>H₂ (red) yield</th>
<th>CO yield</th>
<th>CO₂ yield</th>
<th>H₂/CO yield</th>
<th>Δδ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Ni</td>
<td>600°C</td>
<td>trace</td>
<td>trace</td>
<td>-</td>
<td>97%</td>
<td>83%</td>
</tr>
<tr>
<td></td>
<td>700°C</td>
<td>782</td>
<td>1404</td>
<td>2.2</td>
<td>88%</td>
<td>85%</td>
</tr>
<tr>
<td>20% Ni</td>
<td>600°C</td>
<td>224</td>
<td>593</td>
<td>2.1</td>
<td>95%</td>
<td>89%</td>
</tr>
<tr>
<td></td>
<td>700°C</td>
<td>1539</td>
<td>3011</td>
<td>2.6</td>
<td>95%</td>
<td>89%</td>
</tr>
<tr>
<td>40% Ni</td>
<td>600°C</td>
<td>498</td>
<td>1223</td>
<td>3.2</td>
<td>88%</td>
<td>83%</td>
</tr>
<tr>
<td></td>
<td>700°C</td>
<td>2841</td>
<td>4816</td>
<td>3.1</td>
<td>96%</td>
<td>90%</td>
</tr>
<tr>
<td>60% Ni</td>
<td>600°C</td>
<td>440</td>
<td>1120</td>
<td>3.8</td>
<td>99%</td>
<td>95%</td>
</tr>
<tr>
<td></td>
<td>700°C</td>
<td>2295</td>
<td>3824</td>
<td>3.5</td>
<td>98%</td>
<td>96%</td>
</tr>
<tr>
<td>80% Ni</td>
<td>600°C</td>
<td>548</td>
<td>1081</td>
<td>5.0</td>
<td>92%</td>
<td>93%</td>
</tr>
<tr>
<td></td>
<td>700°C</td>
<td>1883</td>
<td>3115</td>
<td>3.4</td>
<td>97%</td>
<td>94%</td>
</tr>
<tr>
<td>100% Ni</td>
<td>600°C</td>
<td>228</td>
<td>764</td>
<td>174</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>700°C</td>
<td>529</td>
<td>1091</td>
<td>367</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Δδ as in (La₀.₆Sr₀.₄O₀.₉)₀.₉Co₀.₅Fe₀.₅O₃₋₀.₅Niₓ

11.4 Summary

This chapter presents a comparative material study using LSCF-based OCs for CH₄-fueled water splitting. Specifically, we assess LSCF, Hf-modified LSCF, and the mixed LSCF-Ni as OCs for CL H₂O splitting. As compared to the ceria-based OCs established in the previous chapters, perovskite oxides demonstrate superb water splitting properties at temperature above 800°C. Among tested perovskites, LSCF produces the highest amount of H₂ with the fastest kinetics. However, the use of LSCF suffers from material degradation. In an attempt to mitigate the structural evolution, Hf-coated LSCF is tested, which exhibits an activation process with kinetics and overall H₂ yield increasing significantly with redox cycling. PSCFN offers potential carbon-free solution with significant redox kinetics and oxygen carrying capacity, and it also exhibits minor activation of the reactivity. LSCC, on the other hand, is significantly slower with limited oxygen carrying capacity.
Despite the promising results obtained at 800°C, the use of LSCF-based OCs at 700°C or lower temperature is constrained by the slow CH₄ reduction step. The addition of nickel to LSCF effectively catalyzes the reduction reactions at low temperature, leading to an order of magnitude improvement of the H₂ production rate at 700°C as compared to LSCF as well as all ceria-based materials reported in this thesis. The redox kinetics with various nickel content is tested, and 60%LSCF-40%Ni shows the best performance for CL H₂O splitting. The results from this chapter suggest directions for alternative materials applicable for low temperature CL H₂O splitting and syngas coproduction.

11.5 Bibliography

[16] B. Wang, B. Zydorczak, D. Poulidi, I.S. Metcalfe, K. Li, A further investigation of the kinetic demixing/decomposition of La0.6Sr0.4Co0.2Fe0.8O3-δ oxygen separation membranes, Journal of Membrane Science, 369 (2011) 526-535.
Chapter 12

Conclusion

12.1 Summary

Chemical-looping (CL) is a novel and promising option for several applications including oxy-combustion for carbon capture (CC), fuel reforming, CO$_2$ reduction, and syngas/hydrogen production. In this process, oxygen carriers (OC) are utilized to cyclically adsorb and release oxygen, hence enabling a split reaction pathway and resulting in two separated exhaust streams with desirable products. To implement this concept, a rotary reactor design with micro-channel structure was developed in the Reacting Gas Dynamics Lab (RGDL) at MIT, which exhibits superior performance over conversional designs. Key elements determining the CL performance are the OC kinetics and material characteristics, including the redox rates and reaction pathway, material surface structure, and chemical stability.

This thesis examines the fundamentals of the CL reduction and oxidation (redox) processes using both experimental and theoretical approaches, with emphasis on nickel-based OC for oxy-fuel combustion and cerium-based OC for reforming and H$_2$O/CO$_2$ splitting. Experiments are carried out in a button-cell fixed-bed reactor, coupled with an advanced on-line quadruple mass spectrometer (QMS), which enables real-time measurements of the surface chemistry and
transport mechanism under various conditions with sufficiently fast response and high accuracy. With the time-resolved kinetics measurement, the redox processes are modeled taking into account four major elements: thermodynamics, surface chemistry, transport mechanism, and structural evolution. The method developed in this thesis, combining well-controlled experiment and detailed kinetics modeling, enables a new and thorough approach for identifying the rate-limiting mechanism, examining the defect thermodynamics in the bulk and at the surface, as well as designing and optimizing alternative materials for chemical-looping technology.

Applying the kinetics modeling method to nickel-based OCs for oxy-fuel applications, and ceria-based materials for H₂O/CO₂ splitting, key questions regarding the redox fundamentals are answered: reaction mechanism under operating conditions relevant for CL; the effect of redox cycling on the equilibrium state of the OC; the impact of the surface structure on the carrying capacity and kinetics; the optimal size/thickness of the OCs; the synergy of dopant and bimetallic additives, etc. Conclusions and key findings are summarized below.

12.1.1 Nickel-based OCs for oxy-fuel combustion

Redox study with nickel thin foils (2.5 μm, 10 μm, and 100 μm) reveals that structural evolution during the cycling is the major determining factor. Oxidation starts via the anisotropic nucleation of the oxide grains (stage I), followed by a rapid growth of oxide grains driven by the short-circuit diffusion (stage II), which then overlap and annihilate the fast diffusion paths (stage III). Reduction is initiated by the loss of oxygen, forming dense nickel clusters blocking the interior NiO. Macro-pores are formed to accommodate the volume loss, providing the direct gas-diffusion passages. A nucleation-growth model is used to characterize the structural evolution
during oxidation. The model reveals that the growth of the oxide grain follows a parabolic law, with the rate constant decreasing with conversion. The observed structural difference among the three foils contributes to the difference in the oxide grain growth rates. Reduction is characterized as an adsorption/reaction process. The accessible oxygen decreases with conversion and structural evolution. Kinetics modeling reveals that the nickel surface is nearly saturated with adsorbed hydrogen. A simple thumb rule is suggested for designing nickel-based OC: nickel layer with size close to 1 μm suffices to maintain fast redox conversion oxidation and high utilization.

To achieve practical redox repeatability for the CLC applications, NiO particles (with size of 1 μm) prepared on YSZ nanopowder is examined. Superior cyclic stability is observed starting the 2nd cycle, with a complete utilization of the carrying capacity. Compared to nickel foils, significant improvement is achieved on the conversion kinetics. The model reveals that the use of YSZ significantly enhances the ionic transport process for both redox steps. Oxidation follows a shrinking-core model under the control of internal chemistry. Reduction with H₂ or CO undergoes a similar adsorption-reaction pathway with the foil case, and the oxygen removal step remains the rate-limiting step. The presence of H₂O does not affect the reduction rate. The formed CO₂, on the other hand, leads to slower reduction conversion, because of the backward reaction by CO₂.

12.1.2 Ceria-based OCs for CLR and H₂O/CO₂ splitting

Redox measurements with fine ceria nano-powder show over an order of magnitude improvement on the H₂ production rate compared to the state-of-the-art water splitting studies. It
is found that reduction with un-doped ceria is slow, and it determines the total hydrogen yield produced in the following splitting step. A threshold temperature of 700°C is necessary to activate sufficient oxygen carrying capacity. The redox kinetics is modeled as a two-step surface chemistry, taking into account an \( \text{H}_2\text{O} \) adsorption/dissociation step and a charge transfer step, coupled with the bulk-to-surface transport equilibrium. The model reveals that the surface defect concentration is significantly higher compared to the bulk, because of the difference in the defect formation free energy. Charge transfer is the rate-determining step for \( \text{H}_2 \) production. Attempts to improve the low temperature redox reactivity are made following two strategies: reducing the defect formation enthalpy, hence promoting OC reducibility; accelerating the charge-transfer by maintaining a high surface defect concentration.

Following the first strategy, isovalent \( \text{Zr} \) is added to ceria forming a solid solution with significantly enhanced reducibility. The threshold temperature with CZO is lowered to 650°C, with over 60% improvement in the kinetic rates and twice the total \( \text{H}_2 \) yield at low temperature. The kinetics modeling reveals that the improved kinetics is attributed to the over 40% reduction in the defect formation enthalpy for CZO. As oxygen vacancy is gradually filled up during oxidation, the surface \( \text{H}_2\text{O} \) splitting chemistry undergoes a transition from exothermic to endothermic, with the cross-over around \( \delta = 0.04 \sim 0.05 \), which, on the other hand, constrains the further splitting process. The kinetics study identified that \( \text{H}_2\text{O} \) splitting with CZO is kinetics limited at low temperature and transitions to partial-equilibrium with significantly enhanced backward reaction at high temperature. Following the second strategy, praseodymium-doped ceria is examined, in which the dopant acts as an electron-acceptor, freezing a portion of oxygen vacancy. The threshold temperature with Pr\(_{0.2}\)Ce\(_{0.8}\)O\(_2\) is further lowered to 600°C with the peak
rate doubled from that of CZO. The kinetics model reveals that the charge-compensated oxygen vacancy promotes the formation of adsorbates at low temperature, and hence promotes the charge transfer reaction.

The obtained defect formation thermodynamics and transport equilibria from H₂O/H₂ cases are successfully applied to CO₂ splitting. Similarly, significantly higher CO₂ splitting kinetics is obtained in comparison to literature, resulting from the use of fine particles and well-controlled experiments. CZO shows the fastest CO₂ splitting kinetics, because of a lowered charge-transfer energy barrier compared to other two OCs. Kinetics modeling taking into account a two-step mechanism (CO₂ activation and the charge transfer reaction) identifies that the charge transfer remains the rate-controlling step for CO₂ splitting. Compared to H₂O mechanism, it is found that the adsorption step is material specific and less sensitive to the oxidizer (H₂O or CO₂), while the charge-transfer step is similar among the three OCs, and it is mostly related to the properties of surface adsorbates (OH⁻ or CO₃²⁻). The kinetics modeling outlines the critical role of the surface defects on the formation and following evolution of surface adsorbates during the redox conversion.

With the obtained H₂O and CO₂ splitting mechanisms, CH₄-fueled H₂O splitting is examined. Two major reduction stages are identified: the formation of the complete products, CO₂/H₂O, on the oxidized surface, and the formation of syngas species, CO/H₂, on the reduced surface. CZO is found to produce the highest amount of H₂, but suffer from an unfavorable syngas composition and a higher carbon formation tendency. PCO prevails in the syngas quality; however the large oxygen vacancy renders it more prone to degradation. The H₂O splitting kinetics in the CH₄-
fueled tests is perfectly characterized by the previously developed kinetics model. Reduction modeling takes into account the two conversion pathways with \( \text{CH}_4 \) activating over oxidized surface similarly as \( \text{H}_2 \), and the reduced surface similarly as \( \text{H}_2\text{O} \), respectively. Fitted results exhibit a qualitative agreement, although additional work is needed to further examine the reduction mechanism.

CL \( \text{H}_2\text{O} \) splitting is found to be rate-limited by the slow \( \text{CH}_4 \) cracking reaction. Thus, in an attempt to accelerate the low temperature kinetics, perovskite-based OCs are tested. As compared to the ceria-based OCs, LSCF-based OCs demonstrate superior water splitting properties at 800\(^\circ\text{C}\) or higher temperature. However, splitting kinetics at 700\(^\circ\text{C}\) or lower is still limited by the slow \( \text{CH}_4 \) reduction step. The addition of nickel to LSCF effectively catalyzes the reduction reactions at low temperature, leading to an order of magnitude improvement of the \( \text{H}_2 \) production rate at 700\(^\circ\text{C}\) compared to other \( \text{CH}_4 \)-fueled tests. Among various LSCF-Ni composite OCs, 60\%LSCF-40\%Ni shows the best performance for CL \( \text{H}_2\text{O} \) splitting.

The redox kinetics obtained from this study demonstrates the feasibility of CL \( \text{H}_2\text{O}/\text{CO}_2 \) splitting technology as promising carbon-neutral \( \text{H}_2 \) production or \( \text{CO}_2 \) reduction options. With the use of ceria-based or composite pervoskite, CL process potentially offers higher efficiency with lower costs compared to the conventional reforming technology.

12.1.3 Overall summary

This research project has clearly demonstrated that with novel materials, CL technology can provide an efficient solution to \( \text{CO}_2 \) capture and \( \text{H}_2 /\text{syngas} \) co-production. Specifically, the use of
NiO/YSZ achieves fast kinetics, robust stability and sufficient OC utilization from 500 to 1000°C, enabling complete CO₂ capture with minimum energy penalty. The ceria-, and perovskite-based OCs exhibit over an order-of-magnitude faster kinetics compared to the state-of-the-art, enabling improved H₂ production/CO₂ reduction efficiency isothermally at 600-700°C. In-depth understanding of the redox fundamentals have been obtained, enabled by the coupling of the well-controlled experiments and detailed modeling framework on the basis of electrochemistry. Insights gained from these practices will shed light on the design and optimization of the CL applications.

Overall the major contributions of this work to the field of CL oxy-fuel combustion, and H₂O/CO₂ splitting are summarized below, some of which may also be helpful in the area of metallurgy, electrolyzers, solid oxide fuel cells, etc.

1) Demonstrated the potential advantages of CL oxy-fuel combustion with NiO/YSZ to achieve complete CO₂ capture with minimum energy penalty; demonstrated the potential of H₂O/CO₂ splitting with ceria-, perovskite-based OCs to achieve faster kinetics at low temperature;

2) Developed a generalized approach to characterize the surface-oriented electro-chemical process, with the consideration of interactions of mobile ions, electrons between the bulk and the surface, along with the adsorbates and electrostatic fields;

3) Identified the morphological and microstructural evolutions of nickel and their effects on the redox reactions; clarified the diffusional enhancement from the structural support;

4) Established an in-depth understanding of the surface reaction process of ceria; quantified the defect segregation on the surface from the bulk phase; evaluated the contributions
from the surface defects and dopants to the reaction kinetics; obtained a set of kinetics and equilibrium parameters consistent for a wide range of conditions;

5) Explored alternative options for promoting the reaction kinetics.

**12.2 Suggested future work**

12.2.1 Modeling improvement

For the purpose of kinetics fitting, the reaction modeling developed in this study adopts an electro-neutrality assumption. This assumption, however, can break down in the space-charge region near the surface, in which the vacancies and electrons form a double layer, creating a large disturbance of the spatial electrostatic potential field near the surface [1]. This may lead to large interferences of the transport process of the charged species, hence affecting the redox kinetics. A complete understanding of the charge-field interactions requires solving the complete Poisson-Nernst-Planck equations (see Chapter 3) coupled with the surface chemistry. The knowledge gained from this issue may be of particular importance for the design of nano-sized OCs, in which the spacing of grain boundaries or layered structure can drop below the space charge width, resulting in deviations of the bulk properties from defect equilibria [2]. The space charge, on the other hand, can induce additional surface stresses, which also alters the thermodynamic equilibrium as well as key transport properties near the surface, contributing to additional surface segregation effect [3].

12.2.2 Developing detailed CH$_4$ reduction mechanism for nickel and cerium-based OCs

The ultimate goal of CL combustion with carbon capture is to convert CH$_4$ into complete product, i.e., CO$_2$ and H$_2$O, during reduction. Thus, understanding the CH$_4$ reduction kinetics with nickel
oxide is important. CH₄-nickel reactions involve the direct reduction reaction as well as the nickel catalyzed reactions, as listed in Table 12-1. All these reactions should be carefully evaluated within the conditions relevant for CL combustion.

Table 12-1 Possible reactions involved with CH₄-NiO reactions, and summary of some available data from literature

<table>
<thead>
<tr>
<th>Reactions scheme</th>
<th>kinetics from literature</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Direct NiO reduction reaction</strong></td>
<td></td>
</tr>
<tr>
<td>H₂ oxidation</td>
<td>H₂ + NiO ⇌ Ni + H₂O</td>
</tr>
<tr>
<td>CO oxidation</td>
<td>CO + NiO ⇌ Ni + CO₂</td>
</tr>
<tr>
<td>Partial oxidation</td>
<td>CH₄ + 2NiO ⇌ 2Ni + CO₂ + 2H₂</td>
</tr>
<tr>
<td>Partial oxidation</td>
<td>CH₄ + NiO ⇌ Ni + CO + 2H₂</td>
</tr>
<tr>
<td>Complete oxidation</td>
<td>CH₄ + 4NiO ⇌ 4Ni + CO₂ + 2H₂O</td>
</tr>
<tr>
<td><strong>Ni catalyzed reaction</strong></td>
<td></td>
</tr>
<tr>
<td>Steam reforming</td>
<td>CH₄ + H₂O ⇌ 3H₂ + CO</td>
</tr>
<tr>
<td>Dry reforming</td>
<td>CH₄ + CO₂ ⇌ 2H₂ + 2CO</td>
</tr>
<tr>
<td>Water gas shift</td>
<td>CO + H₂O ⇌ H₂ + CO₂</td>
</tr>
<tr>
<td>CH₄ cracking</td>
<td>CH₄ ⇌ 2H₂ + C</td>
</tr>
<tr>
<td>Carbon gasification</td>
<td>C + H₂O ⇌ CO + H₂</td>
</tr>
<tr>
<td>Boudouard reaction</td>
<td>2CO ⇌ C + CO₂</td>
</tr>
</tbody>
</table>

As discussed in Chapter 10, the use of CH₄ as fuel for H₂O splitting with ceria-based OCs involves many more complicated reaction steps. Identification of each elementary step and mapping out the overall reaction roadmaps require much more efforts in elucidating the contribution from each individual reaction pathway. Despite the preliminary efforts made in Chapter 10 to understand the most important pathway, much more work is needed to quantify each elementary reaction. Specifically, the break-down of the four C-H bond with or without the presence of vacancy, dopant, carrier gas, etc., should be examined thoroughly, and thermodynamically consistent reaction mechanism should be developed on the basis of the defect equilibria established with H₂O and CO₂. Additionally, ceria-based OC is also known to catalyze a few reactions, including reforming, water-gas shift, methanation reactions [26]. Therefore, a
complete description of the CH$_4$-fueled reduction should take into account these possible side reactions. Besides, additional work is needed to clarify carbon deposition mechanism.

12.2.3 Exploring new materials for faster kinetics, larger capacity, and enhanced stability

Chapter 11 presents a preliminary test with perovskite oxides as OCs. The use of LSCF provides superior redox kinetics compared to ceria-based OCs. The large perovskite oxide family offers many more potential options, with large redox capacity, fast kinetics of reduction, and desirable stability and durability. Some candidates may include SrCoO$_{3.6}$ and Pr$_2$NiO$_4$. Pr$_2$NiO$_4$ belongs to the Ruddlesden Propper (RP) oxide family, which can accommodate both oxygen vacancies and oxygen interstitials, making their range of oxygen non-stoichiometry much larger.

As shown in Chapter 11, the use of composite pervoskite structure, or pervoskite-metal pair, may lead to further improvement of the splitting kinetics. In such a composite, one material may serve as an oxygen source enabling fast ionic diffusion, while the other providing electrons. LSCF-Ni mixed OC is one of the potential options with significantly enhanced reactivity. The use of Ni catalyzes CH$_4$ cracking reaction, thus promoting the reduction kinetics. The improved kinetics with these composites effectively lowers the operating temperature, leading to improved system efficiency. Besides, materials are subjected to less harsh conditions at lower temperature, leading to better stability and elongated lifetime.

12.2.4 Design and fabrication of rotary reactor to achieve the CL process

Successful operation of the rotary-based CL reactor remains the ultimate goal for CL material study. Thus, preparing and fabrication of the rotary reactor with micro-channels requires effort in the future. Potential challenges still need to be addressed for the construction, the operation, up-
scaling and commercialization of the rotary CLC. This may include, for instance, how to prepare the desirable OC materials onto the channel substrate, how to ensure sufficient loading while maintain large surface area, how to maintain regenerability during the cyclic operation under high temperature and high pressure and prevent potential structural degradation, what are the optimal conditions/off-design behaviors for the system operation, etc. These challenges are significant to the application of the rotary design and they must be approached critically and comprehensively. Bench scale and lab scale prototypes shall be fabricated, and experimental practices shall be performed to examine all the above factors.

12.3 Bibliography