Hydrogen Migration in Monoclinic ZrO₂ and the Effects of Defects and Dopants Assessed by First-Principles Calculations

By

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Submitted to the Department of Nuclear Science and Engineering on September 23rd, 2015 in Partial Fulfillment of the Requirements for the degree of Master of Science in Nuclear Science and Engineering

Abstract

Zirconium-based alloys, which have been employed as cladding materials in nuclear industry, pick up hydrogen during service because of corrosion in water. This is one of the degradation processes that challenge the safe operation of nuclear reactors. Composition of commercial zirconium-based alloys has been developed experimentally, aiming to improve corrosion and hydrogen resistance. The empirical testing process is costly, time-consuming and can provide little knowledge on the underlying mechanisms. In order to understand the critical step of hydrogen entering zirconium-based alloys, we study hydrogen migration in monoclinic zirconium dioxide (m-ZrO$_2$), the oxide phase, which is present in the outer protective oxide layer contacting the cooling water. First principles calculations are casted to study hydrogen migration at atomistic scale. All possible stable sites for hydrogen to take in the structure are determined based on energy minimization. Barriers and saddle point configurations of elemental diffusion paths are obtained using the nudged elastic band method. Each extended diffusion path can be constructed from these elemental migration steps.

Even a small change, at the level of $\sim$0.1\%wt, in composition of alloying elements in zirconium-based alloys can cause large alteration of its neutron absorption property, as well as corrosion resistance and hydrogen pickup ability. Hydrogen exists in the form of proton in m-ZrO$_2$. To find the effect of defects and dopants on the hydrogen diffusion kinetics, we studied proton migration when cation vacancies, $V'_z_{2r}$ or dopants Ni$^{X}_{2r}$, Cr$^{X}_{2r}$, Fe$^{X}_{2r}$, Nb$_{2r}$, Sn$_{2r}$ and U$_{2r}$ are present in m-ZrO$_2$. Ni$^{X}_{2r}$, Cr$^{X}_{2r}$, Fe$^{X}_{2r}$, Sn$_{2r}$ and U$_{2r}$ serve as substitutional defects with neutral charge state while Nb$_{2r}$ takes the same site but with $+1$ charge state in equilibrium. Similar studies on other dopants can be easily conducted using the framework developed here.

Oxygen atoms in m-ZrO$_2$ can be categorized into two planes, namely the O3 and O4, depending on whether they bond with 3 or 4 neighboring Zr atoms. These planes stack layer by layer. This work found that proton migration in m-ZrO$_2$ is constrained in two dimensions within the O3 planes. Intrinsic defect $V''_{2r}$ was found to be a trap for protons with a trapping energy greater than 1.4eV. Alloying additions affect proton migration mainly due to their size and charge. Three of the nearest sites around Ni$^{X}_{2r}$, Cr$^{X}_{2r}$, Fe$^{X}_{2r}$, Sn$_{2r}$ are usually the deepest traps for the proton.
Proton trapping energy increases and the proton migration barriers increase with the Shannon Radii of dopant ions, as Ni$_{Zr}^X$(0.48Å), Cr$_{Zr}^X$(0.55Å), Fe$_{Zr}^X$(0.58Å), Sn$_{Zr}^X$(0.75Å). For Nb$_{Zr}^X$ or U$_{Zr}^X$, none of the nearest proton sites are the deepest trap while one of the second nearest proton sites is the deepest trap. Protons prefer to stay nearest to the Ni$_{Zr}^X$, Cr$_{Zr}^X$, Fe$_{Zr}^X$, Sn$_{Zr}^X$ dopant ions, but they do not approach the closest proton sites around Nb$_{Zr}^X$ and U$_{Zr}^X$. The positive charge of Nb$_{Zr}^X$ and the large size of U$_{Zr}^X$ are thought to be the reasons for this behavior.

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Chapter 1: Introduction

1.1 Motivation and overview of material challenge in nuclear fission industry

Significant worldwide growth in energy demand, especially in developing countries, has led to increased usage of fossil fuels. Annual coal consumption in China has grown steadily from 680 million short tons in 1980 to over 3.88 billion short tons in 2012\[1\]. U.S. energy-related carbon dioxide emissions from coal, oil, natural gas and other natural resources has increased from 650 million tons in 1950 to 1.496 billion tons in 2011, with a peak consumption amount of 1.649 billion tons in 2007\[2\]. Widespread concerns about climate change from these CO\(_2\) emission increases have sparked growing interest in clean forms of energy including solar, wind, hydroelectric and nuclear powers. As of this writing, hydroelectric power systems generate approximately 15% of the world’s electricity\[3\], and nuclear fission generates more than 11%\[4\], while wind turbines and solar panels generate less than 2%\[3\].

The performance of power generators, including nuclear power plants, has always been constrained by the characteristics of their engineering materials. The low (< 30%) conversion efficiency of materials used in solar cells has limited the proliferation of solar panels in clean energy generation\[5\]. In fusion devices, the constraints of neutron resistance and limitations in their capacity to operate as plasma-facing components have restricted the development of fusion as a viable clean energy source\[6\]. The appropriate selection of engineering materials has also been a crucial challenge for safe and economic operation of any fission-based nuclear power plant. At high temperature (~300°C at normal operating conditions, > 800°C when loss of coolant accident occurs), degradation of materials from interaction with harsh environmental conditions can lead to operation failure and nuclear accidents. Therefore, in order to ensure the nuclear fission's leading role in the sustainable energy field, proper design of materials for efficient functioning in corrosive high-temperature and radiative conditions is crucial.

1.2 Nuclear reactor systems and their material challenges

Two types of nuclear reactors are widely used: (1) the pressurized water reactor (PWR) and (2) the boiling water reactor (BWR)\[7\]. In both systems, energy is released from splitting atoms to heat. This transforms water into steam directly in a BWR or through a second loop in a PWR.
Subsequently, as in a conventional thermal power plant, the steam rotates the generator, and electricity is generated.

In each reactor the initial coolant water circulates through the reactors core and transfers heat generated from the core. PWR contains a primary cooling circuit through which water flows through the core under pressure. Water is thereby heated without boiling. In the secondary circuit in PWR, steam is generated through exchanging heat with the primary circuit, and that steam drives the turbine in the generator. In BWR, however, water boils into steam when heated in the reactor, and then pumps the generator directly (Figure 1-1).

Except for the difference in cooling water loop in PWR and BWR, structures of nuclear reactors are quite similar. In both types, fuel-usually uranium oxide-is contained in small ceramic fingertip-sized pellets that are arranged in metal tubes, forming long fuel rods. The rods are then grouped into fuel assemblies inside a reactor vessel, which is enclosed in a concrete and steel containment building (Figure 1-2).

Temperatures in the reactor core are about 325°C in PWR, and 295°C in BWR. In PRW, pressurized water is maintained by steam in a pressurizer at about 150 times the atmospheric pressure, so that the reactor can function well at temperatures above 100°C. BWR, however, is designed to operate with 12%-15% of the water as steam in the top of the core. Relevant information and more details can be found on the World Nucleation Association Website[8].

At 300°C or higher, corrosive and radiative conditions, degradation of fuel cladding materials will threaten the proper functioning of fuel rods, by deteriorating its mechanical properties and corrosion resistivity, as the next section will discuss.
The Pressurized-Water Reactor (PWR) Containment Structure

Pressurizer Steam Generator

Generator

Condenser

(a) The Pressurized-Water Reactor (PWR)

The Boiling-Water Reactor (BWR) Containment Structure

Reactor Vessel

Control Rods

Generator

Turbo

Condenser

(b) The Boiling-Water Reactor (BWR)

Figure 1-1: Comparative schematic diagrams of PWR and BWR. The BWR has only one water-cooling loop, while the PWR has two. The water in the PWR is pressurized to prevent it from cooling at temperatures between 100°C and 325°C. Figures courtesy of the U.S. Nuclear Regulatory Commission website [7].
1.3 Degradation of fuel cladding materials in a nuclear reactor

This section focuses on the zirconium (Zr) alloy cladding material in a specific part of a nuclear reactor vessel.

In the Fukushima Daiichi nuclear disaster in 2011, flooding caused the emergency battery-powered generators in that nuclear reactor complex to fail, thus stopping the active cooling system and causing a loss of reactor control[9]. This in turn caused the Zr alloy fuel cladding material to produce around 1,000 kg of hydrogen gas per reactor during its redox reaction with water, which was expedited at a much higher temperature than 300°C at normal condition.

\[ \text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2 \]  

Explosions occurred in three reactors when the hydrogen-air mixture reached its explosive limits.
In addition to leaving the cladding tube and evolving into the cooling water, some of the liberated hydrogen was absorbed into the Zr alloy, despite the protective oxide layer that formed above the alloy during waterside corrosion[10]. Protons can either reduce into hydrogen gas and leave the cladding material—which may cause the gas to accumulate in the reactor—or diffuse through and penetrate the protective oxide layer and then dissolve into the Zr metal (Figure 1-3). When the concentration of hydrogen in the Zr alloy exceeds the dissolution limit, a second phase of Zr hydride may form, which would deteriorate the mechanical property of the cladding material. This study assumes that the hydrogen evolving into cooling water can be effectively removed from the reactor core without accumulation, but hydride cannot be removed once the hydrogen has entered the metal.

This thesis examines how to retard hydrogen pick-up by engineering the composition of the passive oxide layer that grows on the Zr alloy. The purpose is to be able to slow down the hydrogen in the oxide layer, and make it easier for surface protons to reduce and evolve as hydrogen gas.

The Zr alloy's property of corrosion resistance and hydrogen pickup must be understood to design, test and optimize Zr alloys for use in nuclear systems. The development of commercially usable Zr alloys has been based on knowledge gleaned from experimental testing, which is costly
and time consuming (a single test can last several years[11]) and lends few clues to how these degradation processes occur. A fundamental theory on those processes and how variables affect them is needed to guide alloy design.

Computer simulation techniques have played significant roles in material modeling. Starting from atoms and electrons, material property can be deduced from microscopic simulation results. Scientific knowledge of how atomic reactions and diffusion evolves can also be gathered from computer simulation. A typical computer simulation-assisted material study is the identification of stable binary and ternary compounds[12] through the criteria of formation enthalpy. In comparison, experimental testing of various possible compounds is difficult due to the harsh physical environment, long endurance, and occasional mixture with hazardous, poisonous materials. In spite of the lack of the computational power necessary for the precise simulation of macroscopic-scale atoms, we can simulate small systems, including atoms in hundreds, to gain knowledge of one or several reactions at one time.

This thesis emphasizes proton migration, the dominant form of Hydrogen, as the key phenomenon to study. Conventionally, a protective oxide layer would form above Zr metal (Figure 1-3). Most hydrogen pick-up is from the oxidation reaction between Zr and water. Hydrogen liberated from such a reaction must penetrate the oxide layer before it can dissolve in metal. Since the rate-limiting process involves hydrogen entering into oxide, the study of hydrogen migration in oxide's outer part is crucial to understand the mechanism of hydrogen pickup. Hydrogen diffusion in Zr oxide is the system explored in this thesis.

The initial background introduction, which includes Zr alloy development history, is necessary to assist our understanding of the problem. The second part explains the computation method used and explores hydrogen diffusion in perfect Zr oxide, with no intrinsic defects or dopants. The third part examines hydrogen migration modeling when intrinsic defects or dopants are present. Based on the doping result, the thesis concludes with relations between intrinsic defects or dopants and proton migration.
Chapter 2: Background

In almost all types of water-cooled reactors, including Canada Deuterium Uranium (CANDU) heavy-water reactors and such light-water reactors as PWR and BWR, Zr alloys have been widely used as fuel cladding materials due to its resistance to corrosion[7]. Zircaloy, the Zr-Sn (zirconium-tin) alloy, has shown satisfactory technical behavior in the first commercial nuclear power plant, Shippingport[13]. Zr-2.5Nb alloy is used in CANDU reactors. Zr also has excellent nuclear property: it is almost transparent to neutrons, possessing a tiny neutron absorption cross-section of 0.18 barns[14], while Hf (hafnium), which has an almost identical electron configuration to Zr, absorbs 600 times more neutrons than Zr[14]. Neutrons from fission reaction in uranium fuels penetrate fuel cladding. Then they either enter other uranium fuels to sustain fission reaction, or they slowdown in cooling water so energy can be transferred from a nuclear phase to a heat phase for further transformation. Too much neutron-absorption of neutrons in the reaction core will reduce fuel burn-up. For these reasons, neutron transparent Zr alloys such as Zircaloy are the best option for cladding material.

2.1 Zirconium alloy development history

In the nuclear industry, the crucial requirement of low neutron-absorption cross-section has restricted structural and cladding materials options. Zr has appeared to be competitive after early investigations into possible alternative structural and cladding materials for pressurized water reactors. After Hf, which has 600 times higher thermal neutron absorption than Zr, was removed from Zr specimens, the cross-section declined. The first pressurized water naval reactor used Zr as the candidate for cladding and structural materials[13].

Early tests of pure Zr on its corrosion weight gain in water and steam at elevated temperatures between 200°C and 400°C were unstable. Black adherent oxide could form as a protective layer above some Zr batches; for other supposedly identical specimens, a white corrosion product formed and then spalled and flaked, without protecting the metal underneath[15]. This breakaway was shown to be unstable.

Initially, achieving higher-quality Zr with higher purity was the design strategy for better corrosion resistance performance[16]. However, mechanical properties could not meet this
standard under elevated temperature. Zr alloys were brought to attention to retain advantages while optimizing Zr's performance. It was observed that small amounts of N (Nitrogen), C (Carbon), O (Oxygen), Al (Aluminum), Ti (Titanium) and Si (Silicon) could adversely affect the corrosion behavior, while Sn (Tin), Ta (Tantalum) and Nb (Niobium) could improve corrosion resistance. Adding Sn and Nb could offset some harmful effects from hard-to-eliminate impurities; Nb was less effective than Sn, especially since Sn does not poison Zr severely. Early Zr alloys were always Zircaloy, based on which Zircaloy family (from Zircaloy-I on) was developed. Although Sn hedged the deteriorative effect due to contamination of N, Sn introduced an unacceptably high post-migration oxidation rate.

2.1.1 Zircaloy

Soon, Zircaloy-2 suspended Zircaloy-1. Fe (Iron), Cr (Chromium), Ni (Nickel), and Sn (Tin) were deliberately added into the new alloy, and the Sn content in Zircaloy-2 was less than that in Zircaloy-1. The specification of Zircaloy-2's composition has been fixed by studies of varieties of variables, which ensured its effective performance below 360°C. However, its performance would decline above 400°C due to the presence of Sn. Higher Sn content gives a higher oxidation rate than that with lower concentration of Sn. The quantitative comparisons of compositions in Zircaloy-2 and Zircaloy-4[17] are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition, Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UNS R60001</td>
</tr>
<tr>
<td>Sn (Tin)</td>
<td>...</td>
</tr>
<tr>
<td>Fe (Iron)</td>
<td>...</td>
</tr>
<tr>
<td>Cr (Chromium)</td>
<td>...</td>
</tr>
<tr>
<td>Ni (Nickel)</td>
<td>...</td>
</tr>
<tr>
<td>Nb (Niobium)</td>
<td>...</td>
</tr>
<tr>
<td>O (Oxygen)</td>
<td>A</td>
</tr>
<tr>
<td>Fe + Cr + Ni</td>
<td>...</td>
</tr>
<tr>
<td>Fe + Cr</td>
<td>...</td>
</tr>
</tbody>
</table>

Maximum Impurities, Weight ppm

<table>
<thead>
<tr>
<th>Element</th>
<th>75</th>
<th>75</th>
<th>75</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (Aluminum)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>B (Boron)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Cd (Cadmium)</td>
<td>...</td>
<td>30</td>
<td>30</td>
<td>...</td>
</tr>
<tr>
<td>Ca (Calcium)</td>
<td>270</td>
<td>270</td>
<td>270</td>
<td>270</td>
</tr>
</tbody>
</table>
Then along came Zircaloy-3, which restricted its Sn content to less than 0.5% to resolve this issue. However, the advantage of Zircaloy-3 over Zircaloy-2 is too small for the former to be widely used[10].

A Sn-free alloy, Valloy (Zr-1.2wt%Cr-0.08wt%Fe) was developed to improve corrosion resistance at high temperatures. Its behavior was not stable near 300°C, which denied its wide commercial acceptance. Zircaloy-2 and Zircaloy-4 are listed in the standard specification for cladding tubes, while other developed alloys are no longer in current use[10].

Hydrogen pickup fraction minimization is also necessary, in addition to high temperature corrosion resistance improvement, as hydrogen pickup fraction has no simple relation to the amount of oxide formation, though more oxide generally corresponds to a higher hydrogen pickup fraction.

The cladding corrosion in the early PWR failure was accompanied by internal hydriding. This became the driving force for developing Zr alloys as shields against hydrogen pickup.

<table>
<thead>
<tr>
<th>Element</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr (Chromium)</td>
<td>200</td>
</tr>
<tr>
<td>Co (Cobalt)</td>
<td>20</td>
</tr>
<tr>
<td>Cu (Copper)</td>
<td>50</td>
</tr>
<tr>
<td>Hf (Hafnium)</td>
<td>100</td>
</tr>
<tr>
<td>H (Hydrogen)</td>
<td>25</td>
</tr>
<tr>
<td>Fe (Iron)</td>
<td>1500</td>
</tr>
<tr>
<td>Mg (Magnesium)</td>
<td>20</td>
</tr>
<tr>
<td>Mn (Manganese)</td>
<td>50</td>
</tr>
<tr>
<td>Mo (Molybdenum)</td>
<td>50</td>
</tr>
<tr>
<td>Ni (Nickel)</td>
<td>70</td>
</tr>
<tr>
<td>Nb (Niobium)</td>
<td>...</td>
</tr>
<tr>
<td>N (Nitrogen)</td>
<td>80</td>
</tr>
<tr>
<td>P (Phosphorous)</td>
<td>...</td>
</tr>
<tr>
<td>Si (Silicon)</td>
<td>120</td>
</tr>
<tr>
<td>Sn (Tin)</td>
<td>50</td>
</tr>
<tr>
<td>W (Tungsten)</td>
<td>100</td>
</tr>
<tr>
<td>Ti (Titanium)</td>
<td>50</td>
</tr>
<tr>
<td>U (Uranium)</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 2.1: Chemical requirements for Zr alloy tubes for nuclear reactor fuel cladding. Data and table courtesy of the American Society for Testing and Materials (ASTM) [17]
Later, higher nickel content was found to correspond to a higher hydrogen pickup fraction during corrosion inside or outside the reactor (Figure 2-1). To improve hydrogen pickup property, Ni-free Zircaloy-2 was developed based on such findings.

Figure 2-1: Inclusion of Ni gives higher hydrogen pickup fraction. Figures courtesy of [11].

Besides Ni, optimizations on other alloying element dimensions have improved the corrosion resistance in 400°C steam, which resulted in the new Zircaloy-4. The main modification was the increase in Fe content, and the total migration-metal content remained the same although Ni content decreased.

In foreign nations, other paths were taken, such as Zr-Nb and Zr-Cr-Fe alloys, due to the unique characteristics of each country’s nuclear reactors. We will focus our discussion around Zircalloys.

### 2.2 Mobile species

Zr oxidation is a complex process. Since hydrogen liberation is accompanied by Zr oxidation, some key phenomena are listed here for reference. Detailed information and introduction can be obtained from wherever it is cited.
Oxygen anion is reported to be more mobile than Zr cation[18]. The measured diffusivity of oxygen in stabilized, cubic ZrO$_2$ ceramics with high intrinsic vacancy concentrations is over five orders of magnitude higher than that in ZrO$_2$ with low vacancy concentrations. Thus, the dominant mobile species is oxygen anion, which exchanges with vacancy sites.

However, the diffusivity of Zr ions is low[18]. Their diffusion cannot compensate for the diffusion of oxygen to keep charge-neutrality; this must be achieved by sending electron currents in the opposite direction to that of oxygen diffusion. ZrO$_2$ is almost completely ionic oxide where electrons cannot flow freely. Thus the electron current is probably achieved by a valence change in Zr ions[18].

In summary, Zr oxidation is kinetically achieved by inward diffusion of oxygen ions, while Zr ions are immobile. The charge-neutrality is maintained by electron current outflow assisted by valence change in Zr ions.

Figure 2-2: Diffusivity of oxygen in stabilized, cubic ZrO$_2$ ceramics, with high intrinsic vacancy concentrations. Figure courtesy of [19].
2.3 Three phases

Three phases of the ZrO$_2$ stoichiometric composition exist[20]. The monoclinic phase is the most stable phase at low temperature until $-1478$K at ambient pressure, above which a tetragonal phase becomes more stable. Above $2650$K, the cubic phase is the most stable one until it melts at $\sim 2980$K (Figure 2-3). Structures of three phases are schematically shown in Figure 2-3.

![Figure 2-3: Three phases of the ZrO$_2$ stoichiometric composition exist. Data are from[21]. Figure courtesy of the ASM Alloy Phase Diagrams Center website[22].](image1)

![Figure 2-4: The monoclinic phase is the most stable one at room temperature until 1400K. At a nuclear reactors normal operational temperature of 600K, the monoclinic phase is the most stable ZrO$_2$ phase. Figure courtesy of [20].](image2)
If revisit Figure 1-3, we can find ZrO$_2$ in its tetragonal phase, which would appear in-between the stable monoclinic phase and the original metal. Therefore, at the temperature range where the monoclinic phase is more stable than the tetragonal one, stress at the region close to metal stabilizes the tetragonal phase. As oxide evolves, the tetragonal phase is relaxed and transforms into the monoclinic phase, while a new tetragonal phase would form when metal is further oxidized. In this manner, oxide can grow inward to the metal.

2.4 Hydrogen pick-up
Oxidation corrosion and associated hydrogen pick-up are the two main forms of degradation mechanisms that threatens cladding materials[23]. Early in the development of zirconium for nuclear application in 1953, hydrogen pick-up was pointed out[24].

Hydrogen is intentionally added to the coolant water to combine with oxygen generated from the radiolytic decomposition of water, so that water is formed instead of having oxygen react with nitrogen and form nitric acid. The radiolytic decomposition of water is another source of hydrogen. But the amounts of hydrogen from these two sources are small, compared to those generated from corrosion. Corrosion of the cladding is the main source of hydriding zirconium, since it is in ionic form and close to the metal surface[25].

The dissolved hydrogen in the water is not responsible for hydriding of Zircaloy-2[26]. Zirconium doesn't hydride to gaseous hydrogen at 360°C, with an oxide film that form in high temperature water[26]. Having Zircaloy-2 in high pressure (30 atmospheres) hydrogen does not lead to extensive hydriding[26].

Klepfer[27] introduced four factors determining embrittlement due to corrosion hydrogen:

1. Hydrogen's picked-up by cladding material Zircaloy mainly follows the liberation of the gas during corrosion reaction (1.1). Total hydrogen generated from corrosion is strictly determined by the extent of oxidation reaction (1.1).

2. The amount of hydrogen ingression to the underlying metal ranges from 15 to 50 % of the theoretically available from the corrosion reaction [25, 26, 28, 29].
Since only a fraction of the hydrogen generated by reaction (1.1) penetrates the protective oxide and reaches metal[10]. This fraction can be defined as hydrogen pickup fraction so that the hydrogen pickup extent can be quantified to make comparison. The hydrogen ingress into the metal is normalized to the total hydrogen determined theoretically from corrosion reaction (1.1) [30].

\[ f_H = \frac{H_{\text{absorbed}}}{H_{\text{generated}}} \]  \hspace{2cm} (1.2)

\( f_H \) depends on alloying elements [31], microstructure and microchemistry [32].

Upon fabrication, a protective oxide layer covers the metal. Although this barrier can impede the ingress of hydrogen, cracks form in the barrier due to strain cast on oxides when they provide shortcuts for hydrogen to migrate through. However, the hydrogen diffusion through the coherent oxide phase is crucial as well. In this thesis, hydrogen diffusion through extended defects is not studied specifically. Rather, we study how alloying elements affect hydrogen migration.

3. Solubility of hydrogen in the alloy. Hydrogen solubility is quite limited in Zircaloy. At 400°C, 200 ppm of hydrogen can be dissolved, while only 1 ppm of hydrogen can be dissolved at room temperature[33]. Fuel cladding operates under heat-flux; therefore, the temperature gradient can lead to a hydrogen concentration limit that is lower in the outer side and higher in the inner side. Hydrides are concentrated in the outer layer[34].

4. The effect of hydrogen in the alloy on ductility, which will be related to the amount, orientation and morphology of the hydride precipitate. A Zr hydride phase may precipitate when temperature drops or when hydrogen concentration exceeds its dissolution limit. The new hydride phase is brittle and can harm the mechanical property of cladding materials to a degree determined by the fraction of the hydride phase. Embrittlement of the zirconium from hydrogen could result in cladding rupture and exposure of the less corrosion resistant nuclear fuel to the primary coolant water. Radioactive fission product would be transported to other portions of reactor circuit.
Figure 2-5: Ni addition increases hydrogen absorption. Binary additions of Cr and Fe reduce hydrogen absorption. Sn has little effect on hydrogen absorption. Figure courtesy of [25]

2.5 Effect of alloying elements on hydrogen pickup

We focus specifically on how alloying elements would affect hydrogen pickup in Zr alloys.

There have been abundant data for hydrogen pickup in zirconium alloys containing Ni, Fe, Cr, Sn, Nb, etc. These data guided the development of zirconium alloy. Fe, Cr, Ni have extremely limited solubility in zirconium. Precipitates are formed at several hundred ppms. By presenting as discrete particles, corrosion resistance can be improved markedly.

Berry, et al[25] studied the hydrogen pickup dependence on Fe, Cr, Ni and Sn additions. Ni addition results in increased hydrogen absorption in zirconium while the binary additions of Cr and Fe reduce hydrogen absorption during corrosion. Sn has little or no effect on hydrogen absorption.

It is proposed in [25] that in the case of Fe and Cr alloys, most protons are reduced to hydrogen molecules and evolve into cooling water rather than diffuse through the oxide film, while smaller amount of hydrogen still migrate through the oxide film and reach metal, which occurs near
compound particles. In the Ni case, the pick-up fraction is larger. More hydrogen atoms or ions build up close to nickel compounds.

Couet, et al[30] measured the total and instantaneous hydrogen pickup fraction in zirconium alloys. They derived dependencies of hydrogen pickup on alloying elements as well as microstructure. Nb addition decreases hydrogen pickup fraction whereas Cu addition increases it. The proposed reason for Zr-2.5Nb has the lowest $f_H$ of all the alloys investigated in the study is that the Nb atoms dissolved in the ZrO$_2$ solid solution would dope the oxide layer and act as donors. Electrons are the compensating defect for the positively charged Nb. Zr-2.5Nb has the highest electronic conductivity and lowest hydrogen pickup comparing to Zircaloy-4[35].

In the aspect of alloying element, zirconium-based alloys with application in nuclear fuel cladding are optimized aiming at reducing hydrogen pickup as well as mitigating cladding degradation.

Two design strategies can be proposed[36] that either choosing the alloying composition which gives the lowest hydrogen concentration at equilibrium, or the one corresponding to the longest duration for hydrogen to diffuse into the matrix and reach equilibrium. Regarding the later strategy, as long as the kinetic process is low enough, hydrogen can be effectively blocked by the oxide and will hardly penetrate into metal to form hydride.

The above results are experimentally macroscopic. This thesis aims at studying proton migration and how defects introduced by alloying element affect microscopic diffusion of proton.

The following chapter starts from proton diffusion in perfect m-ZrO$_2$ sites; based on that, intrinsic defects and dopants can be included in the diffusion process.
Chapter 3: Hydrogen diffusion in perfect m-ZrO$_2$

It is known from Chapter 2 that the outer side part of ZrO$_2$ at the interface between metal and cooling water is in monoclinic phase (Figure 2-4). Hydrogen has to diffuse through the monoclinic phase before reaching the metal region, where it either dissolves into metal or precipitates as hydride, supposing shortcut diffusion paths into metal formed by extended defects like cracks, grain boundaries are rare in this model. Starting from this chapter, we study the elemental diffusion paths and corresponding barriers of proton diffusion in m-ZrO$_2$. Each elemental path includes only one hoping or rotating action from one stable site to a neighboring stable site. Based on these complete elemental diffusion paths base, any long distance diffusion path can be constructed. Once the framework of proton diffusion in coherent m-ZrO$_2$ can be built, modifications to perfect m-ZrO$_2$ sites can be made to study the effect of intrinsic defects and those introduced by dopants: how elemental diffusion paths and their barriers alter once a point defect presents at the sight of proton. These results can help understand how proton diffusion is enhanced or impeded with these defects. The scientific explanation would be helpful for designing new Zr alloys, regarding kinetically stopping hydrogen pick-up.

Characterization of symmetry and property of perfect m-ZrO$_2$, as well as proton diffusion in it, is discussed in this chapter. Study on doped m-ZrO$_2$ cell and corresponding hydrogen diffusion will be discussed in the following chapter.

3.1 Method

3.1.1 Density functional theory

Our first-principles calculations in the framework of the density-functional theory (DFT)[37] are performed based on plane-wave pseudopotential approach as implemented in the Vienna ab initio simulation package (VASP)[38, 39]. Projector augmented wave (PAW) method[40] is employed to describe the electron-ion interactions. For the exchange-correlation functional, we use the generalized gradient approximation (GGA) in the Perew-Burke-Ernzerhof (PBE) form.[41] All calculations are carried out spin-polarized with a plane-wave cutoff kinetic energy of 450eV. Monkhorst-Pack scheme[42] $2\times2\times2$ k-point mesh is used for Brillouin zone sampling. The relaxation of electronic degrees of freedom ceases when the total free energy change and the band structure energy change in consecutive two steps are within $10^{-4}$eV. Structural changes
due to presence of dopants and proton are taken into account by relaxing all ions with volume fixed. Ionic relaxations are considered to be achieved when the Hellman-Feynman force on each atom is smaller than $0.01\text{eV}/\text{Å}$. Supercells consisting of $2 \times 2 \times 2 \text{m-ZrO}_2$ conventional unit cells, including 32 Zr and 64 O atoms, are used when calculating energies of protonic stable sites and when surveying proton diffusion with/without the presence of dopants. These cells represent systems with low proton or a dopant concentration of $\sim 1/96$. The proton is treated as a classical ion in our calculation without considering tunneling effect. The PAW atomic data treat as valence electrons the $4s^2 4p^6 4d^2 5s^2$ for Zr (12 electrons), $2s^2 2p^4$ for O (6 electrons), $1s^1$ for H (1 electron), $3p^6 3d^8 4s^2$ for Ni (16 electrons), $3s^2 3p^6 4s^4 3d^5$ for Cr (14 electrons), $3s^2 3p^6 3d^7 4s^1$ for Fe (16 electrons), $4s^2 4p^6 4d^4 5s^1$ for Nb (13 electrons), $4d^{10} 5s^2 5p^2$ for Sn (14 electrons), and $5f^3 6s^2 6p^6 6d^1 7s^2$ for U (14 electrons).

### 3.1.2 Nudged Elastic Band Method

Diffusion paths are completed using climbing image nudged elastic band (CI-NEB) scheme [43, 44] after protonic stable sites are obtained for starting and final configuration. The migration path is constructed from two images of starting and final configurations and several intermediate images to be optimized so a minimum energy path is obtained. For all CI-NEB calculations in this study, three intermediate images are inserted in the path. Images on each path are connected by spring force, to hold imaged from sinking to the minima, when relaxing their positions.

### 3.1.3 Bader Analysis

Electron belongings are crucial when divide molecules into atoms. Bader analysis[45] defines the ionic boundary where electronic charge density is a minimum perpendicular to the boundary. Regions form after boundaries are defined. Inside each region, there is a nucleus claiming all electrons distributed inside the region it locates. The number of electrons is usually not an integer. The total charge and volume inside each region is the Bader charge and Bader volume, respectively. It is a good approximation to the total electronic charge of each atom. Code from Henkelman Group [46-48] has been used to implement Bader analysis.

### 3.1.4 Trapping Energy

In Chapter 4, when dopant/extrinsic defect sites are introduced in the m-ZrO$_2$ cell, trapping energy is used to evaluate trapping strength of stable proton sites near defects sites. In this subsection, we define trapping energy and explain how trapping energy is calculated.
Suppose dopant cation M (M will be Ni, Cr, Fe, Nb, Sn or U in Chapter 4) is the dopant cation to be studied. A proton site, h, close to M is to be evaluated on its ability to trap a proton. Four total energies are calculated to reap trapping energy:

1. Total energy of perfect m-ZrO$_2$, $E_p$. In our case, the calculation cell includes 32 Zr atoms and 64 O atoms.

2. Total energy of m-ZrO$_2$ with one Zr atom substituted by the dopant cation M, $E_M$. The calculation cell includes 31 Zr atoms, 64 O atoms and 1 M atom taking a Zr site. If vacancy $V'''''_Z$ is to be evaluated, the calculation cell includes only 31 Zr atoms and 64 O atoms.

3. Total energy of m-ZrO$_2$ with one Zr atom substituted by the dopant cation M, and with a proton taking the stable proton site h, $E_{M,h}$. The calculation cell includes 31 Zr atoms, 64 O atoms, 1 M atom taking a Zr site and 1 proton taking stable proton site h near dopant cation M.

4. Total energy of m-ZrO$_2$ with a proton taking the same site as the one in 3, but without any Zr atom substituted by the dopant cation M, $E_{p,h}$.

Then trapping energy is defined as the energy difference between (1) proton staying at the trap site and (2) proton staying out of trap region:

$$E_{\text{trap}} = (E_{M,h} + E_p) - (E_M + E_{p,h})$$ (3.1)

3.2 Structure of and symmetry in Perfect m-ZrO$_2$

Atoms of two elements, Zr and O, are present in m-ZrO$_2$ (Figure 3-1). Based on bonding condition of each atom, they can be further classified:
There is only one type of Zr atom in m-ZrO2. Each Zr atom is bonded with 7 O atoms, 4 of which are of one type, the other 3 of which are of the other type, depending on their bonding conditions with Zr atoms.

There are two types of O atoms. They are stacked layer by layer in a-axis alternatively with the other type of O atoms in-between. O atoms in one layer of them are bonded with 3 Zr atoms, while O atoms in the other type of layers are bonded with 4 Zr atoms. The former O atoms can be termed with O3, while the later O4.

Having known classification of O3 and O4, we continue the discussion of symmetry separately in O3 layers and O4 layers. Ionic bonds are formed between Zr atom and O atom. By measuring atomic separation distance, we classify corresponding bonds into 3 types: longer (L), shorter (S), and connecting (C). Sample bonds of each type are denoted in Figure 3-2.
Figure 3-2: O3 layers can be viewed as being put together by elemental identical subplanes. Each subplane is formed by 4 atoms, including 2 Zr atoms and 2 O atoms. 2 longer bonds and 2 shorter bonds are formed between Zr and O inside each subplane. Bonds located in opposite edges in each quadrangle are of the same type, L or S. Thus each subplane is a parallelogram.

Due to symmetry, each O3 layer can be viewed as being constructed from elemental identical subplanes. Each subplane is formed by 4 atoms, including 2 Zr atoms and 2 O atoms. 2 longer bonds and 2 shorter bonds are formed between Zr and O inside each subplane. Bonds located in opposite edges in each quadrangle are of same type, L or S. Thus each subplane is a parallelogram.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Length(Å) in this study</th>
<th>Bond Length(Å) measured in [50]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longer (L)</td>
<td>2.18</td>
<td>2.17</td>
</tr>
<tr>
<td>Shorter (S)</td>
<td>2.10</td>
<td>2.09</td>
</tr>
<tr>
<td>Connecting (C)</td>
<td>2.07</td>
<td>2.07</td>
</tr>
</tbody>
</table>

Table 3.1: Three types of Zr-O bonds in O3 layer. Longer bonds and shorter bonds are inside each subplane as being squared by dashed lines. Neighboring subplanes are connected by connecting bonds.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Angle between neighboring bonds(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longer (L) ↔ Shorter (S)</td>
<td>105.1</td>
</tr>
<tr>
<td>Longer (L) ↔ Connecting (C)</td>
<td>83.2</td>
</tr>
<tr>
<td>Shorter (S) ↔ Connecting (C)</td>
<td>87.3</td>
</tr>
</tbody>
</table>

Table 3.2: Angles between neighboring bonds in O3 layers
Bonding in O4 layers is of less symmetry. Each O atom in O4 layers is bonded with 4 neighboring Zr atoms. But no obvious symmetry exists: 4 bonds connecting with each O atom varies in length, ranging from 2.19 Å to 2.31 Å.

![Figure 3-3: O-Zr bond configuration in O4 layer](image)

As has been mentioned in the former bonding subsection, O3 layers can be viewed as being constructed by elemental subplanes due to symmetry. The microscopic bonding conditions of corresponding atoms in each subplanes are the same. But these subplanes can be further categorized into 2 types based on their normal direction. We can name those share normal direction (0.4753, -0.7512, -0.4579) as α subplane, while those share normal direction (-0.4764, -0.7474, 0.4631) as β subplane. In Figure 3-2, one α subplane is squared by longer dashed lines, while one β subplane is squared by shorter dashed lines. α subplanes and β subplanes are stacked inter between inside each O3 layer.

<table>
<thead>
<tr>
<th>Subplane</th>
<th>Normal direction(normalized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>(0.4753, -0.7512, -0.4579)</td>
</tr>
<tr>
<td>β</td>
<td>(-0.4764, -0.7474, 0.4631)</td>
</tr>
</tbody>
</table>

Table 3.3: Two types of subplanes exist in O3 layers, with two different normal directions

To propose possible stable sites for hydrogen to take, we can look at valance electrons distribution. Higher distribution of valence electrons correspond to sites for proton to take with more chances, compared to the lower distribution of valence electrons. Results of valence electron distribution can be visualized in Figure 3-4, where thick yellow isosurfaces surrounding
atom site correspond to higher valence electron distribution, while thin blue isosurfaces surrounding Zr atom site correspond to scarce valence electron distribution.

A more quantitative analysis is as following. In our calculation, $4s^2 4p^6 4d^2 5s^2$ for Zr (12 electrons), $2s^2 2p^4$ for O (6 electrons) are treated as valence electrons. 32 Zr atoms and 96 O atoms ($2 \times 2 \times 2$ of unit m-ZrO$_2$ cell) are included in the computational cell, thus $32 \times 12 + 64 \times 6 = 768$ electrons are to be distributed in each cell. Bader analysis gives the electron belonging result as in Table 3. 4.

<table>
<thead>
<tr>
<th>Atom</th>
<th># Atom</th>
<th># Valence electrons</th>
<th>Effective Charge State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>32</td>
<td>~9.42</td>
<td>+2.58</td>
</tr>
<tr>
<td>O3</td>
<td>32</td>
<td>~7.26</td>
<td>-1.26</td>
</tr>
<tr>
<td>O4</td>
<td>32</td>
<td>~7.32</td>
<td>-1.32</td>
</tr>
<tr>
<td>Sum</td>
<td>96</td>
<td>768</td>
<td>Neutral</td>
</tr>
</tbody>
</table>

Table 3. 4: Valence electron distribution and charge state of each atoms

The proton, with positive effective charge state, tends to bond with O atoms with negative effective charge state, while is repulsed away from Zr atom with positive effective charge state. An O-H bond is usually formed when a proton is present.

3.3 Stable sites for hydrogen to take at static state

Before searching for possible stable sites for hydrogen to take, it is necessary to find out in what form, or charge states to be specific, hydrogen takes when it is present in m-ZrO$_2$ matrix. Here we include results from Youssef [36], where intrinsic and possible H defects are included in the
m-ZrO$_2$ system with constraint of charge-neutrality. Concentrations of each defect after reaching equilibrium are determined using formation energies of all defects competing for the identical site, assuming Boltzmann distribution is obeyed. The predominant forms for hydrogen to present in m-ZrO$_2$ are H$^+$ and H$_{2zr}^-$. The former is a proton interstitial, while the latter is equivalent to proton sitting at a Zr vacancy with charge -4. We will discuss the latter case in the part of hydrogen diffusion in m-ZrO$_2$ sites with vacancy. In this section, hydrogen is treated as in the form of proton when present in perfect m-ZrO$_2$ sites.

To propose possible stable sites for a proton to take, we have looked at valance electrons distribution. Proton would prefer to stay closer to O and form O-H bond rather than Zr due to Columb forces between charges. Depending on O site type-03 or 04 we can divide our study into (1) stable hydrogen sites bonded with 03, (2) stable hydrogen sites bonded with 04.

3.3.1 **Stable hydrogen sites bonded with 03**

Due to symmetry, all possible stable sites for proton to take are equivalent to stable sites corresponding to a four-atom subplane. Four stable sites have been found in each subplane, or elemental plane.

We denote them with 1, 2, 3 and 4. Their configurations and bonding schemes are depicted in Figure 3-5. O-H bonds formed by hydrogen at stable sites 1, 4 are of the same length. O-H bonds formed by hydrogen at stable sites 2, 3 are of the same length.
Figure 3-5: In O3 layer, a proton can take four stable sites by forming O-H with O atom. We denote them with 1, 2, 3 and 4, whose configurations are depicted in (1), (2), (3) and (4) correspondingly. Large green, small red and little gray spheres represent Zr, O, and H atoms, respectively.

**Bond length**

<table>
<thead>
<tr>
<th>H site</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 4</td>
<td>0.984</td>
</tr>
<tr>
<td>2, 3</td>
<td>0.991</td>
</tr>
</tbody>
</table>

Table 3.5: O-H bonds formed by hydrogen at stable sites 1, 4 are of the same length. O-H bonds formed by hydrogen at stable sites 2, 3 are of the same length. This is consistent with the symmetry property of O in subplane: hydrogen 1, 4(2, 3) are bonded with O atoms of same bonding configuration.

**Angles between bonds**

In addition to bond length, angles between newly formed O-H and O-Zr bonds, which can be longer (L), shorter (S), and connecting (C) types, have been measured. Results are listed in Table 3.6. It is confirmed that symmetry maintains between stable hydrogen sites 1(2) and 4(3).
Table 3.6: Angles between bonds, where O-Zr are of longer (L), shorter (S), and connecting (C) as denoted in Figure 3-2, while O-H are of 1, 2, 3, 4 as denoted in Figure 3-5 for different hydrogen sites. Since the presence of hydrogen break the symmetry of subplane, only bonds connecting to O that are bonded with the hydrogen are included here. Results are consistent with the argument that hydrogen site 1 is equivalent to site 4; site 2 is equivalent to site 3.

<table>
<thead>
<tr>
<th>Angle between</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>L</th>
<th>S</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>109.2</td>
<td>98.7</td>
<td>98.6</td>
<td>108.9</td>
<td>-</td>
<td>102.3</td>
<td>106.8</td>
</tr>
<tr>
<td>S</td>
<td>92.2</td>
<td>86.5</td>
<td>86.5</td>
<td>92.2</td>
<td>102.3</td>
<td>-</td>
<td>147.9</td>
</tr>
<tr>
<td>C</td>
<td>90.7</td>
<td>108.0</td>
<td>108.0</td>
<td>90.9</td>
<td>106.8</td>
<td>147.9</td>
<td>-</td>
</tr>
</tbody>
</table>

**Electron distribution around O-H, charge state**

<table>
<thead>
<tr>
<th>Stable H sites</th>
<th>#Valence electrons around O, bonded with the H (Charge state)</th>
<th>#Valence electrons around H (Charge state)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.288(-1.288)</td>
<td>0.405(+0.595)</td>
</tr>
<tr>
<td>2</td>
<td>7.294(-1.294)</td>
<td>0.398(+0.602)</td>
</tr>
<tr>
<td>3</td>
<td>7.293(-1.293)</td>
<td>0.399(+0.601)</td>
</tr>
<tr>
<td>4</td>
<td>7.281(-1.281)</td>
<td>0.413(+0.587)</td>
</tr>
</tbody>
</table>

Table 3.7: Bader analysis Electron distribution around O, H and corresponding effective charge state. Results at site 1 and 4 are close. Results at site 2 and 3 are close.

Given the following measured equivalencies between 1 and 4, 2 and 3

1. Bond length
2. Angles between O-H and O-Zr; Angles between O-Zr and O-Zr in corresponding cases.
3. Electron distribution and effective charge state

We conclude that hydrogen sites 1 is equivalent to 4, 2 is equivalent to 3.

**3.3.2 Hydrogen bonded with 04**

Hydrogen can also bond with 04. From Figure 3-6, there are at least three stable sites for hydrogen to take in 04 planes. We compare their total energy with those where hydrogen stays bonded with 03, in Table 3.8.
In 04 layers, we proposed four possible sites for H to take and have them relaxed. The relaxed configurations are depicted in (A), (B), (C) and (D). As can be noticed, (A) and (B) are identical after relaxation.

**Comparison between stable H sites bonded with 03 and 04**

It is revealed from Table 3.8 that energies of stable H sites bonded with 04 are at least 0.5 eV (C) higher than the most stable H site, 2(03). Thus the probability for hydrogen to take a H site bonded with 04, compared with energy of those bonded with 03, is

<table>
<thead>
<tr>
<th>Hydrogen sites (03/04)</th>
<th>Total energy (Relative to the lowest, eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 4 (03)</td>
<td>0.0475</td>
</tr>
<tr>
<td>2, 3 (03)</td>
<td>0</td>
</tr>
<tr>
<td>A, B (04)</td>
<td>0.678</td>
</tr>
<tr>
<td>C (04)</td>
<td>0.504</td>
</tr>
<tr>
<td>D (04)</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table 3.8: Energy comparison between possible H sites bonded with 03 and H sites bonded with 04

\[
\frac{P(C(04))}{P(2(03))} = \frac{\exp\left(-\frac{E(C(04))}{kT}\right)}{\exp\left(-\frac{E(2(03))}{kT}\right)} = \exp\left(-\frac{E(C(04))-E(2(03))}{kT}\right) = \exp\left(-\frac{0.504eV}{kT}\right)
\]

At 300°C, the probability ratio would be around 6×10⁻⁵. Even at 1000°C, the probability ratio would be less than 3×10⁻³. We consider for the most of time, hydrogen would migrate inside 03 layer. Even for some time hydrogen can bond with 04, it would immediately hop to a nearest stable hydrogen site bonded with 03, due to a big energy drop. We can safely ignore H staying at
relative stable sites where it is bonded with O4. In further discussions, we assume hydrogen only bonds with O3 atoms and diffuse inside O3 layer.

3.4 Kinetically how proton hops or rotates from one stable site to another

In this section, we only consider H diffusion inside a O3 layer, due to the relative hardness for H to take a H site in O4.

In order to migrate in Zr oxide, hydrogen atom has to hop from bonding with one O atom to another, in the meantime O-H bond breaks and reforms. Or O-H bond rotates without breaking but changes its direction and sometimes length as well.

Having known the relative stable sites for hydrogen to take, we are interested in knowing how hydrogen migrates from one stable site to another. By setting stable starting configuration and ending configuration, we can use nudged elastic bands method[44] to solve for the most likely diffusion paths, and find the energy barrier to overcome in order for the diffusion to occur. An explanation on how nudged elastic works can be referred to in section 3.1.2.

Due to symmetry, as we have discussed in section 3.3.1, proton site 1 is equivalent to site 4, site 2 is equivalent to site 3. There are only 3 non-equivalent cases of migration from one site to another inside each subplane: 1) $i \rightarrow j$, 2) $i \rightarrow 3$, 3) $i \rightarrow 4$. Any other migrations are equivalent to one of these 3 migrations. E.g. 4$\rightarrow$3 is the same as 1$\rightarrow$2. Since $i \rightarrow j$ is exactly the reverse of $j \rightarrow i$, only one calculation is needed for each case and its reverse case.
### 3.4.1 Hopping: 1→3

Since 1 is equivalent to 4, 3 is equivalent to 2, the study of hopping from 1→3 can cover the paths of 4→2 and corresponding reverse paths as well.

Using nudged elastic bands method\cite{44} (details of this method can be referred to in section 3.1.2), by inserting 3 images and locating the migration path, we can find the diffusion barrier to overcome in order for a proton to hop from site 1 to site 3.

![Figure 3- 7: Trajectory of proton hopping from starting configuration 1 to ending configuration 3. Details on two stable sites 1, 3 can be referred in section section 3.3.1. Three intermediate configurations are reaped using nudged elastic band method.](image)

A climbing image method\cite{44} is used, thus one of the images, 02, with highest energy is driven to the saddle point. The difference between energies of images 00 and 02 is the barrier for forward (1 → 3) hopping, while the difference between energies of images 02 and 04 is the barrier for backward (3 → 1) hopping. The forward barrier is 0.468 eV, while the backward barrier is 0.421 eV (Figure 3- 8).
An interesting phenomenon worth mentioning here is the saddle point configuration. For the convenience of elaborating, we denote O atom bonded with hydrogen in image 00 as \( O_1 \), the O atom bonded with hydrogen in image 04 as \( O_f \). Proton doesn't form bond with \( O_f \) as soon as or before breaking bond with \( O_1 \). Proton actually forms bond with another O (Figure 3-7 (c)). The O-H bond length at the saddle point is measured to be 0.996\( \text{Å} \), a little longer than that of H site 1/4(0.984\( \text{Å} \)) and that of H sites 2/3(0.991\( \text{Å} \)).

![Energy barrier](image)

Figure 3-8: Energy barrier for a proton to go from 1 to 3 is 0.468eV, while the energy barrier for a proton to migrate from 3 to 1 is 0.421eV.
3.4.2 Rotation: 1 → 2

Due to symmetry, study of 1 → 2 can cover 4 → 3 and their corresponding reverse paths as well.

![Diagram of proton hopping from configuration 1 to configuration 2.](image)

Figure 3-9: Trajectory of proton hopping from starting configuration 1 to ending configuration 2. Details on two stable sites 1, 2 can be referred in section 3.3.1. Three intermediate configurations are reaped using nudged elastic band method. This specific trajectory pass through the angle between S type O-Zr bond and C type O-Zr bond.

In rotation path O-H bond doesn’t break. Proton rotates around the hydrogen to move to the other stable H sites.

The energy barrier for the forward path from 1 to 2 is 0.468 eV, while the energy barrier for the backward path from 2 to 1 is 0.421 eV. The energy diagram is in Figure 3-10.
Figure 3-10: Energy barrier for a proton to go from 1 to 2 is 0.468 eV, while the energy barrier for a proton to go from 2 to 1 is 0.421 eV.

However, there's a query why H takes the path crossing the angle between Zr-O shorter and connecting bonds, while there should be chances that H takes the path crossing the angle between Zr-O longer and connecting bonds. Now we compare the barriers for proton to overcome for rotation paths in each case.
3.4.3 Alternative rotation path: 1 →* 2

The alternative rotation paths share exactly the same starting and ending configurations with the formal one in Error! Reference source not found., while the intermediate images are rather different. H takes the path crossing the angle between Zr-O longer and connecting bonds.

Figure 3-11: Trajectory of proton hopping from starting configuration 1 to ending configuration 2. Details on two stable sites 1, 2 can be referred in section section 3.3.1. Three intermediate configurations are reaped using nudged elastic band method. This specific trajectory pass through the angle between L type O-Zr bond and C type O-Zr bond.

The energy barrier for the alternative forward path from 1 to 2 is 1.389 eV, while the energy barrier for the alternative backward path from 2 to 1 is 1.342 eV. The energy diagram is in Figure 3-12.
Figure 3-12: Energy barrier for a proton to go from 1 to 2 is 1.389eV, while the energy barrier for a proton to go from 2 to 1 is 1.342eV.

It turns out that in order to take the alternative path (crossing the angle between Zr-O longer and connecting bonds), the energy barrier to overcome is \(1.389\text{eV} - 0.468\text{eV} = 0.921\text{eV}\) higher than that of taking the original path (the angle between Zr-O shorter and connecting bonds), which corresponds to \(\exp\left(-\frac{0.921\text{eV}}{kT}\right)\) relative probability. At 300°C, it is around \(8 \times 10^{-9}\) times of the probability of taking the original path. In other words, proton would cross the angle between Zr-O shorter (S) and connecting (C) bonds, instead of crossing the angle between Zr-O longer (L) and connecting (C) bonds.
3.4.4 Hopping: 1 → 4

Due to symmetry, study of 1 → 4 cannot cover 2 → 3. But both 1 → 4 and 2 → 3 path call for the proton to squeeze through the window formed by 2 Zr and 2 O atoms. They should share the same saddle point configuration. In this subsection we study the path 1 → 4.

Starting configuration and ending configuration of path 1 → 4 are depicted in Error! Reference source not found.. The shortest migration path is the one squeezing through the subplane.

Using NEB, we can get 3 intermediate images in the shortest migration path, as in Figure 3-13.

![Diagram of proton hopping](image)

Figure 3-13: Trajectory of proton hopping from starting configuration 1 to ending configuration 4. Details on two stable sites 1, 4 can be referred in section section 3.3.1. Three intermediate configurations are reaped using nudged elastic band method. This trajectory squeezes through the window formed by 2 O atoms and 2 Zr atoms.

From image 02, we can find the proton inside the subplane, in between 2 O atoms and 2 Zr atoms. However, energy of saddle point configuration is rather unstable, around 1.558 eV higher than that of 1 or 4, see Figure 3-14.
Figure 3-14: Energy barrier for a proton to go from 1 to 4 or reverse path is 1.558 eV. 1 is of the same energy with 4. The forward and backward barriers are the same.

The diffusion barrier corresponding to the path across the subplane is so high that it is energetically inhibited. There's only tiny energy difference (< 0.05 eV << 1.558 eV) between 1 (4) and 2 (3). The migration between 2 and 3 across the subplane is also energetically inhibited.

3.4.5 Hopping between subplanes

So far we have exhausted possible paths inside any subplane in O3. In order for a proton to diffuse in a long distance (longer than the distance between two neighboring O atoms), proton needs to hop from one subplane to a neighboring subplane, and continue hopping or rotating. In this section, we are going to discuss proton hopping inter subplanes.

Similar to former discussions of inner subplane diffusion, we choose starting configuration and ending configuration. The only difference is that starting configuration and ending configuration are in neighboring subplanes instead of in the same subplane now.

Although this diffusion path includes two subplanes, the migration is relatively easier than inner subplane diffusion. The energy barrier is only 0.268 eV forwardly (from a 2(3) in one subplane to
a 1(4) in a neighboring subplane) and 0.220 backwardly (from a 1(4) in one subplane to a 2(3) in a neighboring subplane).

Figure 3-15: Trajectory of proton hopping from starting configuration 2 in one subplane to ending configuration 4 in the neighboring subplane. Details on two stable sites 2, 4 can be referred in section section 3.3.1. Three intermediate configurations are reaped using nudged elastic band method.
Figure 3-16: Energy barrier for a proton to go from a 2(3) site in one subplane to a 1(4) site in a neighboring subplane is 0.268 eV, while the reverse path gives a 0.220 eV energy barrier.

Figure 3-17: Any long distance diffusion can be constructed from elemental hopping and rotating paths. Barriers for each elemental path have been denoted in the schematic plot. Dashed line corresponds to hopping from one subplane to the neighboring subplane. Solid lines correspond to subplanes with two different normal directions as discussed in Table 3.3. Hopping between subplanes are easiest with barriers of only 0.2 to 0.3 eV, while hopping inside subplane and rotating are harder with barriers of 0.4 to 0.5 eV.

3.4.6 Summary

In perfect m-ZrO$_2$, stable H sites are of high symmetry, which shall break when doping sites are present as will be discussed in the next Chapter. Elemental diffusion paths, whose barriers are
less than 0.5 eV, are limited to 2 hopping paths (an old H-O breaks, a new H-O forms) and 1 rotation (the H-O bond doesn't break). Every long distance diffusion path can be constructed from these three elemental diffusion steps. Alternative diffusion steps are of too large barriers (> 1eV), we consider them energetically impeding to be taken.

To sum, proton will take one of four stable sites by bonding with one of the O atoms in O3 plane. Long distance diffusion is constructed by 3 hopping and 1 rotating elemental paths, among which, the hopping inside subplanes and rotating are the diffusion limited steps, with the barriers of 0.421eV and 0.468eV. Diffusion between subplanes is relatively easier, with diffusion barrier of only 0.268eV and 0.220eV. Starting from the next Chapter, intrinsic defects and defects due to dopants are included, to find their effects on hydrogen diffusion.
Chapter 4 : Hydrogen diffusion in defected m-ZrO$_2$

Zircaloy-2 and Zircaloy-4 are listed in ASTM B 811[17] standard for usage as cladding tubes. As has been listed in Table 2.1, Sn, Fe, Cr and Ni are added to Zirconium when Zircaloy-2 is fabricated. In Zircaloy-4, Ni is removed. Only a few ppm of alloying elements are added into the alloy without impacting neutron absorption performance. The effect of alloying element on hydrogen pickup has been studied, see Figure 2-1. The peak exhibits the detrimental effect upon hydrogen pickup due to adding of nickel. For this reason Ni is removed in Zircaloy-4. For similar reasons, the knowledge of how each alloying elements can affect hydrogen diffusion in oxide will be helpful to design alloying composition in the aspect of hydrogen pickup.

Fe, Cr and Ni, as eutectoid elements, were added accidentally by a stainless steel spoon, which turned out to an enhancement in corrosion resistance. Sn can mitigate the deleterious effect of nitrogen impurity, and has positive impact on mechanical properties. Nb is also included in Zr-Nb alloy in cladding in Russian PWRs and BWRs. For their prominent performance in aspects other than hydrogen pickup, it is necessary to find out their performance in the aspect of hydrogen pickup. In this chapter, we study hydrogen migration in the presence of these elements. In addition to Fe, Ni, Cr, Sn and Nb, we also study U as alloying element, to complete the discussion on how size of these alloying elements can affect hydrogen diffusion. The form of alloying elements in Zircaloy is complicated. Alloying elements either dissolve in Zirconium matrix or precipitate as different phases with varied sizes. The sizes of the precipitates play an important role in affecting corrosion resistance and there are special thermo-mechanical treatment to control the precipitate size distribution [10].

The size and the charge of the alloying elements that dissolve into m-ZrO$_2$ can impact the stability and mobility of hydrogen defects. We choose to systematically study the size and charge effect, by assessing the effect of the cations listed in Table 4.1
Since our study focuses on m-ZrO₂ phase, the alloying elements are introduced into m-ZrO₂ as dopant cations. Their charge states are examined and summarized in Table 4.1. Then hydrogen is introduced to find the variation on its diffusion paths and barriers when alloying/dopant defects are present. Results are presented in the following sections.

In order to find the dominant defects in m-ZrO₂ system, with and without doping, we refer to Figure 1 in the study of predominant native and hydrogen defects at equilibrium[36]. At higher $P_{O_2}$ (>10⁻¹¹ atm), $H_{Zr}^{'''''}$ dominates and at lower $P_{O_2}$ (<10⁻¹ atm), $H_{Zr}^{'''}$ predominates. Through comparing the results of undoped m-ZrO₂ and hydrogen only doped cases, the increasing concentration of $V_{Zr}^{'''''}$ absorbs proton and becomes $H_{Zr}^{'''''}$. It is reasonable that $H_{Zr}^{'''}$ concentration is at least one order of magnitude smaller than $H_{Zr}^{'''''}$. $V_{Zr}^{'''''}$ is also several orders of magnitude smaller.

### 4.1 The presence of native defect $V_{Zr}^{'''''}$

Firstly, we examine the interaction between a proton and $V_{Zr}^{'''''}$, to study what role does $V_{Zr}^{'''''}$ play regarding migration of proton.

There's only one type of Zr atom in m-ZrO₂. Bonding condition for each Zr atom is the same. Each Zr atom is bonded with 4 04 and 3 03 atoms, making its coordination number 7. Ionic radius for Zr at charge +4 with coordination 7 is 0.78Å[51].

<table>
<thead>
<tr>
<th>M</th>
<th>Dominant charge</th>
<th>Shannon ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Ni₃ₓ[Zr]</td>
<td>0.48</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr₃ₓ[Zr]</td>
<td>0.55</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe₃ₓ[Zr]</td>
<td>0.58</td>
</tr>
<tr>
<td>Nb</td>
<td>Nb₃ₓ[Zr]</td>
<td>0.69</td>
</tr>
<tr>
<td>Sn</td>
<td>Sn₃ₓ[Zr]</td>
<td>0.75</td>
</tr>
<tr>
<td>Zr</td>
<td>Zr₃ₓ[Zr]</td>
<td>0.78</td>
</tr>
<tr>
<td>U</td>
<td>U₃ₓ[Zr]</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 4.1: Dominant charge state[36] of dopants in m-ZrO₂ and their Shannon ionic radius[51].
At steady image, energies of stable sites for proton to take are calculated after relaxation. It turns out at least 3 sites (v1, v2, v3 in Figure 4-1) can be taken by proton through bonding with one of three neighboring Oxygen. We also compare trapping energies of proton inside V''''_{Zr} (v1, v2, v3 in Figure 4-1) and proton staying away from V''''_{Zr} (nv1, nv2 in Figure 4-1). Details of how to calculate trapping energy can be referred to in subsection 3.1.4

Figure 4-1: Relative stable sites for proton to take, inside V''''_{Zr} (v1, v2 and v3), and outside V''''_{Zr} (nv1, nv2). Large green, small red represent Zr and O atoms, respectively. Smallest colors represent the proton at different sites.

<table>
<thead>
<tr>
<th>Protonic sites inside V''''_{Zr}</th>
<th>Trapping Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v1</td>
<td>-0.986</td>
</tr>
<tr>
<td>v2</td>
<td>-1.222</td>
</tr>
<tr>
<td>v3</td>
<td>-1.232</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Neighboring sites outside V''''_{Zr}</th>
<th>Trapping Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nv1</td>
<td>0.182</td>
</tr>
<tr>
<td>nv2</td>
<td>0.145</td>
</tr>
</tbody>
</table>

Table 4.2: Trapping energy comparison between stable sites that proton can take, when V''''_{Zr} presents in m-ZrO₂. v1, v2 and v3 denote stable proton sites inside V''''_{Zr}, while nv1, nv2 denote stable proton sites outside V''''_{Zr}.

From Table 4.2, protonic sites inside V''''_{Zr} are very strong (~-0.1eV) trapping sites for a proton. To make a comparison, we have found the variances in energies of 4 stable proton sites in perfect m-ZrO₂ are within only 0.04eV. The physical meaning is that once a proton has managed to move into a V''''_{Zr}, the proton will merge with vacancy and form H''''_{Zr}. The energy of latter merged
configuration is 1.4eV lower than that of the proton and \( V'\) being separated. This result is consistent with the study at equilibrium. The three trapping sites inside vacancy \( V''\) are of similar trapping energies, with 0.01eV and 0.3eV energy differences. However, for stable proton sites outside but in vicinity of the vacancy \( V''\) (nv1, nv2), the trapping energies are positive, i.e. they are more unstable than the energy of a proton presenting in a region free of vacancy \( V''\). As we will compare with dopants sites in later sections, \( V''\) is the strongest trapping sites that we have surveyed.

Then is it easy for proton to migrate into the \( V''\) trap? This question can be resolved by studying the diffusion barrier of the path for proton to get into \( V''\). Nudged elastic band method is used to study possible diffusion paths for proton to get into \( V''\).

One path of proton hopping from one stable site (v1) inside \( V''\) to the other (v2) and two possible paths of leaving \( V''\) for (entering \( V''\) from) nearby perfect site (nv1, nv2) are studied.

<table>
<thead>
<tr>
<th>Path</th>
<th>Forward Barrier (eV)</th>
<th>Backward Barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v1 → v2</td>
<td>0.62</td>
<td>0.90</td>
</tr>
<tr>
<td>v3 → nv1</td>
<td>3.06</td>
<td>1.60</td>
</tr>
<tr>
<td>v3 → nv2</td>
<td>1.67</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 4: Diffusion barriers for a proton moving around \( V''\). v1 → v2 is a path of a proton hopping inside \( V''\). v3 → nv1/nv2 are paths of a proton leaving or approaching (reverse direction) \( V''\).

Leaving from the trap for a nearby perfect site is hard, from energy comparison between starting and final configuration, and it is even harder when the barrier is considered. The smallest barrier to overcome in order to exit the trap is 1.67eV, while the smallest barrier to overcome to enter the trap is only 0.25eV, smaller than most diffusion barriers of proton diffusion in perfect m-ZrO\(_2\) region, see Figure 3-17. So there's no excess energy barrier to overcome to enter a \( V''\) trap, if compared with conventional diffusion in perfect matrix. But once proton meets an untaken \( V''\) and has fallen into the trap, it is extremely hard for the proton to exit the trap and become a free proton again. To sum, \( V''\) is a trap for proton migration.

### 4.2 Sn doping

Sn (Tin) takes 1.20-1.70%wt in Zircaloy-2 and Zircaloy-4, the highest concentration in Zircaloy except Zr.
We learn from Youssef's study [36] that the predominant Sn defect is \( \text{Sn}^x_{\text{Zr}} \). At 600K, \( \text{Sn}^x_{\text{Zr}} \) can dissolve to over 0.01% wt. Other Sn related defects are with lower concentration than most intrinsic defects \((10^{-14})\), which can be safely ignored. Thus, we consider hydrogen diffusion when \( \text{Sn}^x_{\text{Zr}} \) is present.

From Kröger-Vink diagram, there's no need for any charged defects to compensate the presence of \( \text{Sn}^x_{\text{Zr}} \) in order to keep charge-neutrality since its charge state is 0. At equilibrium, \( \text{Sn}^x_{\text{Zr}} \) is energetically favorable to form. Now we look at how hydrogen or proton interacts with \( \text{Sn}^x_{\text{Zr}} \). Other than induced charge redistribution when a +1 charge proton present, there's no charge repulsion or attraction force due to neutral \( \text{Sn}^x_{\text{Zr}} \).

\( \text{Sn}^x_{\text{Zr}} \) can be viewed as combination of \( \text{Sn}^{4+} \) and \( \text{V}''``\text{Zr} \). We remove a \( \text{Zr}^{4+} \) from the perfect m-\( \text{ZrO}_2 \), and have \( \text{Sn}^{4+} \) added to the \( \text{V}''``\text{Zr} \) which used to be taken by a \( \text{Zr}^{4+} \), as \( \text{Zr}^x_{\text{Zr}} \). Size of Sn at charge +4 with coordination number of 7 is of radii \( 0.75\AA \)[51], almost the same as that of Zr at charge +4 with coordination number of 7.

We examine proton diffusion in \( \text{O}_3 \) plane.

![Figure 4-2: Relative stable sites for proton to take, when \( \text{Sn}^x_{\text{Zr}} \) presents. 1, 2, 3, 4, 5 and 6 are six stable proton sites bonded with \( \text{O}_3 \) which are directly bonded with \( \text{Sn}^x_{\text{Zr}} \). n1, n2 and n3 are three sub nearest](image)
proton sites to $\text{Sn}^{X}_{\text{Zr}}$ that protons at 4, 5, and 6 can hop to in which way protons migrate away from $\text{Sn}^{X}_{\text{Zr}}$. Large light green, large grass green, small red represent Zr, Sn and O atoms, respectively. Smallest colors represent proton at different sites.

The presence of Sn leads to 1-6 six protonic sites near $\text{Sn}^{X}_{\text{Zr}}$ with trapping energies ranging from -0.109eV to -0.225eV. Comparing typical diffusion path 1 $\rightarrow$ 2, the change is within 0.02eV. The barrier for proton to overcome to leave (approach) Sn is almost the same to the barrier for proton to migrate between subplanes in undefected m-ZrO$_2$ region.

Since there's little charge effect, we focus on size effect. The radius of Sn with identical charge and coronation number, 0.75Å is almost the same as the radii of Zr, 0.78Å. There's no space distortion around the substituted Sn. Size effect should be little, and indeed proton migration around Sn is similar to migration around Zr, comparing Table 4. 5 and Figure 3-17.

![Table 4. 4: Trapping energy comparison between possible stable proton sites that are closest to $\text{Sn}^{X}_{\text{Zr}}$. Among them, proton site 6 is the strongest proton trap site, with trapping energy -0.225eV.](image)

<table>
<thead>
<tr>
<th>Paths</th>
<th>Forward Barrier(eV)</th>
<th>Backward Barrier(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $\rightarrow$ 2</td>
<td>0.437</td>
<td>0.476</td>
</tr>
<tr>
<td>4 $\rightarrow$ n1</td>
<td>0.222</td>
<td>0.250</td>
</tr>
<tr>
<td>5 $\rightarrow$ n2</td>
<td>0.327</td>
<td>0.205</td>
</tr>
<tr>
<td>6 $\rightarrow$ n3</td>
<td>&lt;0.279</td>
<td>&lt;0.246</td>
</tr>
</tbody>
</table>

Table 4. 5: Diffusion barriers for proton moving around $\text{Sn}^{X}_{\text{Zr}}$. 1 $\rightarrow$ 2 is the path of proton rotating around $\text{Sn}^{X}_{\text{Zr}}$. 4 $\rightarrow$ n1, 5 $\rightarrow$ n2, 6 $\rightarrow$ n3 are three paths of proton leaving or approaching (reverse direction) $\text{Sn}^{X}_{\text{Zr}}$.

4.3 Fe doping

Fe is also added to Zircaloy: 0.07-0.20%wt in Zircaloy-2 and 0.18-0.24%wt in Zircaloy-4. We examine Fe dissolved in m-ZrO$_2$ in a dilute limit.

59
We learn from equilibrium study that Fe$_{2r}^X$ dominates when equilibrium is reached[36]. Concentrations of other possible charge states like Fe$_{2r}^Z$, Fe$_{2r}^J$ are at least one order of magnitude smaller. Thus, we consider hydrogen diffusion when Fe$_{2r}^X$ present.

From Kröger-Vink diagram in Youssef's results [36], neutral Fe$_{2r}^X$ doesn't need any charged defects for compensation in order to keep charge-neutrality, since its charge state is 0. At equilibrium, Fe$_{2r}^X$ is energetically favorable to form. This result is at equilibrium. Now we look at how hydrogen or proton migration changes when Fe$_{2r}^X$ presents. There's no charge repulsion or attraction due to neutral Fe$_{2r}^X$ other than induction force as charge redistributes when a +1 charged proton presents near Fe$_{2r}^X$.

Fe$_{2r}^X$ can be viewed as combination of Fe$^{4+}$ and V$_{2r}''''$. A Zr$^{4+}$ is removed from m-ZrO$_2$, and Fe$^{4+}$ is inserted in the V$_{2r}''''$. Shannon ionic radius[51] of Fe at charge +4 with coordination of 6 is 0.58Å, smaller than that of Zr at charge state +4 with coordination of 7, 0.78Å.

We examine proton diffusion in O3 plane.

Figure 4- 3: Relative stable sites for proton to take, when Fe$_{2r}^X$ presents. 1, 2, 3, 4, 5 and 6 are six stable proton sites bonded with O3 atoms which are directly bonded with Fe$_{2r}^X$. n1, n2 and n3 are three sub nearest proton sites to Fe$_{2r}^X$ that protons at 4, 5, and 6 can hop to in which way protons migrate away from Fe$_{2r}^X$. Large green, medium gold, small red represent Zr, Fe and O atoms, respectively. Smallest colors represent proton at different sites.
<table>
<thead>
<tr>
<th>Trapping Energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>

Table 4.6: Trapping energy comparison between possible stable proton sites that are closest to Fe\text{\textgreek{r}}. Among them, proton site 6, 5 are the two strongest proton trap sites, with trapping energy -0.567eV, -0.456eV.

<table>
<thead>
<tr>
<th></th>
<th>Forward Barrier(eV)</th>
<th>Backward Barrier(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>0.151</td>
<td>0.32</td>
</tr>
<tr>
<td>4→n1</td>
<td>0.512</td>
<td>0.237</td>
</tr>
<tr>
<td>5→n2</td>
<td>0.626</td>
<td>0.112</td>
</tr>
<tr>
<td>6→n3</td>
<td>&lt;0.639</td>
<td>&lt;0.220</td>
</tr>
</tbody>
</table>

Table 4.7: Diffusion barriers for a proton moving around Fe\text{\textgreek{r}}. 1 → 2 is the path of proton rotating around Fe\text{\textgreek{r}}. 4 → n1, 5→n2, 6→n3 are three paths of proton leaving or approaching (reverse direction) Fe\text{\textgreek{r}}.

4.4 Cr doping

Cr, one of eutectoids, together with Fe and Ni have been added to the alloy accidentally, but it turns out alloy’s corrosion resistance has been enhanced. In our study here, we examine Cr dissolved in m-ZrO\textsubscript{2} in a dilute limit.

Similarly, we learn from equilibrium study[36] that Cr\textsubscript{\textgreek{x}}\text{\textgreek{r}} dominates when equilibrium is reached. Other possible charge states like Cr\textsubscript{\textgreek{r}} and Cr\textsuperscript{\textgreek{x}}\textsubscript{\textgreek{r}} are at least two orders of magnitude smaller in concentration. Thus, we consider hydrogen diffusion when Cr\textsubscript{\textgreek{x}}\text{\textgreek{r}} presents.

From Kröger-Vink diagram in Youssef's results[36], neutral Cr\textsubscript{\textgreek{x}}\textsubscript{\textgreek{r}} doesn't need any charged defects for compensation in order to keep charge-neutrality, since its charge state is 0. At equilibrium, Cr\textsubscript{\textgreek{x}}\textsubscript{\textgreek{r}} is energetically favorable to form. This result is at equilibrium. Now we look at
how hydrogen or proton interacts with Cr$_{Zr}^X$. To note, there is no charge repulsion or attraction due to neutral Cr$_{Zr}^X$ other than induction force as charge redistributes when a +1 charged proton presents near Cr$_{Zr}^X$.

Cr$_{Zr}^X$ can be viewed as combination of Cr$^{4+}$ and V$^{''''}$. We remove the Zr$^{4+}$ from the perfect m-ZrO$_2$, and have Cr$^{4+}$ inserted in the V$^{''''}$. Radius of Cr at charge +4 with coordination number of 4 or 6 is 0.41 Å and 0.55 Å\[51]\] respectively, smaller than that of Zr at charge +4 with coordination of 7, 0.78 Å.

We examine proton diffusion in O3 plane.

![Figure 4-4](image_url)

Figure 4-4: Relative stable sites for proton to take, when Cr$_{Zr}^X$ presents. 1, 2, 3, 4, 5 and 6 are six stable proton sites bonded with O3 atoms which are directly bonded with Cr$_{Zr}^X$. n1, n2 and n3 are three sub nearest proton sites to Cr$_{Zr}^X$ that protons at 4, 5, and 6 can hop to in which way protons migrate away from Cr$_{Zr}^X$. Large green, medium blue, small red represent Zr, Cr and O atoms, respectively. Smallest colors represent proton at different sites.

<table>
<thead>
<tr>
<th></th>
<th>Trapping Energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.052</td>
</tr>
<tr>
<td>2</td>
<td>0.055</td>
</tr>
<tr>
<td>3</td>
<td>-0.329</td>
</tr>
<tr>
<td>4</td>
<td>-0.319</td>
</tr>
<tr>
<td>5</td>
<td>-0.361</td>
</tr>
<tr>
<td>6</td>
<td>-0.493</td>
</tr>
</tbody>
</table>

Table 4.8: Trapping energy comparison between possible stable proton sites that are closest to Cr$_{Zr}^X$. Among them, proton site 6 is the strongest proton trap site, with trapping energy -0.493 eV.
Table 4.9: Diffusion barriers for a proton moving around \( \text{Cr}_{Zr}^X \). 1 \( \rightarrow \) 2 is the path of proton rotating around \( \text{Cr}_{Zr}^X \). 4 \( \rightarrow n1 \), 5\( \rightarrow n2 \), 6\( \rightarrow n3 \) are three paths of proton leaving or approaching (reverse direction) \( \text{Cr}_{Zr}^X \).

<table>
<thead>
<tr>
<th>Path</th>
<th>Forward Barrier (eV)</th>
<th>Backward Barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1( \rightarrow 3 )</td>
<td>0.172</td>
<td>0.460</td>
</tr>
<tr>
<td>4( \rightarrow n1 )</td>
<td>0.422</td>
<td>0.171</td>
</tr>
<tr>
<td>5( \rightarrow n2 )</td>
<td>0.603</td>
<td>0.301</td>
</tr>
<tr>
<td>6( \rightarrow n3 )</td>
<td>0.639</td>
<td>0.297</td>
</tr>
</tbody>
</table>

4.5 Ni doping

Ni is reported to increase hydrogen pickup fraction to the peak in Figure 4-1. In this section, we examine how Ni affects hydrogen migration in m-ZrO\(_2\), by substituting Zr in charge state \( \text{Ni}_{Zr}^X \). Again, we refer to concentration results at equilibrium from Youssef’s study[36]. The predominant charge state for Ni to take is \( \text{Ni}_{Zr}^X \) at equilibrium.

From Kröger-Vink diagram, \( \text{Ni}_{Zr}^X \) doesn't need any charged defect to compensate its concentration for charge-neutrality, since its charge state is 0. At equilibrium, \( \text{Ni}_{Zr}^X \) is energetically favorable to form. Here we study how hydrogen or proton migration changes when \( \text{Ni}_{Zr}^X \) presents. There is also no charge repulsion or attraction due to neutral \( \text{Ni}_{Zr}^X \) other than induction force as charge redistributes when a +1 charged proton presents near \( \text{Ni}_{Zr}^X \).

\( \text{Ni}_{Zr}^X \) can be viewed as combination of \( \text{Ni}^{4+} \) and \( V_{Zr}'''' \). We remove a \( \text{Zr}^{4+} \) from the perfect m-ZrO\(_2\), and have \( \text{Ni}^{4+} \) inserted in the \( V_{Zr}'''' \). Radius of Ni at charge +4 with coordination number of 6 is 0.48 Å[51], smaller than that of Zr at charge state +4 with coordination of 7, 0.78 Å.

We examine proton diffusion in O\(_3\) plane.
Figure 4-5: Relative stable sites for proton to take, when Ni$_{2zr}^+$ presents. 1, 2, 3, 4, 5, and 6 are six possible stable proton sites that are closest to Ni$_{2zr}^+$. They all serve as proton traps, with negative trapping energy. Among them, proton sites 6, 5, 4 are the 3 strongest proton trap sites, with trapping energies -1.396eV, -1.184eV and 0.883eV, see Table 4.10. Large light green, medium gold, small red represent Zr, Ni and O atoms, respectively. Smallest colors represent proton at different sites.

<table>
<thead>
<tr>
<th></th>
<th>Trapping Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.133</td>
</tr>
<tr>
<td>2</td>
<td>-0.071</td>
</tr>
<tr>
<td>3</td>
<td>-0.269</td>
</tr>
<tr>
<td>4</td>
<td>-0.883</td>
</tr>
<tr>
<td>5</td>
<td>-1.184</td>
</tr>
<tr>
<td>6</td>
<td>-1.396</td>
</tr>
</tbody>
</table>

Table 4.10: Energy comparison between possible stable proton sites that are closest to Ni$_{2zr}^+$. Among them, proton sites 6, 5, 4 are the 3 strongest proton trap sites, with trapping energies -1.396eV, -1.184eV and 0.883eV.

By calculating trapping energies of each possible stable proton sites that are closest to Ni$_{2zr}^+$, we have found three strongest proton trap sites: 6, 5, 4, with trapping energies -1.396eV, -1.184eV and 0.883eV. Then we continue to study barriers to overcome in order for proton to enter or leave such strong proton traps.
Kinetically, we surveyed the proton migration or leaving (approaching) the three deepest traps, 4, 5, and 6. NEB method gives an abnormal energy versus reaction path curve, see Figure 4-6. It turns out the interaction between a proton and the NiIr leads to a large displacement when proton is close enough to NiIr, then a reaction path like Figure 4-6 is resulted. The similar circumstances appear when 5→n2 and 6→n3 is surveyed. It has become a two-body case for Ni. Nevertheless, by comparing energy difference of initial and final configurations, we can reach a safe conclusion that NiIr is a deep trap for proton migration.

<table>
<thead>
<tr>
<th>Paths See Figure 4-5</th>
<th>Energy difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4→n1</td>
<td>0.871eV</td>
</tr>
<tr>
<td>5→n2</td>
<td>1.332eV</td>
</tr>
<tr>
<td>6→n3</td>
<td>1.341eV</td>
</tr>
</tbody>
</table>

Table 4.11: Diffusion barriers for a proton moving around NiIr: 1→2 is the path of proton rotating around NiIr. 1→3 is the path of proton hopping around NiIr. 4→n1 is the path of proton leaving or approaching (reverse direction) NiIr.
4.6 Nb doping

Zr-2.5%Nb (UNS R60901) is used as pressure tube in CANDU reactor[52] as well as advanced alloys for LWRs such as M5[53]. In the study here, we examine dilute levels of Nb dissolved in m-ZrO$_2$, by substituting Zr with Nb in the dominant charge state of Nb$_{2zr}$. Similarly, we refer to concentration results at equilibrium from Otgonbaatar’s[54] and Youssef’s[36] study. The predominant charge state for Nb to take is Nb$_{2zr}^*$. From Kröger-Vink diagram, Nb$_{2zr}^*$ is compensated by V$_{zr}^{**}$. The increasing concentration of V$_{zr}^{**}$ leads to a higher concentration of H$_{zr}^{***}$ after hydrogen join the system. The result is at equilibrium. Now we look at how hydrogen or proton interacts with Nb$_{2zr}^*$. Nb$_{2zr}^*$ can be viewed as combination of Nb$^{5+}$ and V$_{zr}^{**}$. We remove a Zr$^{4+}$ from the perfect m-ZrO$_2$, and have Nb$^{5+}$ inserted in the V$_{zr}^{**}$. Shannon radius of Nb at charge +5 with coordination number of 7 is 0.69Å[51], smaller than that of Zr at charge +4 with coordination number of 7, 0.78 Å.

We still examine proton diffusion in O3 plane.
Figure 4- 7: Relative stable sites for proton to take, when \( \text{Nb}_{\text{Zr}} \) presents. 1, 2, 3, 4, 5, and 6 are six possible stable proton sites that are closest to \( \text{Nb}_{\text{Zr}} \). Only 2 and 4 serve as possible proton traps with tiny (shallower than 0.1 eV) trapping energy, see Table 4. 12. Large light green, medium grass green, small red represent \( \text{Zr}, \text{Nb} \) and \( \text{O} \) atoms, respectively. Smallest colors represent proton at different sites.

The presence of Nb by substituting original Zr doesn't alter energies of nearby stable proton sites too much: energy variances are less than 0.1 eV. Kinetically, we have also studied the diffusion barrier of paths that hydrogen hops and rotates around \( \text{Nb}_{\text{Zr}} \).

<table>
<thead>
<tr>
<th>Trapping Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>

Table 4. 12: Trapping Energy comparison between possible stable proton sites that are closest to \( \text{Nb}_{\text{Zr}} \). Among them, proton site 4 is the strongest proton trap site, with trapping energy -0.087eV.

It turns out that the hopping barrier inside subplane is 0.446eV~0.603eV and 0.234eV~0.270eV for inter subplane, which is within 0.1 eV difference to the original case before Nb substituting Zr.
And one alternation worth noting is the barrier of leaving Nb is increased by 0.016eV while the barrier of approaching Nb remains the same.

<table>
<thead>
<tr>
<th></th>
<th>Forward Barrier(eV)</th>
<th>Backward Barrier(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>0.503</td>
<td>0.603</td>
</tr>
<tr>
<td>1→3</td>
<td>0.446</td>
<td>0.501</td>
</tr>
<tr>
<td>4→n1</td>
<td>0.234</td>
<td>0.269</td>
</tr>
<tr>
<td>5→n2</td>
<td>0.263</td>
<td>0.382</td>
</tr>
<tr>
<td>6→n3</td>
<td>&lt;0.247</td>
<td>&lt;0.524</td>
</tr>
</tbody>
</table>

Table 4.13: Diffusion barriers for a proton moving around Nb<sup>+</sup><sub>Zr</sub>. 1→2 is the path of proton rotating around Nb<sup>+</sup><sub>Zr</sub>. 4→n1, 5→n2, 6→n3 are three paths of proton leaving or approaching (reverse direction) Nb<sup>+</sup><sub>Zr</sub>.

The introduction of Nb causes no severe change to proton migration, although the Nb<sup>+</sup><sub>Zr</sub> is with positive charge state.

### 4.7 U doping

In order to confirm the trend that a smaller dopant size corresponds to a stronger trap, proton migration around U dopant substitutional defect U<sup>x</sup><sub>Zr</sub> is studied, with identical neutral charge state to Sn<sup>x</sup><sub>Zr</sub>, Fe<sup>x</sup><sub>Zr</sub>, Cr<sup>x</sup><sub>Zr</sub>, Ni<sup>x</sup><sub>Zr</sub>, Zr<sup>x</sup><sub>Zr</sub> but a larger Shannon ionic radius.

Neutral U<sup>x</sup><sub>Zr</sub> doesn't need any charged defects for compensation in order to keep charge-neutrality, since its charge state is 0. The most favorable charge state, whether it is U<sup>x</sup><sub>Zr</sub>, U<sup>y</sup><sub>Zr</sub>, U<sup>z</sup><sub>Zr</sub> or other charge state can only be confirmed by systematic calculation of them energetically and Kröger-Vink diagram construction, using same framework in [36]. However we choose U<sup>x</sup><sub>Zr</sub> simply to observe dopant ion’s size effect (radius of U<sup>x</sup><sub>Zr</sub>(0.95Å) with coordination number of 7 is larger than that of Zr<sup>x</sup><sub>Zr</sub>(0.78Å) with same coordination number) on proton diffusion, keeping charge state variable fixed to neutral. There's no charge repulsion or attraction due to neutral U<sup>x</sup><sub>Zr</sub> other than induction force as charge redistributes when a +1 charged proton presents near U<sup>x</sup><sub>Zr</sub>.
We examine proton diffusion in O3 plane.

Figure 4-8: Relative stable sites for proton to take, when U_{Zr}^X presents. 1, 2, 3 and 4 are four stable proton sites bonded with O3 in the subplane where one Zr is substituted by U. 5 is another protonic stable site that is bonded with an O3 atom that is bonded with U_{Zr}^X. n1 denotes a stable proton site away from U_{Zr}^X. Large light green, large grass green, small red represent Zr, U and O atoms, respectively. Smallest colors represent proton at different sites.

Table 4.14: Trapping energy comparison between possible stable proton sites that are closest to U_{Zr}^X. Among them, proton site 1 is the strongest proton trap site, with trapping energy -0.214eV.

<table>
<thead>
<tr>
<th>Trapping Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Forward Barrier (eV)</th>
<th>Backward Barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1→2</td>
<td>0.335</td>
</tr>
<tr>
<td>4→n1</td>
<td>0.408</td>
</tr>
<tr>
<td>5→n2</td>
<td>0.181</td>
</tr>
<tr>
<td>6→n3</td>
<td>0.224</td>
</tr>
</tbody>
</table>
Table 4. 15: Diffusion barriers for proton moving around $U_{Zr}^X$. $1 \rightarrow 2$ is the path of proton rotating around $U_{Zr}^X$. $4 \rightarrow n1$, $5 \rightarrow n2$, $6 \rightarrow n3$ are three paths of proton leaving or approaching (reverse direction) $U_{Zr}^X$.

**Chapter 5: Conclusion**

Proton diffusion inside perfect and defected $m$-$ZrO_2$ was studied. First principles calculations and nudged elastic band method were used to find the stable H sites and the diffusion paths and barriers connecting these stable H sites. Bader analysis was conducted on stable H sites and dopant sites to find their charge state. Bader analysis was also conducted on saddle point configurations (See Appendix A) for each diffusion paths to examine whether charge state changes.

**5.1 Proton diffusion in perfect m-$ZrO_2$**

The combination of total energy, NEB calculation and charge analysis in the case of perfect m-$ZrO_2$ revealed the following results:

- Four stable sites (1, 2, 3, 4), as shown in Figure 3-5, can be taken by proton through bonding with O3. Due to symmetry, 1(2) is equivalent to 4(3).
- Proton can also bond with O4, but with much higher (> 0.5eV) energy than bonding with O3. O3 is the preferential binding layer for protons, therefore the migration is confined to this plane.
- There are only 3 irreducible elemental paths for proton to migrate within the O3 layer. Barriers of diffusion inside the $\alpha$ and $\beta$ subplanes (Figure 3-7, Figure 3-9) are higher (0.42~0.46eV), while barriers of diffusion between the subplanes (Figure 3-13) are lower (0.22~0.26eV).
- Any long distant proton diffusion can be constructed from these 3 paths.

![Diagram of proton diffusion in perfect m-$ZrO_2$](image)

Figure 5-1: Proton diffusion in perfect m-$ZrO_2$
5.2 Proton diffusion around $V_{Zr}'''$ trap

Intrinsic defect $V_{Zr}'''$ was included to study its effect on proton diffusion in its vicinity, and following results have been reached:

- When inside $V_{Zr}'''$, at least three stable sites can be taken by proton through bonding with the nearest O3, with similar total energies (variance $< 0.30$eV).
- Proton staying outside of $V_{Zr}'''$ has much higher (>1.4eV) energy than in vacancy.
- The lowest barrier, among those surveyed, for proton to enter $V_{Zr}'''$ is 0.25eV, similar to the lowest barrier when proton diffuses in perfect ZrO$_2$. No extra energy is needed for proton to enter $V_{Zr}'''$. But the barrier for proton to jump out from $V_{Zr}'''$ is at least 1.67eV. To sum, $V_{Zr}'''$ is a trap for proton diffusion.

From these observations, we can infer an indirect way to affect hydrogen diffusion by doping: doping element can affect concentration of $V_{Zr}'''$, a proton trap. Higher concentration of $V_{Zr}'''$ would impede proton migration in m-ZrO$_2$.

5.3 Proton diffusion around extrinsic defects - dopant cations

Besides the indirect link between alloying addition and hydrogen migration, effects of defects introduced by alloying elements on hydrogen diffusion are studied directly as well.

Dopants either precipitate as another phase in alloy or dissolve into the alloy. We have considered effects of dissolved alloying elements, which then dissolve as dopant cations in m-ZrO$_2$. We first discuss trapping and repulsion energy (details on how to calculate trapping energy can be referred to in section 3.1.4):

5.3.1 Trapping and Repulsion Energy

Trapping energies are summarized in Table 5.1. It is found that:

1. Sites 4, 5, 6 are usually the three deepest traps for Ni$_{Zr}^X$, Cr$_{Zr}^X$, Fe$_{Zr}^X$, Sn$_{Zr}^X$. Among them, 6 is the deepest.
2. Comparing the same site in different dopant cases, e.g site 4, proton trapping energy at site 4 increases as Shannon Radii of dopant ions increase for Ni$_{Zr}^X$ (0.48Å), Cr$_{Zr}^X$ (0.55 Å), Fe$_{Zr}^X$ (0.58Å), Sn$_{Zr}^X$ (0.75Å), Zr$_{Zr}^X$ (0.78Å). Nb$_{Zr}^*$, U$_{Zr}^*$ doesn’t follow the trend, due to charge effect and size effect as explained in the next item.
3. If second nearest proton sites, n1, n2 and n3, are included, see Table 5.1, it turns out none of sites 1-6 are the deepest trap in Nb\textsuperscript{Zr}\textsuperscript{+} or U\textsuperscript{Zr}\textsuperscript{+} cases. n3 becomes the deepest trap in both Nb\textsuperscript{Zr}\textsuperscript{+} and U\textsuperscript{Zr}\textsuperscript{+} cases. Physically, protons prefer to stay nearest to dopant ions when dopant defects are Ni\textsuperscript{Zr}\textsuperscript{+}, Cr\textsuperscript{Zr}\textsuperscript{+}, Fe\textsuperscript{Zr}\textsuperscript{+}, Sn\textsuperscript{Zr}\textsuperscript{+}. But protons wouldn’t approach to the closest proton sites when dopant defects are Nb\textsuperscript{Zr}\textsuperscript{+} and U\textsuperscript{Zr}\textsuperscript{+}, rather protons would stay at n3 at nearest since n3 is a deeper trap in these two cases.

<table>
<thead>
<tr>
<th>Dopant element</th>
<th>Shannon Radii (Å)</th>
<th>Trapping (-) and Repulsion (+) Energy (eV)</th>
<th>At nearest proton sites</th>
<th>At second nearest proton sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>M\textsuperscript{Zr}\textsuperscript{+}</td>
<td>( F_{\text{Shannon}} )</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Ni\textsuperscript{Zr}\textsuperscript{+}</td>
<td>0.48</td>
<td>-0.133</td>
<td>-0.071</td>
<td>-0.269</td>
</tr>
<tr>
<td>Cr\textsuperscript{Zr}\textsuperscript{+}</td>
<td>0.55</td>
<td>-0.052</td>
<td>0.055</td>
<td>-0.329</td>
</tr>
<tr>
<td>Fe\textsuperscript{Zr}\textsuperscript{+}</td>
<td>0.58</td>
<td>-0.252</td>
<td>-0.375</td>
<td>-0.023</td>
</tr>
<tr>
<td>Nb\textsuperscript{Zr}\textsuperscript{+}</td>
<td>0.69</td>
<td>0.027</td>
<td>-0.026</td>
<td>0.019</td>
</tr>
<tr>
<td>Sn\textsuperscript{Zr}\textsuperscript{+}</td>
<td>0.75</td>
<td>-0.135</td>
<td>-0.126</td>
<td>-0.154</td>
</tr>
<tr>
<td>Zr\textsuperscript{Zr}\textsuperscript{+}</td>
<td>0.78</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>U\textsuperscript{Zr}\textsuperscript{+}</td>
<td>0.95</td>
<td>-0.214</td>
<td>-0.120</td>
<td>0.049</td>
</tr>
</tbody>
</table>

Table 5.1: Trapping energy comparison between possible stable proton sites that are closest (1, 2, 3, 4, 5 and 6) and second closest (n1, n2, n3) to the dopant ion M\textsuperscript{Zr}\textsuperscript{+}. Positive charge effect causes n3 to become a deeper trap than 4 for Nb\textsuperscript{Zr}\textsuperscript{+}. Size effect causes n3 to become a deeper trap than 4 in U\textsuperscript{Zr}\textsuperscript{+} case.
5.3.2 Energy barriers of entering and exiting from the traps

<table>
<thead>
<tr>
<th>Dopant element</th>
<th>Site 4</th>
<th>Site 5</th>
<th>Site 6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Approaching</td>
<td>Leaving</td>
<td>Trap/Repulsion</td>
</tr>
<tr>
<td>Ni$^{3+}$</td>
<td>NA</td>
<td>NA</td>
<td>Trap</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>0.171</td>
<td>0.422</td>
<td>Trap</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.237</td>
<td>0.512</td>
<td>Trap</td>
</tr>
<tr>
<td>Nb$^{3+}$</td>
<td>0.270</td>
<td>0.234</td>
<td>Repulsion</td>
</tr>
<tr>
<td>Sn$^{2+}$</td>
<td>0.250</td>
<td>0.222</td>
<td>Trap</td>
</tr>
<tr>
<td>Zr$^{3+}$</td>
<td>0.268</td>
<td>0.220</td>
<td>Reference</td>
</tr>
<tr>
<td>U$^{6+}$</td>
<td>0.674</td>
<td>0.408</td>
<td>Repulsion</td>
</tr>
</tbody>
</table>

Table 5.2: Barriers of approaching proton traps are small, <0.270 eV, comparable with smallest hopping barrier (0.220 eV) in the defect free region. Although site 6 is the deepest trap, it is not the easiest to enter. However, the differences are not significant. Challenges relating to defining barriers in Ni case can be referred to in section 4.5.

1. Sn$^{2+}$ (0.75 Å) has the closest radius to Zr$^{2+}$ (0.78 Å). When Zr$^{2+}$ is substituted by Sn, proton diffusion in vicinity of Sn$^{2+}$ is almost the same as the case of proton diffusion in defect free m-ZrO$_2$ region.

2. Except for positive charged Nb$^{3+}$, for the dopant cations with smaller Shannon ionic radius than Zr$^{3+}$, substitutional defect sites M$^{X+}$ behave as proton traps, see Table 5.1.

3. Barriers of approaching proton traps are small, <0.270 eV, comparable with smallest hopping barrier (0.220 eV) in defect free region.

4. Barriers of leaving the traps are higher than the hopping barrier in the defect free-region.

5. Although site 6 is the deepest trap, it is not the easiest to enter. However, the differences are not significant.

6. U$^{6+}$, with a larger Shannon ionic radius than Zr$^{3+}$, cause the positive energy perturbation in the nearest proton sites (1-6), while gives a deeper proton trap at n3.

In order to explain the correlation of trapping energies to dopant size, following arguments are provided here as possible reasons. Note these are only tentative explanations and more analysis is needed for determining the exact reason.

a) Dopant ions which are smaller than Zr$^{3+}$ do not fill all the space that a missing Zr$^{4+}$ leaves behind. Given the same charge state of these dopant ions, or Coulomb forces between proton and substitutional sites, smaller dopant ions leave more open space available for proton to take, and be associated with less strain energy.
b) After proton is trapped, proton is bonded with an oxygen atom, rather than a substitutional dopant ion. Actually proton site is further away rather than being in the vicinity of dopant ion. The dopant ion is always bonded with the surrounding oxygen atoms. Thus, the smaller dopant ions can leave more space for proton to be bonded with shared $O$.

7. Nb doesn't follow the size trend as the other dopants above. The change in the barrier relative to the undoped case is correlated more closely to its relative charge. Other dopants' dominant charge state is neutral $M_{2+}^\times$, while Nb is in a positive $Nb_{2+}^\ast$. Repulsive forces exist between $Nb_{2+}^\ast$ and proton, both with a positive charge, which increases the proton migration barrier while approaching the Nb site. And results in a proton trap in the second nearest proton site, $n3$. 

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Hopping between subplanes

Hopping inside subplane

<table>
<thead>
<tr>
<th>$r$</th>
<th>$E_{\text{Ni}}$</th>
<th>$E_{\text{Cr}}$</th>
<th>$E_{\text{Fe}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td>0.871 eV</td>
<td>0.422 eV</td>
<td>0.512 eV</td>
</tr>
<tr>
<td>0.55</td>
<td>0.000 eV</td>
<td>0.171 eV</td>
<td>0.237 eV</td>
</tr>
<tr>
<td>0.585</td>
<td>0.322 eV</td>
<td>0.322 eV</td>
<td>0.322 eV</td>
</tr>
</tbody>
</table>

(a) $\text{Ni}_{2r}^x$

(b) $\text{Cr}_{2r}^x$

(c) $\text{Fe}_{2r}^x$
Hopping inside subplane

0.234 eV
0.269 eV

Rotating: 0.503 eV
0.603 eV

(d) Nb_{2r}

Hopping inside subplane

0.220 eV
0.268 eV

Rotating: 0.468 eV
0.421 eV

(f) Zr_{2r}
Figure 5-2: Proton diffusion in vicinity of defects introduced by dopant cations of (a) Ni\textsuperscript{X}_{2r}, (b) Cr\textsuperscript{X}_{2r}, (c) Fe\textsuperscript{X}_{2r}, (d) Nb\textsuperscript{X}_{2r}, (e) Sn\textsuperscript{X}_{2r}, (f) Zr\textsuperscript{X}_{2r}, (g) U\textsuperscript{X}_{2r}. Blue dashed line represents migration towards or leaving dopant cations. Zr is not a dopant. Notation Zr\textsuperscript{X}_{2r} is used to make Zr as a reference case.
Appendix A

Questions

A.1 Does dopants' charge state change at saddle point configuration?

Additional calculations have been casted by fixing ions of configuration at saddle point and having electrons relaxed. Bader analysis is conducted when proton is at stable sites as well as at saddle point. Results are as following.

<table>
<thead>
<tr>
<th>sites/metal/Charge</th>
<th>Fe</th>
<th>Cr</th>
<th>Nb</th>
<th>Ni</th>
<th>U</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7158</td>
<td>1.9434</td>
<td>2.7321</td>
<td>1.4129</td>
<td>2.5372</td>
<td>2.4155</td>
</tr>
<tr>
<td>2</td>
<td>1.7095</td>
<td>1.9478</td>
<td>2.7261</td>
<td>1.4142</td>
<td>2.5246</td>
<td>2.4117</td>
</tr>
<tr>
<td>3</td>
<td>1.7871</td>
<td>1.9432</td>
<td>2.7255</td>
<td>1.4116</td>
<td>2.5093</td>
<td>2.4158</td>
</tr>
<tr>
<td>4</td>
<td>1.7110</td>
<td>1.9407</td>
<td>2.7192</td>
<td>1.4149</td>
<td>2.5232</td>
<td>2.4171</td>
</tr>
<tr>
<td>n1</td>
<td>1.7765</td>
<td>1.9479</td>
<td>2.7353</td>
<td>1.4342</td>
<td>2.5221</td>
<td>2.4147</td>
</tr>
<tr>
<td>n2</td>
<td>1.7867</td>
<td>1.968</td>
<td>2.742</td>
<td>1.4233</td>
<td>2.5157</td>
<td>2.4171</td>
</tr>
<tr>
<td>1→2 saddle point</td>
<td>1.6783</td>
<td>\</td>
<td>2.7361</td>
<td>\</td>
<td>2.541</td>
<td>2.4177</td>
</tr>
<tr>
<td>1→3 saddle point</td>
<td>\</td>
<td>1.9479</td>
<td>2.7397</td>
<td>\</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>1→n1 saddle point</td>
<td>\</td>
<td>1.9522</td>
<td>2.7333</td>
<td>1.4192</td>
<td>\</td>
<td>2.4187</td>
</tr>
</tbody>
</table>

Table A. 1: Bader charges of metal for proton at stable sites and saddle points. Bader charges don't change at saddle point, except for Fe. \ stands for calculations in process.

<table>
<thead>
<tr>
<th>sites/metal/spin</th>
<th>Fe</th>
<th>Cr</th>
<th>Nb</th>
<th>Ni</th>
<th>U</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.1564</td>
<td>2.0230</td>
<td>0.0000</td>
<td>1.8898</td>
<td>1.9218</td>
<td>0.0000</td>
</tr>
<tr>
<td>2</td>
<td>3.1437</td>
<td>1.9816</td>
<td>0.0000</td>
<td>1.9048</td>
<td>1.9169</td>
<td>0.0000</td>
</tr>
<tr>
<td>3</td>
<td>3.2986</td>
<td>2.0214</td>
<td>0.0000</td>
<td>1.8901</td>
<td>1.9099</td>
<td>0.0000</td>
</tr>
<tr>
<td>4</td>
<td>3.2013</td>
<td>1.9628</td>
<td>0.0000</td>
<td>0.0009</td>
<td>1.9078</td>
<td>0.0000</td>
</tr>
<tr>
<td>n1</td>
<td>3.2947</td>
<td>2.0092</td>
<td>0.0000</td>
<td>1.9311</td>
<td>1.8675</td>
<td>0.0000</td>
</tr>
<tr>
<td>n2</td>
<td>3.2583</td>
<td>1.9610</td>
<td>0.0000</td>
<td>0.0001</td>
<td>1.9382</td>
<td>0.0000</td>
</tr>
<tr>
<td>1→2 saddle point</td>
<td>3.1068</td>
<td>\</td>
<td>0.0000</td>
<td>\</td>
<td>1.9234</td>
<td>0.0000</td>
</tr>
<tr>
<td>1→3 saddle point</td>
<td>\</td>
<td>2.0286</td>
<td>0.0000</td>
<td>\</td>
<td>\</td>
<td>\</td>
</tr>
<tr>
<td>1→n1 saddle point</td>
<td>\</td>
<td>2.0092</td>
<td>0.0000</td>
<td>0.0006</td>
<td>\</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Table A. 2: Bader spins of metal for proton at stable sites and saddle points. \ stands for calculations in process.
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