Experimental study and modeling analysis of ion transport membranes for methane partial oxidation and oxyfuel combustion

by

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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering and Computation

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Abstract

The atmospheric concentration of $CO_2$ has recently exceeded 400 (ppm) (up from 285 (ppm) in 1850), largely because of the burning of fossil fuels. Despite the growth of alternatives, these fuels will continue to play a major role in the energy sector for many decades. In accordance with international agreements, action to curtail $CO_2$ emissions is necessary, including carbon capture, reuse and storage. For this purpose, some of the leading technologies are oxy-combustion for power generation and partial oxidation for syngas production. Both require significant quantities of oxygen, whose production can impose considerable energy and economic penalties. Alternative technologies, such as intermediate-temperature ceramic membranes, operating under reactive conditions, promise to ameliorate both. Challenges include the long term stability of the material, reactor design and integration into the overall system.

The goal of this thesis is to develop a framework for the thermochemical and electrochemical modeling of oxygen-conducting membranes that can be used in reactor design, based on experimental measurements and detailed surface exchange kinetics and charged species transport. $La_{0.9}Ca_{0.1}FeO_3$–$\delta$ (LCF) perovskite membranes have been used because of their long term stability in a reducing environment. Using experimental measurements, we examine the impact of hydrogen, carbon monoxide and methane on oxygen permeation and defect chemistry. While LCF exhibits low flux under non-reactive conditions, in the presence of fuel oxygen permeation increases by more than one order of magnitude. Our experiments confirm that hydrogen surface
oxidation is faster compared to carbon monoxide. With methane, syngas production is slow and oxygen permeation is limited by surface exchange on the permeate side. Adding \( \text{CO}_2 \) to the fuel stream doubles the oxygen flux and increases syngas production by an order of magnitude.

Our modeling analysis shows that different oxidation states of Fe participate in the electron transfer process. To account for this dependency, oxygen transport is modeled using a multi-step (fuel dependent) surface reaction mechanism that preserves thermodynamic consistency and conserves site balance and electroneutrality. Charged species diffusion is modeled using the dilute-limit Poisson-Nernst-Planck formulation that accounts for transport due to concentration gradient as well as electromigration. We use the experimental data to extract kinetic parameters of the model. We couple the aforementioned model with CFD of the gas-phase transport and thermochemistry in an effort to develop a numerical tool that allows the design of membrane reactors that exhibit high oxygen permeation and fuel conversion.

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List of Symbols

Abbreviations

ASU  Air Separation Unit  
EDL  Electric Double Layer  
GC  Gas Chromatograph  
GHG  Greenhouse Gases  
Gtoe  Gigatons of Oil Equivalent  
ITM  Ion Transport membrane  
LCF  $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ membrane  
MFC  Mass Flow Controller  
MIEC  Mixed ionic-electronic conducting  
MPI  Message Passing Interface  
MS  Mass Spectrometer  
NIST  National Institute of Standards and Technology  

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PISO  Pressure Implicit Algorithm with Splitting of Operators
PNP  Poisson-Nernst-Planck
ppm  Parts per million
sccm  Standard Cubic Centimeter per Minute

Elements and Molecules

Ar  Argon
C  Carbon
C₂H₂  Acetylene
C₂H₄  Ethylene
C₂H₆  Ethane
C₃H₈  Propane
Ca  Calcium
CH₄  Methane
CO  Carbon Monoxide
CO₂  Carbon Dioxide
Fe  Iron
H₂  Hydrogen molecule
H₂O  Steam
La  
Lanthanum

$N_2O$  
Nitrous oxide

$O$  
Oxygen atom

$O_2$  
Oxygen molecule

**Greek**

$\delta$  
Formula-unit concentration of oxygen vacancies, $[V_O^\bullet]$ (−)

$\delta_{ij}$  
Kronecker delta (−)

$\dot{\omega}_k$  
Volumetric reaction rate of species $k$ in the gas-phase $(kg/m^3/sec)$

$\dot{\omega}_T$  
Volumetric heat release rate in the gas-phase $(W/m^3)$

$\dot{\omega}_{s,k}$  
Surface reaction rate of species $k$ due to heterogeneous reactions $(mole/m^2/sec)$

$\dot{\omega}_{T,s}$  
Surface heat release rate due to heterogeneous reactions $(W/m^2)$

$\epsilon$  
Ratio of the Debye length over the membrane thickness (−)

$\epsilon_k^{L,J}$  
Characteristic Lennard-Jones energy of species $k$ $(J)$

$\epsilon_o$  
Permittivity of vacuum $(F/m)$

$\epsilon_r$  
Relative permittivity of a material (−)

$\epsilon_{mem}$  
Membrane emissivity (−)

$\eta_i$  
Outward facing normal unit vector (−)
\( \lambda \)  
Thermal conductivity of the mixture in the gas-phase \((W/m/K)\)

\( \lambda_D \)  
Debye screening length \((m)\)

\( \lambda_k \)  
Thermal conductivity of species \(k\) in the gas-phase \((W/m/K)\)

\( \lambda_M \)  
Thermal conductivity of the membrane \((W/m/K)\)

\( \mu \)  
Dynamic viscosity of the mixture \((kg/m/sec)\)

\( \mu_k \)  
Dynamic viscosity of species \(k\) \((kg/m/sec)\)

\( \mu_{Fe^e_{Fe}} \)  
Mobility of electron holes, \(Fe^e_{Fe}\) \((m^2/V/sec)\)

\( \mu_{Fe_{Fe}^e} \)  
Mobility of electrons, \(Fe_{Fe}^e\) \((m^2/V/sec)\)

\( \Omega_{\nu,k} \)  
Collision integral of species \(k\) \((-)\)

\( \Omega_D \)  
Diffusion collision integral \((-)\)

\( \phi \)  
Electrostatic potential \((V)\)

\( \rho \)  
Density of the mixture \((kg/m^3)\)

\( \rho_M \)  
Membrane density \((kg/m^3)\)

\( \rho_s \)  
Volumetric or surface charge density \((C/m^3)\) or \((C/m^2)\)

\( \sigma \)  
Stefan-Boltzmann constant \((W/m^2/K^4)\)

\( \sigma_k \)  
Electronic-ionic conductivity of species \(k\) inside the material \((S/m)\)

\( \sigma_{k}^{LJ} \)  
Average diameter of molecular collision of species \(k\) \((\text{Å})\)

\( \sigma_{ij} \)  
Total stress tensor \((N/m^2)\)
Characteristic time scale of the PNP equations \((\text{sec})\)

Viscous stress tensor \((\text{kg/sec}^3)\)

**Kröger-Vink notation**

\(Ca'_{La}\) \(Ca^{+2}\) state incorporated into the \(La^{+3}\) lattice site

\(Fe^*_{Fe}\) \(Fe^{+4}\) iron state incorporated into the \(Fe^{+3}\) lattice site

\(Fe'_{Fe}\) \(Fe^{+2}\) iron state incorporated into the \(Fe^{+3}\) lattice site

\(Fe''_{Fe}\) \(Fe^{+3}\) iron state incorporated into the \(Fe^{+3}\) lattice site

\(h^*\) Electron hole

\(O^z_O\) Oxygen ion inside the oxygen lattice site

\(V^\circ_{O}\) Oxygen vacancy inside the oxygen lattice site

**Roman**

\(\Delta G_i^o\) Standard-state Gibbs free energy of reaction \(i\) \((\text{J/mole})\)

\(\Delta h_{j,k}^o\) Mass specific enthalpy change of formation of species \(k\) \((\text{J/kg})\)

\(\Delta h_{j,k}^{0,m}\) Mole specific enthalpy change of formation of species \(k\) \((\text{J/kmole})\)

\(\Delta H_i^o\) Standard-state enthalpy of reaction \(i\) \((\text{J/mole})\)

\(\Delta S_i^o\) Standard-state entropy of reaction \(i\) \((\text{J/mole/K})\)

\(\dot{m}\) Mass flow rate \((\text{kg/sec})\)

\(\dot{Q}\) Volumetric heat source terms \((\text{W/m}^3)\)
\( \dot{q}_i \) \hspace{1cm} \text{Heat flux vector} \ (W/m^2) \\
\( \dot{s}_m \) \hspace{1cm} \text{Rate of progress of surface reaction} \ m \ (mole/m^2/sec) \\
\( \dot{V} \) \hspace{1cm} \text{Volumetric flow rate} \ (m^3/sec) \ or \ (sccm) \\
\( [i] \) \hspace{1cm} \text{Formula-unit concentration of charged species} \ i \ (-) \\
\( A \) \hspace{1cm} \text{Area} \ (m^2) \\
\( C_k \) \hspace{1cm} \text{Volumetric and surface molar concentration} \ (mole/m^3) \ or \ (mole/m^2) \\
\( c_p \) \hspace{1cm} \text{Specific heat capacity at constant pressure of the mixture} \ (J/kg/K) \\
\( c_{p,k} \) \hspace{1cm} \text{Specific heat capacity at constant pressure of species} \ k \ (J/kg/K) \\
\( c_{p,M} \) \hspace{1cm} \text{Membrane specific heat capacity at constant pressure} \ (J/kg/K) \\
\( C_{ref} \) \hspace{1cm} \text{Reference molar concentration} \ (mole/m^3) \\
\( D_k \) \hspace{1cm} \text{Diffusion coefficient of species} \ k \ \text{in mixture/material} \ (m^2/sec) \\
\( D_k^T \) \hspace{1cm} \text{Thermal diffusion coefficient of species} \ k \ \text{in mixture} \ (m^2/sec) \\
\( D_{kj} \) \hspace{1cm} \text{Binary diffusion coefficient of species} \ k \ \text{into species} \ j \ (m^2/sec) \\
\( D_{ref} \) \hspace{1cm} \text{Reference diffusion coefficient} \ (m^2/sec) \\
\( e \) \hspace{1cm} \text{Specific energy} \ (J/kg) \\
\( e_c \) \hspace{1cm} \text{Electron charge} \ (C) \\
\( E_i \) \hspace{1cm} \text{Electric field} \ (V/m) \\
\( e_t \) \hspace{1cm} \text{Total specific energy} \ (J/kg)
**F**  
Faraday constant $(C/mole)$

$f_{k,i}$  
Volume force acting on species $k$ in direction $i$ $(m/sec^2)$

$g_i$  
Gravitational acceleration vector $(kg * m/sec^2)$

$h$  
Specific enthalpy of the mixture $(J/kg)$

$h_k$  
Specific enthalpy of species $k$ $(J/kg)$

$h_s$  
Sensible specific enthalpy of the mixture $(J/kg)$

$h_t$  
Total specific enthalpy of the mixture $(J/kg)$

$h_{s,k}$  
Sensible specific enthalpy of species $k$ $(J/kg)$

$i_{ext}$  
External current density $(A/m^2)$

$J_{k,i}$  
Molar flux vector of species $k$ $(mole/m^2/sec)$

$j_{k,i}$  
Mass flux vector of species $k$ $(kg/m^2/sec)$

$J_{O_2}$  
Experimentally measured oxygen flux through the membrane $(mole/m^2/sec)$

$k$  
Specific kinetic energy $(J/kg)$

$k_b$  
Boltzmann constant $(J/K)$

$K_g$  
Total number of gas-phase species $(-)$

$K_s$  
Total number of surface species $(-)$

$K_{C_i}$  
Equilibrium constant of reaction $i$ based on molar concentrations $(atm^a mole^b m^c)$
Equilibrium constant of reaction \( i \) based on partial pressures and formula-unit concentrations \((-\))

Thickness of the membrane \((m)\)

Total number of charged species within the material \((-\))

Avogardo’s constant \((1/mole)\)

Total number of gas-phase reactions \((-\))

Total number of heterogeneous reactions \((-\))

Pressure \((Pa)\)

Partial pressure of species \( k \) \((Pa)\)

Pressure at standard conditions \((Pa)\)

Universal gas constant \((J/mole/K)\)

Ionic radii of element \( i \) \((m)\)

Temperature \((K)\)

Time \((sec)\)

Tolerance factor \((-\))

Membrane temperature \((K)\)

Velocity vector \((m/sec)\)

Correction velocity vector \((m/sec)\)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_m$</td>
<td>Molar volume ($m^3/mole$)</td>
</tr>
<tr>
<td>$V_{k,i}$</td>
<td>Diffusion velocity vector of species $k$ ($m/sec$)</td>
</tr>
<tr>
<td>$W$</td>
<td>Molecular weight of the mixture ($kg/kmole$)</td>
</tr>
<tr>
<td>$W_k$</td>
<td>Molecular weight of species $k$ ($kg/kmole$)</td>
</tr>
<tr>
<td>$x$</td>
<td>Calcium doping in the A-site of LCF, $[Ca'_{La}] (-)$</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Position vector ($m$)</td>
</tr>
<tr>
<td>$X_k$</td>
<td>Mole fraction of species $k$ ($-$)</td>
</tr>
<tr>
<td>$Y_k$</td>
<td>Mass fraction of species $k$ ($-$)</td>
</tr>
<tr>
<td>$z_k$</td>
<td>Valence of charged species ($-$)</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

In this chapter, we briefly discuss the motivation behind this work that comes mainly from the global effort to mitigate the environmental impact of global warming by reducing the atmospheric $CO_2$ emissions as well as to improve the efficiency of the current technologies associated to the production of synthesis gas by methane reforming.

1.1 $CO_2$ emissions from fossil fuels

Global warming is a term used to describe the observed increase in the planet’s average temperature and its effect to the Earth’s climate [1]. Climate scientists have observed that the $CO_2$ levels in the atmosphere have been rising significantly during the last decades [2]. In particular, the 2015 average $CO_2$ atmospheric concentration is estimated around 399 (ppm), while the pre-industrial era level was approximately 280 (ppm) [2]. For the month of November 2016, the Earth System Research Laboratory measured an average $CO_2$ concentration of 403.53 (ppm) above Mauna Loa.
in Hawaii. It is evident that reaching the 400 (ppm) value of \( CO_2 \) concentration in the atmosphere has now become a reality. At the same time, the atmospheric concentration of other gases enhancing global warming (such as \( CH_4 \) and \( N_2O \)) is also increasing at a significant rate.

Between the various human activities that produce greenhouse gases, the use of energy represents the largest source of emissions. Figure 1-1 shows that approximately two thirds of the global GHG emissions come from the energy sector, while agriculture and other industrial processes account only for one third. Within the energy sector share, 90 (%) corresponds to \( CO_2 \) release in the atmosphere resulting from fossil fuel combustion, while the \( CH_4 \) and \( N_2O \) concentrations emitted from energy-related applications are much lower.

![Figure 1-1: Estimated shares of global anthropogenic GHG](image)

Despite the growth of other forms of energy considered non-emitting such as nuclear and renewable energy (solar, hydropower etc.), fossil fuel combustion still remains the main source of energy and the situation is unlikely to change within the
next decades. Figure 1-2 shows that the share of fossil fuels in the world’s primary energy supply was around 84 (%) in 2012. Predictions reveal that petroleum and coal combustion will reduce but use of natural gas will increase due to the relatively low current price of the hydrocarbon. The Clean Power Plan announced by the United States in August 2015 will not affect the expected trends significantly [3].

Figure 1-2: World primary energy supply with future predictions [3].

1.2 Action towards $CO_2$ emission reduction

Since $CO_2$ emissions are positively correlated to the use of fossil fuels, it is reasonable to observe an upward trend to the atmospheric $CO_2$ levels. Figure 1-3 shows the $CO_2$ concentration in the atmosphere measured at the Mauna Low Observatory and confirms the aforementioned trend. Given that GHG have a great contribution to the increase of the planet’s temperature, it is evident that action should be taken in order to reduce $CO_2$ emissions from anthropogenic activity. Otherwise, climate
change will become irreversible and such a situation may have extremely negative effects to any form of life on our planet.

Figure 1-3: Atmospheric $CO_2$ concentration between March 1958 and September 2016. The red line corresponds to the monthly mean values, centered on the middle of each month while the black line includes a correction for the average seasonal cycle.

The year 2015 was a milestone for climate action due to the Paris Agreement that was announced during the 21st Conference of the Parties in December 2015. The importance of the Paris Agreement is significant because it is the first international agreement that obligates all countries, both developed and developing, to mitigate their $CO_2$ emissions. In the past, industrialized countries were the ones to emit
most GHG; recently, the trend has changed and it is observed that the GHG share of developing countries has overcome that of developed countries [2]. Hence, an international shift towards a low-carbon world is crucial in order to meet the global climate goals. The Agreement sets the goal of allowing for a $2(\degree C)$ increase in the planet’s temperature compared to the pre-industrial levels and pursuing efforts that would guarantee a temperature rise close to $1.5(\degree C)$. The latter will be attained only through major reductions of GHG in each participant country.

The first effort to enforce $CO_2$ mitigation prior to the Paris Agreement was the Kyoto Protocol. It was signed on December 11 1997 in Kyoto, Japan, and participant countries committed to set emission reduction targets around $5(\%)$ relative to their domestic GHG values of 1990. One of the important features of the Kyoto Protocol was the opportunity of participant countries to make use of flexible mechanisms that allowed industrialized countries to obtain emission credits from emission reduction projects. Despite its extensive participation (192 Parties), the Kyoto Protocol is limited in its potential to address global emissions. The United States remain outside of the Protocol’s jurisdiction, and developing countries do not face emissions targets [2].

The second effort to constrain $CO_2$ emissions from both developed and developing countries was set by the Cancún Agreement signed on December 11 2010 in Cancún, Mexico, during the United Nations Climate Change Conference. The agreement recognizes that climate change represents an urgent and potentially irreversible threat to human societies and the planet, which needs to be urgently addressed by all parties. The share of participating countries on $CO_2$ emission was more than $80(\%)$ and the agreement included a voluntary emission reduction effort for 2020. The Agreement proposed participating countries should establish clear objectives for GHG reduction and mobilized the development of clean and carbon free technology.
The aforementioned agreements have boosted the development of alternative technologies that guarantee low CO₂ emissions or reuse CO₂ instead of tossing it to the atmosphere. One of the objectives of this thesis is to explore whether CO₂ can be used in the chemical industry for the production of syngas via methane conversion facilitated by ITM integration. However, before describing this novel technology, it is important to discuss why syngas production is significant, what is the current state of the art in terms of its production and why ITM are promising candidates for reducing the energetics of methane reforming to syngas.

1.3 Syngas production technologies

Syngas (or synthesis gas) is a mixture of gaseous H₂ and CO and its production is one of the most important processes in chemical industry [4]. The name comes from its use as an intermediate during the production of synthetic natural gas or during ammonia or methanol production. Besides its use for chemical conversion, syngas is also fed into fuel cells to produce electricity. Sometimes, it can also be used as a fuel for internal combustion engines. In addition, syngas is the source for liquid hydrocarbon production via the Fisher-Tropsch process. Hence, given the wide range of applications using syngas as a primary feedstock, various technologies have been developed to allow for a high efficiency and low production cost.

The primary feedstock for syngas production is natural gas, which consists primarily of methane. Large scale industrial reformers use steam for the conversion of methane to syngas to achieve high H₂ yields. The process is represented by the following reaction:

\[ CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H^\circ = 206.1 \text{ (kJ/mole)} \]  (1.1)
Typically, the reaction takes place at temperatures around 500 – 900 (°C), pressures of 20 – 35 (atm) and steam to carbon ratios of 2.5 – 3 [5]. Conversion of methane is favorable at high temperature, low pressure and high steam to carbon ratios. Although the latter reduces the possibility of carbon deposition within the reformer, modern power plants use a low steam to carbon ratio to achieve higher efficiency and reduce the operating cost. Hydrogen plants with old reforming technology operate at temperatures well below 900 (°C) and high steam to carbon ratios, but their efficiency is poor [6]. As a result, a typical steam reformer nowadays operates at temperatures higher than 900 (°C) while the steam to carbon ratio is around 2.5. These reformers can achieve methane conversions above 90 (%) [7].

It can be seen by reaction 1.1 that steam reforming of methane is a highly endothermic process. Heat is supplied to the reformer externally, while the reformer is frequently designed as a packed bed reactor. To allow conversion close to the equilibrium limits, various catalysts can be used with Nickel being the most popular one due to its high activity and low cost [5]. To control the $H_2$ to $CO$ ratio, the water-gas shift reaction is usually employed. Carbon monoxide reacts with additional steam to form hydrogen and carbon dioxide according to the following exothermic reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^\circ = -41.2 \, (kJ/mole) \quad (1.2)$$

To allow for carbon dioxide emission reduction from power plants, dry reforming of methane can be used instead of steam methane reforming. Replacing $H_2O$ with $CO_2$ aims at the reuse of this greenhouse gas by converting it into useful products. Dry reforming of methane takes place according to the following reaction:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H^\circ = 247.3 \, (kJ/mole) \quad (1.3)$$
Reaction 1.3 shows that dry reforming of methane yields to a lower $H_2$ yield compared to steam reforming. At the same time, dry reforming is more energetically demanding compared to steam reforming. Given the high endothermicity of reaction 1.3, catalysts are frequently used to allow for operation at lower temperatures. Typical catalysts used during the process are Platinum, Palladium, Ruthenium, Rhodium or Iridium; these however are more expensive compared to Nickel [8]. Another disadvantage is catalyst deactivation due to carbon deposition which remains a serious obstacle for scaling up the catalytic dry-reforming system. Because of the higher energy needs, the lower $H_2$ yield and the carbon deposition issue, steam reforming of methane is more popular compared to dry reforming.

Besides steam and dry reforming of methane, syngas can also be produced by partial oxidation of methane. The process is dictated by the following chemical reaction:

$$ CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \quad \Delta H^\circ = -35.7 \text{ (kJ/mole)} \quad (1.4) $$

An advantage of partial oxidation of methane is that the reaction is exothermic and is favorable at low temperatures, hence operation between $300 - 500 \, (^\circ C)$ reduces the energy consumption significantly [8]. However, the methane to oxygen ratio has to be controlled precisely in order to avoid full oxidation of methane into steam and carbon dioxide:

$$ CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \quad \Delta H^\circ = -802.4 \text{ (kJ/mole)} \quad (1.5) $$

It can be seen from reaction 1.5 that full oxidation of methane is highly exothermic and hence the temperature of the system should be controlled to minimize the
possibility of reactor overheat.

An alternative approach that increases the efficiency of syngas production is to combine steam reforming and partial oxidation of methane into a hybrid system. In this case, the process is called auto-thermal reforming since the heat released from methane partial oxidation is provided to the methane steam reforming, hence the energy requirement is lower.

However, partial oxidation of methane requires the addition of $O_2$ into the fuel stream. Usually, pure $O_2$ is preferred since the use of air may enhance the formation of $NO_x$, another heavily regulated pollutant. In addition, $N_2$ exists in the air stream at a mole fraction of 78 (%) but does not participate in the syngas production reactions, hence significant energy penalties arise from the unnecessary heating of $N_2$. However, air is preferred when the syngas is going to be used for ammonia synthesis [5]. When pure $O_2$ is needed, its production requires considerable amount of energy. The next section describes the current industrial method for pure $O_2$ production and discusses the advantages of using ITM reactors as an alternative and low cost technology.

1.4 Pure $O_2$ production from cryogenic distillation and comparison with ITM reactors

1.4.1 Cryogenic distillation

Oxygen is the third largest volume chemical produced worldwide [9]. It is a very important gas because $O_2$ is used in chemical industries, metallurgy, glassmaking, clean power generation and environmental protection [10]. More than 90 (%) of the commercially available oxygen and nitrogen are produced through cryogenic distillation of the atmospheric air. During cryogenic distillation, air is cooled down until
its components are liquefied. For atmospheric pressure, oxygen’s boiling point is approximately $-183 \, ^\circ C$, while that of nitrogen is around $-195.8 \, ^\circ C$. Argon’s boiling point is in-between, close to $-185.8 \, ^\circ C$. Hence, by reducing the temperature of the air mixture, the components of air can be separated efficiently.

The first to apply the process of cryogenic distillation in large scale was Carl von Linde in 1895. Using the Joule-Thompson effect, he successfully liquefied air on a continuous basis by separating approximately 70\% $O_2$ [11]. In 1902, he produced pure oxygen by introducing air in a distillation column and in 1908, Linde introduced the double-column to increase efficiency and allow for nitrogen capture [11]. One column operates at low pressure while the other one is at high pressure; the two columns are coupled with a condenser, which is a key feature during air separation.

Cryogenic air separation is currently the most efficient and cost-effective technology for producing large quantities of oxygen, nitrogen, and argon as gaseous or liquid products. It is a mature technology that results in high-purity oxygen production but this maturity means that there is little room for efficiency improvements when an ASU operates using cryogenic distillation. The highest energy consumption comes from the compression of the feed air, while additional energy is required to regenerate the molecular sieves used to remove components that may affect the cryogenic process [12]. According to Pfaff and Kather, ASUs show a specific energy consumption of approximately $0.25 \, (kWh/kg \, O_2)$ when delivering 99.5\% pure $O_2$ by volume at atmospheric pressures, however this value is not fixed and can vary depending on the compression process. In addition, the specific energy consumption of an ASU decreases with decreasing $O_2$ purity. For example, Air Liquide proposes that the specific energy can decrease around $0.16-0.20 \, (kWh/kg \, O_2)$ with an oxygen product purity of 95\% by volume [12, 13, 14].

As a result, to allow for high purity $O_2$ production, alternative methods that
gurantee low energy consumption should be considered. The use of pressure swing adsorption with zeolites as the absorbents is still at its early stages, while the $O_2$ purity is lower than 95(%) [10]. An alternative technology to cryogenic distillation that has the potential to reduce the energy requirements of $O_2$ separation while maintaining the $O_2$ purity around 100(%) is the use of Ion Transport Membranes described in the next section.

1.4.2 Ion Transport Membranes

ITM are dense ceramic materials selective to oxygen ions only. Given that nothing else passes through the membrane but oxygen ions, purity of 100(%) can be achieved assuming air leaks can be avoided. To enable oxygen permeation, ITM operate at temperatures $T > 700 (^{\circ} C)$. The oxygen flux through the material is a strong function of temperature and oxygen partial pressure around the material. Although the permeation steps will be discussed in the following section, ITM are thin enough to reduce limitations related to diffusion of species within the material. For laboratory purposes, ITM have thicknesses in the order of 1 ($mm$); for industrial applications, membranes approximately 100 ($\mu m$) thick will be used either with a porous support or catalyst or both applied on the gas-membrane interfaces.

The first to propose the use of ITM for pure $O_2$ separation from air was Teraoka et. al. in 1985 by investigating $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ under different stoichiometries and temperature ranges [15]. From that point further, significant progress has been made due to both academic and industrial research activities. In the industrial area, Air Products and Ceramatec have been the pioneers in the development of ITM for the production of pure oxygen and syngas [16]. The ITM team holds more than 90 US patents in the ITM technology, while generous funding has been provided by the US
Department of Energy to assist the scaling up of the technology. Working towards industrial commercialization, Air Products has developed a 1(MW) intermediate scale cogeneration plant in Convent, LA, capable of producing 100 tons of pure $O_2$ per day [16]. According to the company, the capital cost can decrease by 30(%) with the use of ITM. However, on September 2015, Air Products decided to spin off its Materials Technologies business. The spin off was completed during October 2016 and the new company has been renamed Versum Materials. Until this point, it is unclear whether Versum Materials will continue working on the ITM technology.

1.5 Fundamentals of Ion Transport Membranes

Ceramic membranes for oxygen separation belong to two different categories: pure oxygen conducting membranes and mixed ionic-electronic conducting membranes [17]. In the first case, oxygen in the form of ions are flowing through the material while in the second case, both oxygen ions and electronic charge carriers are moving to allow for net change neutrality within the material. In the remaining of this section we will describe the fundamentals of MIEC given that they constitute the majority of ITM.

1.5.1 MIEC structure

The performance of MIEC depends highly on the material composition and structure, hence significant work has been done in the past decades on the exploration of possible material candidates that optimize oxygen permeation and stability. Most MIEC satisfy the aforementioned criteria when their structure exhibits either a perovskite or a fluorite type [17]. Perovskite-type materials have an orthorhombic structure;
an orthorhombic lattice results from a stretch of a cubic lattice along two of its orthogonal directions such that the lattice parameters are distinct, i.e. $a \neq b \neq c$. In addition, perovskite-type materials are described by the general formula $ABO_3$, where $A$ and $B$ stand for different elements [18]. Different valence combinations of $A$ and $B$ site can be used; the most typical ones are $A^{1+}B^{5+}O_3^{2-}$, $A^{2+}B^{4+}O_3^{2-}$ and $A^{3+}B^{3+}O_3^{2-}$ [18]. The A-site is frequently occupied by large alkali earth metals such as Barium, Lanthanum, Strontium, while the B-site is usually a transition metal like Iron, Copper, Cobalt etc. Although the same structure is obtained in all cases, the use of different elements leads to perovskites with completely different properties due to the differences in the electronic structure of the material that results from the solid state chemistry and the bonding that takes place between the various elements [18]. A typical perovskite lattice is shown in figure 1-4.

![Figure 1-4: Structure of a $ABO_3$ perovskite: A is located at the body center position, B is located at the corners while O exists at the edge centers [18].](image-url)
The size of the A-site is larger than that of the B-site and hence an important parameter associated with the perovskite structure is the tolerance factor \( t_f \). The tolerance factor is defined as:

\[
\begin{align*}
    t_f &= \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}
\end{align*}
\]  

(1.6)

A perovskite structure is preserved if \( 0.8 \leq t_f \leq 1.0 \) [17, 19]. The tolerance factor is an empirical relationship that confirms the impact of the element size on the structure stability.

On the other hand, the fluorite structured oxides exhibit a simple cubic oxygen lattice with alternate body centers occupied by eight coordinated cations. The general formula is \( AO_2 \), where \( A \) is a tetravalent cation. More information about the fluorite-type structure can be obtained in [20].

1.5.2 Defect chemistry and oxygen transport within ITM

The perfect perovskite structures described in the previous section will never be able to conduct oxygen ions within their bulk. To allow for oxygen ion incorporation, the material needs to experience defects in the oxygen lattice site. In practice, all materials contain defects in temperatures higher than \( 0 \) (K). Thermodynamically, the presence of these defects permits the material to obtain its minimum Gibbs free energy. Creation of defects increases the entropy within the material because the number of possible configurations that can be occupied by defects becomes higher [17].

Defects can be classified into the following categories:

- Point defects: point defects constitute a local disruption in the regularity of
the lattice. They occur only at or around a single lattice point and are not extended in space in any dimension. This is why sometimes they are called 0-dimensional defects. The most frequently occurred point defects are vacancies, interstitial impurities or substitutional impurities.

Point defects in ionic solids are created in such a way that allows the material to maintain charge neutrality. The most characteristic type of point defects in ionic solids are the Schottky and Frenkel defects.

- Line defects: line defects are related to the misalignment of atoms in the crystal lattice.

- Planar defects: grain boundaries are a general planar defect that separate regions of different crystalline orientation (i.e. grains) within a polycrystalline solid.

To allow for oxygen ion diffusion within the volume of ITM, a driving force is required. The driving force that enables oxygen ion transport is the difference in the electrochemical potential of oxygen between the two membrane sides. Oxygen permeation through the material is the outcome of two different processes: surface exchange and material diffusion.

Figure 1-5 shows a schematic of this process. Oxygen vacancies within ITM constitute one type of point defects associated with the material. In the next chapters, we will show that point defects other than oxygen vacancies may exist within ITM; for example, within LCF, three iron states are found to coexist and two of these behave as localized point defects.

Starting with an oxygen molecule $O_2$ in the gas-phase of the oxygen rich side, advection and diffusion drive the molecule close to the membrane surface. As soon
Figure 1-5: Oxygen permeation process within ITM. The transport mechanism includes surface exchange and material diffusion.

As $O_2$ reaches the oxygen rich membrane surface, it adsorbs on the membrane side, it dissociates into two oxygen atoms $O$ and then two electron transfer processes take place to ionize each $O$ into $O^{-2}$. Once $O^{-2}$ is formed, it reacts with an oxygen vacancy and is incorporated into the oxygen lattice site of the ITM as $O_O^X$. This entire process is the surface exchange on the gas-membrane interface of the oxygen rich side. Note that this is just one proposed mechanism of the surface exchange on ITM and other possible mechanisms may exist depending on the material solid state chemistry.

Within ITM, $O_O^X$ will move from the oxygen rich to the oxygen lean side due to a
difference in the electrochemical potential between the two sides. This means that $O_\delta^X$ will start hoping into neighboring vacancies due to this driving force until it reaches the oxygen lean side. This charged species diffusion process has two contributions: the first is related to the diffusion due to concentration gradient, while the second is associated with electromigration. Electromigration is the driving force due to the presence of an electrostatic field created by the movement of charged species within the material. While $O_\delta^X$ moves from the oxygen rich to the oxygen lean side, oxygen vacancies diffuse on the opposite direction. The transport of the rest of the charged species within the material is such so that electroneutrality (in the bulk) is held.

Once $O_\delta^X$ reach the oxygen lean membrane side, the reverse surface exchange mechanism described previously takes place. In this way, $O_2$ is formed in the gas-phase and is free to move due to both convection and diffusion.

1.5.3 Oxygen permeation through $La_{0.9}Ca_{0.1}FeO_{3-\delta}$

In this thesis, we have selected to use a Lanthanum Ferrite perovskite with 10 (%) Calcium substitution in the A-site; the resulting material has the general formula $La_{0.9}Ca_{0.1}FeO_{3-\delta}$. The choice of the material was made based on the high stability that the structure exhibits at high temperatures and under a reducing environment. However, the increased stability of LCF is associated with low oxygen permeation under non-reactive conditions. Figure 1-6 shows a comparison of the oxygen permeation that has been measured under inert conditions for various materials; LCF is shown to have a poor performance compared to other materials but it is not susceptible to phase transformations which is a significant problem for high $O_2$ permeation perovskites, like BSCF. Nevertheless, the next chapters describe the $O_2$ permeation increase through LCF when fuel is introduced at the sweep side.
LCF is the perovskite used by Air Products for pure $O_2$ and syngas production. Although the ITM team working for Air Products has published various papers on the performance of LCF, none of them provides information in terms of the oxygen flux that can be achieved under different operating conditions and with the use of different catalysts or porous layers. Given the potential use of LCF in large scale industrial applications, the scope of this thesis is to provide experimental data for the same material under different operating conditions and to create a framework for the modeling of the oxygen permeation process that will be used further for the design of high efficiency ITM modules.

Figure 1-6: Oxygen permeation within perovskites of different structure and stoichiometry [21].
1.6 Research Objectives

Given the global effort for $CO_2$ emission reduction and the need to explore high efficiency alternative technologies for gas conversion using pure oxygen, the objectives of this thesis are:

1. Characterization of LCF under a $CH_4 - CO_2$ reactive mixture by measuring the oxygen permeation, syngas production and fuel conversion under different temperatures, flow rates, inlet $CH_4$ concentrations and membrane thicknesses.

2. Development of a framework to model the surface exchange and charged species diffusion within LCF (or similar perovskites) using the PNP model:
   a. Proposal of a model that accounts for the exact defect mechanism of LCF with the additional constrain of thermodynamic consistency.
   b. Determination of the reaction rate coefficients and bulk diffusion properties by fitting experimental data during pure $O_2$ production.
   c. Development of a multi-step surface reaction mechanism that accounts for the impact of $H_2$ and $CO$ on the oxygen permeation and defect chemistry.

3. Development of a CFD model that couples gas-phase transport with the PNP model towards the design of ITM modules of optimized performance.
Chapter 2

A large scale reactor for ITM characterization

In this chapter, we describe the experimental apparatus and the equipment used to characterize the LCF membrane of our study. Given the interest of testing the material in the presence of fuel, emphasis will be given to the experimental setup under reactive conditions. This chapter provides a quick overview of the apparatus and the equipment used during the experiments; more detailed information about the design of the reactor is available in [22].

2.1 Objectives of ITM reactor design

Laboratory scale ITM reactors are generally designed in a way to allow for the measurement of system-level properties, such as the oxygen permeation through the membrane or the fuel conversion/production. Although such information is vital for the determination of whether a material can be considered as a promising candi-
date for future integration in industrial scale ITM reactors, little knowledge can be obtained in terms of the impact of the mixture composition on the oxygen permeation. In addition, numerical simulations resolving the gas-phase transport within ITM reactors have shown that, depending on the operating conditions and the reactor design, the species composition on the membrane surface can be different when compared to the outlet, well-mixed measurements [23, 24]. This is certainly the case when the inlet mixture is combustible in the gas-phase. But even for inert mixtures, the evolution of a diffusive boundary layer on the membrane sides can lead to a concentration gradient within the reactor. Hence, knowledge of the species mole fractions as close as possible to the membrane surface is required. This can be achieved either by direct measurement of the chemical composition locally or by using numerical simulations. Numerical simulations can be quite useful when the inlet mixture is an inert gas since the rate of the corresponding surface reactions involving $O_2$ ionization, dissociation and incorporation can be quantified. For reactive mixtures though, if the chemical reactions that take place on the membrane surface are unknown, numerical simulations are not useful because they cannot capture the impact of heterogeneous reactions on the oxygen permeation and species evolution. This means that experimental measurements near the membrane surface is the key to determine the species concentration locally and understand their impact on the material performance.

Measurement of the mixture composition as close as possible to the membrane surface provides the possibility to develop universal models independent of the experimental apparatus used during the testing of the material. Towards this direction, the reactor used in this work has been designed in a way that allows to measure the species concentration locally. This is attained with a use of a quartz probe that is inserted within the sweep side of the reactor. Quartz is chemically inert and can
withstand high temperatures, hence it is an ideal candidate for high temperature applications operating under a reactive environment. This measurement technique can be applied for both inert and reactive cases and it will be shown that it is compatible when either a Mass Spectrometer (MS) or a Gas Chromatograph (GC) is used for the quantification of the mixture composition.

2.2 Stagnation flow reactor

The processes that occur when ITM are introduced in a reactor are inherently complicated. Besides the chemistry that takes place on the gas-membrane interfaces and the diffusion of species within the material, one also has to account for the role of the flow field and the gas-phase transport within the air and fuel sides. When designing a laboratory scale reactor to be used for the investigation of the fundamentals of these materials, reducing the complexity is the key in order to isolate the processes directly related to the presence of the material.

The reactor geometry is a crucial choice during the design stage since it is strongly related to the flow field. As discussed before, a probe should be inserted to allow for the measurement of the local species concentration. If the mixture composition along the material is not uniform, one has to conduct multiple measurements at different membrane locations to capture the non-uniformity; this certainly increases the duration of the experiment and the associated operating cost.

A better approach is to design an ITM reactor having a geometry that leads to a uniform species distribution along the membrane. A geometry that meets this criterion is the stagnation flow configuration. A stagnation flow has the advantage of creating a flow field which is self-similar in the direction parallel to the membrane surface, while species concentration varies only in the direction perpendicular to the
Figure 2-1: Numerical simulations of the stagnation flow ITM reactor when air is introduced at the feed (top) side and $H_2$-$Ar$ mixtures at the fuel (bottom) side. The flow-field is self-similar in the $X$-direction at both sides. Species concentration varies only in the $Y$-direction. White dashed lines correspond to the contours of each species while black solid lines correspond to the streamlines.

membrane surface. The flow field of a stagnation flow is shown in figure 2-1; the flow has been determined by solving the CFD model described in chapter 3 assuming the exact geometry of the ITM reactor used during the experiments (described below). This self-similarity in the flow field is very important during the experiments because
the mixture composition along the entire area of the membrane can be quantified simply by probing gases at one location. Given that spatial variations are present only in the direction perpendicular to the membrane surface, moving the probe downwards allows for the quantification of the mixture composition away from the material.

Figure 2-2: Stagnation flow ITM reactor used during the experiments [22].

Figure 2-2 shows the exterior of the stagnation flow ITM reactor which was first introduced in [25]. The top side is the air/feed side while the bottom side is the fuel/sweep side. The reactor was built using Inconel 601 which is proven to
have great oxidation resistance at high temperatures. The reactor is enclosed in an insulating box that allows to reach temperatures up to \( T = 1100 (\degree C) \); this is achieved with the use of six silicon carbide radiant heating elements supplied by I Squared R Element Co. The total power supply of these elements is 16 (kW). The heating rate was controlled by thermocouple-feedback positioned at the top of the enclosure. The reactor enclosure design was made of the insulating material Gemcolite® NS, laminated in layers up to 8" thick, from Refractory Specialties Inc. This material was rated for continuous use in temperatures up to 1260 (\degree C), and is designed with an inorganic binder so that harmful gases are not released when first heated.

The Arrhenius dependent nature of chemical reactions and conductivities make the oxygen permeation processes very sensitive to temperature variations; hence, establishing isothermal conditions within the reactor is necessary. To achieve this, the preheating box shown in figure 2-2 was installed before the inlet of the sweep side. In this way, the residence time of the sweep mixture before entrance to the inlet of the ITM reactor increases significantly; as a result, temperature variations within the reactor can be eliminated.

2.3 Membrane geometry and quartz probe

After the short description of the exterior of the reactor, the next step is to describe the placement of the membrane and the probe within the reactor. Figure 2-3 shows the position of the membrane with respect to the rector. The figure shows the side of the membrane that is exposed to the air stream. To reveal the membrane, one has to remove the feed side of the reactor, which is a separate part assembled to the entire reactor.

The membrane used during the experiments is a square, planar LCF membrane
Figure 2-3: Position of the membrane during the experiments. Figure shows the side exposed to air.

with dimensions $85 \times 85 (mm^2)$. Due to sealing with the use of a gasket material, the effective area of the membrane (i.e. the area of the membrane exposed to the flow stream) is $73 \times 73 (mm^2)$. The LCF membranes have been produced in a variety of thickness by Ceramatec; although membranes with thickness around 0.1 (mm) were provided, it was found that sealing is very difficult to achieve because these thin membranes would easily break due to the applied thermal and mechanical stresses. As a result, membranes with thickness between $0.9 (mm) - 1.5 (mm)$ were used during the experiments.

The sweep side of the reactor is revealed once the membrane is removed from
Figure 2-4: Sweep side of the reactor. Figure shows the quartz probe used to measure the mixture composition as close as possible to membrane surface, the thermocouple that measures the membrane temperature and the flow straightener that minimizes the swirling motion of the inflow stream.

the mounting position shown in figure 2-3: the interior of the sweep side is shown in figure 2-4. The figure shows the quartz probe that is used to measure the local species concentration near the vicinity of the membrane. The probe is straight except from the tip which is slightly bent to ensure contact with the membrane and sampling from a point undisturbed by the presence of the probe. The other end of the probe (not shown in figure 2-4) exits the reactor and is connected to the MS or GC sampling line. Sealing is attained using a 1/8" Swage-Lok® Ultra-Torr Connector with an O-ring configuration that guarantees leak-free connection. If measurement of the spatial
variation of the mixture composition is required, the probe can be adjusted vertically or can be twisted to allow for the measurement at other membrane locations.

Figure 2-4 also shows the position of a thermocouple that is inserted at the sweep side of the reactor to allow for the temperature measurement on the membrane surface; another thermocouple (not shown in figure 2-4) is inserted at the feed side in a similar way. A Swage-Lok® configuration is used to ensure high performance sealing of the reactor due to the thermocouple insertion. The thermocouple is of K-type with a closed tip which allows it to be radiation insensitive. It can be adjusted vertically to allow for the temperature measurement away from the material. Although it is desired to have the thermocouple in contact to the membrane surface during the experiments, it was found that the thermocouple can have catalytic effects because part of the material contains Nickel which is known to be a good catalyst for various fuels. To ensure that the thermocouple is not participating in any chemical reaction during reactive experiments, it was removed from the sweep side at the beginning of the experiment and after the membrane temperature was measured under an inert environment. The temperature changes were then monitored only with the corresponding thermocouple at the feed side of the membrane. No significant temperature variations were observed during the reactive experiments.

Although Inconel 601 shows good oxidation resistance, it was found that it may also catalyze certain reactions. This is due to the presence of nickel in the alloy. To reduce the contact of the gas-stream with the catalytic walls, the sweep side of the reactor was covered with quartz. This ensures that Inconel does not participate in any catalytic reactions and that hence, fuel conversion happens due to gas-phase reactions and heterogeneous reactions on the membrane surface.
2.4 Flow control

The flow control within ITM reactors is probably one of the most important parameters during the experiments. The first necessity that needs to be satisfied requires the flow to have small fluctuations around the set point to guarantee steady state operation. If the flow field within the reactor does not reach steady (or quasi-steady) conditions, the temperature and mixture composition measurements will have high uncertainty that makes the post-processing of the data quite difficult. In addition, the flow control setup should also allow measurements to be conducted under different operating conditions that include the mixing of different gases with no constrain in the desired concentration. Moreover, the equipment should be versatile enough to permit the control of different gases using the same mass flow controller.

To meet these requirements, the experimental apparatus was equipped with 4 GF40 Elastomer Sealed Thermal Mass Flow Controllers provided by Brooks Instrument. One MFC is used to control the flow at the feed side and the remaining ones are used for the sweep side flow control where a blend of gases is usually added at the inlet. These MFCs are quite flexible given that multiple gases can be controlled using one device. At the same time, the gas type and maximum flow rate can be adjusted during run-time. They have high accuracy and control and they provide fast response. The MFCs are powered and controlled by the 0254 Four Channel Power Supply, Readout & Set Point Controller purchased by Brooks Instrument. The 0254 is a microcomputer-based controller that allows various operations including blending of different gases. One of the most important functions of the controller is the compatibility with LabView; Brooks Instrument provides an online application that allows the remote control of the MFCs. Figure 2-5 shows the previously described system used to accurately control the inlet mass flow rates.
2.5 Analysis of mixture composition

To measure the mixture composition, we have used both Gas Chromatography and Mass Spectrometry instruments. Although these two measurement techniques are quite accurate, their operation is based on different principles. According to the measurement type and the operating conditions, the use of one instrument can be beneficial when compared to the other. For example, the use of an MS is required when the measurement of the time-dependent concentration of species is required; a GC can only be used to measure the species concentrations under steady-state conditions. In addition, collecting data using an MS is much faster because the
mixture is analyzed during run-time; when using a GC, a vacuum pump draws a portion of the mixture from the reactor to the GC where it will be driven into the analytical column for gas separation and then, the species concentration will be quantified using a detector. This entire process requires 1-3 minutes depending on the species that exist in the mixture to be analyzed. Moreover, an MS can measure the steam concentration in the mixture, while for a GC steam cannot be measured and at the same time steam entrainment into the GC should be avoided because it may deteriorate the performance of the analytical columns. Because of this, the experimental apparatus should be designed accordingly to allow for steam removal prior to the GC entrance.

On the other hand, calibration using an MS is very sensitive and has to be performed using a mixture that contains the same gases that also appear during the experimental measurements; attention has also to be given to the calibration points since the calibration concentrations of species have to be close to the ones that are present during the experiment. A GC is free of such a drawback given that a calibration curve for each species is generated; different mixture compositions can be used with multiple calibration points. Hence, the calibration of a GC is an easier and more reliable task compared to an MS. However, the GC cannot measure all species in the mixture; this is constrained by the capability of the analytical columns to separate the species. Hence, the mixture quantification depends on the type of the analytical columns installed in the GC. An MS can detect all species except from the ones having the same mass to charge ratio. For example, the most common issue with an MS is that the concentration of $N_2$ cannot be distinguished with that of $CO$ because the charge to mass ratio is the same. To achieve this, other special calibration of the instrument is required.

Because of the latter deficiency, air leaks at the sweep side cannot be accurately
measured when both $N_2$ and $CO$ exist in the mixture. This is why in this thesis it was decided to use an MS for non-reactive cases while a GC was used for reactive measurements. 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 [26]. Under reactive conditions, a 490 MicroGC from Agilent Technologies was used. The GC is equipped with 3 analytical columns:

- MolSieve 5A: operates using a Helium carrier gas and can detect $H_2$, $O_2$, $Ar$, $N_2$, $CH_4$, $CO$. The column is very sensitive to $CO_2$, hence the back-flush option is enabled when $CO_2$ is present in the mixture. Otherwise, the baseline of the chromatogram is disturbed significantly and the quantification of the species composition becomes difficult.

- COX: operates using an Argon carrier gas and can detect $He$, $H_2$, $CO$, $CH_4$, $CO_2$ and combined $O_2 - N_2$. The back-flush option is not enabled for the operating conditions under investigation.

- PPQ: operates using a helium carrier gas and can detect combined $O_2 - N_2$, $CH_4$, $CO_2$, combined $C_2H_2 - C_2H_4$, $C_2H_6$, $C_3H_8$. The back-flush option is not enabled for the operating conditions under investigation.

During the experiments, the mixture composition is measured at three different points: one is located at the inlet of the ITM reactor and another one at the outlet; the third measurement aims to evaluate the mixture composition near the vicinity of the membrane at the sweep side using the quartz probe. No measurement of the $O_2 - N_2$ composition at the feed side is conducted. To automate the process, the tubes at the sampling points where connected to a VICI Valco automatic selector.
valve which can be controlled by the GC software or manually. To estimate the uncertainty of the measured values, at least 20 measurements are conducted at each location; the average and standard deviation can then be calculated.

2.6 Use of desiccant for steam removal

One of the major problems to solve when conducting reactive experiments is the way \( H_2O \) is treated during the measurements. When using an MS, steam can only be measured when it remains in the gas-phase without condensing into water. If the latter happens, then the analysis of the mixture using an MS will result into an erroneous species concentration because steam condensation will change the mixture composition analyzed by the instrument. This means that all the lines exiting the reactor have to be heated-up in order to avoid steam condensation. Note that if steam condenses into water within the sampling line, this may block the flow in the tube which may then lead to erroneous measurements or even damage the instrument.

While dealing with steam when using an MS seems to be straightforward, the use of a GC makes things slightly more complicated. Recall that a GC cannot directly measure steam while at the same time we should avoid the entrainment of steam within the GC because the analytical columns may be contaminated or severely damaged. One way to prevent steam from entering the GC is to use a cold trap. However, a cold trap increases the dead volume between the sampling lines and as a result the measurement duration increases significantly.

A better approach is to use a desiccant prior to the GC inlet. A desiccant is a solid substance that has the ability to absorb water. Silica gel is the most popular desiccant material. The solid particles are blue prior to their use and become pink when they have absorbed 8% of their weight. To achieve best performance, steam
Figure 2-6: Configuration of sampling lines. The lines are connected to the VICI Valco autosampler which then leads the mixture to the GC. All sampling lines are heated-up when steam is present in the mixture. The desiccant is added in a 3/4" tube prior to the GC entrance. The mixture is kept hot to prevent steam condensation until it is adsorbed by the desiccant.

has to be in gaseous form before it comes into contact with the desiccant. As a result, even in this case the sampling lines leading to the GC need to be heated-up during the experiment. Figure 2-6 shows the configuration of the sampling lines. The sampling lines were heated-up using an extreme-temperature heat cable that surrounded the exterior of the tubes. This first layer was covered by a second layer of insulation to reduce heat losses to the environment. Then, a third layer of aluminum foil was added to guarantee uniform temperature distribution along the lines. The
configuration is presented in figure 2-7. The figure also shows the part of the quartz probe that exits the reactor as well as the Swage-Lok® connectors that allow for a leakage-free operation of the reactor. Given that the quartz needs to be positioned during the experiment, part of it was not insulated, however no steam condensation was observed inside the quartz tube.

Figure 2-7: Sampling line heat-up configuration.
Chapter 3

Numerical investigation of ITM reactors: modeling the gas-phase and material transport

In this chapter, we describe the numerical tools used for the investigation of ITM reactors. These tools represent the transport of species that convect and diffuse in the gas-phase as well as the diffusion of charged species within the material. As will be shown in the next chapters, coupling these two models allows for the development of a numerical tool that will be used for the design of novel ITM reactors suitable for industrial applications that involve fuel conversion to useful products.
3.1 Modeling the transport of gas-phase species

3.1.1 Equations of state

The numerical model used in this study to resolve the gas-phase is a 2D/3D, compressible, finite volume solver based on the Pressure Implicit Algorithm with Splitting of Operators (PISO) for the solution of the Navier-Stokes equations [27, 28]. The code was developed using the open source software OpenFOAM [29]. For laminar flow and using index notation, conservation of momentum, mass, energy and the ideal gas law are considered according to Poinsot [30]. The following subsections provide more information regarding the equations of state and the evaluation of thermodynamic and transport properties required for the solution of the multispecies transport problem.

Conservation of momentum

The conservation of momentum is described by the following equation:

\[
\frac{\partial}{\partial t} (\rho u_j) + \frac{\partial}{\partial x_i} (\rho u_i u_j) = -\frac{\partial p}{\partial x_j} + \frac{\partial \tau_{ij}}{\partial x_i} + \rho \sum_{k=1}^{K_g} Y_k f_{k,j} \tag{3.1}
\]

Assuming that the only volumetric force acting on species \( k \) comes from the gravitational field, \( f_{k,j} = g_j = (0, 0, -9.81) \), which is considered constant for all species \( k \). Then, equation 3.1 becomes:

\[
\frac{\partial}{\partial t} (\rho u_j) + \frac{\partial}{\partial x_i} (\rho u_i u_j) = -\frac{\partial p}{\partial x_j} + \frac{\partial \tau_{ij}}{\partial x_i} + \rho g_j \tag{3.2}
\]
The viscous stress tensor is given by the following equation:

\[
\tau_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial u_m}{\partial x_m} \delta_{ij} \tag{3.3}
\]

To solve equation 3.2, knowledge of the dynamic viscosity of the mixture, \( \mu \), is required. This is evaluated using the following expression that arises from the kinetic theory of gases [31, 32]:

\[
\mu (\text{Pa} \cdot \text{sec}) = \sum_{k=1}^{K_a} \frac{X_k \mu_k}{\sum_{p=1}^{K_a} X_p \Phi_{kp}} \tag{3.4}
\]

In equation 3.4, \( \mu_k \) is the dynamic viscosity of the species \( k \) evaluated using the following expression:

\[
\mu_k (\text{Pa} \cdot \text{sec}) = 26.69 \times 10^{-7} \times \frac{(W_k T)^{1/2}}{(\sigma_k^{L,J})^2 \Omega_{\nu,k}} \tag{3.5}
\]

In equation 3.5, \( \sigma_k^{L,J} \) is the average diameter of molecular collision for species \( k \) and \( \Omega_{\nu,k} \) the collision integral for species \( k \). The parameter \( \sigma_k^{L,J} \) is a tabulated value that is easily found in the literature for all species [31] while \( \Omega_{\nu,k} \) is evaluated using the equation below:

\[
\Omega_{\nu,k} = A_{\nu} \left( \frac{k_B T}{\epsilon_k^{L,J}} \right) B_{\nu} + C_{\nu} \exp \left( -D_{\nu} \frac{k_B T}{\epsilon_k^{L,J}} \right) + E_{\nu} \exp \left( -F_{\nu} \frac{k_B T}{\epsilon_k^{L,J}} \right) \tag{3.6}
\]

where \( k_B = 1.380 \times 10^{-23} \, \text{(J/K)} \) is the Boltzmann constant, \( A_{\nu} = 1.16145 \), \( B_{\nu} = 0.14874 \), \( C_{\nu} = 0.52478 \), \( D_{\nu} = 0.77320 \), \( E_{\nu} = 2.16178 \) and \( F_{\nu} = 2.43787 \). The parameter \( \epsilon_k^{L,J} \) is the characteristic Lennard-Jones energy, which is also tabulated for all species.
In addition, $\Phi_{kp}$ in equation 3.4 is given by the following equation:

$$\Phi_{kp} = \left[ 1 + \left( \frac{\mu_k}{\mu_p} \right)^{1/2} \left( \frac{W_p}{W_k} \right)^{1/4} \right]^2 \left[ 8 \left( 1 + \frac{W_k}{W_p} \right) \right]^{1/2}$$  \hspace{1cm} (3.7)

Conservation of mass

The mass conservation equation for species $k$ is written in the following form [30, 32]:

$$\frac{\partial}{\partial t} (\rho X_k) + \frac{\partial}{\partial x_i} (\rho (u_i + V_{k,i}) X_k) = 0 \quad \text{for} \quad k = 1, \ldots, K_g \hspace{1cm} (3.8)$$

The modeling of the volumetric reaction rate of species $k$, $\dot{\omega}_k$, is identical to [30] and hence will not be repeated here. To calculate the diffusion velocities $V_{k,i}$, the solution of the Maxwell-Stefan diffusion problem is required [33]:

$$\frac{\partial}{\partial x_i} \left( X_k \rho \frac{D_{k,j}}{D_{k,j}^T} \frac{\partial T}{\partial x_i} \right) = \sum_{j=1}^{K_g} X_k X_j \frac{\partial p}{\partial x_i} + \sum_{j=1}^{K_g} \frac{X_k X_j}{\rho D_{k,j} T} \left( \frac{D_{j}^T}{Y_j} - \frac{D_{k}^T}{Y_k} \right) \frac{\partial T}{\partial x_i} \hspace{1cm} (3.9)$$

The system of equations 3.9 used to obtain the diffusion velocities $V_{k,i}$ is a linear system of size $K_g^2$ which must be solved in all 3 directions for each computational cell and at each time step [30]. To reduce the computational cost associated with this kind of calculation, instead of solving the exact Maxwell-Stefan diffusion problem, we shall use the Hirschfelder and Curtiss approximation which is the best first-order approximation to the system of equations 3.9 [30, 34]. In addition, the Soret effect (diffusion of mass due to temperature gradients) and the Dufour effect (diffusion of mass due to pressure gradients) are neglected.

According to the Hirschfelder and Curtiss approximation, the diffusion velocities
\( V_{k,i} \) are evaluated using the following expression:

\[
V_{k,i} \, (m/sec) = -\frac{D_k \partial X_k}{X_k \partial x_i}
\]  
(3.10)

In equation 3.10, the diffusion coefficient of species \( k \) in the mixture, \( D_k \), is evaluated according to the equation below:

\[
D_k \, (m^2/sec) = \frac{1 - Y_k}{\sum_{j=1, j \neq k}^{K} \frac{X_{j}}{D_{jk}}}
\]  
(3.11)

where \( D_{jk} = D_{kj} \) is the binary diffusion coefficient of species \( k \) into species \( j \) evaluated using the following expression:

\[
D_{kj} \, (m^2/sec) = 0.0266 \times \frac{T^{3/2}}{p \left( \frac{2}{w_k + w_j} \right)^{1/2} \left( \frac{\sigma_{k}^{LJ} + \sigma_{j}^{LJ}}{2} \right)^2 \Omega_D}
\]  
(3.12)

In equation 3.12, the pressure \( p \) is in \((Pa)\). Also, the parameter \( \Omega_D \) is calculated as follows:

\[
\Omega_D = \frac{A_D}{\left( \frac{k_B T}{\epsilon_{kj}} \right)^{B_D}} + \frac{C_D}{\exp \left( D_D \frac{k_B T}{\epsilon_{kj}} \right)} + \frac{E_D}{\exp \left( F_D \frac{k_B T}{\epsilon_{kj}} \right)} + \frac{G_D}{\exp \left( H_D \frac{k_B T}{\epsilon_{kj}} \right)}
\]  
(3.13)

where \( A_D = 1.06036, B_D = 0.15610, C_D = 0.19300, D_D = 0.47635, E_D = 1.03587, F_D = 1.52996, G_D = 1.76474 \) and \( H_D = 3.89411 \). Additionally in equation 3.13:

\[
\epsilon_{kj} = \left( \epsilon_k^{LJ} \epsilon_j^{LJ} \right)^{1/2}
\]  
(3.14)

Until this point we have expressed the way the mixture-average diffusion coefficient
$D_k$ is evaluated at each computational cell. Since we used the Hirschfelder and Curtiss approximation, substitution of equation 3.10 in equation 3.8 leads to the following species equation:

$$\frac{\partial}{\partial t} (\rho Y_k) + \frac{\partial}{\partial x_i} (\rho u_i Y_k) = \frac{\partial}{\partial x_i} \left( \rho D_k \frac{W_k}{W} \frac{\partial X_k}{\partial x_i} \right) + \dot{\omega}_k \quad \text{for } k = 1, \ldots, K_g \quad (3.15)$$

Summation of equation 3.15 over all $K_g$ species should lead to the mass conservation equation:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i) = 0 \quad (3.16)$$

However, given that $D_k$ is evaluated using the Hirschfelder and Curtiss approximation, summation of equation 3.15 over all $K_g$ species will conserve mass up to a small value close to zero. The right-hand side of the species conservation would have been strictly zero only if the exact diffusion problem was solved. This is the disadvantage of not solving for the Maxwell-Stefan diffusion problem, which would conserve mass exactly.

To ensure compatibility between mass and species conservation, a correction velocity $V_{i}^c$ is added to the convection velocity in the species equation 3.15:

$$\frac{\partial}{\partial t} (\rho Y_k) + \frac{\partial}{\partial x_i} \left( \rho (u_i + V_{i}^c) Y_k \right) = \frac{\partial}{\partial x_i} \left( \rho D_k \frac{W_k}{W} \frac{\partial X_k}{\partial x_i} \right) + \dot{\omega}_k \quad \text{for } k = 1, \ldots, K_g \quad (3.17)$$

This correction velocity is evaluated using the following expression:

$$V_{i}^c (m/sec) = \sum_{k=1}^{K_g} D_k \frac{W_k}{W} \frac{\partial X_k}{\partial x_i} \quad (3.18)$$

The correction velocity $V_{i}^c$ is evaluated to ensure global mass conservation. If all species equations are now summed, the mass conservation equation is recovered.
To numerically solve equation 3.17, the mole fraction $X_k$ that appears on the right-hand side is transformed into mass fractions $Y_k$. Hence, the following species conservation equation is solved:

$$\frac{\partial}{\partial t}(\rho Y_k) + \frac{\partial}{\partial x_i} (\rho (u_i + V_i^c) Y_k) = -\frac{\partial j_{k,i}}{\partial x_i} + \omega_k \quad \text{for } k = 1, \ldots, K_g$$

(3.19)

$$j_{k,i} = -\rho D_k \frac{\partial Y_k}{\partial x_i} - \frac{\rho D_k}{W} \frac{\partial W}{\partial x_i} Y_k$$

(3.20)

The reason behind this transformation is to allow for the implicit discretization of the laplacian term which increases the stability of the system during the numerical solution. During the computation, $K_g - 1$ species equations are solved and the last one is evaluated through global mass conservation $Y_{K_g} = 1 - \sum_{k=1}^{K_g-1} Y_k$.

**Conservation of energy**

The conservation of energy requires attention because multiple forms exist. We start from the conservation equation for the total specific energy $e_t$:

$$\frac{\partial}{\partial t} (\rho e_t) + \frac{\partial}{\partial x_i} (\rho u_i e_t) = -\frac{\partial \dot{q}_i}{\partial x_i} + \frac{\partial}{\partial x_j} (\sigma_{ij} u_i) + \dot{Q} + \rho \sum_{k=1}^{K_g} Y_k f_{k,i} (u_i + V_{k,i})$$

(3.21)

In equation 3.21, the heat flux $\dot{q}_i$ is given by the following equation:

$$\dot{q}_i = -\lambda \frac{\partial T}{\partial x_i} + \rho \sum_{k=1}^{K_g} h_k Y_k V_{k,i} \quad \text{Fourier's Law}$$

(3.22)

Interdiffusion term
The following equation relates the total specific energy \( e_t = e + \frac{1}{2} u_m u_m \) and the total specific enthalpy \( h_t = h + \frac{1}{2} u_m u_m \):

\[
e_t = h_t - \frac{p}{\rho}
\]  

(3.23)

Substitution of equation 3.23 into equation 3.21 yields the following expression:

\[
\begin{align*}
\frac{\partial}{\partial t} (\rho h_t) + \frac{\partial}{\partial x_i} (\rho u_i h_t) - \frac{\partial p}{\partial x_i} - \frac{\partial}{\partial x_i} (u_i p) &= -\frac{\partial q_i}{\partial x_i} + \frac{\partial}{\partial x_j} (\sigma_{ij} u_i) + \\
&+ \dot{Q} + \rho \sum_{k=1}^{K_g} Y_k f_{k,i} (u_i + V_{k,i})
\end{align*}
\]  

(3.24)

We next make use of the total stress tensor relation:

\[
\sigma_{ij} = \tau_{ij} - p \delta_{ij}
\]  

(3.25)

Substitution of equation 3.25 into equation 3.24 leads to the following expression:

\[
\begin{align*}
\frac{\partial}{\partial t} (\rho h_t) + \frac{\partial}{\partial x_i} (\rho u_i h_t) &= \frac{\partial p}{\partial t} - \frac{\partial q_i}{\partial x_i} + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \dot{Q} + \rho \sum_{k=1}^{K_g} Y_k f_{k,i} (u_i + V_{k,i})
\end{align*}
\]  

(3.26)

The next step is to rearrange equation 3.26 so that the specific enthalpy of the mixture \( h \) appears. For this reason, we make use of the following expression:

\[
h_t = h + \frac{1}{2} u_m u_m = h + k
\]  

(3.27)
Using the aforementioned formula, equation 3.26 now becomes:

\[
\frac{\partial}{\partial t}(\rho h) + \frac{\partial}{\partial x_i} (\rho u_i h) + \frac{\partial}{\partial x_i} (\rho u_i k) = \frac{\partial p}{\partial t} - \frac{\partial q_i}{\partial x_i} + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \\
+ \dot{Q} + \rho \sum_{k=1}^{K_g} Y_{k,f,i} (u_i + V_{k,i})
\]  

(3.28)

The specific enthalpy $h_k$ is related to the specific sensible enthalpy $h_s$ and the formation enthalpies of species $k$, $\Delta h_{f,k}$, through the following expression:

\[
h = h_s + \sum_{k=1}^{K_g} Y_{k} \Delta h_{f,k}
\]

(3.29)

Substitution of equation 3.29 into equation 3.28 leads to:

\[
\frac{\partial}{\partial t}(\rho h_s) + \frac{\partial}{\partial x_i} (\rho u_i h_s) + \frac{\partial}{\partial x_i} (\rho u_i k) = \frac{\partial p}{\partial t} - \frac{\partial q_i}{\partial x_i} + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \\
+ \dot{Q} + \rho \sum_{k=1}^{K_g} Y_{k,f,i} (u_i + V_{k,i})
\]

(3.30)

To further simplify equation 3.30, we will multiply the transport equation 3.8 of each species $k$ with $\Delta h_{f,k}$ and then sum these $K_g$ equations over all species $k$. This process leads to the following equation:

\[
\frac{\partial}{\partial t} \left( \rho \sum_{k=1}^{K_g} Y_{k} \Delta h_{f,k} \right) + \frac{\partial}{\partial x_i} \left( \rho u_i \sum_{k=1}^{K_g} Y_{k} \Delta h_{f,k} \right) + \frac{\partial}{\partial x_i} \left( \rho \sum_{k=1}^{K_g} Y_{k} \Delta h_{f,k} V_{k,i} \right) = -\dot{\omega}_T
\]

(3.31)
where the heat release rate $\dot{\omega}_T$ due to combustion in the gas-phase is defined as:

$$\dot{\omega}_T = - \sum_{k=1}^{K_g} \Delta h^o_{f,k} \dot{\omega}_k.$$  

(3.32)

Note that the Hirschfelder-Curtiss approximation has not been used up to this point.

Substitution of equation 3.31 into equation 3.30 results to:

$$\frac{\partial}{\partial t} (\rho h_s) + \frac{\partial}{\partial x_i} (\rho u_i h_s) + \frac{\partial}{\partial t} (\rho k) + \frac{\partial}{\partial x_i} (\rho u_i k) - \frac{\partial}{\partial x_i} \left( \rho \sum_{k=1}^{K_g} Y_k \Delta h^o_{f,k} V_{k,i} \right) - \dot{\omega}_T = \frac{\partial p}{\partial t} - \frac{\partial q_i}{\partial x_i} + \frac{\partial}{\partial x_j} \left( \tau_{ij} u_i \right) + \dot{Q} + \rho \sum_{k=1}^{K_g} Y_k f_{k,i} (u_i + V_{k,i})$$

(3.33)

At this point, we will also substitute equation 3.22 into equation 3.33 and this leads to:

$$\frac{\partial}{\partial t} (\rho h_s) + \frac{\partial}{\partial x_i} (\rho u_i h_s) + \frac{\partial}{\partial t} (\rho k) + \frac{\partial}{\partial x_i} (\rho u_i k) - \frac{\partial}{\partial x_i} \left( \rho \sum_{k=1}^{K_g} Y_k \Delta h^o_{f,k} V_{k,i} \right) - \dot{\omega}_T = \frac{\partial p}{\partial t} + \frac{\partial}{\partial x_i} \left( \lambda \frac{\partial T}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \left( \rho \sum_{k=1}^{K_g} h_k Y_k V_{k,i} \right) + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \dot{Q} + \rho \sum_{k=1}^{K_g} Y_k f_{k,i} (u_i + V_{k,i})$$

(3.34)

Equation 3.34 can be further simplified by using the definition of the specific enthalpy for one species:

$$h_k = h_{s,k} + \Delta h^o_{f,k}$$

(3.35)

Similarly to the momentum equation, we shall assume that $f_{k,j} = g_j$ constant for all species $k$. Substitution of equation 3.35 into equation 3.34 results to the final form
of the energy equation:

\[
\frac{\partial}{\partial t} (\rho h_s) + \frac{\partial}{\partial x_i} (\rho u_i h_s) + \frac{\partial}{\partial t} (\rho k) + \frac{\partial}{\partial x_i} (\rho u_i k) = \dot{\omega}_T + \frac{\partial p}{\partial t} + \frac{\partial}{\partial x_i} \left( \lambda \frac{\partial T}{\partial x_i} \right) \\
- \frac{\partial}{\partial x_i} \left( \rho \sum_{k=1}^{K_g} h_{s,k} Y_k V_{k,i} \right) + \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \dot{Q} + \rho g_i \sum_{k=1}^{K_g} Y_k (u_i + V_{k,i})
\]

(3.36)

Note that equation 3.36 is written in conservative form. As will be seen in the boundary condition section, using the conservative form of the energy equation is important for the derivation of the corresponding boundary conditions on the gas-membrane interfaces. These boundary conditions result from the integration of the conservative form of the state equations in a control volume that includes the gas-membrane interface. In addition, \( V_{k,i} \) in equation 3.36 can now be calculated using equation 3.10 after use of the Hirschfelder-Curtiss approximation.

Equation 3.36 is solved for the specific sensible enthalpy \( h_s \). Once \( h_s \) is evaluated, the temperature \( T \) on each computational cell is calculated by numerical integration of the definition of \( h_s \):

\[
h_s (J/kg/K) = \int_{T_0}^{T} c_p dT
\]

(3.37)

In equation 3.37, \( c_p \) is the specific heat capacity of the mixture at constant pressure, evaluated as:

\[
c_p (J/kg/K) = \sum_{k=1}^{K_g} Y_k c_{p,k}
\]

(3.38)

The specific heat capacity of species \( k \) at constant pressure, \( c_{p,k} \), is expressed in polynomial form according to the NIST database.

Equation 3.36 requires evaluation of the thermal conductivity of the mixture \( \lambda \) at each computational cell. This is defined in a similar mixing rule as the dynamic
viscosity of the mixture [31, 35]:

\[
\lambda(W/m/K) = \sum_{k=1}^{K_g} \frac{X_k \lambda_k}{\sum_{p=1}^{P_g} X_p \Phi_{kp}}
\] (3.39)

In equation 3.39, \( \Phi_{kp} \) is evaluated using equation 3.7 while \( \lambda_k \) is defined using the kinetic theory of gases [31, 35]:

\[
\lambda_k(W/m/K) = \frac{15}{4} \frac{R}{W_k \mu_k} \left[ \frac{4}{15} \frac{c_{pk} W_k}{R} + \frac{1}{3} \right]
\] (3.40)

Note that in equation 3.40, the universal gas constant enters as \( R = 8314 \, (J/kmole/K) \).

Also, \( \mu_k \) is evaluated using equation 3.5.

**Alternative form of conservation of energy**

Equation 3.36, although exact, is numerically stable for small time steps. To increase the stability of the numerical solution and allow for the use of larger time steps during the time marching, an alternative form of the energy conservation exists. The latter is achieved by transforming Fourier’s law into an expression that includes the laplacian of \( h_s \). We start from the definition of the specific enthalpy \( h \) and evaluate the gradient:

\[
\frac{\partial h}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \sum_{k=1}^{K_g} Y_k h_k \right) = \sum_{k=1}^{K_g} Y_k \frac{\partial h_k}{\partial x_i} + \sum_{k=1}^{K_g} h_k \frac{\partial Y_k}{\partial x_i} = \sum_{k=1}^{K_g} Y_k \frac{\partial h_k}{\partial T} \frac{\partial T}{\partial x_i} + \sum_{k=1}^{K_g} h_k \frac{\partial Y_k}{\partial x_i}
\] (3.41)

where the chain rule has been used for the first term in the right-hand side. However, from the definition of \( c_{p,k} \) we know that at constant pressure \( c_{p,k} = \left( \frac{\partial h_k}{\partial T} \right)_p \). Hence,
equation 3.41 can be written as:

\[ \frac{\partial h}{\partial x_i} = \sum_{k=1}^{K_g} Y_k c_{p,k} \frac{\partial T}{\partial x_i} + \sum_{k=1}^{K_g} h_k \frac{\partial Y_k}{\partial x_i} = c_p \frac{\partial T}{\partial x_i} + \sum_{k=1}^{K_g} h_k \frac{\partial Y_k}{\partial x_i} \]  

(3.42)

We next substitute \( h \) and \( h_k \) from equations 3.29 and 3.35, respectively, into equation 3.42. After some algebra, we end up to the following expression:

\[ \frac{\partial h_s}{\partial x_i} = c_p \frac{\partial T}{\partial x_i} + \sum_{k=1}^{K_g} h_{s,k} \frac{\partial Y_k}{\partial x_i} = \frac{1}{c_p} \frac{\partial h_s}{\partial x_i} - \frac{1}{c_p} \sum_{k=1}^{K_g} h_{s,k} \frac{\partial Y_k}{\partial x_i} \]  

(3.43)

Equation 3.43 can now be inserted into equation 3.36:

\[ \frac{\partial}{\partial t} (\rho h_s) + \frac{\partial}{\partial x_i} (\rho u_i h_s) + \frac{\partial}{\partial t} (\rho k) + \frac{\partial}{\partial x_i} (\rho u_i k) = \dot{\omega}_T + \frac{\partial}{\partial t} + \\
+ \frac{\partial}{\partial x_i} \left( \frac{\lambda}{c_p} \frac{\partial h_s}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \left( \frac{\lambda}{c_p} \sum_{k=1}^{K_g} h_{s,k} \frac{\partial Y_k}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \left( \rho \sum_{k=1}^{K_g} h_{s,k} Y_k V_{k,i} \right) + \\
+ \frac{\partial}{\partial x_j} (\tau_{ij} u_i) + \dot{Q} + \rho g_i \sum_{k=1}^{K_g} Y_k (u_i + V_{k,i}) \]  

(3.44)

This new formulation of the energy conservation has multiple advantages. First, the energy conservation is still written in conservative form. Second, the appearance of \( h_s \) in the right-hand side of equation 3.44 as a diffusive term allows for the implicit discretization which significantly increases the stability of the system. Hence, in all the calculations of this thesis, equation 3.44 will be used.
Ideal gas law

The last equation to be solved is the ideal gas law:

$$\rho = \frac{pW}{RT}$$  \hspace{1cm} (3.45)

This equation is used to evaluate the density $\rho$ at each computational cell.

3.1.2 Computational domain of ITM reactor

The state equations described in the previous sections will be solved numerically using a computational domain that replicates the exact ITM reactor described in chapter 2; the computational domain is shown in figure 3-1. The same figure includes the different boundaries associated with each side.

For the numerical solution, a 2D structured mesh is generated. The mesh is refined very close to the gas-membrane interfaces, as shown in figure 3-2. To reduce the computational cost, a geometric progression for the mesh size is used; this means that the size of the cells is decreasing as we approach the membrane. Assuming symmetry along the $x = 0$ axis allows us to solve half of the reactor and this choice reduces the computational cost significantly. The membrane extends from $x = 0 \ (mm)$ to $x = 36.5 \ (mm)$ and the thickness in the $y$ direction varies according to the membrane under investigation.

To accelerate the numerical solution, the case is solved in parallel using the Open MPI interface provided by OpenFOAM. This means that the computational domain is decomposed in smaller regions and different processors perform the required calculations in parallel. As will be shown in the next section, coupled boundary conditions are used for the feed and sweep side of the membrane, hence each side of
Figure 3-1: Computational domain of ITM reactor. Top side is the feed/air side while bottom side is the sweep/fuel side. Symmetry along the $x = 0$ axis allows for the numerical solution of half of the reactor. Figure also includes the inlet, outlet, wall, membrane and symmetry axis boundaries of each side.

the membrane is discretized with the same number of cells to ensure boundary compatibility. When running parallel simulations of coupled domains in OpenFOAM, the boundaries that exchange information should be included in the same sub-region during the mesh decomposition. This means that, when decomposing the entire mesh, we should ensure that the faces of the membrane feed and sweep side are as-
signed to the same processor. In OpenFOAM, this is achieved by creating a *faceSet* that generates a list of the faces of each side using the command *setSet*. Once the *faceSet* is created, the next step is to use the option *singleProcessorFaceSets* in the *system/decomposePar* dictionary to allow for the preservation of both faces in the same sub-region that will be solved by the same processor.

![Mesh of the laboratory ITM reactor](image)

*Figure 3-2: Mesh of the laboratory ITM reactor for the solution of the gas-phase state equations. Figure shows the position of the membrane with respect to the reactor. Mesh is refined close to the gas-membrane interfaces.*
3.1.3 Initial and boundary conditions

At every computational cell, the initial condition selected for the problem imposes a zero velocity vector \( u_i \), a pressure equal to \( p = 101325 \) (Pa) = 1 (atm) and a temperature \( T \) equal to the temperature at the inlet of the domains. Initially the reactor is assumed to be filled with air with a composition of \( X_{O_2} = 21 \) (%), \( X_{N_2} = 78 \) (%) and \( X_{Ar} = 1 \) (%) (conversion to mass fraction \( Y_k \) is performed).

The boundary conditions of the computational domain are of great importance when simulating reactive flows that involve more than one species, especially when an ITM is included in the simulation. For each boundary, we require appropriate conditions that allow for the estimation of the velocity vector, temperature, pressure, and species mass fractions. In this section we provide a detailed description of the boundary conditions used in this study and we focus our attention on the boundary conditions applied on the gas-membrane interfaces.

**Inlet boundaries**

At the inlet of the computational domain, the mass flow rate \( \dot{m}_{in} \) is imposed as a boundary condition. At each time step, the velocity vector \( u_i \) is estimated by the following expression:

\[
u_i = -\frac{\dot{m}_{inlet}}{\rho A_{inlet}} \eta_i \quad i = 1, 2, 3
\]

For the pressure, a zero-Neumann boundary condition is imposed:

\[
\frac{\partial p}{\partial x_j} \eta_j = 0
\]

Attention is required for the mass fraction of species \( k \), \( Y_k \), at the inlet of the computational domain. A common but risky approach is to use Dirichlet boundary
conditions for the mass fractions $Y_k$. This approach is appropriate only when the inlets of the domain are at some distance from high diffusion gradients. However, if the flow is highly diffusive very close to the inlet of the domain, Dirichlet boundary conditions may not preserve the correct species mass flow rates. Moen has shown that an alternative approach is to use a diffusive inlet boundary condition that specifies the normal total mass flux of each species $k$ as follows [36]:

$$
\left[ \rho \left( u_j + V_j^c \right) \eta_j Y_k - \rho D_k \frac{\partial Y_k}{\partial x_j} \eta_j - \frac{\rho D_k}{W} Y_k \frac{\partial W}{\partial x_j} \eta_j \right]_{\text{inlet}} = \frac{\dot{m}_{\text{in}}}{A_{\text{inlet}}} Y_k^{\text{desired}}
$$

(3.48)

where $Y_k$ is the mass fraction of species $k$ on the inlet boundary while $Y_k^{\text{desired}}$ is the desired mass fraction of species $k$ at the inlet (which would have been applied using a Dirichlet boundary condition otherwise). During the time marching, $Y_k$ at the inlet is updated at each time step using equation 3.48 until the value $Y_k^{\text{desired}}$ is obtained. Note that equation 3.48 arises by integrating equation 3.19 over a control volume that includes the inlet boundary neglecting unsteady and volumetric terms and then applying Gauss’s theorem to convert the volume integrals to surface integrals.

For the temperature $T$ at the inlet, a Dirichlet boundary condition is imposed. Similarly to the inlet boundary condition of mass fraction $Y_k$, if the inlet is located close to regions of high thermal gradients, the normal heat flux of the mixture should be specified as follows [37]:

$$
\left[ \rho u_i \eta_i \left( h_s + k \right) - \frac{\lambda}{c_p} \left( \frac{\partial h_s}{\partial x_i} - \sum_{k=1}^{K_q} h_{s,k} \frac{\partial Y_k}{\partial x_i} \right) \eta_i + \rho \sum_{k=1}^{K_q} h_{s,k} Y_k V_{k,i} \eta_i - \tau_{ij} u_i \eta_j \right]_{\text{inlet}} = \frac{\dot{m}_{\text{in}}}{A_{\text{inlet}}} h_s^{\text{desired}}
$$

(3.49)

where $h_s^{\text{desired}}$ is the specific sensible enthalpy of the mixture at the inlet calculated
using equation 3.37 based on the desired temperature and species composition. During the time marching, $h_s$ at the inlet is updated until the desired value $h_{s \text{desired}}$ is obtained.

**Outlet boundaries**

At the outlet of the computational domain, the velocity is extrapolated from the cell value adjacent to the boundary using a zero-Neumann boundary condition:

$$\frac{\partial u_i}{\partial x_j} = 0 \quad i = 1, 2, 3$$

(3.50)

To prevent inflow from the outlet of the domain, OpenFOAM provides the *inletOutlet* boundary condition. At each time-step, the aforementioned condition checks the outlet mass flow rate. If the outlet mass flow rate is positive, equation 3.50 is applied. However, if the outlet mass flow rate becomes negative leading to inflow from the exit of the domain, a Dirichlet boundary condition is imposed; a common practice is to set a zero velocity vector as a Dirichlet boundary condition in case of flow reversal.

For the pressure, a non-reflective wave boundary condition is used. Poinsot et. al. provides a detailed analysis on how the eigenvalue analysis can be used to generate an appropriate non-reflecting wave boundary condition [38]. OpenFOAM provides the *waveTransmissive* boundary condition that incorporates a similar but simpler procedure. In particular, the boundary condition performs some basic thermodynamic calculations and tries to create a tendency towards a farfield pressure $p_\infty$ while setting the instantaneous outlet pressure value to be something as consistent as possible with the outgoing characteristics. An important input in the boundary condition is the length between the exit of the computational domain and the distance where $p_\infty$ is satisfied; this distance is denoted as $L_\infty$. The larger the value of $L_\infty$, the further
the pressure at the outlet of the domain will deviate from the value specified as $p_\infty$. However, the smaller the value of $L_\infty$, the more reflective the boundary tends to be as the pressure at the outlet is closer to $p_\infty$.

For the mass fraction of species $k$, $Y_k$, and the temperature at the outlet, $T$, zero-Neumann boundary conditions are imposed:

$$\frac{\partial Y_k}{\partial x_j} n_j = 0$$

$$\frac{\partial T}{\partial x_j} n_j = 0$$

Similarly to the outlet boundary condition for the velocity vector, the inletOutlet boundary condition is selected for $Y_k$ and $T$. In case of flow reversal, the Dirichlet boundary conditions are the values used for the initial solution of the problem.

**Wall boundaries**

The no-slip boundary condition for the velocity vector is applied at non-reactive walls of the computational domain:

$$u_i = (u_x, u_y, u_z) = (0, 0, 0)$$

For the pressure, a zero-Neumann boundary condition is imposed that sets the normal of the pressure gradient equal to zero:

$$\frac{\partial p}{\partial x_j} n_j = 0$$
For the mass fraction of species $k$, a zero-flux boundary condition is imposed:

$$
\left[ \rho \left( u_j + V_c^j \right) \eta_j Y_k - \rho D_k \frac{\partial Y_k}{\partial x_j} \eta_j - \frac{\rho D_k}{W} Y_k \frac{\partial W}{\partial x_j} \eta_j \right]_{\text{wall}} = 0 \quad (3.55)
$$

Note that the boundary condition described by equation 3.55 is not equivalent to a zero-Neumann boundary condition that appears to be used frequently in the literature for the mass fraction of species $k$ on non-reactive walls. Equation 3.55 is the appropriate boundary condition that satisfies a zero-flux condition on the walls. It arises by integrating equation 3.19 over a control volume that includes the wall boundary neglecting unsteady and volumetric terms (since no reaction takes place) and then applying Gauss’s theorem to convert the volume integrals into surface integrals.

In this work, we shall assume that the walls of the computational domain are adiabatic, hence no heat is allowed to transfer to the external environment. We first integrate equation 3.36 over a control volume that includes the wall boundary and the exterior of the computational domain neglecting unsteady terms and assuming no reaction terms. Applying Gauss’s theorem leads to the following condition:

$$
q_i^{\text{wall}} \eta_i = 0 \Rightarrow \left[ -\lambda \frac{\partial T}{\partial x_i} \eta_i + \rho \sum_{k=1}^{K_g} h_{s,k} Y_k V_{k,i} \eta_i \right]_{\text{wall}} = 0 \quad (3.56)
$$

In equation 3.56, terms including the mixture velocity vector have been dropped out due to the no-slip condition. However, we can easily prove that the heat conduction term due to interdiffusion is zero on non-reactive walls. To show this, we first integrate equation 3.8 over a control volume that includes the wall boundary and the exterior of the computational domain neglecting unsteady terms and assuming no reaction terms. We then apply Gauss’s theorem and multiply each $k$ equation with
$h_{s,k}$. Summation of these new $k$ equations over all species $K_g$ leads to the following expression:

$$
\left[ \sum_{k=1}^{K_g} \rho \left( u_i + V_{k,i} \right) \eta_i h_{s,k} Y_k \right]_{\text{wall}} = 0 \quad \text{no-slip condition} \quad \left[ \rho \sum_{k=1}^{K_g} h_{s,k} Y_k V_{k,i} \eta_i \right]_{\text{wall}} = 0 \quad (3.57)
$$

Hence, with the use of equation 3.57, the wall temperature 3.56 becomes a zero-Neumann boundary condition for the temperature $T$:

$$
q_i^{\text{wall}} \eta_i = 0 \Rightarrow -\lambda \frac{\partial T}{\partial x_i} \eta_i = 0 \Rightarrow \frac{\partial T}{\partial x_i} \eta_i = 0 \quad (3.58)
$$

Considering the reactor walls as adiabatic is not restrictive. One can also assume isothermal walls by specifying a constant temperature. Other boundary conditions consider the heat conduction flux to be constant or the possibility of allowing for heat transfer with the external environment.

**Symmetry plane**

At symmetry planes no flow is allowed to cross. Hence, a slip boundary condition is applied for the velocity vector that sets the normal component equal to zero:

$$
u_j \eta_j = 0 \quad (3.59)
$$

To calculate the tangential velocity, a mirroring is performed according to the Householder transformation [39]. For the pressure, a zero-Neumann boundary condition is imposed that sets the normal of the pressure gradient equal to zero:

$$
\frac{\partial p}{\partial x_j} \eta_j = 0 \quad (3.60)
$$
No species are allowed to cross the symmetry plane boundary. Hence, a no-flux boundary condition is imposed, similar to the case of inert walls:

\[
\rho \left( u_j + V_j^c \right) \eta_j Y_k - \rho D_k \frac{\partial Y_k}{\partial x_j} \eta_j - \frac{\rho D_k}{W} Y_k \frac{\partial W}{\partial x_j} \eta_j \right]_{\text{sym}} = 0 \quad (3.61)
\]

In addition, no heat is allowed to cross the symmetry plane boundary, hence, the symmetry plane is considered to be adiabatic. It has been shown earlier that equation 3.56 that applies for the case of an adiabatic wall evolves into a zero-Neumann boundary condition for the temperature \( T \) given that the normal component of the velocity vector is zero at symmetry planes:

\[
\dot{q}_{i,\text{sym}}^\eta = 0 \Rightarrow \left[ -\lambda \frac{\partial T}{\partial x_i} \eta_i + \rho \sum_{k=1}^{K_g} h_{s,k} Y_k V_k i \eta_i \right]_{\text{sym}} = 0 \quad \text{Eq. (3.57)} \Rightarrow \frac{\partial T}{\partial x_i} \eta_i = 0 \quad (3.62)
\]

**Ion transport membrane wall**

In this section, we present the boundary conditions applied on the gas-membrane interface for cases that involve the numerical solution of the gas-phase problem only. In such cases, the experimentally measured oxygen flux \( J_{O_2} \) is used in the boundary condition and the solution of the multi-species problem allows for the prediction of the mixture composition on the membrane sides. Hence, in the equations presented in this subsection, the membrane is treated as a black box that consumes oxygen at the air/feed side and produces oxygen at the sweep/fuel side, although this applies for cases where no surface reactions of other species but oxygen are taking place. For reactive cases that involve fuel surface reactions (e.g. hydrogen or carbon monoxide surface oxidation), the membrane acts as source-sink of the corresponding species. At the end of this chapter, we will discuss the coupling of the multi-species problem with
the PNP equations that will give rise to a new (but similar) set of boundary conditions applicable for the coupled problem that incorporates the numerical solution of both gas and solid phases.

For the cases where the membrane is treated as a species source-sink, the membrane boundary is discretized using the same number of cells at each side and the boundary conditions are satisfied at each opposite set of cells. The conditions to be satisfied arise by integrating the conservative form of continuity, species and sensible enthalpy equations in a control volume that contains the interface of the gas and the solid phases. The derivation leads to the following general conditions, applied for either the feed or sweep side (using the corresponding quantities of each side).

To begin with, the velocity vector on the gas-membrane interfaces is evaluated using the following equation that arises from the continuity equation:

\[ u_i = -\frac{1}{\rho} \sum_{k=1}^{K_g} \omega_{s,k} \frac{W_k}{1000} \eta_i \]  \hspace{1cm} (3.63)

For the pressure, a zero-Neumann boundary condition is imposed since the membrane boundary acts similar to a wall:

\[ \frac{\partial p}{\partial x_j} \eta_j = 0 \]  \hspace{1cm} (3.64)

For the species \( k \) on the gas-membrane interface, the total flux of species \( k \) should equal the surface reaction rate:

\[ \left[ \rho (u_j + V_j^c) \eta_j Y_k - \rho D_k \frac{\partial Y_k}{\partial x_j} \eta_j - \rho D_k W_k \frac{\partial W}{\partial x_j} \eta_j \right]_{TM} = \dot{\omega}_{s,k} \frac{W_k}{1000} \]  \hspace{1cm} (3.65)

Regarding the temperature calculation on the gas-membrane interfaces, here we shall assume that the thermal resistance due to conduction inside the membrane
is very small compared to the convection and radiation thermal resistances in the gas-phase. This means that the temperature gradient within the two membrane sides is negligible and hence the approximation of equal temperature on the two sides \( T_{\text{feed}} = T_{\text{sweep}} = T_{\text{mem}} \) can be made. As a result, we can consider a heat balance at the feed and sweep sides as follows:

\[
\dot{q}_{i}^{\text{feed}} \eta_{i}^{\text{feed}} + \dot{q}_{i}^{\text{sweep}} \eta_{i}^{\text{sweep}} = 0
\]  

(3.66)

where \( \dot{q}_{i}^{\text{feed}} \) and \( \dot{q}_{i}^{\text{sweep}} \) are calculated using equation 3.67, expressed in terms of feed/sweep side quantities:

\[
\dot{q}_{i} = \dot{\omega}_{T,s} \eta_{i} - \lambda \frac{\partial T}{\partial x_{i}} + \rho \sum_{k=1}^{K_{g}} h_{s,k} Y_{k} V_{k,i} - u_{j} K_{ij} - \sigma \epsilon_{\text{mem}} (T_{\text{mem}}^4 - T_{\infty}^4) \eta_{i}
\]  

(3.67)

In Equation 3.67, \( \dot{\omega}_{T,s} \) is the surface heat release rate per unit area due to heterogeneous reactions defined as:

\[
\dot{\omega}_{T,s} = - \sum_{n=1}^{N_{s}} \dot{s}_{n} \Delta H_{n}^{o}
\]  

(3.68)

The radiation term on the gas-membrane interface has been added for completeness. In case of gas-phase combustion of gaseous oxygen with other species, Ahmed et. al. have shown the importance of accounting for the surface radiation on the gas-membrane interfaces [40]. In equation 3.67, the emissivity of the membrane is \( \epsilon_{\text{mem}} = 0.8 \) while the Stefan-Boltzmann constant has its regular value \( \sigma = 5.67 \times 10^{-8} \) (\( W/m^2/K^4 \)).

The presence of \( T_{\text{mem}}^4 \) in equation 3.67 requires an iterative process to obtain the membrane temperature at each time step. For this reason, we shall use a Newton-
Raphson method as follows:

\[
T_{\text{mem}}^{t+\Delta t} |_{l+1} = T_{\text{mem}}^{t+\Delta t} |_{l} - \frac{F (T_{\text{mem}}^{t+\Delta t} |_{l})}{F' (T_{\text{mem}}^{t+\Delta t} |_{l})}
\]  

(3.69)

where \( F(x) = \dot{q}_{i}^{\text{feed}} \xi_{i}^{\text{feed}} + \dot{q}_{i}^{\text{sweep}} \xi_{i}^{\text{sweep}} \) and \( l \) is the index of the iterative process until convergence to the value \( T_{\text{mem}}^{t+\Delta t} \) is achieved. The initial guess \( T_{\text{mem}}^{t+\Delta t} |_{l=0} \) corresponds to the temperature at the previous time step \( T_{\text{mem}}^{t} \). In addition, we shall assume that the interdiffusion term in equation 3.67 is not a strong function of temperature given that small time-steps as used during the time marching. This allows to evaluate the derivative \( F' (T_{\text{mem}}^{t+\Delta t}) \) analytically and reduce the computational cost.

At the air/feed side, the membrane acts as an \( O_{2} \) sink at a rate equal to the experimentally measured \( J_{O_{2}} \). This implies that for \( k = O_{2} \) we set \( \dot{\omega}_{s,O_{2}} = -J_{O_{2}} \) (note \( J_{O_{2}} \) is always positive) in equations 3.63 and 3.65 while \( \dot{\omega}_{s,N_{2}} = \dot{\omega}_{s,Ar} = 0 \) given that no \( N_{2} \) or \( Ar \) can cross the membrane boundary.

At the fuel/sweep side and for non-reactive cases, the membrane acts as an \( O_{2} \) source and hence for \( k = O_{2} \) we set \( \dot{\omega}_{s,O_{2}} = J_{O_{2}} \) while \( \dot{\omega}_{s,k} \) is zero for all other species. However, for reactive cases assuming surface reactions on the sweep side only, \( \dot{\omega}_{s,O_{2}} = 0 \) since no oxygen enters the gas-phase computational domain. Instead, the surface reaction rate of the species produced/consumed on the gas-membrane interface should be equated with the experimentally measured flux. In the next chapters will show how this can be achieved for \( H_{2} \) and \( CO \) surface oxidation by applying the experimentally measured \( J_{O_{2}} \) to predict the local \( H_{2} \), \( H_{2}O \), \( CO \) and \( CO_{2} \) sweep side concentrations.
3.2 Modeling the transport of charged species within the material

3.2.1 Charged species within LCF

Four mobile charged species exist within LCF. Using Kröger-Vink notation, these charged species correspond to oxygen vacancies \( V_O^{\bullet\bullet} \) and three different iron states \( Fe^{\bullet}_{Fe}, Fe^{\pi}_{Fe} \) and \( Fe^{\prime}_{Fe} \) which represent the \( Fe^{+4}, Fe^{+3} \) and \( Fe^{+2} \) iron states incorporated into the \( Fe^{+3} \) lattice site, respectively. Besides these mobile charged species, one also has to account for the presence of \( Ca \) in the \( La \) site which gives rise to the fixed charged species \( Ca^{\prime}_{La} \). Hence, \( Ca^{\prime}_{La} \) is not mobile, but is accounted for in the calculation of the charge density \( \rho_s \).

For LCF, addition of Calcium in the Lanthanum site of \( LaFeO_3 \) generates oxygen vacancies. Since \( Ca^{+2} \) while \( La^{+3} \), the charge imbalance is compensated by the oxidation of \( Fe^{+3} \) to \( Fe^{+4} \) in the B-site according to the following reaction:

\[
LaFe^{+3}O_3 + xCa^{+2} - xLa^{+3} \rightarrow La_{1-x}Ca_xFe^{+3_y}Fe^{+4_{1-y}}O_{3-\delta} + \frac{\delta}{2}O_2
\]  \( (3.70) \)

Ciambelli et al. shows that the \( Fe^{+3} \) oxidation to \( Fe^{+4} \) increases as more oxygen vacancies are generated during Calcium addition to \( LaFeO_3 \) [56]. The same mechanism of oxygen vacancy creation and \( Fe^{+3} \) oxidation is also found in materials such as \( La_{1-x}Sr_xCoO_{3-\delta} \) [57]. Since \( Fe^{+3} \) can disproportionate into \( Fe^{+4} \) and \( Fe^{+2} \), \( Fe^{+2} \) is also present in the B-site, but in lower concentrations at high oxygen partial pressures. Hence, while equation 3.70 shows how the addition of Calcium impacts the formation of vacancies and the oxidation of \( Fe^{+3} \) to \( Fe^{+4} \), the resulting perovskite is a \( La_{1-x}Ca_xFe^{+2_z}Fe^{+3_y}Fe^{+4_{1-y-z}}O_{3-\delta} \) including all three iron states in the B-site.
3.2.2 LCF nonstoichiometry at equilibrium

Using a coulometric titration cell and LCF powder, Geary and Adler investigated the dependence of the equilibrium concentration of oxygen vacancies and iron states on the temperature and $P_{O_2}$ under a non-reactive environment [58]. To predict the defect concentrations, a point-defect model was used. The model accounts for the following two reactions:

1. \[ \frac{1}{2}O_2 (g) + V_{O}^{\bullet} + 2Fe_{Fe}^{\pm} \rightleftharpoons O_{O}^{X} + 2Fe_{Fe}^{\bullet} \] (3.71)

2. \[ 2Fe_{Fe}^{\pm} \rightleftharpoons Fe_{Fe}^{\bullet} + Fe_{Fe}^{\prime} \] (3.72)

Reaction 3.71 corresponds to the oxygen incorporation reaction while reaction 3.72 corresponds to the iron disproportionation. The equilibrium constants based on partial pressures and formula-unit concentrations for the aforementioned reactions can be defined as:

\[ KP_1 = \frac{1}{\left( \frac{P_{O_2}}{P_{ref}} \right)^{1/2} \left[ V_{O}^{\bullet} \right] \left[ Fe_{Fe}^{\pm} \right]^2} \] (3.73)

\[ KP_2 = \frac{\left[ Fe_{Fe}^{\bullet} \right] \left[ Fe_{Fe}^{\prime} \right]}{\left[ Fe_{Fe}^{\pm} \right]^2} \] (3.74)

In equations 3.73 and 3.74, $P_{ref} = 1 \text{ (atm)}$ while the brackets denote formula-unit concentrations. The molar concentration of species $k$, $C_k$, is related to the formula-unit concentration $[X_k]$ through the expression:

\[ C_k (\text{mole/cm}^3) = \frac{[X_k]}{V_m} \] (3.75)
The equilibrium constant $K_{P_i}$ of reaction $i$ is related to the Gibbs free energy change $\Delta G_{i}^{\circ}$ through the following equation:

$$K_{P_i} = \exp\left(\frac{-\Delta G_{i}^{\circ}}{RT}\right) = \exp\left(\frac{-\Delta H_{i}^{\circ} - T\Delta S_{i}^{\circ}}{RT}\right)$$ (3.76)

In addition to equations 3.73 and 3.74, the model includes oxygen site conservation, Fe site conservation and strict electroneutrality both at the gas-membrane interfaces as well as in the interior of the material. The corresponding equations are:

$$[O_{O}^{V}] + [V_{O}^{\bullet \bullet}] = 3 \Rightarrow C_{O_{O}^{V}} + C_{V_{O}^{\bullet \bullet}} = \frac{3}{V_{m}}$$ (3.77)

$$[Fe_{Fe}^{2+}'] + [Fe_{Fe}^{3+}'] + [Fe_{Fe}^{4+}'] = 1 \Rightarrow C_{Fe_{Fe}^{2+}'} + C_{Fe_{Fe}^{3+}'} + C_{Fe_{Fe}^{4+}'} = \frac{1}{V_{m}}$$ (3.78)

$$[Ca_{La}'] + [Fe_{Fe}^{3+}'] = 2[V_{O}^{\bullet \bullet}] + [Fe_{Fe}^{3+}'] \Rightarrow \frac{x}{V_{m}} + C_{Fe_{Fe}^{3+}'} = 2C_{V_{O}^{\bullet \bullet}} + C_{Fe_{Fe}^{3+}'}$$ (3.79)

Mizusaki et al. was the first to apply the same model for $La_{1-x}Sr_{x}FeO_{3-\delta}$ [59]. By measuring $\delta_{eq} = [V_{O}^{\bullet \bullet}]_{eq}$ at different $T$ and $P_{O_2}$, Geary and Adler fitted $\Delta H_{1}^{\circ}$, $\Delta S_{1}^{\circ}$, $\Delta H_{2}^{\circ}$ and $\Delta S_{2}^{\circ}$ and hence determined $K_{P_1}$ and $K_{P_2}$ [58]. These values are summarized in table 3.1. Knowledge of these equilibrium constants is essential for the concept of thermodynamic consistency that will be introduced in the development of the corresponding electrochemical model for finite rate kinetics.

Figure 3-3 shows the equilibrium formula-unit concentration of oxygen vacancies and iron states as a function of oxygen partial pressure $P_{O_2}$ at $\theta = 950$ (°C) using the aforementioned point-defect model [58]. Given that three iron states coexist in the B-site, electron transfer in LCF can take place in two different ways depending on the partial pressure. Oxygen production occurs through an electron transfer process in which either $Fe_{Fe}^{3+}$ reduces to $Fe_{Fe}^{2+}$ or $Fe_{Fe}^{4+}$ to $Fe_{Fe}^{3+}$, as described by the following
0 Formula unit concentrations at equilibrium: $\theta = 950 \, (^\circ \text{C})$

Figure 3-3: Formula-unit concentration of $V_{O}^{**}$, $Fe_{Fe}^{*}$, $Fe_{Fe}^{x}$, and $Fe_{Fe}'$ as a function of oxygen partial pressure $P_{O_2}$ at $\theta = 950 \, (^\circ \text{C})$ under equilibrium conditions [58].

reactions:

\begin{align*}
O_{O}^{X} + 2Fe_{Fe}^{*} & \rightleftharpoons \frac{1}{2}O_{2} \, (g) + V_{O}^{**} + 2Fe_{Fe}^{x} \tag{3.80} \\
O_{O}^{X} + 2Fe_{Fe}^{x} & \rightleftharpoons \frac{1}{2}O_{2} \, (g) + V_{O}^{**} + 2Fe_{Fe}' \tag{3.81}
\end{align*}

At high $P_{O_2}$, $Fe_{Fe}^{*}$ is abundant and the electron transfer takes place by reduction of $Fe_{Fe}^{*}$ to $Fe_{Fe}^{x}$. As $P_{O_2}$ decreases, $Fe_{Fe}^{*}$ is depleted and electrons move from $Fe_{Fe}^{x}$ to $Fe_{Fe}'$ during oxygen production. At the point where the oxygen vacancy formula-unit concentration equals half of the $Ca$ doping, there exists a crossover in the formula-unit concentration of $Fe_{Fe}^{*}$ and $Fe_{Fe}'$. At the crossover, electronic conduc-
Table 3.1: Standard-state enthalpy and entropy change of reactions 3.71 and 3.74 determined by Geary and Adler using a coulometric titration cell [58].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_1^o$ (kJ/mole)</th>
<th>$\Delta S_1^o$ (J/mole/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}O_2(g) + VO^{2+} + 2Fe^{2+}<em>{Fe} \rightleftharpoons O^{2-} + 2Fe^{3+}</em>{Fe}$</td>
<td>$-152 \pm 6$</td>
<td>$-94$</td>
</tr>
<tr>
<td>Reaction</td>
<td>$\Delta H_2^o$ (kJ/mole)</td>
<td>$\Delta S_2^o$ (J/mole/K)</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>$2Fe^{2+}<em>{Fe} \overset{k</em>{f2}}{\rightleftharpoons} 2Fe^{3+}<em>{Fe} + Fe^{3+}</em>{Fe}$</td>
<td>$66 \pm 5$</td>
<td>$-55$</td>
</tr>
</tbody>
</table>

Activity changes from p-type to n-type, while the total electronic conductivity reaches a minimum value [58]. The same behavior has been observed for similar perovskites such as $La_{1-x}Sr_xFeO_{3-8}$ [59] and $La_{0.5}Sr_{0.5}Fe_{1-x}Mn_xO_{3-8}$ [60]. Depending on the electron transfer type, kinetics of surface reactions on the gas-membrane interfaces vary significantly.

3.2.3 Poisson-Nernst-Planck (PNP) model

In the dilute limit, i.e. neglecting interactions between defects, the diffusion of charged species within a material can be described by the PNP model. Cohen and Cooley were the first to report calculations of the time-dependent Nernst-Planck equations for a thin permeable membrane between electrolytic solutions [41]. Soon after this paper was released, several authors published papers dealing with the numerical solution of the PNP equations for different applications that involve ion transport. A few of these include studies on porous media [42, 43], mixed-conductors [44], electrodes [45] and membranes [46]. One of the most representative papers on the numerical solution of the PNP equations is that by Brumleve and Buck [47] where the authors present a detailed analysis for the development a fully implicit finite difference scheme of the time-dependent PNP equations solved using the Newton-Raphson
The PNP equations have become very popular in the field of electrochemistry for the study of batteries and mixed ionic-electronic conducting materials. Bazant et al. used a PNP model to study the DC response of electrochemical thin films, such as separators for microbatteries [48]. Detailed surface exchange coupled with the PNP model has been applied for gadolinium-doped ceria mixed-conductors [49] and yttrium-doped barium zirconates [50, 51, 52]. In this thesis, we will formulate a PNP model applicable to the LCF membrane under investigation for both inert and reactive cases. The model formulation is general and can be used for materials similar to the LCF.

To begin with, the PNP model includes conservation equations for the transport of charged species within the material and Gauss’s law for the electrostatic potential. Using the Einstein summation convention, the conservation equation for a charged species $k$ within the material can be expressed as:

$$\frac{\partial C_k}{\partial t} + \frac{\partial J_{k,i}}{\partial x_i} = 0 \quad k = 1, ..., M_c$$

(3.82)

The defect flux of a charged species $k$, $J_{k,i}$, is given by:

$$J_{k,i} = -D_k \frac{\partial C_k}{\partial x_i} - D_k z_k F \frac{C_k}{RT} \frac{\partial \phi}{\partial x_i} \quad k = 1, ..., M_c$$

(3.83)

The first term in the right hand side of equation 3.83 is the diffusive flux of species $k$ due to concentration gradient, while the second term is the diffusive flux due to electromigration. The latter contribution arises from the development of an electrostatic field due to charged species movement within the material which affects the diffusion process.
The electrostatic potential $\phi$ is related to the local charge density $\rho_s$ through the Gauss equation:

$$\frac{\partial}{\partial x_i} \left( -\varepsilon_r \varepsilon_0 \frac{\partial \phi}{\partial x_i} \right) = \rho_s = F \sum_{k=1}^{M_e} z_k C_k \tag{3.84}$$

The local charge density $\rho_s$ includes the summation of molar concentrations for both mobile and fixed charged species; this means that for LCF, we also account for the charge of Calcium into the Lanthanum lattice site. Although the relative permittivity $\varepsilon_r$ is a function of temperature and frequency, in this study it is considered constant. To solve the Poisson equation 3.84, the relative permittivity of LCF is required. However, no experimental data of $\varepsilon_r$ is available for the same material. For similar perovskites like $LaFeO_{3-\delta}$, literature suggests that $\varepsilon_r$ is in the range of $\varepsilon_r = 200$ [53, 54].

A subtle but very important point when using a PNP model is related to the assumption of strict electroneutrality on the gas-membrane interfaces. If charge is allowed to accumulate on the interface, an EDL evolves and the electrostatic potential $\phi$ is evaluated by solving the Poisson equation 3.84. When an EDL evolves, the two sides of the interface (i.e. the solid and the gas phase) have opposite charge. For example, if the net charge of ions that adsorb on the interface of the gas-phase is negative, then a net positive charge of species will evolve on the interface of the solid solution, as shown in figure 3-4. This charge accumulation will lead to charge separation on the interface due to Coulomb interactions of the charged species and this can affect the surface reaction kinetics significantly. The aforementioned model formulation is more realistic in the modeling of electrochemical systems but the computational cost increases significantly. This happens because the characteristic length scale that dictates the screening of the charge separation (called the Debye length) should be resolved during the numerical solution of the PNP equations. The
Debye length will be defined later in this chapter, but the order of magnitude for perovskites is around $1 - 10$ (nm).

To simplify the analysis, the EDL can be neglected by assuming a strict electroneutrality condition on the gas-membrane interfaces. By strict we mean that the charge density $\rho_s$ is strictly zero on the interface. However, this assumption has the following significant implication: charge can only build up inside the material through faradaic charge transfer reactions that take place on the interface; due to charge conservation, the charge then diffuses to the interior of the material. This means that an assumption of strict electroneutrality on the interface implies elec-
troneutrality of the entire material and it reduces the Poisson equation 3.84 into a Laplace equation for the electrostatic potential $\phi$. Hence, $\phi$ becomes independent of $\epsilon_r$, the electric field $E_i = -\frac{\partial \phi}{\partial x_i}$ is constant inside the material and the same solution is obtained for any value of $\epsilon_r$. This is a very important point and should not be neglected in the modeling of electrochemical systems assuming strict electroneutrality on the gas-membrane interfaces. However, in this thesis we shall still solve the Poisson equation for the electrostatic potential because it is more general compared to Laplace’s equation and at the same time we would like Poisson’s equation to enforce strict neutrality within the material instead of making an a priori assumption. We note here that solving for either Poisson’s or Laplace’s equation for $\phi$ is nearly equivalent and this is an implication of assuming strict electroneutrality at the interfaces.

3.2.4 Modeling the diffusion coefficients $D_k$

Because of the simultaneous presence of $Fe'_Fe$, $Fe^+_Fe$ and $Fe^+_Fe$, both n-type and p-type electronic conductivities co-exist [61]. According to [61], these depend on $[Fe'_Fe]$ and $[Fe^+_Fe]$:

$$\sigma_n = \sigma_{Fe'_Fe} = [Fe'_Fe] \frac{N_{Ae}}{V_m} (1 - [Fe'_Fe]) \mu_{Fe'_Fe}$$  \hspace{1cm} (3.85)

$$\sigma_p = \sigma_{Fe^+_Fe} = [Fe^+_Fe] \frac{N_{Ae}}{V_m} (1 - [Fe^+_Fe]) \mu_{Fe^+_Fe}$$  \hspace{1cm} (3.86)

In equations 3.85 and 3.86, $\mu_{Fe'_Fe}$ and $\mu_{Fe^+_Fe}$ are the mobilities of electrons and electron holes, respectively, which are constant values dependent on the membrane type and stoichiometry [61, 62, 63]. To relate the diffusion coefficients of $Fe'_Fe$ and $Fe^+_Fe$.

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to the electronic conductivities $\sigma_n$ and $\sigma_p$, the Nernst-Einstein expression is used:

$$\sigma_k = \frac{z_k^2 F^2 C_k D_k}{RT} \quad (3.87)$$

For the diffusion coefficient of oxygen vacancies $D_V$ we use the following expression that accounts for the dependence of $D_V$ on the oxygen vacancy concentration [61]:

$$D_V = D_V^* \left(1 - \frac{\delta}{3}\right) = A D_V^* e^{-E_D V_0 / RT} \left(1 - \frac{\delta}{3}\right) \quad (3.88)$$

### 3.2.5 Dimensionless form of the PNP model

Before solving numerically the PNP model, it is desired to express the equations in dimensionless form. To simplify the analysis, we will consider equations 3.82 and 3.84 in one dimension along the thickness for the membrane; we define the spatial coordinate as $y$. Note that expansion of the model in 2D or 3D is straightforward.

We begin by defining the following dimensionless parameters:

$$\tilde{y} = \frac{y}{L}, \quad \tilde{t} = \frac{t}{\tau}, \quad \tilde{C}_k = \frac{C_k}{C_{ref}}, \quad \tilde{D}_k = \frac{D_k}{D_{ref}}, \quad \tilde{\phi} = \frac{F}{RT} \phi \quad (3.89)$$

where the tilde sign expresses dimensionless parameters. According to 3.89, the transport equations 3.82 become:

$$\left( \frac{L^2}{\tau D_{ref}} \right) \frac{\partial \tilde{C}_k}{\partial \tilde{t}} = \frac{\partial}{\partial \tilde{y}} \left( \tilde{D}_k \frac{\partial \tilde{C}_k}{\partial \tilde{y}} \right) + \frac{\partial}{\partial \tilde{y}} \left( \tilde{D}_k z_k \tilde{C}_k \frac{\partial \tilde{\phi}}{\partial \tilde{y}} \right) \quad k = 1, ..., M_c \quad (3.90)$$

Without loss of generality, we can define the dimensionless time $\tau$ as:

$$\tau = \frac{L^2}{D_{ref}} = 1 \Rightarrow D_{ref} = L^2 \quad \text{and} \quad C_{ref} = \frac{1}{V_m} \quad (3.91)$$
Hence, the dimensionless transport equations become:

\[
\frac{\partial \tilde{C}_k}{\partial t} = \frac{\partial}{\partial \tilde{y}} \left( \tilde{D}_k \frac{\partial \tilde{C}_k}{\partial \tilde{y}} \right) + \frac{\partial}{\partial \tilde{y}} \left( \tilde{D}_k z_k \tilde{C}_k \frac{\partial \tilde{\phi}}{\partial \tilde{y}} \right) \quad k = 1, \ldots, M_c \tag{3.92}
\]

Using the same scaling arguments (3.89 and 3.91), the Poisson equation (3.84) can be expressed as:

\[
\frac{\partial}{\partial \tilde{y}} \left( -\epsilon^2 \frac{\partial \tilde{\phi}}{\partial \tilde{y}} \right) = \sum_{k=1}^{M_c} z_k \tilde{C}_k = \tilde{\rho}_s \tag{3.93}
\]

In equation (3.93), \(\tilde{\rho}_s\) is the dimensionless charge density, while \(\epsilon\) is the ratio of the Debye screening length \(\lambda_D\) over the thickness of the membrane \(L\):

\[
\epsilon = \frac{\lambda_D}{L}, \quad \lambda_D = \sqrt{\frac{\epsilon_r \epsilon_o RT}{F^2 C_{ref}}} \tag{3.94}
\]

The Debye screening length, named after the Dutch physicist and physical chemist Peter Debye, is typically in the order of nanometers and expresses the distance away from the interface over which the electrostatic effects prevail.

### 3.2.6 Numerical solution of the PNP model

For the numerical solution of equations (3.92) and (3.93), we will use the Finite Volume Method. In the Finite Volume Method, the computational domain is discretized in finite volumes and the equations of interest are integrated over the finite volume.

Figure 3-5 shows the spatial discretization along the thickness of the membrane using a non-uniform mesh. Non-uniform meshes are preferred when solving the PNP equations given that high gradients may appear close to the interfaces and until the Debye length is reached. The feed/air side of the membrane is located at \(\tilde{y} = 0\) and the sweep/fuel side at \(\tilde{y} = 1\). The thickness is discretized using \(N\) finite volumes.
stored at the cell-center. The boundary condition at the feed side is denoted with the superscript 0 while the sweep side is denoted with the superscript $N+1$; this leads to a total of $N+2$ values for each equation.

![Finite Volume Method Space Discretization](image)

Figure 3-5: Finite Volume mesh for the solution of the PNP equations in 1D. The feed/air side of the membrane corresponds to $\tilde{y} = 0$ while the sweep/fuel side corresponds to $\tilde{y} = 1$. The domain is discretized using $N$ finite volumes while $N+2$ values of $\tilde{C}_k$ and $\tilde{\phi}$ are obtained.

To allow for the use of large time steps during the time marching, an implicit finite volume method will be used. Explicit schemes suffer from the need to maintain a time step less than $0.5 \hat{D}_k$ during the time marching in order for stability requirements to be met. The implicit schemes are stable for very large time steps and this choice significantly reduces the computational cost. However, the floating point operations increase given that implicit schemes require the solution of a matrix while in explicit schemes, the solution at the next time step is updated using an algebraic equation.
Mass conservation

The first step in a finite volume implementation is to integrate the equation of interest over a control volume. Hence, we start by integrating equation 3.92 over the control volume $\Delta \tilde{y}_p$ and applying Gauss’s theorem for the diffusive terms assuming that the normal unit vector is pointing outwards the finite volume. Hence, we end up into the following expression:

$$
\frac{\partial \check{C}_k}{\partial t} \Delta \tilde{y}_p = \left( \check{D}_k \frac{\partial \check{C}_k}{\partial \tilde{y}} \right)_e - \left( \check{D}_k \frac{\partial \check{C}_k}{\partial \tilde{y}} \right)_w + \left( \check{D}_k z_k \check{C}_k \frac{\partial \check{\phi}}{\partial \tilde{y}} \right)_w - \left( \check{D}_k z_k \check{C}_k \frac{\partial \check{\phi}}{\partial \tilde{y}} \right)_e \quad (3.95)
$$

Equation 3.95 shows that the terms on the right-hand side must be expressed at the interfaces $w$ and $e$. The next step is to use a time discretization scheme for the unsteady term and a space discretization scheme to approximate the first derivative of $\check{C}_k$ and $\check{\phi}$ with respect to $\tilde{y}$ on the interfaces $w$ and $e$. We choose the forward Euler for the time derivative, but other schemes can be used as well. For the spatial derivatives, we use the central difference scheme. As a result, equation 3.95 becomes:

$$
\frac{\check{C}_k^{P,m+1} - \check{C}_k^{P,m}}{\Delta t} \Delta \tilde{y}_p = \check{D}_k^{c,m} \check{C}_k^{E,m+1} - \check{C}_k^{P,m+1} - \check{D}_k^{w,m} \check{C}_k^{P,m+1} - \check{C}_k^{W,m+1} + \check{D}_k^{e,m} z_k \check{C}_k^{e,m+1} - \check{\phi}_k^{E,m+1} - \check{\phi}_k^{P,m+1} + \check{D}_k^{w,m} z_k \check{C}_k^{w,m+1} - \check{\phi}_k^{W,m+1} \quad (3.96)
$$

At this point we should make a few important observations: first, $m$ corresponds to the current discrete time step while $m + 1$ is the next discrete time step for which the solution is looked for. Second, the discretization scheme selected here is not fully implicit given that the dimensionless diffusion coefficients $\check{D}_k$ and the dimensionless electrostatic potential $\check{\phi}$ are evaluated at the current time step $m$; in a fully implicit scheme, the dimensionless diffusion coefficients $\check{D}_k$ and the dimensionless electrostatic
potential $\tilde{\phi}$ would be expressed at $m + 1$, but to solve this equation, one has to iterate using the Newton-Raphson method as described in [47]. The choice of the implicit formulation used in equation 3.96 allows to solve the transport equation of the charged species $k$ by matrix inversion without using the Newton-Raphson method; this approach is computationally cheaper, but less stable compared to the fully implicit scheme.

After some algebra, equation 3.96 can be expressed in the following compact form:

$$
\tilde{C}_k^{w,m+1} \left( - \frac{2\tilde{D}_k^{w,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_W} \right) + \tilde{C}_k^{e,m+1} \left( \frac{2\tilde{D}_k^{e,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_E} + \frac{2\tilde{D}_k^{w,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_W} \right) + \\
+ \tilde{C}_k^{E,m+1} \left( - \frac{2\tilde{D}_k^{e,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_E} \right) - \tilde{C}_k^{e,m+1} \frac{2\tilde{D}_k^{e,m} z_k (\tilde{\phi}_E^{m} - \tilde{\phi}_P^{m})}{\Delta \tilde{y}_E + \Delta \tilde{y}_P} + \\
+ \tilde{C}_k^{w,m+1} \frac{2\tilde{D}_k^{w,m} z_k (\tilde{\phi}_P^{m} - \tilde{\phi}_W^{m})}{\Delta \tilde{y}_P + \Delta \tilde{y}_W} = \frac{\Delta \tilde{y}_P}{\Delta t} \tilde{C}_k^{P,m}
$$

(3.97)

In equation 3.97, $\tilde{C}_k^{w,m+1}$ and $\tilde{C}_k^{e,m+1}$ need to be expressed using cell-center values. Although several techniques exist that allow to express the aforementioned values on the interfaces $w$ and $e$, the best approach is to use an upwind scheme. The reason for this is that the electromigration flux has convective characteristics and an upwind scheme provides additional computational benefits.

To develop an upwind scheme, one has to check the sign of the electromigration flux at each time step. There are two different cases described below:

1: $-z_k (\tilde{\phi}_P^{P,m} - \tilde{\phi}_W^{W,m}) \leq 0$ and $-z_k (\tilde{\phi}_E^{E,m} - \tilde{\phi}_P^{P,m}) \leq 0$

In this case, the electromigration flux is negative meaning that diffusion due to electromigration happens to the negative $\tilde{y}$ direction. Hence, $\tilde{C}_k^{w,m+1}$ and
$\tilde{C}_{k}^{v,m+1}$ can be approximated by:

$$\tilde{C}_{k}^{w,m+1} = \tilde{C}_{k}^{P,m+1} \quad \text{and} \quad \tilde{C}_{k}^{e,m+1} = \tilde{C}_{k}^{E,m+1}$$

(3.98)

At the same time, the dimensionless diffusion coefficients at the interfaces $w$ and $e$ are evaluated by:

$$\tilde{D}_{k}^{w,m} = \tilde{D}_{k} \left( \tilde{C}_{k}^{P,m} \right) \quad \text{and} \quad \tilde{D}_{k}^{e,m} = \tilde{D}_{k} \left( \tilde{C}_{k}^{E,m} \right)$$

(3.99)

2: $-z_{k} \left( \bar{\phi}_{k}^{e,m} - \bar{\phi}_{k}^{P,m} \right) > 0$ and $-z_{k} \left( \bar{\phi}_{k}^{E,m} - \bar{\phi}_{k}^{P,m} \right) > 0$

In this case, the electromigration flux is positive meaning that diffusion due to electromigration happens to the positive $\bar{y}$ direction. Hence, $\tilde{C}_{k}^{w,m+1}$ and $\tilde{C}_{k}^{e,m+1}$ can be approximated by:

$$\tilde{C}_{k}^{v,w,m+1} = \tilde{C}_{k}^{W,m+1} \quad \text{and} \quad \tilde{C}_{k}^{v,e,m+1} = \tilde{C}_{k}^{P,m+1}$$

(3.100)

At the same time, the dimensionless diffusion coefficients at the interfaces $w$ and $e$ are evaluated by:

$$\tilde{D}_{k}^{w,m} = \tilde{D}_{k} \left( \tilde{C}_{k}^{W,m} \right) \quad \text{and} \quad \tilde{D}_{k}^{e,m} = \tilde{D}_{k} \left( \tilde{C}_{k}^{P,m} \right)$$

(3.101)

For both cases, another option for the estimation of $\tilde{D}_{k}^{w,m}$ and $\tilde{D}_{k}^{e,m}$ is to use the average value of the cell-centered dimensionless diffusion coefficients around the corresponding interface.

One can combine these two cases into a single stencil that can be expressed as
follows:
\[
\alpha^W_{\tilde{C}_k} C_k^{W,m+1} + \alpha^P_{\tilde{C}_k} C_k^{P,m+1} + \alpha^E_{\tilde{C}_k} C_k^{E,m+1} = \frac{\Delta \tilde{y}_P}{\Delta t} \tilde{C}_k^P
\]  
(3.102)

The coefficients \( \alpha^W_{\tilde{C}_k} \), \( \alpha^P_{\tilde{C}_k} \) and \( \alpha^E_{\tilde{C}_k} \) have the following form:

\[
\alpha^W_{\tilde{C}_k} = -\frac{2 \tilde{D}_k^{w,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_W} - \max \left( 0, -\frac{2 \tilde{D}_k^{w,m} z_k (\tilde{\phi}_P^m - \tilde{\phi}_W^m)}{\Delta \tilde{y}_P + \Delta \tilde{y}_W} \right)
\]  
(3.103)

\[
\alpha^P_{\tilde{C}_k} = \frac{\Delta \tilde{y}_P}{\Delta \tilde{t}} + \frac{2 \tilde{D}_k^{e,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_E} + \frac{2 \tilde{D}_k^{w,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_W} + \\
+ \max \left( 0, -\frac{2 \tilde{D}_k^{e,m} z_k (\tilde{\phi}_E^m - \tilde{\phi}_P^m)}{\Delta \tilde{y}_E + \Delta \tilde{y}_P} \right) - \\
- \min \left( 0, -\frac{2 \tilde{D}_k^{w,m} z_k (\tilde{\phi}_P^m - \tilde{\phi}_W^m)}{\Delta \tilde{y}_P + \Delta \tilde{y}_W} \right)
\]  
(3.104)

\[
\alpha^E_{\tilde{C}_k} = -\frac{2 \tilde{D}_k^{e,m}}{\Delta \tilde{y}_P + \Delta \tilde{y}_E} + \min \left( 0, -\frac{2 \tilde{D}_k^{e,m} z_k (\tilde{\phi}_E^m - \tilde{\phi}_P^m)}{\Delta \tilde{y}_E + \Delta \tilde{y}_P} \right)
\]  
(3.105)

At this point, we have expressed the solution of the dimensionless transport equations in full detail. We note here that equation 3.102 applies only for the intermediate finite volumes. For the first finite volume (next to the feed side), equation 3.102 still applies but at the same time, \( \Delta \tilde{y}_W \) has to be set zero. Equivalently, \( \Delta \tilde{y}_E \) in equation 3.102 has to be set to zero for the last finite volume (next to the sweep side).

As a result, the dimensionless concentration of the charged species \( k \) at the next time step can be calculated by solving the linear system of equations 3.102 subject to appropriate boundary conditions. Equations 3.102 constitute a tridiagonal matrix on the left-hand side that can be solved using the well-known Thomas algorithm.
The finite volume formulation of the Poisson equation is similar to that of the transport equations. We first integrate equation 3.93 over the control volume $\Delta \tilde{y}_P$ and we apply Gauss’ theorem. This leads to the following expression:

$$
\left( -\epsilon^2 \frac{\partial \tilde{\phi}}{\partial \tilde{y}} \right)_e - \left( -\epsilon^2 \frac{\partial \tilde{\phi}}{\partial \tilde{y}} \right)_w = \sum_{k=1}^{M_c} z_k \tilde{C}_k^{P,m+1} \Delta \tilde{y}_P = \tilde{\rho}_s^{P,m+1} \Delta \tilde{y}_P 
$$

(3.106)

In equation 3.106, $\tilde{\rho}_s$ is expressed in the next time step because we assume that the transport equations for all charged species $k$ are solved first and the Poisson equation is solved last. Hence, the updated $\tilde{C}_k^{P,m+1}$ values are used in the evaluation of the dimensionless charge density $\tilde{\rho}_s$.

In addition, equation 3.106 shows that evaluation of the dimensionless potential gradient at the interfaces $w$ and $e$ is required. To estimate this gradient, we will use a central difference method as follows:

$$
-\epsilon^2 \frac{\tilde{\phi}_{E,m+1} - \tilde{\phi}_{P,m+1}}{\frac{\Delta \tilde{y}_E + \Delta \tilde{y}_P}{2}} + \epsilon^2 \frac{\tilde{\phi}_{P,m+1} - \tilde{\phi}_{W,m+1}}{\frac{\Delta \tilde{y}_P + \Delta \tilde{y}_W}{2}} = \tilde{\rho}_s^{P,m+1} \Delta \tilde{y}_P
$$

(3.107)

As a result, we can express the system of equations for the dimensionless potential using the following stencil:

$$
\alpha^W_\phi \tilde{\phi}_{W,m+1} + \alpha^E_\phi \tilde{\phi}_{E,m+1} + \alpha^P_\phi \tilde{\phi}_{P,m+1} = \tilde{\rho}_s^{P,m+1} \Delta \tilde{y}_P
$$

(3.108)

The coefficients $\alpha^W_\phi$, $\alpha^P_\phi$ and $\alpha^E_\phi$ have the following form:

$$
\alpha^W_\phi = -\frac{2\epsilon^2}{\Delta \tilde{y}_P + \Delta \tilde{y}_W}
$$

(3.109)
Similarly to the transport equations, we note that equation 3.108 applies only for the intermediate finite volumes. For the first finite volume (next to the feed side), equation 3.108 still applies but at the same time, $\Delta \tilde{y}_W$ has to be set zero. Equivalently, $\Delta \tilde{y}_E$ in equation 3.108 has to be set to zero for the last finite volume (next to the sweep side).

As a result, the dimensionless electrostatic potential at the next time step can be calculated by solving the linear system of equations 3.108 subject to appropriate boundary conditions.

**Initial and boundary conditions of the PNP model**

The PNP model is solved numerically subject to an appropriate initial condition in the entire computational domain and boundary conditions at the feed ($\tilde{y} = 0$) and sweep ($\tilde{y} = 1$) sides. For the initial condition, we assume that the material has a uniform distribution of charged species that satisfy equilibrium, Fe site conservation and electroneutrality. In addition, the dimensionless electrostatic potential is set to zero.

Regarding the boundary conditions for the transport equations 3.92, if the species molar concentration $\tilde{C}_k$ is known, a Dirichlet boundary condition for a species $k$ is imposed:

\[
\tilde{C}_k|_{\tilde{y}=0} = \tilde{C}_{k,\text{known}}|_{\tilde{y}=0} \quad (3.112)
\]

\[
\tilde{C}_k|_{\tilde{y}=1} = \tilde{C}_{k,\text{known}}|_{\tilde{y}=1} \quad (3.113)
\]
When finite rate kinetics is considered, the molar concentration of a species $k$ at the boundary is evaluated by applying a Robin boundary condition that accounts for chemical reactions on the gas-membrane interfaces [48, 49, 64]:

$$
\tilde{J}_{k,i} |_{y=0} = (\tilde{\omega}_{s,k} \eta_k) |_{y=0} \quad (3.114)
$$

$$
\tilde{J}_{k,i} |_{y=1} = (\tilde{\omega}_{s,k} \eta_k) |_{y=1} \quad (3.115)
$$

where $\tilde{J}_{k,i}$ is the dimensionless flux of charged species $k$ and $\tilde{\omega}_{s,k}$ is the dimensionless net molar reaction rate of species $k$ at the corresponding side (which will be defined in the next chapters). The dimensionless flux of charged species $k$, $\tilde{J}_{k,i}$, is given by the following equation:

$$
\tilde{J}_{k,i} = -\tilde{D}_k \frac{\partial \tilde{C}_k}{\partial y} - \tilde{D}_k z_k \tilde{C}_k \frac{\partial \tilde{\phi}}{\partial y} \quad (3.116)
$$

For the electrostatic potential and assuming a strict electroneutrality condition on the gas-membrane interfaces, we set $\tilde{\phi}(\tilde{y} = 0) = 0$ at the feed side as a reference value. At the sweep side, the following equation imposes an external current density $i_{ext}$ through the material:

$$
i_{ext} = F \sum_{k=1}^{M_c} z_k J_k + \frac{\partial}{\partial t} \left( -\epsilon_r \epsilon_0 \frac{\partial \tilde{\phi}}{\partial x} \right)_{i_D} \quad (3.117)
$$

Given that the LCF of our study operates under open-circuit conditions, we impose $i_{ext} = 0$ at the sweep side and equation 3.117 becomes an implicit boundary condition that can be used to evaluate the potential gradient $\frac{\partial \tilde{\phi}}{\partial y} |_{y=L}$ during the time-marching. In equation 3.117, $i_F$ is the Faradaic current density due to redox reactions while $i_D$
is the displacement current density that accounts for the time-varying electric field. By non-dimensionalizing equation 3.117, we get the following expression:

\[ i_{ext} = \frac{i_{ext}}{E_{ref}/C_{ref}} = \frac{i_{ext}}{i_{ref}} = \frac{\partial}{\partial t} \left( -\varepsilon \frac{\partial \phi}{\partial y} \right) - \sum_{k=1}^{M_c} \tilde{D}_k \tilde{z}_k \frac{\partial \tilde{C}_k}{\partial y} - \frac{\partial \tilde{\phi}}{\partial y} \sum_{k=1}^{M_c} \tilde{D}_k \tilde{z}_k^2 \tilde{C}_k \] (3.118)

Equation 3.118 can be discretized at \( \tilde{y} = 1 \) as follows:

\[
\begin{align*}
\left( \tilde{\phi}^{N+1,m+1} - \tilde{\phi}^{N+1,m+1} \right) \\
\left( \varepsilon^2 + \Delta t \sum_{k=1}^{M_c} \tilde{D}_k^{N+1,m} \tilde{z}_k^2 \tilde{C}_k^{N+1,m+1} \right) = \varepsilon^2 \left( \tilde{\phi}^{N,m} - \tilde{\phi}^{N+1,m} \right) + \\
+ \frac{\tilde{i}_{ext} \Delta t \Delta y_N}{2} + \Delta t \sum_{k=1}^{M_c} \tilde{D}_k^{N+1,m} \tilde{z}_k \left( \tilde{C}_k^{N+1,m+1} - \tilde{C}_k^{N,m+1} \right)
\end{align*}
\] (3.119)

At steady-state, \( i_D \) is zero; however, this term is retained during the solution of the PNP equations since the system of equations evolves over time. The algorithm stops when the solution of the dimensionless molar concentrations \( \tilde{C}_k \) and the electrostatic potential \( \tilde{\phi} \) within the material reach steady-state. Note that within the bulk of the membrane, the concentration of \( F_{Fe}^{2+} \) as a function of position is calculated through the Fe-site conservation.

**Heat transfer within the material**

In the cases presented above, we assumed that the material is isothermal, so the temperature along the thickness has been considered uniform. However, one can also solve the heat equation within the material to allow for a non-uniform temperature distribution. This is very important during the coupling of the gas-phase problem with the PNP equations given that heat may transfer due to gas-phase or heterogeneous chemical reactions from the sweep to the feed side and vice versa.
The heat equation within the material is given by the following equation assuming no volumetric source terms:

\[
\rho_M c_{p,M} \frac{\partial T_M}{\partial t} - \frac{\partial}{\partial x_i} \left( \lambda_M \frac{\partial T_M}{\partial x_i} \right) = 0
\] (3.120)

Air Products and Chemicals has provided the thermal properties required to solve equation 3.120. First, the density of the membrane has been specified as:

\[\rho_M = 6.235 \times 10^6 \text{ (kg/m}^3\text{)}\] (3.121)

In addition, the specific heat capacity \(c_{p,M}\) and the thermal conductivity \(\lambda_M\) of the membrane have been measured as a function of temperature. Figure 3-6 includes the corresponding temperature dependencies.

Regarding the specific heat capacity of LCF, we observe a significant dispersion in the measurements as the temperature goes over 500 (°C). At temperatures higher than 900 (°C), the membrane specific heat capacity is between \(c_{p,M} = 520 - 600 \text{ (J/kg/K)}\); given that we are interested in the high temperature regime, we shall use the value \(c_{p,M} = 560 \text{ (J/kg/K)}\) when solving the heat equation for LCF. In addition, the membrane thermal conductivity has been measured up to 700 (°C), hence extrapolation for high temperatures is required. As a result, we shall use the value \(\lambda_M = 1.8 \text{ (W/m/K)}\) when solving the heat equation 3.120.

### 3.3 Coupling the gas-phase and material transport

Until this point, we have presented the equations and the numerical solution of the gas-phase and material transport separately. To investigate complex ITM reac-
Figure 3-6: Specific heat capacity and thermal conductivity of LCF as a function of temperature. Data provided by Air Products and Chemicals during private communications.

tors, one should couple the gas-phase problem with the material diffusion of charged species expressed by the PNP equations. The coupling of these two problems happens by applying appropriate boundary conditions at the gas-membrane interfaces.

In the gas-phase, the velocity vector on the gas-membrane interfaces is evaluated using the following equation that arises from the continuity equation:

\[ u_i = -\frac{1}{\rho} \sum_{k=1}^{K_g} \dot{\omega}_{s,k} \frac{W_k}{1000} \eta_i^{gas} \]  

(3.122)

120
For the pressure, a zero-Neumann boundary condition is imposed:

\[
\frac{\partial p}{\partial x_j} \eta_j^{\text{gas}} = 0 \tag{3.123}
\]

For the species \( k \) on the gas-membrane interface, the total flux of species \( k \) should equal the net surface reaction rate of the corresponding species:

\[
\left[ \rho \left( u_j + V_j^c \right) \eta_j^{\text{gas}} Y_k - \rho D_k \frac{\partial Y_k}{\partial x_j} \eta_j^{\text{gas}} - \frac{\rho D_k}{W} Y_k \frac{\partial W}{\partial x_j} \eta_j^{\text{gas}} \right]_{TM} = \dot{\omega}_{s,k} \frac{W_k}{1000} \tag{3.124}
\]

For the temperature on the gas-membrane interfaces we impose continuity of the heat flux as follows:

\[
\rho u_i \left( h_s + K \right) \eta_i^{\text{gas}} + \dot{\omega}_{T,s} \frac{\partial T_i}{\partial x_i} \eta_i^{\text{gas}} + \rho \sum_{k=1}^{K_g} h_{s,k} Y_k V_{k,i} \eta_i^{\text{gas}} - u_j \tau_{ji} \eta_i^{\text{gas}} - \sigma \epsilon_{mem} \left( T_{mem}^4 - T_{\infty}^4 \right) = \lambda_M \frac{\partial T_i}{\partial x_i} \eta_i^{TM} \tag{3.125}
\]

In equation 3.125, \( T_i = T = T_M \) is the interfacial temperature. Equation 3.125 is solved iteratively using the Newton-Raphson method, as described in earlier chapters.

Note that equations 3.122-3.125 are general and apply at both the feed and sweep gas-membrane interfaces.

For the PNP model, the boundary conditions are exactly the same as described in section 3.2.6.
Chapter 4

$CO_2$-assisted methane partial oxidation to syngas using ITM

This chapter is devoted to the discussion of using ion transport membranes for the production of synthesis gas via methane dry-reforming. We show that partial oxidation of methane to syngas using LCF and $CH_4$-$Ar$ mixtures at the membrane sweep side has a low fuel conversion rate, while the oxygen permeation rise levels off at low inlet fuel concentrations. The performance is improved when $CO_2$ is added in the inlet mixture. The oxygen flux through the membrane and the methane conversion rate increase considerably; at the same time, $CO_2$ is converted into useful products instead of being emitted to the atmosphere. This $CO_2$ reuse can have a significant impact on the global effort to mitigate the negative effects of global warming on the planet’s temperature rise.
4.1 Catalytic activity of methane decomposition on LCF

Several studies suggest that iron can catalyze methane pyrolysis. For example, Ibrahim et al. used an iron catalyst to promote methane pyrolysis for hydrogen production at $\theta = 700 \, ^\circ C$ [65]. Jin et al. have shown that activated carbon supported $Fe - Al_2O_3$ catalysts can be used in hydrogen production via catalytic methane pyrolysis [66]. In a recent study, Maneerung et al. observed higher $CH_4$ pyrolysis rates when $LaNiO_{3-\delta}$ was doped with $Fe$ at the B-site to form $LaNi_{1-x}Fe_xO_{3-\delta}$ [67].

Given the presence of $Fe$ in the B-site of an LCF, it is important to investigate any interactions of the surface with the fuel under zero oxygen flux conditions.

To examine possible catalytic activity of LCF leading to methane decomposition, we conducted two different experiments using pure nitrogen ($N_2$) at the feed side (instead of air) and methane-argon mixtures at the sweep side. Using pure $N_2$ at the feed side allows for the investigation of interaction of the sweep surface with the fuel. Figure 4-1 shows the sweep side surface measurements of $CH_4$ and $H_2$ as a function of the inlet $CH_4$ mole fraction. Solid lines correspond to an LCF separating the feed and sweep side, while dashed lines correspond to measurements using a quartz plate instead of the LCF membrane under the same conditions. Quartz is chemically inert under a reactive environment and can withstand high temperatures, hence it is an ideal candidate to isolate catalytic effects of the LCF membrane. The modified apparatus is shown in figure 4-2. The experiment was conducted at $\dot{V}_{\text{sweep}}^{\text{total}} = 2000 \, (sccm)$ and temperature around $\theta = 750 \, ^\circ C$ to suppress gas-phase kinetics. According to figure 4-1, $CH_4$ decomposition on the surface of the membrane is not significant; gas-phase reactions contribute most to the methane decomposition.
Figure 4-1: Sweep side $X_{CH_4}^{mem}$ and $X_{H_2}^{mem}$ using an LCF and a quartz plate. Operating conditions: feed volumetric flow rate $\dot{V}_{N_2} = 3000 \pm 2(sccm)$, sweep volumetric flow rate $\dot{V}_{sweep}^{total} = 2000 \pm 2(sccm)$.

4.2 Reactive $CH_4 - Ar$ experiments under finite oxygen flux conditions

Figure 4-3 shows the dependency of the oxygen flux $J_{O_2}$ and the methane conversion as a function of inlet methane mole fraction and temperature when air is used at the feed side. The sweep side volumetric flow rate is kept constant at $\dot{V}_{sweep}^{total} =$
Figure 4-2: Use of a quartz plate instead of an ITM to quantify the importance of gas-phase reactions under different operating conditions. Figure shows the gasket material and the position of the probe and thermocouple at the sweep side during the experiment.

2000 (secm); an $L = 1.5\ (mm)$ thick membrane is used at $\theta = 905\ (^{\circ}C)$ while a thinner $L = 1.0\ (mm)$ membrane is used at $\theta = 960\ (^{\circ}C)$. For a fixed temperature, figure 4-3 shows that $J_{O_2}$ increases by one order of magnitude compared to inert cases as more fuel is introduced at the sweep side of the reactor, but levels off at about $X_{CH_4}^{in} \approx 5\%$. The highest flux is $J_{O_2} = 0.35\ (\mu m o l e / c m^2 / s e c)$ at $\theta = 960\ (^{\circ}C)$. The same figure includes the methane conversion at the same conditions. For a fixed temperature, as the oxygen flux levels off as a function of inlet fuel concentration, the conversion rate follows the same trend.
Examining the mechanism under which the oxygen flux increases requires knowledge of the chemical species composition near the vicinity of the membrane sweep surface; this is achieved with the quartz probe. Figure 4-4 shows the mole fractions of CO, H₂, CH₄, CO₂, O₂ and C at the membrane surface. Carbon mole fraction is obtained using a carbon/hydrogen balance between inlet and probe measurements since no advanced instrumentation for measurement of C was available. Mole fractions lower than 0.01 (%) of higher hydrocarbons like acetylene (C₂H₂), ethylene

Figure 4-3: \( J_{O_2} \) and methane conversion as a function of \( X_{CH_4}^{in} \) and temperature. Operating conditions: feed volumetric flow rate \( \dot{V}_{air} = 4000 \pm 2(\text{sccm}) \), sweep volumetric flow rate \( \dot{V}_{sweep}^{total} = 2000 \pm 2(\text{sccm}) \).
(C$_2$H$_4$) and ethane (C$_2$H$_6$) were detected in the flow stream for the entire range of our operating conditions.

Figure 4-4: Membrane species mole fractions as a function of X$_{CH_4}^{co}$ and temperature. Left: measurements at $\theta = 905 \pm 1 (^\circ C)$, right: measurements at $\theta = 960 \pm 2 (^\circ C)$. Operating conditions: feed volumetric flow rate $V_{air} = 4000 \pm 2 (sccm)$, sweep volumetric flow rate $V_{sweep}^{total} = 2000 \pm 2 (sccm)$. 

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In the presence of fuel, $J_{O_2}$ increases due to consumption of $O_2$ at the sweep side that results to an increase in the chemical potential difference of $O_2$ across the membrane. There are two possible mechanisms of $O_2$ consumption: a) $O_2$ desorbs into the gas phase, then reacts with the fuel and other products of gas-phase combustion, b) consumption of oxygen occurs heterogeneously on the surface of the membrane. In the latter case, reactants adsorb on the sweep side and react with oxygen ions in the oxygen lattice site. Given that $CH_4$ decomposes into $C$ and $H_2$ in the gas-phase, the presence of $C$ and $H_2$ may consume oxygen ions directly at the membrane surface. However, direct carbon oxidation on a solid surface is known to be slower than that of gaseous species [68, 69] and hence is discounted here. This conclusion is also supported by the fact that $J_{O_2}$ levels off as a function of inlet fuel concentration despite the carbon increase (figure 4-4). Instead $CO$, which can be produced in the gas-phase, is more likely to participate in gas-solid reactions as follows:

$$O_O^X + 2Fe^\bullet_{Fe} \rightleftharpoons \frac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2Fe^{\pi}_{Fe}$$ (4.1)

$$CO(g) + O_O^X + 2Fe^\bullet_{Fe} \rightleftharpoons CO_2(g) + V_O^{\bullet\bullet} + 2Fe^{\pi}_{Fe}$$ (4.2)

$$H_2(g) + O_O^X + 2Fe^\bullet_{Fe} \rightleftharpoons H_2O(g) + V_O^{\bullet\bullet} + 2Fe^{\pi}_{Fe}$$ (4.3)

$$2Fe^{\pi}_{Fe} \rightleftharpoons Fe^{\prime}_{Fe} + Fe^\bullet_{Fe}$$ (4.4)

Reactions 4.2 and 4.3 show the 2 possible routes of oxygen ion consumption on the gas-membrane interface hence increasing $J_{O_2}$, while reaction 4.1 corresponds to oxygen ion charge transfer, association into $O_2$ and desorption into the gas-phase. Non-reactive measurements (at $X_{CH_4}^{in}$ = 0%) show a much lower flux. Moreover, Dimitrakopoulos and Ghoniem [64] determined the reaction rate constants of reaction 4.1 for non-reactive cases. This rate is an order of magnitude lower than the measured
flux under the reactive conditions of this study. As a result, reaction 4.1 has a much smaller contribution to $J_{O_2}$ rise. Reaction 5.8 describes the disproportionation of Fe.

While determining the reaction rate constants of the aforementioned reactions will be discussed extensively in the following chapters, we can qualitatively get information in terms of the reactions that contribute most to $J_{O_2}$ rise. Figure 4-4 shows that the CO mole fraction at the surface remains low and nearly constant as $X_{CH_4}^{in}$ increases; hence, the rate of reaction 4.2 is low. On the other hand, figure 4-4 shows that the surface $H_2$ mole fraction at $\theta = 905 \, (^\circ C)$ is lower than those shown in figure 4-1 under zero oxygen flux conditions at $\theta = 750 \, (^\circ C)$. Thus, $H_2$ produced through $CH_4$ pyrolysis is consumed at the surface. Moreover, $X_{CO_2}^{mem}$ is very low over the entire range of operating conditions, i.e. reaction 4.2 is also slow. Thus, most of oxygen consumption can be attributed to reaction 4.3. In addition, we observe that $J_{O_2}$ and the sweep side $X_{H_2}$ follow the same trends with respect to the inlet fuel concentration, supporting the conclusion that reaction 4.3 contributes most to the $J_{O_2}$ increase.

On the other hand, syngas is produced via reactions uncorrelated with consumption of $O_2$. The following reactions can take place either in the gas-phase or on the surface of the membrane:

$$CH_4 \rightleftharpoons C + 2H_2 \quad (4.5)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (4.6)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad (4.7)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (4.8)$$

$$C + H_2O \rightleftharpoons CO + H_2 \quad (4.9)$$
Figure 4-1 confirms that reaction 4.5 proceeds faster in the gas-phase and produces significant amounts of $C$ and $H_2$. For the case of $CH_4 - Ar$ mixtures and given the previous observation that reaction 4.2 is slow, the rate of reactions 4.7 and 4.10 do not play an important role in $CH_4$ reforming (note the absence of $CO_2$ and the abundance of $C$). Within the temperature regime of our experiments, the water-gas shift reaction takes place; however, using the same arguments, one expects the rate of this reaction to be slow given the absence of $CO_2$, the low $CO$ concentrations and the presence of $H_2$ in the gas-phase.

As a result, it appears that reaction 4.3 is responsible for most of the surface consumption of oxygen ions and $J_{O_2}$ increase, with a much smaller contribution through reaction 4.2. $H_2$ in reaction 4.3 is the product of the $CH_4$ decomposition in the gas-phase. Therefore, there are 2 possible ways to further produce syngas: either the produced $H_2O$ reacts with $C$ to form $H_2$ and $CO$ through reaction 4.9 or $H_2O$ reacts directly with $CH_4$ to produce syngas through steam reforming described by reaction 4.8; estimating the rates of these reactions in the gas-phase or on the membrane surface will be examined in the next chapters.

### 4.3 Impact of $CO_2$ in $J_{O_2}$ increase and syngas production

Results in the previous section provide information in terms of $J_{O_2}$ enhancement and syngas production when using $CH_4 - Ar$ mixtures at the sweep side of an ITM reactor. We observe that $J_{O_2}$ reaches saturation at low values of $X_{CH_4}^{in}$. An alternative that will be shown to increase $J_{O_2}$ and syngas production is to substitute $Ar$ with
$CO_2$; this choice allows for the reuse of $CO_2$. Another benefit is the conversion of carbon arising from methane decomposition into useful products through reaction 4.10. The kinetics of the Boudouard reaction favors $CO$ production for temperatures higher than $\theta = 700\ (^\circ C)$ [70]. Moreover, the presence of carbon may have a negative impact on the stability of the membrane, hence decreasing carbon concentration protects the surface from phase changes associated with oxygen flux reduction [71].

Figure 4-5: $J_{O_2}$ and methane conversion as a function of $X_{CO_2}^{in}$. Operating conditions: feed volumetric flow rate $\dot{V}_{air} = 4000 \pm 2\ (sccm)$, sweep volumetric flow rate $\dot{V}_{sweep} = 2000 \pm 2\ (sccm)$, $X_{CH_4}^{inlet} = 9.85 \pm 0.1\ (%)$, $\theta = 968 \pm 2\ (^\circ C)$, $L = 1.0\ (mm)$.

Figure 4-5 shows the $J_{O_2}$ and methane conversion as a function of the inlet $CO_2$ mole fraction. For this experiment, we substitute some of $Ar$ with $CO_2$ at the
inlet of the reactor, while keeping the total sweep side volumetric flow rate and the inlet methane mole fraction constant at $V_{sweep}^{total} = 2000(\text{sccm})$ and $X_{\text{CH}_4}^{\text{inlet}} = 9.85\%$, respectively. The experiment was conducted at temperature $\theta = 968^\circ C$ using an $L = 1.0(\text{mm})$ thick membrane. We observe an increase in both the oxygen flux $J_O^2$ and the fuel conversion as more $CO_2$ enters the sweep side of the reactor. Compared to the case without $CO_2$, as the $CO_2$ mole fraction reaches $X_{CO_2}^{in} \approx 9\%$, the oxygen flux increases by approximately 50%, while methane conversion reaches 100%. Next, we examine the underlying mechanism of this performance enhancement.

In terms of the oxygen flux enhancement when $CO_2$ is added in the sweep stream, clearly more oxygen ions $O^X_0$ are consumed at the surface; the concentration of gaseous oxygen is close to zero. Figure 4-6 shows a decrease in methane mole fraction at the membrane surface as a function of inlet $CO_2$; this suggests that reactions involving conversion of methane to syngas play a role. Given the previous results regarding $CO$ and $H_2$ consuming $O^X_0$ at the surface, the reason for the $J_O^2$ enhancement when $CO_2$ is added to the inlet stream is the rise in the concentrations of $H_2$ and $CO$ in the gas-phase; these adsorb on the membrane surface and react with oxygen ions. Surface oxidation of $H_2$ and $CO$ produce more $H_2O$ and $CO_2$, respectively, that can be further consumed in other gas-phase or surface reactions not related to the oxygen flux increase.

Figure 4-6 shows the species composition at the sweep side of the membrane when $CO_2$ is added to the inlet stream. We observe a significant increase in syngas production compared to the case without $CO_2$. When $X_{CO_2}^{in} \approx 9\%$, the hydrogen and carbon monoxide mole fractions at the surface, $X_{H_2}^{mem}$ and $X_{CO}^{mem}$, respectively, increase by approximately one order of magnitude compared to the case without $CO_2$. We also observe that for an inlet ratio $X_{H_2}^{in} / X_{CO_2}^{in} \approx 1$, the syngas composition at
Figure 4-6: Membrane species mole fractions as a function of $X_{CO_2}^{in}$. Operating conditions: feed volumetric flow rate $V_{air} = 4000 \pm 2(sccm)$, sweep volumetric flow rate $V_{sweep} = 2000 \pm 2(sccm)$, $X_{CH4}^{inlet} = 9.85\pm0.1(\%)$, $T = 968\pm2(\degree C)$, $L = 1.0(mm)$.

Figure 4-6 shows excess of $CO_2$ close to the membrane surface. As discussed earlier, the Boudouard reaction 4.10 favors the production of $CO$ given the temperature of our experiments. This is further confirmed by the significant reduction of $C$ at the membrane surface. Given the possibility of steam being present in the flow stream through reaction 4.3 or the reverse water-gas shift reaction 4.6, one should also consider reaction 4.6 as another step for carbon reduction. However, given that carbon is $X_C^{mem} \approx 1(\%)$ in the absence of $CO_2$, we can estimate bounds for the pro-
duction of $CO$ and $H_2$ through reactions 4.9 and 4.10: for the case of $X_{CO_2}^{in} = 9\%$, if only reaction 4.9 takes place, we estimate a contribution of approximately 1\% $CO$ and 1\% $H_2$ in the total $X_{CO}^{mem}$ and $X_{H_2}^{mem}$ values, while we estimate a contribution of 2\% of $CO$ if only the Boudouard reaction 4.9 takes place; this means that the contribution of these reactions in the total $X_{CO}^{mem}$ and $X_{H_2}^{mem}$ production is small and other reactions are responsible for the high syngas concentrations measured at the membrane surface. Reducing the carbon levels is beneficial since useful products can be formed and the risk of carbon altering the membrane structure is minimized.

After elimination of certain reactions as possible candidates for the significant syngas production, we conclude that reactions 4.6, 4.7 and 4.8 should be the main contributors. We examine the case of $X_{CO_2}^{in} \approx 9\%$ and focus on the surface measurements of figure 4-6. Approximately 8\% of $CH_4$ has been converted into other products; approximately 1\% is related to methane decomposition, so the remaining 7\% is converted via reactions 4.6, 4.7 and 4.8. We also observe that approximately 7\% of $CO_2$ has been consumed. In addition, $X_{CO}^{mem} = X_{H_2}^{mem} \approx 13\%$. These measurements suggest that dry reforming is the main contributor of syngas production when $CO_2$ is added to the system.

The reverse water-gas shift and the steam reforming reactions are responsible for the conversion of the remaining methane. However, our GC cannot measure steam and hence it is difficult to directly quantify the impact of reactions 4.6 and 4.8 on syngas production. Future studies will confirm the capability of LCF to catalyze dry reforming as a combination of steam reforming followed by the water-gas shift reaction.
4.4 Conclusion

This chapter investigates the performance of the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ perovskite when methane is introduced at the oxygen lean side. Using experimental measurements, we show that the LCF membrane can pyrolize $CH_4$ at the membrane surface. When a mixture of $CH_4 - Ar$ is added to the sweep side with air in the feed side, $J_{O_2}$ increases by one order of magnitude but levels off at approximately $\chi_{CH_4}^{in} \approx 5\%$. This results in low fuel conversion and syngas production. The aforementioned oxygen flux enhancement is due to heterogeneous reactions consuming oxygen ions on the membrane surface. Given the possible candidates of $J_{O_2}$ increase, we show evidence that the $H_2$ surface oxidation is mainly responsible for this performance enhancement.

To further promote the performance of the membrane, $CO_2$ is added to the sweep side stream. Using $CO_2$ leads to higher methane conversion via dry reforming. The latter protects the material from possible phase change that may deteriorate the performance. When $CO_2$ is introduced into the system, the concentrations of $CO$ and $H_2$ at the membrane surface rise by one order of magnitude. We provide a qualitative analysis through which we show that dry reforming is the main contributor of syngas production. Determining the rates of all possible reactions as well as the possibility of some reactions taking place at the membrane surface is the subject of the following chapters.
Chapter 5

Performance and modeling of LCF under non-reactive conditions

This chapter is devoted to the investigation of the LCF membrane under inert conditions, i.e. when Ar is introduced at the sweep side of the ITM reactor. Measurements under different temperatures and oxygen partial pressures provide insight in the role of the surface exchange and the diffusion of charged species within the material. Fitting of the experimental data using the PNP model identifies the surface exchange as the rate-limiting step.

5.1 Introduction

Production of pure oxygen via air separation is an energy intensive process that works similarly to distillation: air is introduced into a column after steam and carbon dioxide have been removed and then, the temperature is reduced below zero. At atmospheric pressure and around $\theta = -183 (^{\circ}C)$, $O_2$ enters the liquid phase
while $N_2$ remains in the gas-phase given that its boiling point is approximately $\theta = -195.8\,({}^\circ C)$. This is how chemical companies can produce a high purity feedstock of $O_2$ and $N_2$. However, one can easily understand that a system that has the potential to decrease the temperature at such low levels requires significant amounts of energy. As a result, alternative ways that reduce the energetics and the cost associated to $O_2$ separation are becoming very popular.

Compared to cryogenic methods, ITM can serve as a better substitute in reducing the overall energy requirements [72]. A stable candidate under both oxidative and reducing conditions is LCF [73, 74, 75, 76, 77]. Due to its high stability, the LCF membrane has been studied extensively in the literature. The defect mechanism of this perovskite is well understood [56, 58, 78, 79, 80, 81]. Multiple Fe states are found to coexist inside the material and their concentrations depend on the oxygen partial pressure on the two sides of the membrane. Mizusaki et al. were the first to report a crossover between the concentrations of $Fe_{Fe}^{\bullet}$ and $Fe_{Fe}'$ at low oxygen partial pressures for an LSF membrane [59]. Geary et al. verified the presence of the same crossover behavior for an $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ membrane, which undergoes the same defect mechanism as the LSF [58]. However, all studies published so far deal with the equilibrium case under no flux conditions; investigations using this theory under finite oxygen flux conditions were first published in [64] and the model formulation will be presented in this chapter.

Existing oxygen permeation models for materials similar to the LCF suffer from weaknesses that restrict their applicability to a certain range of operating conditions [24, 75, 76, 77, 82, 83]. These models can only be applied in the high oxygen partial pressure regime; if the oxygen partial pressure is reduced significantly, assumptions associated with these models break down. In addition, these models fail to accurately represent the exact defect mechanism of ITM. Although evidence on how the oxygen
flux depends on the concentration of Fe states exist [58], current models do not account for this dependency. In particular, surface exchange and bulk diffusion steps do not respect the Fe site conservation and the electroneutrality condition. Furthermore, surface reactions do not preserve microscopic reversibility; given a set of experimental data, the reaction rate coefficients of a single reaction are fitted independently. Since the reaction rate coefficients are related to their equilibrium constants, these models are not thermodynamically consistent. Thus, new models with the aforementioned conditions are required so that they are applicable under all operating conditions.

Recently, efforts to improve the modeling of the surface reactions and bulk diffusion have appeared in the literature. Detailed surface exchange coupled with the Planck-Nernst-Poisson (PNP) equations is the most general approach [41]; other approaches assume strict electroneutrality in the bulk of the material to decouple the Poisson equation. For example, instead of solving for the exact PNP equations, Zhu et al. used strict electroneutrality coupled with detailed surface exchange to model gadolinium-doped ceria $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ [49]. Vollestad et al. used the PNP equations and detailed surface exchange to study the mixed-conductor $BaZr_{0.8}Y_{0.2}O_{3-\delta}$; however, this study assumes equilibrium for the surface reactions [50]. The same model formulation is used by Kee et al. in the study of a tubular reactor made of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$; a similar assumption of surface reactions being equilibrated is also retained in that study [51].

Here we set the framework for a general representation of the charge transfer kinetics and the transport of charged species within $La_{1-x}Ca_xFeO_{3-\delta}$ perovskites. Our work uses the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ as a model material but the same concepts can be directly extended to other perovskites with defect chemistry similar to the LCF. Our modeling includes detailed surface exchange; diffusion of charged species within
the material is modeled using the PNP equations. Compared to previous studies assuming all surface reactions being at equilibrium, our experimental measurements at the oxygen lean side of the membrane allow for the determination of the finite rate kinetics of the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$. Given separate equilibrium experiments [58], a thermodynamically consistent surface exchange mechanism is proposed.

### 5.2 Weaknesses of existing models

Various models for the oxygen flux through an ITM have been proposed in the literature [24, 75, 76, 82, 83]. The most representative of these account for the two oxygen transport steps: surface exchange and bulk diffusion [18]. For the surface exchange, the following 1-step reversible reaction is considered to describe the overall oxygen adsorption/desorption, dissociation/association and incorporation/exclusion mechanism at the feed/sweep side of the membrane, respectively:

$$\frac{1}{2}O_2(g) + V_{O^+}^{\bullet} \xrightleftharpoons[k_r]{k_f} O_X^\bullet + 2h^\bullet$$  \hspace{1cm} (5.1)

In reaction 5.1, $k_f$ and $k_r$ are the forward and backward reaction rate coefficients, respectively. Using the law of mass action and assuming that the concentration of oxygen ions inside the oxygen lattice sites as well as the concentration of electron holes are constant, the oxygen flux $J_{O_2}$ for reaction 5.1 can be expressed at both the feed and sweep side:

$$J_{O_2}^{\text{feed}} \text{ (mole/cm}^2/\text{sec)} = k_fP_{O_2,f}^{0.5}C_{V_f} - k_r$$  \hspace{1cm} (5.2)

$$J_{O_2}^{\text{sweep}} \text{ (mole/cm}^2/\text{sec)} = k_r - k_fP_{O_2,s}^{0.5}C_{V_s}$$  \hspace{1cm} (5.3)
In equations 5.2 and 5.3, $C_{V_f}$ (mole/cm$^3$) and $C_{V_s}$ (mole/cm$^3$) are the molar concentration of oxygen vacancies on the feed and sweep side, respectively, while $P_{O_2,f}$ (atm) and $P_{O_2,s}$ (atm) are the feed and sweep side oxygen partial pressures, respectively.

The Planck-Einstein equation is used to express the oxygen flux through the membrane for the bulk diffusion step. Following the detailed derivation in [18], we end up in the following expression for the oxygen flux through the membrane:

$$J_{O_2} (mole/cm^2/sec) = \frac{D_V}{2L} (C_{V_s} - C_{V_f})$$

In equation 5.4, $L$ (cm) is the membrane thickness and $D_V$ (cm$^2$/sec) the diffusion coefficient of oxygen vacancies. Assuming steady state ($J_{O_2}^{feed} = J_{O_2}^{sweep} = J_{O_2}$) and by substituting equations 5.2 and 5.3 into equation 5.4, we get the following expression for the oxygen flux:

$$J_{O_2} (mole/cm^2/sec) = \frac{D_V k_f (P_{O_2,f}^{0.5} - P_{O_2,s}^{0.5})}{2L k_f (P_{O_2,f} P_{O_2,s})^{0.5} + D_V (P_{O_2,f}^{0.5} + P_{O_2,s}^{0.5})}$$

To characterize an ITM, $k_f$, $k_r$, and $D_V$ in equation 5.5 have to be specified. These kinetic parameters are fitted using an Arrhenius expression of the form:

$$\beta_i = A_i \exp \left( -\frac{E_a^i}{RT} \right)$$

where $\beta_i$ can be either $k_f$, $k_r$ or $D_V$. $A_i$ is the pre-exponential factor and $E_a^i$ the activation energy.

Although the model given by equation 5.5 is simple enough that it can be used for the design of ITM reactors, it does not account for the exact defect mechanism of an ITM. For example, the defect mechanism of the LCF membrane is well understood.
and has been documented in several papers [56, 58, 78, 79, 80, 81]. A review of the aforementioned modeling approach led to the conclusion that there are many misconceptions and unjustified assumptions that may very well compromise any results, especially when equation 5.5 is utilized for predictions outside the range of operating conditions used for the fitting of \( k_f \), \( k_r \), or \( D_v \). We list these assumptions below and focus in particular to the modeling of the LCF membrane:

a. The model described by equation 5.5 does not preserve reversibility since \( k_f \) and \( k_r \) are fitted as independent parameters. We know that \( k_f \) and \( k_r \) should be related to each other through the equilibrium constant to account for microscopic reversibility.

b. The model does not preserve site balances and does not respect the electroneutrality condition at the gas-membrane interface when the effect of the electric double layer is neglected. It will be shown later that these two conditions are an important part of the modeling of \( J_{O_2} \). We note here that equation 5.5 accounts for strict electroneutrality in the bulk of the membrane [18]. Later in this paper, we will assess the assumption of strict electroneutrality within the LCF perovskite.

c. Several studies of membranes with the same defect mechanism under no flux conditions [50, 51, 58, 59] show that there are multiple B-site oxidation states and their concentration depends on the oxygen partial pressure. Reaction 5.1 does not account for the multiple B-site states. More importantly, the concentrations of the different B-site states are not included in the law of mass action for the oxygen flux \( J_{O_2} \). Even the assumption of constant electron holes should be questioned given the data in [58, 59].
d. In the limit of $P_{O_{2,s}} \to 0 \text{ (atm)}$ (i.e. in the case of vacuum at the sweep side),
the flux predicted using equation 5.5 becomes independent of the membrane thickness: $J_{O_2} \to k_r$. However, one should expect that the oxygen permeation of a very thin membrane should be higher compared to the oxygen permeation of a very thick membrane due to the larger distance that oxygen ions have to travel inside the membrane. As a result, even when vacuum is applied, $J_{O_2}$ should still be a function of membrane thickness and equation 5.5 fails to capture this dependency.

e. The derivation of equation 5.4 assumes higher mobility of electron holes compared to the mobility of oxygen vacancies. This assumption is also questioned given the different B-site oxidation states and their dependency on the oxygen partial pressure.

f. The model formulation assumes the concentration gradient as the only mechanism for oxygen vacancy diffusion within the material (equation 5.4) and neglects the contribution of electromigration. Using a PNP model offers several advantages: first, the PNP model accounts for diffusion due to both concentration gradient and electromigration and the relative contribution of the two can be quantified. In addition, the diffusion of all charged species within the material can be modeled. Also, the PNP model can be easily integrated with heterogeneous reactions at the gas-membrane interfaces.

To close the gap and to relax some of the assumptions associated with the LCF membrane of our study, we present a general formulation of the surface exchange chemistry and bulk diffusion steps. The model can be used for materials with defect mechanism similar to the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$, such as $La_{1-x}Ca_xFeO_{3-\delta}$,
$La_{1-x}Sr_xFeO_{3-\delta}$, $La_{1-x}Ba_xFeO_{3-\delta}$ of any doping percentage. It satisfies thermodynamic consistency by relating $k_f$ and $k_r$ with the equilibrium constant and accounts for B-site conservation on the gas-membrane interfaces as well as in the interior of the membrane.

5.3 Inert oxygen flux model

5.3.1 Defect chemistry

A two-step reaction mechanism is proposed for both the feed and sweep side of the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ membrane [58, 59]:

\[
\frac{1}{2}O_2(g) + V'^{\bullet\bullet} + 2Fe'^{\bullet}_{Fe} \xrightleftharpoons[k_{r_1}]{k_{f_1}} O^{X}_{O} + 2Fe'^{\bullet}_{Fe} \tag{5.7}
\]

\[
2Fe'^{\bullet\bullet}_{Fe} \xrightleftharpoons[k_{r_2}]{k_{f_2}} Fe'^{\bullet}_{Fe} + Fe'^{\bullet}_{Fe} \tag{5.8}
\]

In reactions 5.7 and 5.8, $k_{f_1}$, $k_{r_1}$, $k_{f_2}$ and $k_{r_2}$ are the reaction rate coefficients of the aforementioned reactions. Using the law of mass action, we express the rate of progress of reactions 5.7 and 5.8 at both the feed/sweep side:

\[
\dot{s}_1 \text{ (mole/cm}^2/\text{sec) = } k_{f_1}C_{O_2}^{1/2}C_{V'^{\bullet\bullet}}C_{Fe'^{\bullet}_{Fe}} - k_{r_1}C_{O^{X}_{O}}C_{Fe'^{\bullet}_{Fe}} \tag{5.9}
\]

\[
\dot{s}_2 \text{ (mole/cm}^2/\text{sec) = } k_{f_2}C_{Fe'^{\bullet}_{Fe}} - k_{r_2}C_{Fe'^{\bullet}_{Fe}}C_{Fe'^{\bullet}_{Fe}} \tag{5.10}
\]
The molar concentration of species $k$, $C_k$, is related to the formula-unit concentration $[X_k]$ through the expression:

$$C_k \; (\text{mole/cm}^3) = \frac{[X_k]}{V_m} \quad (5.11)$$

In equation 5.11, $V_m$ is the molar volume. Using XRD analysis, the molar volume of the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ membrane is estimated $V_m = 36.14 \; (\text{cm}^3/mole)$ [64] and this value agrees with other studies [71]. At equilibrium, $\dot{s}_1 = 0$ and $\dot{s}_2 = 0$. This leads to the definition of the equilibrium constants based on molar concentrations, $K_{C_1}$ and $K_{C_2}$:

$$K_{C_1} = \frac{k_{f_1}}{k_{r_1}} = \frac{1}{C_{O^2}^{1/2} C_{V^•}^2 C_{Fe^•_{F_e}}^2} \; (5.12)$$

$$K_{C_2} = \frac{k_{f_2}}{k_{r_2}} = \frac{C_{Fe^•_{F_e}} C_{Fe^•_{F_e}}}{C_{Fe^•_{F_e}}^2} \; (5.13)$$

According to equations 5.12 and 5.13, the rate of progress of reactions 5.7 and 5.8 can be rewritten as:

$$\dot{s}_1 = k_{r_1} \left[ K_{C_1} C_{O^2}^{1/2} C_{V^•}^2 C_{Fe^•_{F_e}}^2 - C_{O^X} C_{Fe^2_{F_e}} \right] \; (5.14)$$

$$\dot{s}_2 = k_{r_2} \left[ K_{C_2} C_{Fe^•_{F_e}}^2 - C_{Fe^•_{F_e}} C_{Fe^•_{F_e}} \right] \; (5.15)$$

The relationship between the equilibrium constants based on molar concentrations $K_{C_1}$, $K_{C_2}$ and the equilibrium constants based on partial pressures and formula-units $K_{P_1}$, $K_{P_2}$ is:

$$K_{P_1} = \frac{1}{\left( \frac{P_{O_2}}{P_{ref}} \right)^{1/2} \left[ \frac{[O^X]^{1/2}}{V^•^{1/2}} \left[ \frac{[Fe^•_{F_e}]^2}{RT} \right] \right]} = \left( \frac{P_{ref}}{RT} \right)^{1/2} \frac{1}{C_{O^2}^{1/2} C_{V^•}^2 C_{Fe^•_{F_e}}^2} = \left( \frac{P_{ref}}{RT} \right)^{1/2} K_{C_1} \; (5.16)$$
\[ K_{P_2} = \frac{[Fe^{\bullet}_{Fe}][Fe^{\prime}_{Fe}]}{[Fe^{\prime \prime}_{Fe}]^2} = \frac{C_{Fe^{\bullet}_{Fe}}C_{Fe^{\prime}_{Fe}}}{C_{Fe^{\prime \prime}_{Fe}}^2} = K_C \]  \hspace{1cm} (5.17)

In equation 6.42, \( P_{\text{ref}} = 1 \text{ (atm)} \) is the standard-state pressure. The equilibrium constant \( K_{P_i} \) of reaction \( i \) is related to the Gibbs free energy change \( \Delta G_i^\circ \) through the following equation:

\[ K_{P_i} = \exp \left( -\frac{\Delta G_i^\circ}{RT} \right) = \exp \left( -\frac{\Delta H_i^\circ - T\Delta S_i^\circ}{RT} \right) \]  \hspace{1cm} (5.18)

In equation 5.18, \( \Delta H_i^\circ \) and \( \Delta S_i^\circ \) are the standard-state enthalpy and entropy change of reaction \( i \), respectively. In a separate study for the \( La_{0.9}Ca_{0.1}FeO_3-\delta \) perovskite, Geary and Adler determined \( K_{P_1} \) and \( K_{P_2} \) and the associated thermodynamic properties after measuring the membrane's nonstoichiometry \( \delta = [V_{O^{\bullet \bullet}}] \) at different temperature and \( P_{O_2} \) conditions using a coulometric titration cell [58]. These values are summarized in table 3.1.

Oxygen site conservation allows to relate the concentration of oxygen vacancies and oxygen ions:

\[ [O^{\bullet \bullet}_O] + [V_{O^{\bullet \bullet}}] = 3 \Rightarrow C_{O^{\bullet \bullet}} + C_{V_{O^{\bullet \bullet}}} = \frac{3}{V_m} \]  \hspace{1cm} (5.19)

Equation 5.19 is valid both at the interior of the membrane as well as at the gas-membrane interfaces. The same applies for the Fe site conservation:

\[ [Fe^{\bullet\prime\prime}_{Fe}] + [Fe^{\bullet}_{Fe}] + [Fe^{\prime\prime}_{Fe}] = 1 \Rightarrow C_{Fe^{\bullet\prime\prime}_{Fe}} + C_{Fe^{\bullet}_{Fe}} + C_{Fe^{\prime\prime}_{Fe}} = \frac{1}{V_m} \]  \hspace{1cm} (5.20)

An assumption that is frequently invoked in modeling mixed-conductors is to neglect the electric double layer on the gas-solid interfaces [49, 50, 51, 52, 64, 84]. The validity of this assumption depends on whether charge separation on the interfaces is important. In contrast to electrolytic-galvanic cells where the electric double layer
is found to be significant [48, 55], the LCF membrane operates under open circuit conditions. No external current flows through the material and hence, the electric double layer, although present, is expected to have less influence compared to the case where the material was polarized. As a result, the following strict electroneutrality condition will be enforced at the gas-membrane interfaces:

\[
[Ca'_{La}] + [Fec'] = 2[V_{O}^{**}] + [Fe_{Fe}^*] \Rightarrow \frac{x}{V_m} + C_{Fe_{Fe}} = 2C_{V_{O}^{**}} + C_{Fe_{Fe}}^* \quad (5.21)
\]

The formula-unit concentration of Calcium in the Lanthanum lattice site for the La_{0.9}Ca_{0.1}FeO_{3-δ} mixed-conductor is \([Ca'_{La}] = x = 0.1\). It is important to note that our modeling assumes strict electroneutrality at the feed and sweep sides and it has already been discussed in chapter 3 that this is equivalent to strict electroneutrality within the entire material since charge can diffuse at the bulk of the membrane only through the interfaces.

In the rest of our analysis, the Fe disproportionation reaction 5.8 is assumed to be at equilibrium, both at the gas-membrane interfaces as well as in the interior [64]. The oxygen incorporation reaction 5.7 is treated as rate-limiting. Combining the Fe-site conservation (equation 3.78), the strict-electroneutrality condition (equation 5.21) and the definition of the equilibrium constant \(K_{P_2}\) (equation 6.43), the formula-unit concentration of the different Fe states can be calculated using an analytical expression applicable on both the feed and sweep sides [64]:

\[
[Fe_{Fe}^*] = \frac{1 - \sqrt{1 + [4K_{P_2} - 1] \left[1 - (2δ - x)^2\right]}}{1 - 4K_{P_2}} \quad (5.22)
\]

\[
[Fe'_{Fe}] = \frac{1 - x}{2} + δ - \frac{1 - \sqrt{1 + [4K_{P_2} - 1] \left[1 - (2δ - x)^2\right]}}{2(1 - 4K_{P_2})} \quad (5.23)
\]
According to this equilibrium assumption, observe that the formula-unit concentration of the iron states becomes a function of the oxygen vacancy formula-unit concentration $\delta$, the Calcium doping $x$ and $K_{P_2}$.

### 5.3.2 Boundary conditions and fitting process

To model oxygen permeation, we use oxygen flux measurements combined with surface $P_{O_2}$ values obtained under different operating conditions. Our fitting process includes the determination of seven parameters related to surface reactions and species material diffusion: $[A_{D_0}, E_{a_0}^{D_0}, A_{k_1}, E_{a_1}^{k_1}, \mu_{FeF_{Fe}}, \mu_{FeF_e}, \epsilon_r]$. Although using seven parameters in the fitting process may introduce some uncertainty, our aim is to provide the foundations for an accurate modeling of the LCF membrane and of similar perovskites. As more data related to these parameters becomes available, one can reduce the uncertainty by fitting fewer parameters, but the overall model formulation presented here remains unchanged.

Given a set of $[A_{D_0}, E_{a_0}^{D_0}, A_{k_1}, E_{a_1}^{k_1}, \mu_{FeF_{Fe}}, \mu_{FeF_e}, \epsilon_r]$, the dimensionless molar concentration of oxygen vacancies at the feed ($\bar{y} = 0$) and sweep ($\bar{y} = 1$) side is calculated by applying a Robin boundary condition that accounts for chemical reactions at the gas-membrane interfaces [48, 49, 64]:

$$\tilde{J}_{V_0^{**}}^{\bar{y}=0} = \tilde{w}_{s, V_0^{**}} \eta_{\bar{y}}^{\bar{y}=0} \Rightarrow -\tilde{D}_{V_0^{**}} \frac{\partial \tilde{C}_{V_0^{**}}}{\partial \bar{y}} ]_{\bar{y}=0} - \tilde{D}_{V_0^{**}} z_{V_0^{**}} \tilde{C}_{V_0^{**}} \frac{\partial \tilde{\phi}}{\partial \bar{y}} ]_{\bar{y}=0} = \tilde{w}_{s, V_0^{**}} \eta_{\bar{y}}^{\bar{y}=0}$$

$$\tilde{J}_{V_0^{**}}^{\bar{y}=1} = \tilde{w}_{s, V_0^{**}} \eta_{\bar{y}}^{\bar{y}=1} \Rightarrow -\tilde{D}_{V_0^{**}} \frac{\partial \tilde{C}_{V_0^{**}}}{\partial \bar{y}} ]_{\bar{y}=1} - \tilde{D}_{V_0^{**}} z_{V_0^{**}} \tilde{C}_{V_0^{**}} \frac{\partial \tilde{\phi}}{\partial \bar{y}} ]_{\bar{y}=1} = \tilde{w}_{s, V_0^{**}} \eta_{\bar{y}}^{\bar{y}=1}$$

$$[Fe_{Fe}^{*}] = \frac{1 + x}{2} - \delta - \frac{1 - \sqrt{1 + [4K_{P_2} - 1] [1 - (2\delta - x)^2]}}{2(1 - 4K_{P_2})}$$

5.24
In equations 5.25 and 5.26, the dimensionless molar reaction rate of oxygen vacancies \( \tilde{\omega}_{s, V^\bullet} \) is defined as:

\[
\tilde{\omega}_{s, V^\bullet} = -\tilde{s}_1 = -\frac{L}{D_{ref} C_{ref}} \tilde{s}_1
\]  

(5.27)

while \( \tilde{s}_1 \) at both sides is calculated using equation 5.9 and the corresponding values at each side. Note that for equation 5.9, \( C_{O_2}^{\text{ref}} \) is known since \( P_{O_2} \) at the sweep side is measured experimentally; at the feed side, we assume air composition and hence, \( P_{O_2}^{\text{feed}} = 0.21 \text{ (atm)} \).

Equations 5.25 and 5.26 are the boundary conditions for the dimensionless molar concentration of oxygen vacancies at the gas-membrane interfaces. Using equations 5.23 and 5.24 (and the corresponding concentration conversions using equation 5.11), the dimensionless molar concentration of \( Fe_{Fe}^{e'} \) and \( Fe_{Fe}^{e} \) at the feed and sweep side are determined and correspond to the applied Dirichlet boundary conditions for the conservation equations 3.92. The concentration of \( Fe_{Fe}^{e} \) is evaluated using the Fe-site conservation.

The PNP model is solved for each experimental point and the numerical solution terminates once steady-state has been obtained. At the end of the numerical solution, we can evaluate the predicted flux \( J_{O_2}^{\text{predicted}} \) and check whether it agrees with the experimentally measured flux \( J_{O_2} \). We are interested in determining the set of \( \left[ A_{D_\psi}, E_{a_\psi}, A_{k_{\psi 1}}, E_{a_{k_{\psi 1}}}, \mu_{Fe_{Fe}^{e'}}, \mu_{Fe_{Fe}^{e}} \right] \) that minimize the objective function:

\[
G = \min \left[ \sum_{m=1}^{M} \left( \frac{J_{O_2,m} - J_{O_2,m}^{\text{predicted}}}{J_{O_2,m}} \right)^2 \right]
\]  

(5.28)

In equation 5.28, \( M \) is the total number of experimental measurements for the oxygen flux. We use MATLAB and a gradient based optimization method to get the optimal solution that minimizes \( G \) and best fits the experimental data.
5.4 Experimental measurements

To assess the new model, inert Ar experiments have been conducted using the stagnation flow reactor described in chapter 2. The composition of the mixture is evaluated by sampling gases and analyzing them using the Quadrupole Mass Spectrometer HPR20 from Hiden Analytical Inc. Given the absence of steam from the mixture, the sampling lines were not heated-up during the measurements.

Figure 5-1: Oxygen flux $J_{O_2}$ and local $P_{O_2}$ as a function of temperature. Experimental data using $Ar$ as the inert carrier at the sweep side of the ITM reactor. Operating conditions: feed side volumetric flow rate $V_{feed} = 6000(sccm)$, sweep side volumetric flow rate $V_{sweep} = 1999 \pm 3(sccm)$, membrane thickness $L = 1.00(mm)$. Solid lines correspond to the best fit of the data.
Figure 5-1 shows the dependency of the oxygen flux $J_{O_2}$ on temperature. The highest oxygen flux that can be achieved at about 1050 ($^\circ$C) is in the order of 0.06 ($\mu$ mole/cm$^2$/sec). The experimental data is collected at $V_{sweep} = 2000$ (sccm) for an $L = 1.00$ (mm) thick membrane. Figure 5-1 also includes the temperature dependency of the surface value of $P_{O_2}$ on the sweep side measured using the quartz probe.

![Graph showing $J_{O_2}$ as a function of volumetric flow rate: $\theta_{mem} = 1072 \pm 5$ ($^\circ$C), $L = 1$ (mm)]

![Graph showing $P_{O_2}$ as a function of volumetric flow rate: $\theta_{mem} = 1072 \pm 5$ ($^\circ$C), $L = 1$ (mm)]

Figure 5-2: $J_{O_2}$ and local $P_{O_2}$ as a function of $Q_{sweep}$. Operating conditions: feed side volumetric flow rate $V_{feed} = 6000$ (sccm), temperature $\theta = 1072 \pm 5$ ($^\circ$C), membrane thickness $L = 1.00$ (mm). Solid lines correspond to the best fit of the data.

Figure 5-2 shows the dependency of $J_{O_2}$ and local $P_{O_2}$ on the sweep volumetric flow rate, $V_{sweep}$. For this case, the temperature was fixed at $\theta = 1072$ ($^\circ$C). As the flow rate increases, oxygen is removed faster from the sweep side of the mem-
brane. This leads to a reduction of the local $P_{O_2}$ and as a result in an increase of $J_{O_2}$. Regarding the large error bar in the oxygen permeation flux, this comes from deviations in the measurement of the outlet species using the MS because the flow in our reactor is quasi steady-state.

Figure 5-3 shows the XRD spectra of an unused $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ membrane together with the XRD spectra of the feed and sweep side of the membrane after experiments. Clearly the LCF membrane did not experience a phase change during experiments and this confirms the stability of the membrane under an inert environment. Using XRD analysis, the unit cell dimensions are estimated and from there, the
molar volume of the LCF membrane was determined to be $V_m = 36.14 (cm^3/mole)$. This value agrees with other reported values in the literature for the same membrane [56, 75, 77].

### 5.5 Model results and discussion

Given the aforementioned experimental results, we investigate the distribution of charged species within the material and the way these affect the oxygen flux. Table 5.1 shows the values of the parameters that minimize equation 5.28. The lower and upper bounds for $A_{D_V}$ and $E_{a}^{D_V}$ have been established from transient dilatometry studies for the LCF membrane under investigation.

Table 5.1: Parameter estimation after fitting the oxygen flux measurements of this study. Table includes the lower and upper bounds used during the fitting process.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Estimated values</th>
<th>Lower Limit</th>
<th>Upper Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{D_V} (cm^2/sec)$</td>
<td>$9.84 \times 10^{-3}$</td>
<td>$2.52 \times 10^{-3}$</td>
<td>$9.84 \times 10^{-3}$</td>
</tr>
<tr>
<td>$E_{a}^{D_V} (kJ/mole)$</td>
<td>53.4</td>
<td>53.4</td>
<td>65.9</td>
</tr>
<tr>
<td>$A_{k_{r_1}} (cm^7/mole^2/sec)$</td>
<td>$3.021 \times 10^7$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$E_{a}^{k_{r_1}} (kJ/mole)$</td>
<td>193.93</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\mu_{Fe_{Fe^*}} (cm^2/V/sec)$</td>
<td>0.0556</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\mu_{Fe_{Fe^*}} (cm^2/V/sec)$</td>
<td>0.0977</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\epsilon_r (-)$</td>
<td>205</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5-4 shows the $J_{O_2}$ predictions of the model developed in this study based on detailed surface exchange and charged species transport, while figure 5-5 shows the predicted formula-unit concentration of oxygen vacancies $\delta$ at the feed and sweep side. We observe that the difference $\delta_s - \delta_f$ increases as the temperature rises leading
to a higher flux. Since the oxygen flux at a fixed temperature remains almost constant at high volumetric flow rates, the same applies to the $\delta_s - \delta_f$ difference.

![Graph showing $J_{O_2}$ as a function of temperature and volumetric flow rate.](image)

Figure 5-4: $J_{O_2}$ predictions using detailed surface exchange and the Planck-Nernst-Poisson model.

In addition, the predictions are in the same order of magnitude as $\delta$ measurements reported in [58] for our range of temperature and measured $P_{O_2}$ conditions. In a recent study for the LCF membrane using $CO_2$ as the inert carrier at the sweep side, Hunt et al. predicted the formula-unit concentration of oxygen vacancies $\delta$ to
be slightly higher as compared to the $\delta$ predictions reported in this study, yet the order of magnitude is the same [76]. Clearly the simple model given by equation 5.5 overpredicts the $\delta$ dependence within the reported operating conditions. Besides the fact that the local sweep side $P_{O_2}$ values are such that the $\delta$ predictions are less than $\frac{\pi}{2} = 0.05$ (and hence no crossover between $F_{C_{Fe}}$ and $F_{C'_e}$ is observed), the assumptions associated with equation 5.5 would break down. Figure 5-6 shows

![Graph showing $\delta_f$ and $\delta_s$ as a function of temperature and volumetric flow rate.](image)

Figure 5-5: Prediction of $\delta_f$ and $\delta_s$ (formula-unit concentrations) for the entire range of our operating conditions.
the formula-unit concentrations of the multiple Fe states as a function of temperature, while figure 5-7 includes the volumetric flow rate dependency of the Fe states. According to reaction 5.7, $Fe_{Fe}^{x}$ is produced at the feed side and consumed at the sweep side; hence it should be expected that $[Fe_{Fe}^{x}]_f > [Fe_{Fe}^{x}]_s$. The proposed surface exchange mechanism successfully captures this characteristic. The predictions show that there is a spatial dependency of $[Fe_{Fe}^{x}]$ and $[Fe_{Fe}^{x}]$ within the membrane.
however the difference between the two sides is small. This is confirmed from figure 5-8 showing the spatial distribution of δ and the multiple Fe states within the bulk of the membrane. As a result, the assumption of constant electron holes made in the derivation of equation 5.4 is reasonable given the small deviation in the formula-unit concentrations of $Fe^*_{Fe}$ and $Fe^{'*}_{Fe}$ within the bulk of the membrane. Again, this is true only within the range of our experimental conditions for which $P_{O_2,e}$ is relatively high and no crossover between $[Fe^*_{Fe}]$ and $[Fe^{'*}_{Fe}]$ is observed.
For a fixed temperature, as the flow rate increases, the local oxygen partial pressure drops so that the material remains electrically neutral. On the other hand, with temperature, more oxygen vacancies are produced and hence rise, while $\frac{\partial}{\partial F}$ happens for this. The reason for this lies in electronic transitions as $\frac{\partial}{\partial F}$ increases. Furthermore, we observe that [\frac{\partial}{\partial F}] increases with temperature, the opposite.

Figure 28. Spatial distribution of $N_0$ and $\frac{\partial}{\partial F}$.
drops and reaches a saturation limit; this behavior reveals the kinetic limitations of the oxygen incorporation reaction. The same trend is also reflected in figure 5-7; the formula-unit concentration of the multiple Fe states remains constant as the flow rate increases. Given that $\delta$ at the feed and sweep side is less than $\frac{\pi}{2} = 0.05$, no crossover in the concentration of Fe states is observed in the range of our operating conditions. Under these conditions, the electronic conductivity of the LCF membrane is of the p-type.

As discussed earlier, to avoid solving for the exact Poisson equation, strict electroneutrality within the bulk of the material is usually enforced. However, applying a strict electroneutrality condition at the interfaces is equivalent to solving Laplace’s equation for the electrostatic potential. To demonstrate this, we present a parametric analysis to quantify the sensitivity of our predictions to $\epsilon_r$. Figure 5-9 shows the electrostatic potential profiles for $\theta = 1072 \pm 5 (^\circ \text{C})$, $\dot{V}_{\text{sweep}} = 1999 \pm 3 \text{ (sccm)}$ and 4 cases: (a) assuming strict electroneutrality in the bulk $\rho = 0$, (b) solving equation 3.84 using $\epsilon_r = 205$, (c) solving equation 3.84 using $\epsilon_r = 10$, (d) solving equation 3.84 using $\epsilon_r = 2$. We observe that the electrostatic potential $\phi$ is not highly sensitive in $\epsilon_r$; solving the PNP model using strict electroneutrality and $\epsilon_r = 205$ produce nearly identical results for the electrostatic potential and the species concentrations. This is an outcome of the fact that applying strict electroneutrality at the gas-membrane interfaces leads to strict electroneutrality within the entire material. Figure 5-9 also shows that the electrostatic potential $\phi$ changes slightly when $\epsilon_r = 10$ or $\epsilon_r = 2$; this change has a negligible impact on the species concentration; the maximum observed relative change between cases (b) and (c) regarding the predicted species concentrations is less than 0.1%. Similar conclusion was reported in Kee et al. for $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ mixed conductors [51]. The authors report that the predicted concentrations are not affected if $\epsilon_r$ is in the range of 10 – 100.
Figure 5-9: Parametric analysis of the dependence of the electrostatic potential \( \phi \) on the relative permittivity \( \epsilon_r \); comparison with the assumption of a strict electroneutrality condition in the membrane bulk. Results correspond to the experimental point of \( \theta = 1072 \pm 5 \, (^{\circ}\text{C}) \) and \( V_{\text{sweep}} = 1999 \pm 3 \, (\text{sccm}) \). Feed side of the membrane is located at \( y = 0 \,(cm) \), while the sweep side corresponds to \( y = L = 0.1 \,(cm) \).

We end this section by comparing the parameters of the fitting process with available data in the literature. Bounds for the diffusion coefficient of oxygen vacancies \( D_V \) have been provided through separate transient dilatometry studies conducted by Air Products on LCF\(^1\): LCF bars of dimensions \( 25 \times 5 \,(mm) \) with thicknesses varying from 1 to 5 \( mm \) were subjected to \( P_{O_2} \) changes from \( 4 \times 10^{-6} \,(atm) \) to 1 \( (atm) \) and bar dimension changes were measured; the technique is outlined in [85]. Hence, we
would like to compare the order of magnitude of $D_V$ determined in this study with other available data in the literature. In a recent study of the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ membrane, Burger et. al. measured the ionic conductivity which was found to be around $6.3 \times 10^{-7} \leq D_V \text{ (cm}^2/\text{sec}) \leq 2.5 \times 10^{-6}$ at $700 - 800 \degree C$ [86]. In addition, Bidrawin et. al. measured the ionic conductivity of $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ in the temperature range of $\theta = 650 - 800 \degree C$ [87]. However, our experimental measurements were conducted in the temperature range of $\theta = 880 - 1050 \degree C$. Using the Nernst-Einstein equation and by extrapolating the $\delta$ values predicted in our experiments for lower temperatures, $D_V$ using the ionic conductivity measurements for the $La_{0.8}Ca_{0.2}FeO_{3-\delta}$ membrane at $\theta = 800 \degree C$ is found to be in the order of $O(D_V) = 2 \times 10^{-5} \text{ (cm}^2/\text{sec})$, while $D_V$ in our study is estimated to be in the order of $O(D_V) = 1 \times 10^{-5} \text{ (cm}^2/\text{sec})$. The latter values are in very good agreement with the ionic conductivity measurements of $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ provided in [86].

Furthermore, for the mobilities of electrons and electron holes $\mu_{Fe^e_{Fe}}$ and $\mu_{Fe^{+}_{Fe}}$, respectively, the values obtained in this study agree very well with reported values of $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ and of similar perovskites. Berger et. al. estimated $\mu_{Fe^e_{Fe}} = 0.125 - 0.15 \text{ (cm}^2/\text{V/sec})$ in the temperature range of $\theta = 700 - 800 \degree C$, which is slightly higher compared to the fitted value obtained in this study. Furthermore, Mizusaki et al. estimated the mobilities of the $LaFeO_{3-\delta}$ to be $\mu_{Fe^e_{Fe}} = 0.056 \text{ (cm}^2/\text{V/sec})$ and $\mu_{Fe^+_{Fe}} = 0.107 \text{ (cm}^2/\text{V/sec})$ [63]. In addition, the same authors estimated the mobilities in $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ to be $\mu_{Fe^e_{Fe}} = 0.07 \text{ (cm}^2/\text{V/sec})$ and $\mu_{Fe^+_{Fe}} = 0.10 \text{ (cm}^2/\text{V/sec})$ [61, 62].

Finally, fitting our experimental results provides a prediction for the relative permittivity; this is estimated to be $\epsilon_r = 205$. For the similar perovskite $LaFeO_3$, the value of $\epsilon_r = 220$ is reported in [54, 53]. Although our estimate for $\epsilon_r$ is in the

\footnote{Private communication with Air Products & Chemicals}
same order of magnitude as in [54, 53] for the LaFeO$_3$, we already showed that the predictions of the concentrations of charged species are not strongly sensitive to $\varepsilon_r$.

### 5.6 Coupling the PNP equations with CFD

In the previous section, we used experimental measurements to extract the kinetics of the oxygen incorporation reaction under non-reactive conditions. In this section, we have coupled the CFD model with the PNP equations in order to resolve simultaneously the gas-phase transport and the diffusion of charged species within the material.

For the sake of brevity, we will restrict our analysis to one case considering an $L = 0.5 \text{ (mm)}$ thick membrane operating at $\theta = 1050 \text{ (C)}$. Air is flown at the feed side with $\dot{V}_{\text{feed}} = 4000 \text{ (sccm)}$, while pure Argon is introduced at the sweep side with $\dot{V}_{\text{sweep}} = 2000 \text{ (sccm)}$. At $t = 0$, the gas-phase of the reactor is filled with air, while the charged species within the material have a uniform distribution equal to the equilibrium concentration at the corresponding temperature and $P_{O_2}$. At both the feed and sweep sides, the common interface is discretized using the same number of finite volumes to allow for a consistent coupling of the two problems.

Figure 5-10 shows the gas-phase mole fraction of $O_2$, $X_{O_2}$ and the formula-unit concentrations of oxygen vacancies, $\delta$, at $t = 20 \text{ (sec)}$, $t = 30 \text{ (sec)}$ and $t = 40 \text{ (sec)}$. Steady-state is achieved after approximately $50 \text{ (sec)}$. Initially, the material is at equilibrium with the gas-phase oxygen, hence the rate of reaction 5.7 at both the feed and sweep sides is zero. As pure Argon is flown at the sweep side, $X_{O_2}$ around the sweep side drops and the rate of progress of reaction 5.7 at the sweep gas-membrane interface becomes positive indicating that equilibrium is no longer satisfied and hence, $V_{O^*}$ are produced at this interface. Production of $V_{O^*}$ at the sweep side results in
Figure 5-10: $X_{O_2}$ and $\delta$ contours as a function of time. Top left subplot shows the $X_{O_2}$ contours at steady-state, while the rest of the subplots show both $X_{O_2}$ and $\delta$ by zooming close to the membrane.

diffusion towards the feed side due to a difference in the electrochemical potential of the charged species. This diffusion process shifts the equilibrium concentration of charged species at the feed side resulting in a non-zero reaction rate for reaction 5.7. The latter allows $V_O^{**}$ to be consumed by a subsequent incorporation of $O_2$ within the material in the form of oxygen ions. Figure 5-11 shows the formula-unit concentration of $Fe_{Fe}^{**}$ within the material for the same time intervals. Given that
Figure 5-11: $X_{O_2}$ and $[Fe^{\bullet}_{Fe}]$ contours as a function of time. Top left subplot shows the $X_{O_2}$ contours at steady-state, while the rest of the subplots show both $X_{O_2}$ and $[Fe^{\bullet}_{Fe}]$ by zooming close to the membrane.

$Fe^{\bullet}_{Fe}$ is consumed at the sweep side, a lower formula-unit concentration is observed at this interface. On the other hand, $Fe^{\bullet}_{Fe}$ is produced at the feed side and hence $[Fe^{\bullet}_{Fe}]_{feed} > [Fe^{\bullet}_{Fe}]_{sweep}$. 

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5.7 Conclusions

This chapter deals with the modeling of surface chemistry and charged species transport within LCF under non-reactive conditions. Existing models are valid only in the sweep side high oxygen partial pressure regime and overestimate the concentration of oxygen vacancies; the model developed in this study is detailed and applicable under a wide range of conditions. Using the $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ membrane, a two-step surface exchange reaction mechanism has been proposed under finite oxygen flux conditions; the same mechanism has already been applied successfully at equilibrium conditions. This mechanism is thermodynamically consistent; the reaction rate coefficients are related through the equilibrium constants determined from separate experiments. Additionally, the model accounts for electroneutrality and Fe-site conservation at the two membranes sides. Detailed transport of charged species within the membrane is achieved using the PNP model. Seven parameters are fitted during the fitting process but the estimations agree well with the reported values of similar perovskites in the literature.

Using argon at the sweep side, we predict the concentrations of oxygen vacancies and Fe states. No crossover between the concentrations of $Fe^{\bullet}_{Fe}$ and $Fe^{\prime}_{Fe}$ is observed within the range of local $PO_2$ at the feed and sweep side. The spatial distribution of the mobile charged species within the membrane is predicted; results show that this spatial deviation is insignificant for the range of our experimental measurements.

Given the absence of data for the relative permittivity and the LCF membrane, a parametric analysis shows that the predicted concentrations and the electrostatic potential profiles slightly change when $\epsilon_r$ is between 2 – 205. The same applies when a strict electroneutrality condition is imposed within the material.

The mathematical tools presented in this study can be directly used for the
modeling of materials with defect chemistry similar to the LCF: $La_{1-x}Ca_xFeO_{3-δ}$, $La_{1-x}Sr_xFeO_{3-δ}$, $La_{1-x}Ba_xFeO_{3-δ}$ of different doping percentage in the A site fall into this category. The model formulation is exactly the same as presented in this study; the only change is that the equilibrium constants, molar volume, diffusion coefficients and relative permittivity of the material under consideration should be used. In the dilute limit, the PNP equations constitute a detailed modeling approach for the transport of charged species within a material. For other perovskites, coupling detailed transport with the corresponding defect chemistry of the membrane of interest allows for the accurate modeling of surface reactions and species diffusion within the material.

5.8 Appendix

The oxygen flux $J_{O_2}$ is calculated by solving a linear system of equations which describes the conservation of argon (Ar), nitrogen (N) and oxygen (O) atoms as well as an equation for the molecular weight of the mixture at the outlet. The conservation of nitrogen takes into account the finite leak of air into the sweep side of the reactor. By measuring the nitrogen concentration at the outlet, we can keep track of the oxygen due to air leak. The following system of equations is considered:

$$\frac{\dot{m}_{in}}{W_{in \text{ mix}}} X_{in}^{Ar} = \frac{\dot{m}_{out}}{W_{out \text{ mix}}} X_{out}^{Ar}$$

(5.29)

$$\frac{\dot{m}_{\text{leak}}}{W_{\text{leak} \text{ mix}}} X_{\text{leak}}^{N_2} = \frac{\dot{m}_{out}}{W_{out \text{ mix}}} X_{out}^{N_2}$$

(5.30)

$$2 \frac{\dot{m}_{\text{leak}}}{W_{\text{leak} \text{ mix}}} X_{\text{leak}}^{O_2} + \frac{\dot{m}_{\text{mem}}}{W_{\text{mem} \text{ mix}}} X_{\text{mem}}^{O} = 2 \frac{\dot{m}_{out}}{W_{out \text{ mix}}} X_{out}^{O_2}$$

(5.31)
\[ W_{\text{out}}^{\text{mix}} = X_{N_2}^{\text{out}} W_{N_2} + X_{O_2}^{\text{out}} W_{O_2} + X_{Ar}^{\text{out}} W_{Ar} \] (5.32)

\[ X_{N_2}^{\text{out}} + X_{O_2}^{\text{out}} + X_{Ar}^{\text{out}} = 1 \] (5.33)

\( X \) denotes mole fractions, \( \dot{m} \) is the mass flow rate and \( W_{\text{mix}} \) the molecular weight of the mixture. Equations 5.29-6.39 involve a system of 5 equations with 5 unknowns: \( \dot{m}_{\text{leak}}, \dot{m}_{\text{mem}}, \dot{m}_{\text{out}}, W_{\text{mix}}^{\text{out}} \) and \( X_{Ar}^{\text{out}} \). The input is the inlet mass flow rate \( \dot{m}_{\text{in}} \) as well as the experimentally measured \( X_{N_2}^{in} \) and \( X_{O_2}^{in} \). The following assumptions have been made:

- Inlet is pure Ar: \( X_{Ar}^{in} = 1, W_{\text{mix}}^{in} = W_{Ar} \)
- Composition of air leak: \( \frac{X_{N_2}^{\text{leak}}}{X_{O_2}^{\text{leak}}} = \frac{79}{21} \)
- Only air leaks into the sweep side of the reactor: \( X_{N_2}^{\text{leak}} + X_{O_2}^{\text{leak}} = 1, W_{\text{mix}}^{\text{leak}} = X_{N_2}^{\text{leak}} W_{N_2} + X_{O_2}^{\text{leak}} W_{O_2} \)
- Oxygen ions enter into the membrane: \( X_{O}^{\text{mem}} = 1, W_{\text{mix}}^{\text{mem}} = W_{O} \)
- The effective area of the membrane is: \( A_{\text{mem}} = 0.005329(m^2) \)

Assuming that the oxygen flux is uniformly distributed along the membrane, the magnitude of \( J_{O_2} \) is calculated using the following equation:

\[ \|J_{O_2}\| (\mu\text{mole/cm}^2/\text{sec}) = \frac{\|J_{O}\|}{2} = \frac{\dot{m}_{\text{mem}} \times 10^5}{2 \times W_{O} \times A_{\text{mem}}} = \frac{\dot{m}_{\text{mem}} \times 10^5}{W_{O_2} \times A_{\text{mem}}} \] (5.34)

For the uncertainty and the corresponding error bars, the standard deviation of the experimental measurements is used. To get the uncertainty for the oxygen flux
$J_{O_2}$ (as well as the uncertainty for the rest of the variables appearing in equations 5.29-6.39), another set of equations has been solved in accordance to equations 5.29-6.39 using the basic rules of error propagation. In this way, the uncertainty for the oxygen flux can be quantified. The system of equations to get the uncertainties is omitted here for the sake of brevity.

To account for the additional oxygen resulting from air leak, the value of $P_{O_2}$ shown in figures 5-1 and 5-2 is the leak-free value, i.e. the value of $O_2$ after subtracting the amount of $O_2$ due to air leak. The calculation is made using the following expression:

$$P_{O_2}^{\text{no leak}} (Pa) = 101325 \times \frac{X_{O_2}^{\text{with leak}} - \frac{21}{79} X_{N_2}^{\text{with leak}}}{1 - \frac{100}{79} X_{N_2}^{\text{with leak}}}$$

(5.35)

In equation 5.35, $X_{O_2}^{\text{with leak}}$ and $X_{N_2}^{\text{with leak}}$ are the mole fractions of the direct measurements after analysis of the mixture using the MS. $P_{O_2}^{\text{no leak}}$ is the $P_{O_2}$ value (shown in figures 5-1 and 5-2) after removing the oxygen that corresponds to air leak.
Chapter 6

Impact of $H_2$ and $CO$ on the oxygen permeation and defect chemistry of LCF

In chapter 4 we presented experimental data for the performance of LCF and the methane conversion under a $CH_4 - CO_2 - Ar$ environment. Chapter 5 dealt with the oxygen permeation under non-reactive conditions and the determination of the reaction constants for the $O_2$ incorporation reaction. In this chapter we will discuss the impact of $H_2$ and $CO$ on the oxygen permeation and defect chemistry of LCF. We present experimental data under a wide range of operating conditions and we expand the model that was discussed in previous chapters to account for chemical reactions of fuel with lattice oxygen ions on the sweep side of the membrane.
6.1 Introduction

In chapter 1, we discussed why methane reforming to syngas, a mixture of hydrogen and carbon monoxide, is an important industrial process in the energy and chemical sectors, yet it requires elevated temperatures and significant heat input to energize the associated endothermic reactions [88]. Partial oxidation of methane reduces this energy barrier but requires pure oxygen. Conventional air separation units use cryogenic methods which are characterized by a significant energy penalty related to the oxygen separation from air [14]. Mixed ionic-electronic conductors can reduce the aforementioned energy requirements given that oxygen can separate from air once an oxygen electrochemical potential difference is established between the two sides of the material [7, 9]. At the same time, the capital cost can decrease since MIEC reactors combine both separation and reaction [89]. In addition, these materials allow for surface modifications using porous supports or catalysts that can enhance the performance significantly [84]. Materials that support an oxygen flux around $0.7 - 7 \mu\text{mole/cm}^2/\text{sec}$ and remain stable under a reactive environment are very good candidates for integration in syngas production through methane reforming [9, 90].

A stable mixed-conductor that meets this performance criterion under reducing conditions is $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ [73]. The defect mechanism of this perovskite is well studied [56, 58, 78, 79, 80, 81]. We have seen that the oxygen flux under non-reactive conditions is low [64, 75, 76] but in the presence of fuel it increases significantly [74]. In particular, when a mixture of methane and carbon dioxide is introduced at the fuel side, syngas production increases the oxygen permeation through heterogeneous reaction of $H_2$ and $CO$ with lattice oxygen ions [74]. Using LCF for syngas production has been studied by other groups which investigated...
interaction of fuel with the material. Although showing performance enhancement in terms of oxygen flux, the underlying mechanism that leads to higher flux has not been examined. For example, Yu et al. [91] report oxygen flux measurements under a reactive CO environment during which significant surface limitations are present. To raise the oxygen permeation, Pt and CeO$_2$ catalysts were incorporated on a porous support at the fuel side while La$_{0.8}$Sr$_{0.2}$O$_3$ was added on the air side. Miller et al. shows the positive effect of adding porous layers on the fuel side or to both sides [92]. In chapter 4 we reported oxygen flux increase and the associated syngas production under a CH$_4$ – CO$_2$ – Ar environment using an unmodified LCF [74]. The goal of this chapter is to model the mechanism that leads to oxygen flux increase and to quantify the impact of H$_2$ and CO on the oxygen permeation. This is achieved by introducing either H$_2$ – Ar or CO – Ar mixtures at the fuel side [93].

Another goal of this chapter is to construct electrochemical models for interfacial reactions. Given that three iron states coexist in the B-site, electron transfer in LCF can take place in two different ways depending on the partial pressure and temperature. Oxygen production occurs through an electron transfer process in which either Fe$^{*}_{Fe}$ reduces to Fe$^{*}_{Fe}$ or Fe$^{*}_{Fe}$ to Fe$^{*}_{Fe}$, as described by the following reactions:

\[
O^X_O + 2Fe^{*}_{Fe} \rightarrow \frac{1}{2}O_2(g) + V^{**}_O + 2Fe^{*}_{Fe} \quad (6.1)
\]

\[
O^X_O + 2Fe^{x}_{Fe} \rightarrow \frac{1}{2}O_2(g) + V^{**}_O + 2Fe^{*}_{Fe} \quad (6.2)
\]

Using a point-defect model at equilibrium, Geary and Adler investigated the role of these two reactions under a non-reactive environment [58]; Mizusaki et al. was the first to apply the same model for La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ [59].

To account for H$_2$ and CO surface oxidation and examine the role of the Fe states
in the charge transfer kinetics, we develop two multistep surface reaction mechanisms based on separate experiments for the two fuels. We couple these mechanisms with detailed modeling of charged species diffusion within the material using a Poisson-Nernst-Planck model in the dilute limit [41]. The model includes Fe site conservation and a strict electroneutrality condition on the gas-membrane interfaces; surface reactions are thermodynamically consistent [58, 94]. Detailed surface exchange coupled with the PNP model has been applied for gadolinium-doped ceria mixed-conductors [49] and yttrium-doped barium zirconates [50, 51, 52]. In these studies, the materials exhibit diffusion limitations and hence, the surface reaction equilibrium is assumed; this assumption is not valid in our case [64, 74, 91, 93].

LCF belongs to a family of perovskites with similar structure and properties, for example $La_{1-x}Ca_xFeO_3-\delta$, $La_{1-x}Sr_xFeO_3-\delta$, $La_{1-x}Ba_xFeO_3-\delta$ of different doping percentage in the A-site. Given the applicability of the model of this study for similar materials, the next section presents a detailed formulation of the oxygen permeation model for LCF under the presence of fuel. Next, we analyze our experimental measurements under a $H_2-Ar$ or $CO-Ar$ environment and we discuss how the electron transfer process on LCF affects the oxygen flux under reducing conditions.

6.2 Oxygen permeation model

6.2.1 Defect chemistry on the feed side

On the feed side, gaseous oxygen molecules adsorb on the membrane surface and react with oxygen vacancies to form oxygen ions incorporated into the oxygen lattice sites. The oxygen ionization process happens through an electron transfer that involves a subsequent oxidation of the corresponding Fe states. It is evident that the overall
oxygen adsorption, dissociation and incorporation mechanism at the feed side of the membrane includes a series of elementary reactions, but the process can be represented by the following two-step reaction mechanism [58, 64, 84]:

\[
\frac{1}{2} O_2 (g) + V_O^{\bullet\bullet} + 2Fe^{x}_{Fe} \xrightarrow{k_{r_1}} O_O^X + 2Fe^{\bullet}_{Fe}
\]  

(6.3)

\[
2Fe^{x}_{Fe} \xrightarrow{k_{r_2}} Fe^{\bullet}_{Fe} + Fe^{\prime}_{Fe}
\]  

(6.4)

Given the high $P_{O_2}$ at the feed side, only one type of electron transfer is considered here. In the aforementioned reactions, $k_{f_1}$ and $k_{r_1}$ are the reaction rate coefficients of the oxygen incorporation reaction while $k_{f_2}$ and $k_{r_2}$ are the reaction rate coefficients of the Fe disproportionation reaction. The rate of progress of these reactions can be expressed as follows:

\[
\dot{s}_1 \text{ (mole/cm}^2/\text{sec)} = k_{f_1} C_{O_2}^{1/2} C_{V_O^{\bullet\bullet}} C_{Fe^{x}_{Fe}} - k_{r_1} C_{O_O^X} C_{Fe^{\bullet}_{Fe}}
\]  

(6.5)

\[
\dot{s}_2 \text{ (mole/cm}^2/\text{sec)} = k_{f_2} C_{Fe^{x}_{Fe}} - k_{r_2} C_{Fe^{\bullet}_{Fe}} C_{Fe^{\prime}_{Fe}}
\]  

(6.6)

In equations 6.5 and 6.6, $\dot{s}_1$ and $\dot{s}_2$ are the rates of progress of reactions 6.3 and 6.4, respectively.

The model for the $O_2$ incorporation reaction has been presented in chapter 5 and hence, the rest of our analysis will focus on the reactive case.

### 6.2.2 Defect chemistry on the sweep side

Under non-reactive conditions, reactions 6.3 and 6.4 describe the production of gaseous oxygen and the Fe state disproportionation [64]. In the presence of fuel, we investigated the equilibrium defect concentration of oxygen vacancies and Fe.
states assuming a mixture of $H_2 - H_2O$ at $\theta = 950\, (^\circ C)$. These defect concentrations were calculated as a function of $H_2$ partial pressure, $P_{H_2}$ (balance is $H_2O$), assuming strict electroneutrality, Fe site conservation coupled with reactions 6.3, 6.4 and the gas-phase hydrogen oxidation reaction 6.7:

$$H_2(g) + \frac{1}{2}O_2(g) \xrightleftharpoons[k_{r3}]{k_{f3}} H_2O(g)$$

(6.7)

Similar trends are observed when calculating the defect concentrations under $CO - CO_2$ mixtures and using the gas-phase $CO$ oxidation instead of reaction 6.7:

$$CO(g) + \frac{1}{2}O_2(g) \xrightleftharpoons[k_{r4}]{k_{f4}} CO_2(g)$$

(6.8)

The standard-state enthalpy and entropy change of reactions 6.7 and 6.8 are known. Using the definition of the Gibbs free energy (equation 3.76), the corresponding equilibrium constants $K_{P_3}$ and $K_{P_4}$ can be estimated. Assuming no other intermediate species besides $H_2$, $O_2$ and $H_2O$, we end up with a system of 5 equations with 5 unknowns: $P_{O_2}$, $\delta$, $[Fe_e^{\delta}]$, $[Fe_e^\bullet]$ and $[Fe_e']$. Figure 6-1 shows a similar behavior to the non-reactive case under equilibrium [58]. At very low fuel concentrations, $Fe_e^\bullet$ is abundant and electrons transfer by $Fe_e^\bullet$ reduction. The crossover in the $Fe_e^\bullet$ and $Fe_e'$ concentration happens at $P_{H_2} \approx 0.003\, (atm)$; at higher $P_{H_2}$, electronic conductivity within LCF is purely n-type and charge transfer happens by $Fe_e^\bullet$ reduction. At the same time, $P_{O_2}$ around the material decreases significantly.

Given the existence of two electron transfer types when introducing fuel, we propose the overall surface reaction mechanism under hydrogen oxidation that consists
of reactions 6.3-6.4 and 6.9-6.10:

\[ H_2 (g) + O_2^X + 2Fe^{x}_{Fe} \xrightleftharpoons[k_{10}]{k_{15}} H_2O \ (g) + V_O^{**} + 2Fe^{x}_{Fe} \quad (6.9) \]

\[ H_2 (g) + O_2^X + 2Fe^{x}_{Fe} \xrightleftharpoons[k_{10}]{k_{15}} H_2O \ (g) + V_O^{**} + 2Fe^{x}_{Fe} \quad (6.10) \]

Figure 6-1: Formula-unit concentration of \( V_O^{**} \), \( Fe^{x}_{Fe} \), \( Fe^{x}_{Fe} \), \( Fe^{x}_{Fe} \), and \( P_{O_2} \) as a function of hydrogen partial pressure, \( P_{H_2} \), at \( \theta = 950 \, ^\circ C \) assuming a \( H_2 - H_2O \) mixture at equilibrium.
For the case of carbon monoxide, the hydrogen surface reactions are replaced by reactions 6.11-6.12:

\[
CO(g) + O_0^X + 2Fe_{Fe}^{*} \overset{k_{r_7}}{\longrightarrow} CO_2(g) + V_{O}^{**} + 2Fe_{Fe}^{x}
\] (6.11)

\[
CO(g) + O_0^X + 2Fe_{Fe}^{x} \overset{k_{r_8}}{\longrightarrow} CO_2(g) + V_{O}^{**} + 2Fe_{Fe}^{x'}
\] (6.12)

We emphasize that the goal of this study is to investigate the impact of fuel on the oxygen permeation without accounting for any interaction of \( H_2 \) with \( CO \) or with other products on the membrane surface. Hence, reactions 6.9-6.12 apply for the case of a single fuel being present in the sweep side. Here, \( k_{f_6}/k_{r_5}, k_{f_6}/k_{r_6}, k_{f_7}/k_{r_7} \) and \( k_{f_8}/k_{r_8} \) are the reaction rate coefficients of reactions 6.9, 6.10, 6.11 and 6.12, respectively. These charge transfer reactions are treated as rate-limiting given that they constitute a series of elementary steps involving absorption/desorption and two electron transfer processes.

In conjunction to the equilibrium case and the transition from high to low oxygen partial pressures under a non-reactive environment [58], each fuel is associated with two surface reactions with lattice oxygen ions. As discussed in the introduction, the difference in these two reactions is the way the electron transfer process takes place: reducing either of \( Fe_{Fe}^{*} \) to \( Fe_{Fe}^{x} \) or \( Fe_{Fe}^{x} \) to \( Fe_{Fe}^{x'} \). As will be seen, the kinetic rates can vary significantly depending on which electron transfer happens.

**6.2.3 Thermodynamic consistency**

An important ingredient of the model is thermodynamic consistency. Under non-reactive conditions [64], we demonstrated how to satisfy thermodynamic consistency by fitting \( k_{r_1} \) and constraining \( k_{f_1} \) using the equilibrium constant \( K_{P_1} \), which was
determined in [58]. This work extends the concept of thermodynamic consistency for the reaction network 6.9-6.10 and 6.11-6.12. For this purpose, knowledge of the equilibrium constants $K_{P_5}$, $K_{P_6}$, $K_{P_7}$, and $K_{P_8}$ is required. These parameters can be determined since they constitute the combination of the oxygen incorporation reaction 6.3, the Fe disproportionation reaction 6.4 and the gas-phase hydrogen/carbon monoxide oxidation reactions 6.7 and 6.8. Table 6.1 summarizes the calculated standard-state enthalpy and entropy change of reactions 6.9-6.12. We observe that the hydrogen and carbon monoxide surface oxidation reactions where the electron transfer happens by reducing $Fe^f_{Fe}$ to $Fe^{f'}_{Fe}$ are exothermic, while the surface reactions where the electron transfer happens by reducing $Fe^{f'}_{Fe}$ to $Fe^f_{Fe}$ are endothermic.

Following a similar approach to the modeling at the feed side, the rate of progress for reactions 6.9-6.12 can now be expressed as follows:

\[
\dot{s}_5 \ (mole/cm^2/sec) = \frac{k_{r5}}{RT} \left[ K_{P_5} P_{H_2} C_{O_2}^x C_{Fe^f_{Fe}}^2 - P_{H_2O} C_{V_2O} C_{Fe^{f'}_{Fe}}^2 \right] \times 101325 \times 10^{-6} \tag{6.13}
\]

\[
\dot{s}_6 \ (mole/cm^2/sec) = \frac{k_{r6}}{RT} \left[ K_{P_6} P_{H_2} C_{O_2}^x C_{Fe^f_{Fe}}^2 - P_{H_2O} C_{V_2O} C_{Fe^{f'}_{Fe}}^2 \right] \times 101325 \times 10^{-6} \tag{6.14}
\]

\[
\dot{s}_7 \ (mole/cm^2/sec) = \frac{k_{r7}}{RT} \left[ K_{P_7} P_{CO} C_{O_2} C_{Fe^f_{Fe}}^2 - P_{CO_2} C_{V_2O} C_{Fe^{f'}_{Fe}}^2 \right] \times 101325 \times 10^{-6} \tag{6.15}
\]

\[
\dot{s}_8 \ (mole/cm^2/sec) = \frac{k_{r8}}{RT} \left[ K_{P_8} P_{CO} C_{O_2} C_{Fe^f_{Fe}}^2 - P_{CO_2} C_{V_2O} C_{Fe^{f'}_{Fe}}^2 \right] \times 101325 \times 10^{-6} \tag{6.16}
\]

In equations 6.13-6.16, $P_{H_2}$, $P_{H_2O}$, $P_{CO}$ and $P_{CO_2}$ (units: atm) are the partial pressures of hydrogen, steam, carbon monoxide and carbon dioxide on the membrane sweep side, respectively. These partial pressures are either measured experimentally or estimated.
6.2.4 Poisson-Nernst-Planck (PNP) model

In the dilute limit, i.e. neglecting interactions between defects, the diffusion of charged species within a material can be described by the PNP model. The PNP model includes conservation equations for the transport of charged species within the material and Gauss's law for the electrostatic potential. The conservation equations have the following form:

\[ \frac{\partial C_k}{\partial t} + \nabla \cdot \mathbf{J}_k = 0 \]  

(6.17)

The flux of charged species \( \mathbf{J}_k \) is given by:

\[ \mathbf{J}_k = -D_k \left( \nabla C_k + \frac{z_k F}{RT} C_k \nabla \phi \right) \]  

(6.18)

The first term in the right hand side of equation 6.18 is the diffusive flux of species \( k \) due to concentration gradient, while the second term is the diffusive flux due to electromigration. The electrostatic potential \( \phi \) is related to the local charge density \( \rho \) through the Gauss equation:

\[ \nabla \cdot (\varepsilon_r \varepsilon_o \nabla \phi) = -\rho_s = -F \sum_{k=1}^{N} z_k C_k \]  

(6.19)

In equation 6.19, \( \varepsilon_r \) and \( \varepsilon_o \) are the relative and vacuum permittivities, respectively; \( \varepsilon_r \) in this study is considered constant. The local charge density \( \rho_s \) includes the summation of molar concentrations for both mobile and fixed charged species; for LCF, we also account for the charge of Calcium into the Lanthanum lattice site. As discussed in other studies [49, 50, 51, 52, 64], solving the Gauss equation is more general than imposing strict electroneutrality \( \rho = F \sum_{k=1}^{N} z_k C_k = 0 \); a complication with applying a strict electroneutrality condition is that small variations in \( \rho \) can
produce large variations in the electrostatic potential $\phi$ since the permittivity is also a small number [48].

No experimental data for the relative permittivity $\varepsilon_r$ is available for LCF. For the same material, Dimitrakopoulos and Ghoniem estimated $\varepsilon_r = 205$ by fitting non-reactive oxygen flux measurements [64]; this value agrees with the reported relative permittivity of similar perovskites like $LaFeO_{3-\delta}$ [53, 54]. We have already shown that applying a strict electroneutrality condition in the bulk of the LCF material does not change predictions compared to the case when the Gauss equation 3.84 is solved and $\varepsilon_r$ is between $2-205$ [64]. The same conclusion is verified for the reactive measurements of this study; the model predictions are almost identical when a strict electroneutrality condition is imposed in the interior of the material compared to the case of solving for equation 3.84.

The model parameters for the diffusion coefficients of charged species within the material are the same as described in chapter 5 and hence are not repeated for the shake of brevity.

### 6.2.5 Boundary conditions of the PNP model

The molar concentration of oxygen vacancies at the feed $\tilde{y} = 0$ and sweep $\tilde{y} = 1$ side is calculated by applying a Robin boundary condition that accounts for chemical reactions on the gas-membrane interfaces [48, 49, 64]:

$$
\tilde{J}_{\tilde{y}=0} = \tilde{\omega}_{s,\tilde{y}=0} \eta_{\tilde{y}=0} \Rightarrow -\tilde{D}_{\tilde{y}=0} \frac{\partial \tilde{C}_{V_{O}^{\bullet \bullet}}}{\partial \tilde{y}} |_{\tilde{y}=0} = \tilde{\omega}_{s,\tilde{y}=0} \eta_{\tilde{y}=0} \quad (6.20)
$$

$$
\tilde{J}_{\tilde{y}=1} = \tilde{\omega}_{s,\tilde{y}=1} \eta_{\tilde{y}=1} \Rightarrow -\tilde{D}_{\tilde{y}=1} \frac{\partial \tilde{C}_{V_{O}^{\bullet \bullet}}}{\partial \tilde{y}} |_{\tilde{y}=1} = \tilde{\omega}_{s,\tilde{y}=1} \eta_{\tilde{y}=1} \quad (6.21)
$$
where $\tilde{\omega}^{\gamma=0}_{s,V^\star}$ and $\tilde{\omega}^{\gamma=1}_{s,V^\star}$ are the dimensionless molar reaction rates at the feed and sweep side, respectively. These are given by the following equations:

$$\tilde{\omega}^{\gamma=0}_{s,V^\star} = -\tilde{s}_{1}^{\text{feed}} = - \frac{L}{D_{\text{ref}}C_{\text{ref}}} \tilde{s}_{1}^{\text{feed}}$$  \tag{6.22}

$$\tilde{\omega}^{\gamma=1}_{s,V^\star} = -\tilde{s}_{\text{sweep}}^{\text{in}} + \tilde{s}_{5} + \tilde{s}_{6} = \frac{L}{D_{\text{ref}}C_{\text{ref}}} (-\tilde{s}_{1}^{\text{sweep}} + \tilde{s}_{5} + \tilde{s}_{6}) \quad (H_2 \text{ oxidation}) \tag{6.23}$$

$$\tilde{\omega}^{\gamma=1}_{s,V^\star} = -\tilde{s}_{1} + \tilde{s}_{7} + \tilde{s}_{8} = \frac{L}{D_{\text{ref}}C_{\text{ref}}} (-\tilde{s}_{1}^{\text{sweep}} + \tilde{s}_{7} + \tilde{s}_{8}) \quad (CO \text{ oxidation}) \tag{6.24}$$

Equations 6.20 and 6.21 are the boundary conditions for the molar concentration of oxygen vacancies at the gas-membrane interfaces. Using equations 5.22 and 5.24 (and the corresponding concentration conversions using equation 5.11), the molar concentration of the different Fe states at the feed and sweep side are determined and correspond to Dirichlet boundary conditions for the conservation equations 6.17.

The boundary conditions for the electrostatic potential at the feed and sweep side are the same as described in chapter 3.

### 6.2.6 Fitting of the reaction rate coefficients

Fitting the oxygen flux measurements of this study allows estimating the backward reaction rate coefficients $k_{r_5}$, $k_{r_6}$, $k_{r_7}$, and $k_{r_8}$. This means that 4 parameters will be fitted using the $H_2 - Ar$ data and 4 parameters will be estimated using the $CO - Ar$ data. In this section we describe this iterative process.

Equations 5.22-5.24 depend on the Calcium doping, the formula-unit concentration of oxygen vacancies $\delta$ and the equilibrium constant of the Fe disproportionation reaction, $K_{P_2}$. Given that $x$ and $K_{P_2}$ are known, the formula-unit concentration of
the different Fe states becomes a function of \( \delta \) only and using equation 5.11, formula-unit concentrations can be transformed into molar concentrations. Hence, the system at the feed side is now closed: if \( \delta \) and \( P_{O_2} \) at the feed side are known, the molar concentrations of the three Fe states and the rate of progress of reaction 5.7, \( \dot{s}_1^{feed} \), can be evaluated. The oxygen partial pressure \( P_{O_2} \) can be either measured or estimated using numerical models. In our study, \( P_{O_2} \) at the feed side is estimated using the CFD model described in chapter 3 by applying the experimentally measured \( J_{O_2} \) as a boundary condition and the predicted values are shown in the next section.

At the sweep side, equations 5.22-5.24 still apply since we are also assuming that reaction 6.4 is equilibrated. Hence, the system at the sweep side is also closed: given \( \delta \), the Fe states can be evaluated and the same is true for the rates of progress of reactions 6.9-6.12.

The fitting process starts with a guess for \( k_{r_5}, k_{r_6}, k_{r_7} \) and \( k_{r_8} \) using an Arrhenius expression of the form 
\[
k_{r_i} = A_{kr_i} e^{-E_{kr_i}/RT};
\]  
where \( A_{kr_i} \) is the pre-exponential factor while \( E_{kr_i} \) is the activation energy of reaction \( i \). Then, the PNP model is solved until steady-state. At the end of this process, \( C_{V\odot} \) as well as \( C_{Fe^{*}_{Fe}}, C_{Fe^{x}_{Fe}} \) and \( C_{Fe^{\circ}_{Fe}} \) at the feed and sweep side are determined. The oxygen vacancy flux is used to estimate \( J_{O_2} \) through the expression 
\[
|J_{V\odot}| = 2 |J_{O_2}|.
\]  
Using MATLAB and a gradient-based optimization algorithm, the pre-exponential factor and activation energies for \( k_{r_5}, k_{r_6}, k_{r_7} \) and \( k_{r_8} \) are updated and the process is repeated until the best fit is obtained.
6.3 Results and discussion

6.3.1 Experimental results

Figure 6-2 shows the measured oxygen flux \( J_{O_2} \) for different concentrations of \( H_2 \) and \( CO \) at the sweep side and temperature \( \theta \). In all cases, the feed side volumetric flow rate is \( \dot{V}_{\text{feed}} = 4000 \, (sccm) \). At the sweep side, the total volumetric flow rate is also kept constant at \( \dot{V}_{\text{sweep}}^{\text{total}} = 2000 \, (sccm) \). When fuel is introduced at the sweep side, the oxygen flux increases significantly. Using hydrogen, the maximum value of the oxygen flux at 1060 ('C) is \( J_{O_2} \approx 1.2 \, (\mu\text{mole/cm}^2/\text{sec}) \) when \( X_{H_2}^{\text{in}} \approx 30 \, (\%) \). At the same temperature, use of carbon monoxide also increases the flux of oxygen to \( J_{O_2} \approx 0.8 \, (\mu\text{mole/cm}^2/\text{sec}) \) when \( X_{CO}^{\text{in}} \approx 40 \, (\%) \), but at a slower rate compared to \( H_2 \). Previous work under a non-reactive environment revealed that surface reactions limit the oxygen flux rise when using a 1 (mm) thick membrane [64]. The current results confirm that surface exchange is still the rate-limiting step in the presence of fuel.

Figure 6-3 compares the XRD spectra of the used membranes before and after the reactive experiments. Both sides show good LCF peaks and no phase change is observed for both \( H_2 - Ar \) and \( CO - Ar \) cases. This confirms the high stability of the LCF membrane under reactive conditions, this time tested in an extreme environment with high fuel concentrations. Same stability performance has been reported by Wu et al. for the LCF membrane in a \( H_2 - H_2O - Ar \) environment with excess of \( H_2O \) [77]. Yu et al. also reports similar stability characteristics for an LCF membrane exposed to a pure \( CO \) environment for 4 hours [91]; in our case, the \( CO - Ar \) measurements lasted approximately 6 days while the \( H_2 - Ar \) measurements had a duration of approximately 3 days. A new peak is identified at the feed side.
Figure 6-2: Oxygen flux as a function of inlet fuel mole fraction (balance gas is Ar) and temperature. Operating conditions: feed side volumetric flow rate $V_{\text{feed}} = 4000 \pm 2(\text{scm})$, sweep side total volumetric flow rate $V_{\text{sweep}}^{\text{total}} = 2000 \pm 2(\text{scm})$, membrane thickness $L = 1.00(\text{mm})$ ($H_2$ measurements) and $L = 1.45(\text{mm})$ ($CO$ measurements). Lines correspond to the best fit of the data.

of the membrane used during the $H_2 - Ar$ experiments at angle $2\theta \approx 36^\circ$. This peak corresponds to silica; silica exists in the gasket material used for the sealing of the sweep side in an effort to avoid air moving from the feed to the sweep side through gaps near the membrane edges. Despite the presence of this peak, the oxygen permeation performance of the membrane did not change during the experiments.
Figure 6-3: Comparison of the XRD spectra of an unused LCF membrane with the feed and sweep side spectra of an LCF membrane exposed to $H_2 - H_2O - Ar$ and $CO - CO_2 - Ar$ flow streams.

Figures 6-4 and 6-5 show the gas-phase $H_2$, $H_2O$, $CO$ and $CO_2$ mole fractions close to the membrane surface as a function of inlet fuel mole fraction and temperature. Further detail on the sweep side $X_{H_2O}^{mem}$ estimation and $X_{H_2}^{mem}$ correction is provided in the Appendix at the end of the chapter. As the temperature rises, less fuel is measured at the surface due to faster reaction with surface oxygen. Figure 6-5 shows that the sweep side $X_{CO}^{mem}$ and $X_{CO_2}^{mem}$ slightly changed when the temperature
Figure 6-4: Sweep side surface mole fraction of $H_2$ and $H_2O$, $X_{H_2}^{mem}$ and $X_{H_2O}^{mem}$, as a function of inlet $X_{H_2}^{in}$ and temperature $\theta$. Operating conditions: feed side volumetric flow rate $\dot{V}_{feed} = 4000 \pm 2(scncm)$, sweep side total volumetric flow rate $\dot{V}_{sweep} = 2000 \pm 2(scncm)$, membrane thickness $L = 1.00(mm)$. Lines correspond to the best fit of the data.

was elevated from $\theta = 953.1(\degree C)$ to $\theta = 1060.1(\degree C)$. The reason for this lies on the rise of air leak as the temperature increased given that thermal expansion of the reactor materials becomes considerable at high temperatures. However, this air leak can be quantified given that the nitrogen mole fraction on the membrane surface is also measured. At $\theta = 953.1(\degree C)$, the nitrogen mole fraction was $X_{N_2}^{mem} \approx 0.2(\%)$
while at $\theta = 1060.1 (^{\circ}C)$, it changed to $X^m_{CO} \approx 0.3 (%)$. This means that, at $\theta = 1060.1 (^{\circ}C)$, the addition of $O_2$ in the gas-phase and the mixture dilution reduces the $CO$ mole fraction at the sweep side by approximately 0.5 (%); hence, the air leak is not significant and does not compromise the results of our analysis. The effect of the air leak is to simply lower the $CO$ and increase the $CO_2$ mole fractions.

Figure 6-5: Sweep side surface mole fraction of $CO$ and $CO_2$, $X^m_{CO}$ and $X^m_{CO_2}$, as a function of inlet $X^m_{CO}$ and temperature $\theta$. Operating conditions: feed side volumetric flow rate $\dot{V}_{feed} = 4000 \pm 2 (sccm)$, sweep side total volumetric flow rate $\dot{V}_{sweep} = 2000 \pm 2 (sccm)$, membrane thickness $L = 1.45 (mm)$. Lines correspond to the best fit of the data.
on the membrane surface compared to the case of zero leak and hence, the material will adjust the oxygen flux depending on the sweep side surface species concentration under finite leak conditions.

Furthermore, for the same reactive operating conditions, small mole fractions around 0.04 (\%) of gaseous oxygen are measured on the sweep side of the membrane. The absence of high $O_2$ mole fractions in the gas-phase and the simultaneous increase of the oxygen flux as the inlet fuel concentration rises confirms that the aforementioned $J_{O_2}$ increase is due to surface activity related to the consumption of oxygen ions on the membrane sweep side. Hydrogen or carbon monoxide adsorb on the membrane surface, react with oxygen ions, form steam and carbon dioxide, respectively, which then desorb into the gas-phase.

Figure 6-6 compares the hydrogen and carbon monoxide conversion as a function of inlet fuel concentration and temperature calculated using equation 6.25:

$$\hat{H}_{H_2/CO} = \left(1 - \frac{\dot{n}_{H_2/CO}^{out}}{\dot{n}_{H_2/CO}^{in}}\right) \times 100\% = \left(1 - \frac{\dot{m}_{out}}{\dot{m}_{in}} \frac{X_{H_2/CO}^{out} W_{mix}^{in}}{X_{H_2/CO}^{in} W_{mix}^{out}}\right) \times 100\% \quad (6.25)$$

In equation 6.25, $\dot{n}_{H_2/CO}^{in}$ and $\dot{n}_{H_2/CO}^{out}$ are the inlet and outlet mole flow rates of $H_2$ or $CO$, respectively; the rest of the parameters are defined in the Appendix at the end of the chapter. Given that higher oxygen fluxes can be achieved when introducing $H_2$ in the sweep side, $H_2$ conversion is higher compared to $CO$ conversion at the same operating conditions. For both fuels, the higher the operating temperature, the higher the conversion associated with higher oxygen flux. In addition, at the same temperature, the fuel conversion decreases as more fuel is introduced in the reactor.
Figure 6-6: Hydrogen (left) and carbon monoxide (right) conversion as a function of inlet fuel mole fraction and temperature. Operating conditions: feed side volumetric flow rate $V_{\text{feed}} = 4000 \pm 2 (sccm)$, sweep side total volumetric flow rate $V_{\text{sweep}} = 2000 \pm 2 (sccm)$, membrane thickness $L = 1.00 (mm)$ ($H_2$ measurements) and $L = 1.45 (mm)$ ($CO$ measurements). Lines correspond to the best fit of the data.

6.3.2 Validation of the CFD model in the presence of fuel

Before fitting the experimental data obtained for the case of $H_2$ and $CO$, we would like to compare the measurements near the vicinity of the membrane with the CFD model predictions. Recall that during the experiments, measurement of the inlet
and outlet of the ITM reactor allows us to estimate \( J_{O_2} \) using mass conservation equations. At the same time, we also measure the local species concentration as close as possible to the membrane surface using the quartz probe.

For a particular experimental point the temperature, flow rate and inlet concentrations at both reactor sides are known. Given that \( J_{O_2} \) is also determined experimentally, we can apply this value as a boundary condition at the feed side of the membrane to predict the feed side \( P_{O_2} \). At the sweep side, we will assume that oxygen ions are consumed only on the membrane surface due to fuel surface reactions without any gas-phase reactions taking place. According to the reaction on the interface, one mole of \( O_2^\circ \) will react with one mole of \( H_2 \) to form one mole of \( H_2O \). In terms of fluxes on the interface, this relation can be expressed as:

\[
J_{H_2} + J_{O_2^\circ} = J_{H_2O} \quad \text{where} \quad J_{H_2} = -J_{H_2O} = -\frac{1}{2}J_{O_2^\circ} = J_{O_2} \tag{6.26}
\]

where the last equality in equation 6.26 holds from the \( O_2^\circ \) and \( O_2 \) stoichiometry of the reaction at the feed side while the equality \( J_{H_2} = -J_{H_2O} \) is true given the stoichiometry of the \( H_2 \) reaction to produce \( H_2O \) on the membrane sweep side (based on reactions 6.9 and 6.10). Similarly for the case of \( CO \):

\[
J_{CO} + J_{O_2^\circ} = J_{CO_2} \quad \text{where} \quad J_{CO} = -J_{CO_2} = -\frac{1}{2}J_{O_2^\circ} = J_{O_2} \tag{6.27}
\]

Equations 6.26 and 6.27 are the boundary conditions for the \( H_2 \), \( H_2O \) and \( CO \), \( CO_2 \) concentration at the sweep side gas-membrane interface, respectively. Solving for the gas-phase transport equations using the CFD model described in chapter 3 together with the aforementioned boundary conditions (at the feed and sweep sides) allows the determination of the feed side \( P_{O_2} \) and the sweep side \( P_{H_2}, P_{H_2O} \) or \( P_{CO}, \)
The latter can then be compared with the direct measurements near the vicinity of membrane to allow for the validation of the numerical model.

Figure 6-7 compares the 2D model predictions with the experimental measurements for the case of \( \theta = 959.1^\circ C \) by resolving the gas-phase transport equations using the geometry of the exact ITM reactor described in chapter 2. The same figure confirms that the \( H_2 \) mole fractions predicted by the model (averaged over the membrane length) are in very good agreement with the experimental measurements. Given that the GC cannot measure steam, the CFD model provides an alternative

Figure 6-7: Numerical prediction of \( X_{H_2}^{mem} \) (left) and \( X_{H_2O}^{mem} \) (right) as a function of \( X_{H_2}^{in} \) and comparison with experiment. Operating conditions: temperature \( \theta = 959.1^\circ C \), feed side volumetric flow rate \( V_{feed} = 4000 \pm 2(sccm) \), sweep side total volumetric flow rate \( V_{sweep} = 2000 \pm 2(sccm) \), membrane thickness \( L = 1.00(mm) \).
way for the estimation of $H_2O$ on the membrane sweep side. Very good agreement is also observed for the case of $CO - Ar$ according to figure 6-8 that compares the local mixture composition numerical predictions with experimental data for the case of $\theta = 1060.1 (^{\circ}C)$.

Until this point we have shown the capabilities of the CFD model in terms of predicting the species concentration on the sweep side of the membrane for reactive cases. Another important test for the algorithm is to examine whether it can resolve the gas-phase transport equations in the vicinity of the membrane with reasonable

![Graph](image_url)

Figure 6-8: Numerical prediction of $X_{CO}^{mem}$ (left) and $X_{CO_2}^{mem}$ (right) as a function of $X_{CO}$ and comparison with experiment. Operating conditions: temperature $\theta = 1060.1 (^{\circ}C)$, feed side volumetric flow rate $V_{feed} = 4000 \pm 2(sccm)$, sweep side total volumetric flow rate $V_{sweep}^{total} = 2000 \pm 2(sccm)$, membrane thickness $L = 1.45(mm)$. 

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accuracy. For this reason, we conducted spatial profile measurements for the species concentration by moving the quartz probe downwards. Figure 6-9 compares the measured distribution of $X_{CO}$ and $X_{CO_2}$ across the sweep side of the membrane with numerical predictions when $X_{CO}^{in} = 9.6\%$, $\theta = 1054\, ^\circ C$ and $L = 1\, (mm)$. We observe that the CFD model predictions have excellent agreement with the measurements.

Figure 6-9: Numerical prediction of the $X_{CO}$ and $X_{CO_2}$ as a function of the distance from the sweep side of the membrane and comparison with experiment. Operating conditions: inlet fuel mole fraction $X_{CO}^{in} = 9.6 \pm 0.1\%$, temperature $\theta = 1053.6 \pm 2.2\, ^\circ C$, feed side volumetric flow rate $\dot{V}_{feed} = 4000 \pm 2\,(sccm)$, sweep side total volumetric flow rate $\dot{V}_{sweep} = 1500 \pm 2\,(sccm)$, membrane thickness $L = 1.00\,(mm)$. 

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Last but not least, the CFD model provides us with the feed side $P_{O_2}$ values. As discussed in previous chapters, the feed side $P_{O_2}$ is not measured during the experiment but it can be easily obtained from numerical simulations by applying $J_{O_2}$ as a boundary condition at the feed side. Figure 6-10 shows the feed side $P_{O_2}$ predictions (average values along the membrane length) for the entire range of $H_2 - Ar$ and $CO - Ar$ measurements. For the same temperature, $P_{O_2}$ decreases as the flux increases.

Figure 6-10: Feed side $P_{O_2}$ as a function of inlet fuel mole fraction (balance gas is Ar) and temperature. Operating conditions: feed side volumetric flow rate $\dot{V}_{feed} = 4000 \pm 2(sccm)$, sweep side total volumetric flow rate $\dot{V}_{sweep} = 2000 \pm 2(sccm)$, membrane thickness $L = 1.00(mm)$ ($H_2$ measurements) and $L = 1.45(mm)$ ($CO$ measurements).
6.3.3 Goodness of fit and defect concentrations

Figure 6-11 compares the experimental $J_{O_2}$ measurements with the model predictions using the two 4-step reaction mechanisms developed for each fuel. The model fits the measurements very well for the entire range of operating conditions.

Figure 6-11: Oxygen flux predictions using the two surface reaction mechanisms developed in this study and comparison with experiments. Operating conditions: feed side volumetric flow rate $V_{feed} = 4000 \pm 2(sccm)$, sweep side total volumetric flow rate $V_{sweep}^{total} = 2000 \pm 2(sccm)$, membrane thickness $L = 1.00(mm)$ ($H_2$ measurements) and $L = 1.45(mm)$ ($CO$ measurements).
In the rest of our analysis, we will focus on the $H_2 - Ar$ case only; the $CO - Ar$ case follows similar trends. Figure 6-12 shows the rates of progress $\dot{s}_5-\dot{s}_6$ and the reaction rate $\dot{s}_{\text{sweep}}$ (equation 6.23 in dimensional form) at $\theta = 1060 (^\circ C)$. The model predictions confirm that the kinetics of fuel surface oxidation depend on the electron transfer step. In particular, reaction 6.10 in which electrons move by reducing $Fe^+_{Fe}$ is much faster compared to reaction 6.9 in which reduction of $Fe^\bullet_{Fe}$ is taking place.

![Figure 6-12: Rate of progress of reactions 6.9-6.12 calculated using equations 6.13-6.16 and sweep side molar reaction rate calculated using equations 6.23-6.24 in dimensional form. Operating conditions: feed side volumetric flow rate $\dot{V}_{\text{feed}} = 4000 \pm 2 (sccm)$, sweep side total volumetric flow rate $\dot{V}_{\text{total}} = 2000 \pm 2 (sccm)$, temperature $\theta = 1060.1 (^\circ C)$, membrane thickness $L = 1.00 (mm)$ ($H_2$ measurements) and $L = 1.45 (mm)$ ($CO$ measurements).]
Figure 6-13 shows the feed and sweep side formula-unit concentration of the three Fe states at $\theta = 1060\, ^\circ C$. As the inlet fuel concentration increases, reaction 6.14 produces $Fe_{Fe}^{\bullet}$ at the sweep side. At the same time, the $O_2$ incorporation at the feed side occurs by oxidation of $Fe_{Fe}^{x}$ to $Fe_{Fe}^{\bullet}$; the latter diffuses to the sweep side and maintains electronic conductivity within LCF in a p-type regime. 

Figure 6-13: Formula-unit concentration of Fe states as a function of inlet fuel mole fraction $X_{H_2}^{in}$ and $X_{CO}^{in}$. Top: $[Fe_{Fe}^{x}]$, center: $[Fe_{Fe}^{\bullet}]$, bottom: $[Fe_{Fe}^{\prime}]$. Operating conditions: feed side volumetric flow rate $V_{feed} = 4000 \pm 2\,(sccm)$, sweep side total volumetric flow rate $V_{sweep}^{total} = 2000 \pm 2\,(sccm)$, temperature $\theta = 1060.1\,(^\circ C)$, membrane thickness $L = 1.00\,(mm)$ ($H_2$ measurements) and $L = 1.45\,(mm)$ ($CO$ measurements). Lines correspond to the best fit of the data.
6-13 confirms this given that no crossover between $[Fe'_{Fe}]$ and $[Fe_{Fe}^{\bullet}]$ takes place. However, $[Fe_{Fe}^{\bullet}]$ drops slowly due to reaction 6.9. Addition of more fuel at the sweep side (which is outside the range of our operating conditions) will further consume $Fe_{Fe}^{\bullet}$ and will lead in a transition to n-type condution under finite oxygen flux conditions.

Figure 6-14 shows the feed and sweep side formula-unit concentration of oxygen vacancies at $\theta = 1060 (^\circ C)$ under finite $J_{O_2}$ conditions. The same plot includes the equilibrium $\delta$ using the local measurements of $H_2$ and $H_2O$. We observe that the oxygen vacancy formula-unit concentration rises compared to the non-reactive case. At the sweep side, chemical reactions of fuel with lattice oxygen ions increase the concentration of oxygen vacancies; oxygen vacancies then diffuse to the feed side. Since $[O_{Fe}^{\delta}] = 3 - \delta$, the oxygen content within the membrane reduces as more fuel is introduced in the sweep side of the reactor. For the same inlet fuel mole fraction and temperature, LCF generates more vacancies at the gas membrane-interfaces when using hydrogen; the same trend is observed for the equilibrium case and confirms that $H_2$ surface oxidation is faster compared to $CO$ surface oxidation.

Furthermore, figure 6-15 shows the role of diffusion due to electromigration within the bulk of LCF. In this figure, the spatial distribution of the oxygen vacancy flux due to concentration gradient, electromigration and total oxygen vacancy flux are presented for 3 different inlet fuel concentrations. Vacancy fluxes due to concentration gradient and electromigration have the same sign and hence increase the value of the total oxygen vacancy flux. At low inlet fuel concentrations, both vacancy fluxes are at the same order of magnitude. However, as the inlet fuel concentration rises, the magnitude of the vacancy flux due to concentration gradient reduces while that of electromigration increases. At $X_{H_2}^{in} = 29.7(\%)$, the vacancy flux due to electromigration dominates.
Figure 6-14: Oxygen nonstoichiometry $\delta$ at the feed and sweep side as a function of inlet fuel mole fraction $X_{H_2}^{in}$ and $X_{CO}^{in}$. Comparison with equilibrium values. Operating conditions: feed side volumetric flow rate $\dot{V}_{feed} = 4000 \pm 2$ (sccm), sweep side total volumetric flow rate $\dot{V}_{sweep}^{total} = 2000 \pm 2$ (sccm), temperature $\theta = 1060.1$ (°C), membrane thickness $L = 1.00$ (mm) ($H_2$ measurements) and $L = 1.45$ (mm) ($CO$ measurements). Lines correspond to the best fit of the data.

Given the surface limitation, modification of the membrane interfaces using a catalyst with faster charge transfer kinetics can promote the electron transfer significantly. For example, Yu et al. show that the surface resistance on LCF is reduced in a pure $CO$ environment with the addition of a porous support and a platinum-cerium oxide catalyst on the fuel side [91]. It is known that cerium oxide exhibits
Figure 6-15: Spatial distribution of oxygen vacancy flux due to concentration gradient (solid red), electromigration (dashed blue) and total (dotted green) oxygen vacancy flux for 6 different cases: top left: $X_{in}^{H_2} = 5.2\%$, center left: $X_{in}^{H_2} = 15.2\%$, bottom left: $X_{in}^{H_2} = 29.7\%$, top right: $X_{in}^{CO} = 4.6\%$, center right: $X_{in}^{CO} = 15.7\%$, bottom right: $X_{in}^{CO} = 30.7\%$. Operating conditions: feed side volumetric flow rate $V_{feed} = 4000 \pm 2 (sccm)$, sweep side total volumetric flow rate $V_{total\ sweep} = 2000 \pm 2 (sccm)$, temperature $\theta = 1060.1 (^{\circ}C)$, membrane thickness $L = 1.00 (mm)$ ($H_2$ measurements) and $L = 1.45 (mm)$ ($CO$ measurements).
a $Ce^{+3} \leftrightarrow Ce^{+2}$ redox cycle [26, 95], which is similar to the Fe redox cycle of LCF. Cerium electron transfer is fast [26], hence addition of cerium oxide on LCF facilitates charge transfer kinetics.

### 6.4 Conclusions

Motivated by the use of $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ mixed-conductors in methane reforming resulting in flux increase and high syngas yields [74], the goal of this chapter is to investigate the impact of $H_2$ and $CO$ surface oxidation to the oxygen flux and defect chemistry. Experimental measurements reveal significant enhancement in the oxygen flux as hydrogen or carbon monoxide are introduced in the sweep side. At $\theta = 1060$ ($^\circ$C) and $V_{\text{sweep}}^{total} = 2000$ (sccm), $J_{O_2} \approx 1.2$ ($\mu$mole/cm$^2$/sec) when the inlet hydrogen mole fraction reaches $X_{H_2}^{in} \approx 30$ ($\%$) and $J_{O_2} \approx 0.8$ ($\mu$mole/cm$^2$/sec) when $X_{CO}^{in} \approx 40$ ($\%$); these flux values correspond to an increase of more than one order of magnitude compared to the corresponding non-reactive case. Furthermore, we show that this performance is achieved without degradation of the membrane’s stability.

Analysis of the gas-phase mixture composition near the membrane sweep side suggests that the aforementioned $J_{O_2}$ increase is due to surface reaction of fuel with lattice oxygen ions. Two 4-step surface reaction mechanisms are proposed at the fuel side of the membrane to account for the hydrogen and carbon monoxide kinetics. To couple surface reactions with the diffusion of charged species within the material, a PNP model is used. Previous work under inert argon conditions determined the reaction rate coefficient of the oxygen incorporation reaction. This work estimates the reaction rate coefficients of hydrogen and carbon monoxide surface reactions with lattice oxygen ions. The equilibrium constants of oxygen incorporation and Fe disproportionation reactions were used to determine the equilibrium constants for
fuel surface reactions.

Our experimental measurements suggest that the LCF membrane exhibits surface limitations. In addition, the model predictions show that, between the two possible paths for electron transfer, the reduction of $Fe^\bullet_{Fe}^*$ to $Fe'_{Fe}^*$ is faster compared to the reduction of $Fe^\bullet_{Fe}^*$ to $Fe^\tau_{Fe}^*$. Furthermore, the model reveals that diffusion due to both concentration gradient and electromigration play a role at low $\delta$ values. At high inlet fuel concentrations, the oxygen nonstoichiometry increases further and the flux due to electromigration becomes the dominant mechanism of oxygen vacancy diffusion. Given that $\delta < 0.05$ for the entire range of operating conditions, no crossover in the concentration of $Fe^\bullet_{Fe}^*$ and $Fe'_{Fe}^*$ is observed.

The mathematical tools presented in this study can be directly used for the modeling of materials with defect chemistry similar to the LCF: $La_{1-x}Ca_xFeO_{3-\delta}$, $La_{1-x}Sr_xFeO_{3-\delta}$, $La_{1-x}Ba_xFeO_{3-\delta}$ of different doping percentage in the A-site fall into this category. The model formulation is exactly the same as presented in this study; the only change is that the equilibrium constants, molar volume, diffusion coefficients and relative permittivity of the material under consideration should be used. The model can be expanded for other perovskites doped in the B-site as well.

6.5 Appendix A: $J_{O_2}$, fuel conversion, sweep side

$X_{H_2O}$ estimation and uncertainty quantification

The oxygen flux $J_{O_2}$ is calculated by solving a linear system of equations which describes the conservation of hydrogen ($H$), carbon ($C$), nitrogen ($N$), argon ($Ar$) and oxygen ($O$) atoms as well as an equation for the molecular weight of the mixture at the outlet. The conservation of nitrogen takes into account the finite leak of air
into the sweep side of the reactor. By measuring the nitrogen concentration at the outlet, we can keep track of the oxygen due to air leak. The following system of equations is considered for CO – Ar mixtures at the inlet of the sweep side:

\[
\frac{\dot{m}_{\text{in}}}{W_{\text{mix}}} X_{\text{CO}}^\text{in} = \frac{\dot{m}_{\text{out}}}{W_{\text{mix}}} (X_{\text{CO}}^\text{out} + X_{\text{CO}_2}^\text{out}) \quad (6.28)
\]

\[
\frac{\dot{m}_{\text{leak}}}{W_{\text{mix}}} X_{\text{N}_2}^\text{leak} = \frac{\dot{m}_{\text{out}}}{W_{\text{mix}}} X_{\text{N}_2}^\text{out} \quad (6.29)
\]

\[
\frac{\dot{m}_{\text{in}}}{W_{\text{mix}}} X_{\text{Ar}}^\text{in} = \frac{\dot{m}_{\text{out}}}{W_{\text{mix}}} X_{\text{Ar}}^\text{out} \quad (6.30)
\]

\[
\frac{\dot{m}_{\text{in}}}{W_{\text{mix}}} X_{\text{CO}}^\text{in} + 2 \frac{\dot{m}_{\text{leak}}}{W_{\text{mix}}} X_{\text{O}_2}^\text{leak} + \frac{\dot{m}_{\text{mem}}}{W_{\text{mix}}} X_{\text{O}}^\text{mem} = \frac{\dot{m}_{\text{out}}}{W_{\text{mix}}} (2X_{\text{O}_2}^\text{out} + X_{\text{CO}}^\text{out} + 2X_{\text{CO}_2}^\text{out}) \quad (6.31)
\]

\[
W_{\text{mix}}^\text{out} = X_{\text{CO}}^\text{out} W_{\text{CO}} + X_{\text{CO}_2}^\text{out} W_{\text{CO}_2} + X_{\text{N}_2}^\text{out} W_{\text{N}_2} + X_{\text{O}_2}^\text{out} W_{\text{O}_2} + X_{\text{Ar}}^\text{out} W_{\text{Ar}} \quad (6.32)
\]

Here \( X \) denotes the mole fraction, \( \dot{m} \) is the mass flow rate and \( W \) the molecular weight. Equations 6.28-6.32 involve a linear system of 5 equations with 5 unknowns: \( \dot{m}_{\text{leak}}, \dot{m}_{\text{mem}}, \dot{m}, W_{\text{mix}}, X_{\text{out}}^\text{out} \). The input is the inlet mass flow rate \( \dot{m}_{\text{in}} \) as well as the experimentally measured \( X_{\text{CO}}^\text{in}, X_{\text{CO}_2}^\text{in}, X_{\text{CO}_2}^\text{out}, X_{\text{N}_2}^\text{out}, \) and \( X_{\text{O}_2}^\text{out} \).

For \( H_2 – Ar \) mixtures, the situation is more complicated since steam cannot be measured directly. To protect the columns of the GC from steam contamination, the Genie 170 membrane separator prevents steam from entering the GC. Hence, the true mole fraction of species \( k \) at the outlet of the reactor, \( X_{\text{out}}^k \), is always lower than the measured mole fraction of species using the GC, \( X_{\text{out,GC}}^k \); these two are related through the following equation:

\[
X_{\text{out,GC}}^k = \frac{X_{\text{out}}^k}{1 - X_{\text{H}_2\text{O}}^\text{out}}, \quad k = H_2, N_2, O_2 \quad (6.33)
\]
In equation 6.33, $X'_{H_2O}$ is the mole fraction of steam at the outlet of the reactor. The following system of equations is considered for $H_2 - Ar$ mixtures:

$$\frac{\dot{m}_{in}}{W_{mix}} W_{in} X'_{H_2} = \frac{\dot{m}_{out}}{W_{mix}} W_{out} (X'_{H_2} + X'_{H_2O})$$ (6.34)

$$\frac{\dot{m}_{leak}}{W_{mix}} X_{leak} = \frac{\dot{m}_{out}}{W_{mix}} X'_{out}$$ (6.35)

$$\frac{\dot{m}_{in}}{W_{mix}} X^{in}_{Ar} = \frac{\dot{m}_{out}}{W_{mix}} X_{out}$$ (6.36)

$$2\frac{\dot{m}_{leak}}{W_{mix}} X_{leak} O_2 + \frac{\dot{m}_{mem}}{W_{mix}} X_{mem} O_2 = \frac{\dot{m}_{out}}{W_{mix}} (2X_{out} O_2 + X'_{H_2O})$$ (6.37)

$$W_{out}^{mix} = X'_{H_2} W_{H_2} + X'_{H_2O} W_{H_2O} + X_{N_2} W_{N_2} + X_{O_2} W_{O_2} + X_{Ar} W_{Ar}$$ (6.38)

$$X'_{H_2} + X'_{H_2O} + X'_{N_2} + X_{O_2} + X_{Ar} = 1$$ (6.39)

Equations 6.33-6.39 involve a linear system of 9 equations with 9 unknowns: $\dot{m}_{leak}$, $\dot{m}_{mem}$, $\dot{m}_{out}$, $W_{mix}$, $X_{out}^{in}$, $X_{out}^{out}$, $X_{out}^{out}$, $X_{out}^{out}$, $X_{out}^{out}$. The input is the inlet mass flow rate $\dot{m}_{in}$ as well as the experimentally measured $X_{H_2}^{in}$, $X_{H_2}^{out}$, $X_{N_2}^{out}$, $X_{O_2}^{out}$.

For both $H_2 - Ar$ and $CO - Ar$ mixtures, the following assumptions have been made:

- **Sweep inlet mixture consists of Ar and the corresponding fuel:** $X_{Ar}^{in} + X_{CO/H_2}^{in} = 1$ and $W_{mix}^{in} = X_{Ar}^{in} W_{Ar} + X_{CO/H_2}^{in} W_{CO/H_2}$

- **Composition of air leak:** $\frac{X_{N_2}^{leak}}{X_{O_2}^{leak}} = 79 \frac{21}{21}$

- **Only air leaks into the sweep side of the reactor:** $X_{N_2}^{leak} + X_{O_2}^{leak} = 1$, $W_{mix}^{leak} = X_{N_2}^{leak} W_{N_2} + X_{O_2}^{leak} W_{O_2}$

- **Oxygen ions is the only species that enters the sweep side of the reactor through**
the membrane: $X_{O_{mem}}^m = 1$, $W_{mix}^m = W_O$

- The effective area of the membrane is: $A_{mem} = 73 \times 73 (mm^2)$

Assuming that the oxygen flux is uniformly distributed along the membrane, the magnitude of $J_{O_2}$ shown in figure 6-2 is calculated using the following equation:

$$|J_{O_2}| \left( \frac{\mu \text{mole/cm}^2}{\text{sec}} \right) = \frac{|J_O|}{2} = \frac{\dot{m}_{mem} \times 10^5}{2 \times W_O \times A_{mem}} = \frac{\dot{m}_{mem} \times 10^5}{W_{O_2} \times A_{mem}} \quad (6.40)$$

For the uncertainty and the corresponding error bars, the standard deviation of the experimental measurements is used. To get the uncertainty for the oxygen flux $J_{O_2}$ (as well as the uncertainty for the rest of the variables appearing in equations 6.28-6.39), another set of equations has been solved in accordance to equations 6.28-6.39 using the basic rules of error propagation. In this way, the uncertainty for the oxygen flux can be quantified. The system of equations to get the uncertainties is omitted for the sake of brevity. All the experimental measurements presented in this study include error bars, which are small and sometimes cannot be visually observed.

Although steam does not enter the GC, $X_{H_2O_{mem}}^m$ can be estimated assuming that all the hydrogen conversion happens on the membrane surface (given the absence of $O_2$ in the gas-phase of the sweep side). The following equation was used to estimate the mole fraction of steam on the membrane sweep side:

$$X_{H_2O_{mem}}^m = X_{H_2}^m - X_{H_2}^{mem} \quad \text{Eqn. (6.33)}$$

$$X_{H_2O_{mem}}^m = X_{H_2}^m - X_{H_2}^{mem,GC} (1 - X_{H_2}^{mem}) \Rightarrow$$

$$\Rightarrow X_{H_2O_{mem}}^m = \frac{X_{H_2}^m - X_{H_2}^{mem,GC}}{1 - X_{H_2}^{mem,GC}} \quad (6.41)$$

The mole fractions of steam presented in figure 6-4 are the values calculated using equation 6.41. We note that $X_{H_2}^{mem,GC}$ is the hydrogen mole fraction measured using

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the GC after steam has been removed from the mixture, while \( X_{H_2}^{\text{m,ref}} \) is the true value within the reactor where the mixture includes steam. Because of this removal of steam prior to the GC, once \( X_{H_2}^{\text{m,ref}} \) is estimated, the \( H_2 \) mole fractions should also be corrected using equation 6.33 and these adjusted values are the ones shown in figure 6-4.

### 6.6 Appendix B: Relationship between \( K_{C_i} \) and \( K_{P_i} \)

For completeness, this section includes the relationship between \( K_C \) and \( K_P \) for all surface reactions associated with this study:

\[
K_{P_1} = \frac{1}{\left( \frac{P_{O_2}}{P_{ref}} \right)^{1/2}} \frac{[O]^X [Fe^{*}_{Fe}]}{[V^{*}_{O}][Fe^{*}_{Fe}]} = \left( \frac{P_{ref}}{RT} \right)^{1/2} \frac{1}{C_{O_2}^{1/2}} \frac{C_{O_X}^{2}C_{Fe^{*}_{Fe}}}{C_{V^{*}_{O}}^{2}C_{Fe^{*}_{Fe}}} = \left( \frac{P_{ref}}{RT} \right)^{1/2} K_{C_1}
\]

\[
K_{P_2} = \frac{[Fe^{*}_{Fe}][Fe^{*}_{Fe}]}{[Fe^{*}_{Fe}]^{2}} = \frac{C_{Fe^{*}_{Fe}}^{2}C_{Fe^{*}_{Fe}}}{C_{Fe^{*}_{Fe}}} = K_{C_2}
\]

\[
K_{P_3} = \frac{\left( \frac{P_{H_2O}}{P_{ref}} \right)}{\left( \frac{P_{O_2}}{P_{ref}} \right)^{1/2}} \frac{1}{\left( \frac{P_{ref}}{RT} \right)^{1/2}} \frac{C_{H_2O}}{C_{H_2}} \frac{1}{C_{O_2}^{1/2}} = \left( \frac{P_{ref}}{RT} \right)^{1/2} K_{C_3}
\]

\[
K_{P_4} = \frac{\left( \frac{P_{CO_2}}{P_{ref}} \right)}{\left( \frac{P_{O_2}}{P_{ref}} \right)^{1/2}} \frac{1}{\left( \frac{P_{ref}}{RT} \right)^{1/2}} \frac{C_{CO_2}}{C_{CO}} \frac{1}{C_{O_2}^{1/2}} = \left( \frac{P_{ref}}{RT} \right)^{1/2} K_{C_4}
\]

\[
K_{P_5} = \frac{\left( \frac{P_{H_2O}}{P_{ref}} \right)}{\left( \frac{P_{O_2}}{P_{ref}} \right)^{1/2}} \frac{[V^{*}_{O}][Fe^{*}_{Fe}]}{[O]^X [Fe^{*}_{Fe}]} = \frac{C_{H_2O}}{C_{H_2}} \frac{C_{V^{*}_{O}}^{2}C_{Fe^{*}_{Fe}}}{C_{O_X}^{2}C_{Fe^{*}_{Fe}}} = K_{C_5}
\]

\[
K_{P_6} = \frac{\left( \frac{P_{H_2O}}{P_{ref}} \right)}{\left( \frac{P_{O_2}}{P_{ref}} \right)^{1/2}} \frac{[V^{*}_{O}][Fe^{*}_{Fe}]}{[O]^X [Fe^{*}_{Fe}]} = \frac{C_{H_2O}}{C_{H_2}} \frac{C_{V^{*}_{O}}^{2}C_{Fe^{*}_{Fe}}}{C_{O_X}^{2}C_{Fe^{*}_{Fe}}} = K_{C_6}
\]

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\[ K_{P_7} = \left( \frac{P_{CO_2}}{P_{ref}} \right) \frac{[V_{O}^{**}][Fe^{t}_{Fe}]}{[O_{O}^{X}][Fe^{t}_{Fe}]} = \frac{C_{CO_2} C_{V_{O}^{**}} C_{Fe^{t}_{Fe}}^2}{C_{CO} C_{O_{O}^{X}} C_{Fe^{t}_{Fe}}^2} = K_{C_7} \]  \hfill (6.48)\\

\[ K_{P_8} = \left( \frac{P_{CO_2}}{P_{ref}} \right) \frac{[V_{O}^{**}][Fe^{t}_{Fe}]}{[O_{O}^{X}][Fe^{t}_{Fe}]} = \frac{C_{CO_2} C_{V_{O}^{**}} C_{Fe^{t}_{Fe}}^2}{C_{CO} C_{O_{O}^{X}} C_{Fe^{t}_{Fe}}^2} = K_{C_8} \]  \hfill (6.49)
Table 6.1: Modeling parameters for the surface reaction mechanisms proposed in this study. $k_{r1}$, $k_{r5}$, $k_{r6}$, $k_{r7}$ and $k_{r8}$ are modeled using an Arrhenius expression of the form $k_{ri} = A_{kr_i} e^{-E_{kr_i}/RT}$. Values in bold correspond to fitted parameters using the reactive measurements of this study.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A_{kr_1}$ (cm$^2$/mole$^2$/sec)</th>
<th>$E_{kr_1}$ (kJ/mole)</th>
<th>$\Delta H^*_1$ (kJ/mole)</th>
<th>$\Delta S^*_1$ (J/mole/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}O_2 (g) + V^{**}<em>O + 2Fe^*</em>{Fe} \xrightarrow{k_{r1}} O^X_0 + 2Fe^*_{Fe}$</td>
<td>$3.021 \times 10^7$</td>
<td>193.93</td>
<td>-152</td>
<td>-94</td>
</tr>
<tr>
<td>Reaction</td>
<td>$A_{kr_2}$ (cm$^4$/mole/sec)</td>
<td>$E_{kr_2}$ (kJ/mole)</td>
<td>$\Delta H^*_2$ (kJ/mole)</td>
<td>$\Delta S^*_2$ (J/mole/K)</td>
</tr>
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<td>--------------------------</td>
</tr>
<tr>
<td>$2Fe^<em><em>{Fe} \xrightarrow{k</em>{r2}} Fe^{</em>}<em>{Fe} + Fe^{*}</em>{Fe}$</td>
<td>--</td>
<td>--</td>
<td>66</td>
<td>-55</td>
</tr>
<tr>
<td>Reaction</td>
<td>$A_{kr_3}$ (1/sec)</td>
<td>$E_{kr_3}$ (kJ/mole)</td>
<td>$\Delta H^*_3$ (kJ/mole)</td>
<td>$\Delta S^*_3$ (J/mole/K)</td>
</tr>
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<td>--------------------------</td>
</tr>
<tr>
<td>$H_2 (g) + \frac{1}{2}O_2 (g) \xrightarrow{k_{r3}} H_2O (g)$</td>
<td>--</td>
<td>--</td>
<td>-241.826</td>
<td>-44.4</td>
</tr>
<tr>
<td>Reaction</td>
<td>$A_{kr_4}$ (1/sec)</td>
<td>$E_{kr_4}$ (kJ/mole)</td>
<td>$\Delta H^*_4$ (kJ/mole)</td>
<td>$\Delta S^*_4$ (J/mole/K)</td>
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</tr>
<tr>
<td>$CO (g) + \frac{1}{2}O_2 (g) \xrightarrow{k_{r4}} CO_2 (g)$</td>
<td>--</td>
<td>--</td>
<td>-282.98</td>
<td>-86.5</td>
</tr>
<tr>
<td>Reaction</td>
<td>$A_{kr_5}$ (cm$^{10}$/mole$^3$/sec)</td>
<td>$E_{kr_5}$ (kJ/mole)</td>
<td>$\Delta H^*_5$ (kJ/mole)</td>
<td>$\Delta S^*_5$ (J/mole/K)</td>
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</tr>
<tr>
<td>$H_2 (g) + O^X_0 + 2Fe^<em><em>{Fe} \xrightarrow{k</em>{r5}} H_2O (g) + V^{**}_O + 2Fe^</em>_{Fe}$</td>
<td>$9.9994 \times 10^8$</td>
<td>213.82</td>
<td>-89.826</td>
<td>49.6</td>
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<tr>
<td>Reaction</td>
<td>$A_{kr_6}$ (cm$^{10}$/mole$^3$/sec)</td>
<td>$E_{kr_6}$ (kJ/mole)</td>
<td>$\Delta H^*_6$ (kJ/mole)</td>
<td>$\Delta S^*_6$ (J/mole/K)</td>
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</tr>
<tr>
<td>$H_2 (g) + O^X_0 + 2Fe^<em><em>{Fe} \xrightarrow{k</em>{r6}} H_2O (g) + V^{**}_O + 2Fe^</em>_{Fe}$</td>
<td>$1.4572 \times 10^{10}$</td>
<td>28.48</td>
<td>42.174</td>
<td>-60.4</td>
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<tr>
<td>Reaction</td>
<td>$A_{kr_7}$ (cm$^{10}$/mole$^3$/sec)</td>
<td>$E_{kr_7}$ (kJ/mole)</td>
<td>$\Delta H^*_7$ (kJ/mole)</td>
<td>$\Delta S^*_7$ (J/mole/K)</td>
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</tr>
<tr>
<td>$CO (g) + O^X_0 + 2Fe^<em><em>{Fe} \xrightarrow{k</em>{r7}} CO_2 (g) + V^{**}_O + 2Fe^</em>_{Fe}$</td>
<td>$2.7251 \times 10^9$</td>
<td>217.75</td>
<td>-130.98</td>
<td>7.5</td>
</tr>
<tr>
<td>Reaction</td>
<td>$A_{kr_8}$ (cm$^{10}$/mole$^3$/sec)</td>
<td>$E_{kr_8}$ (kJ/mole)</td>
<td>$\Delta H^*_8$ (kJ/mole)</td>
<td>$\Delta S^*_8$ (J/mole/K)</td>
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<tr>
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</tr>
<tr>
<td>$CO (g) + O^X_0 + 2Fe^<em><em>{Fe} \xrightarrow{k</em>{r8}} CO_2 (g) + V^{**}_O + 2Fe^</em>_{Fe}$</td>
<td>$1.7833 \times 10^{11}$</td>
<td>50.90</td>
<td>1.02</td>
<td>-102.5</td>
</tr>
</tbody>
</table>
Chapter 7

Thesis conclusions

The goal of this thesis is the development of a framework that allows for the investigation of ion transport membranes under a non-reactive or reactive environment. Throughout this thesis, we have shown how experiments combined with numerical simulations can provide insight towards the fundamental understanding of the permeation process and defect chemistry of the LCF membrane. LCF exhibits surface limitations over the entire range of operating conditions examined in this study. Hence, surface treatment using porous supports with or without a catalyst can speed-up surface reactions and enhance the oxygen permeation significantly.

In chapter 4, we presented experimental measurements when a $CH_4 - Ar$ mixture is introduced at the fuel side of the ITM reactor. In the presence of fuel, oxygen permeation increases by one order of magnitude compared to non-reactive cases but syngas production through methane partial oxidation is low. Addition of $CO_2$ at the inlet fuel stream doubles the oxygen flux while syngas production increases by an order of magnitude. At the same time, the presence of $CO_2$ helps in the long-term stability of the material by converting carbon (that is present for $CH_4 - Ar$ inlet
mixtures) into useful products.

Chapter 5 dealt with the case of pure oxygen production when argon is introduced at the fuel side of the ITM reactor. The oxygen flux is found to exhibit a strong dependence on temperature and $P_{O_2}$. In addition, the oxygen permeation is limited by surface exchange while material diffusion is fast. To model the oxygen permeation process, we coupled detailed surface chemistry with material diffusion using a PNP model in the dilute limit. The model preserves macroscopic reversibility and conserves site balances within the material.

Chapter 6 extends the aforementioned model under reactive mixtures of $H_2 - Ar$ and $CO - Ar$ for a wide range of temperature and inlet fuel compositions. Through experimental measurements, we show that the oxygen flux increases by almost two orders of magnitude for the case of hydrogen; carbon monoxide yields lower fluxes. Two 4-step surface reaction mechanisms have been proposed for each fuel case, yet this mechanism does not account for their interactions. XRD analysis before and after the measurements verifies that LCF is a stable perovskite under high fuel concentrations. The model predictions show that in the presence of fuel, the electron transfer takes place by $Fe^{3+}_{Fe}$ reduction to $Fe^{2+}_{Fe}$ due to the low $P_{O_2}$ at the fuel side of the membrane.

To allow for the design of high efficiency ITM reactors, the PNP model has been coupled with an in-house gas-phase transport solver. The algorithm is general and can be applied for every membrane or reactor geometry. Given that $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ belongs to a family of perovskites with similar defect chemistry, the proposed model can be applied for a large number of materials either directly or with minor modifications.
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