Computational modeling investigation of electrolyte materials in solid oxide electrolyser cell

Wang, Jianfeng

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**COMPUTATIONAL MODELING INVESTIGATION OF
ELECTROLYTE MATERIALS IN SOLID OXIDE
ELECTROLYSER CELL**

WANG JIANFENG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

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ELECTROLYTE MATERIALS IN SOLID OXIDE
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WANG JIANFENG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

5th Aug 2016

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Date

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Wang Jianfeng

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

22 Jan 2019

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Date

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Su, Haibin

Authorship Attribution Statement

This thesis contains material from one paper accepted to be published in the following peer-reviewed journal where I was the first and/or corresponding author.

Chapter 6 is accepted to be published as Jianfeng Wang, Electronic structure of gadolinium-doped ceria system – a DFT study. *Modern Physics Letters B*.

The contributions of the co-authors are as follows:

- A/Prof Haibin Su provided the initial project direction.
- I conducted the DFT simulations and wrote the drafts and revised version of the manuscript.

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Date

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Wang, Jianfeng

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Summary

Solid oxide electrolyser cell (SOEC) is regarded as a promising device for future energy storage and for the deduction of carbon dioxide emission. This thesis aims at finding ways to help improve the long-term stability of SOEC from theoretical perspective. With the background and motivation discussed, we focus on improving the cell performance and seeking for better understanding in the electrolyte materials, especially in the electrolyte material yttria stabilized zirconia (YSZ) and gadolinium doped ceria (GDC).

We find that the maximum ionic conductivity of YSZ may come from the competitive interaction between the positive effect from the increase of oxygen vacancies and the negative effect from the increasing of yttrium ions. We also find that oxygen ion diffusion is hindered by the existence of GB in YSZ. With further investigation, we find that the oxygen ions diffuse faster along the GB interface than across it. The results suggest that GB shall be avoided in synthesizing if possible, and that the direction of GB interface shall be aligned parallel to the ion conducting direction to improve cell performance.

A minimal layer thickness requirement is found on the thickness of the GDC interlayer, which blocks reactions between electrolyte and electrode. The minimal thickness is found to be $\sim 10\text{nm}$ and $\sim 2\mu\text{m}$ under 700°C and 1000°C , which provides useful advices for researchers in the designing and synthesizing of SOEC components. A relationship between the lattice parameter and overall thickness of CeO_x laminated structure is given as a tool for researchers to estimate the oxygen conducting property based on the thickness of GDC interlayer.

Electronic structures and work function in ceria (CeO_2) and GDC are studied. Doping of gadolinium significantly decreases the band gap of ceria, while thin film structure of GDC raises up the band gap a lot. The existence of oxygen vacancy is found to be responsible for the decrease in band gap and helps explain the electronic conductivity of GDC under low oxygen partial pressure.

In conclusion, the results of this thesis help improve the understanding in SOEC electrolyte materials and provide useful information and advices to researchers who are interested in designing and making SOECs with improved performance.

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Abbreviations

CG	Conjugate Gradient
CSL	Coincidence Site Lattice
DFT	Density Functional Theory
DOS	Density of State
EAM	Embedded Atom Model
EXAFS	Extended X-ray Absorption Fine Structure
GB	Grain Boundary
GDC	Gadolinium Doped Ceria
GGA	Generalized Gradient Approximation
HK	Hohenberg-Kohn
HRTEM	High Resolution Transmission electron microscopy
KLMC	Kinetic Lattice Monte Carlo
KS	Kohn-Sham
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
LDA	Local Density Approximation
LDOS	Local Density of States
LNO	$La_2NiO_{4+\delta}$
LPAW	Linear Augmented Plane Wave
LSCF	Lanthanum Strontium Cobalt Ferrite
LSM	Lanthanum Strontium Manganite
LSGM	$La_{1-x}Sr_xGa_{1-y}Mg_yO_{2.85}$
MD	Molecular Dynamics
MSD	Mean Square Displacement
NEB	Nudged Elastic Band
PAW	Projector Augmented Wave
SIE	Self-Interaction Error
SIMS	Secondary Ion Mass Spectrometry
SOEC	Solid Oxide Electrolyser Cell
SOFC	Solid Oxide Fuel Cell
STO	$SrTiO_3$
TEM	Transmission Electron Microscopy
TPB	Triple Phase Boundary
VASP	Vienna Ab Initio Simulation Program
VESTA	Visualization for Electronic and Structural Analysis
WGS	Water-Gas Shift
YSZ	Yttria Stabilized Zirconia

Chapter 1

Introduction

As the reduction of carbon dioxide emission and the demand on energy have become critical global problems, extensive studies have been carried out in solid oxide electrolyser cell (SOEC), a promising device for future energy storage, trying to find a practical way towards a future with less carbon emission and a future that depends less on fossil fuels. The study of this thesis focuses on behavior and properties of materials in SOEC. In this introduction chapter, the motivation and objectives of this thesis are introduced, after which a brief overview of the contents for each chapter is given. The major outcomes are summarized at the end of this chapter.

1.1 Problem Statement

The problem of high CO₂ emissions is a common problem for many countries in the world, especially so with the growing of economic activities. As a response to the global climate change, it has become an increasingly critical mission to reduce the emission of greenhouse gases, or at least, to have a finite CO₂ budget in order to stabilize the global mean temperature change¹⁻⁶. Another problem of great importance the world faces is the challenge of renewable energy. In a world with limited storage of fossil fuels and a world that has increasing demand on energy, it has been a critical mission for researchers and scientists to find ways to utilize renewable energies. While fossil fuels can supply electricity on demand, renewable energies, such as wind, solar, and tide energy only supply power when there is wind blowing or sun shining or when the sea rises or falls. Hence, economic large-scale energy storage solution is essential to balance the supply-demand mismatch to make it possible for these renewable energies to account for a relatively large fraction of total energy demand^{7,8}. **Table 1.1** shows a summary of comparison between SOEC and other H₂ production techniques which can be used as energy storage solution currently or in the future. While the existing energy storage solutions are expensive to scale up, the solid oxide electrolyser cell (SOEC), which can store electricity as chemical fuels by converting CO₂ and H₂O into syngas catalytically, deducing the amount of CO₂ emitted into the atmosphere, acts as a promising energy storage device for the future. If the electricity used for such conversion is from renewable energy, the utilization of SOEC to convert CO₂, with the help of renewable energy, into syngas or synfuels, provides a promising and elegant way towards the solving of the two challenging problems.

Table 1.1 Comparison between SOEC and other H₂ production techniques

	<i>SOEC</i>	<i>Alkaline water electrolysis</i>	<i>Photoelectro-chemical</i>	<i>Stream Reforming</i>
<i>Efficiency (%)</i>	85.5-119	55.6-69.4	1.0-12.4	72-77
<i>Stability</i>	Lack long term stability	Insufficient stability	N/A	High stability
<i>Cost</i>	Low	High	N/A	High
<i>Working Temperature (°C)</i>	900-1000	70-90	60-80	700-1100
<i>Scalability</i>	Large scale	Scalable	Potentially scalable	Scalable
<i>Pros</i>	High efficiency, energy storage issue	Low working temperature, commercial experience	Pure H ₂	Low cost, most extensive industrial experience
<i>Cons</i>	Lack long term stability, high working temperature	High cost, high maintenance cost, low durability	No industrial experience	Unsustainable, highest air emissions

An SOEC works, with the help of external electricity, by converting CO₂ and H₂O into synthetic gas (syngas), which is a building block for chemical fuels⁹. Since CO₂ and H₂O are the main ingredients of the flue gas, this conversion process provides an environmentally friendly way to reduce the emission of CO₂ and implicitly addresses the energy storage issue. **Figure 1.1** shows the co-electrolysis of CO₂ and H₂O as part of renewable fuel cycle.

Figure 1.1 Diagram of co-electrolysis CO_2 and H_2O as part of renewable fuel cycle (Adapted from Ref⁹ with permissions).

The working principles of co-electrolysis of CO_2 and H_2O in SOECs are illustrated in **Figure 1.2**. SOECs, ceramic based cells, usually work at high temperature ($600\text{--}1000^\circ\text{C}$). Exhausted CO_2 and H_2O gases are fed to the cathode, where they meet the electrons and are reduced to H_2 and CO gases, leaving oxygen ions in the cathode. The cathode usually consists of a porous composite of Ni and stabilized zirconia, to achieve both high electronic and high ionic conductivity. It provides triple phase boundary (TPB) where the catalyst particles (Ni), the electrolyte (YSZ), and the gas phase meet together. The thermal and chemical stability of the TPB has key influence to the performance of the cell. The oxygen ions then move through electrolyte, which blocks the transport of electrons at the meantime, towards the anode, where the oxygen ions turn into oxygen gas, releasing electrons and forming a closed circuit.

Figure 1.2 The working principle of SOEC (Adapted with permissions from Ref^[10].)

The reactions that happen at an SOEC are:

at the cathode, where CO_2 and H_2O are fed,

at the anode, where oxygen gases are emitted and hence called air electrode,

Besides the abundant nature of CO_2 and H_2 , SOEC has another advantage, that is, high efficiency^{9,11-13}. Producing H_2 and O_2 from seawater electrolysis using SOEC has been proved possible, and the results promise high efficiency (85.5-119%). The high operating temperature (typically 600-1000°C) of SOEC enables such high energy efficiency at high reaction rates that are not possible for low-temperature cells.

However, being unable to maintain this high performance for long-term stability, SOEC's widespread has been hindered in these years^{9,11-14}. Hence it has been a critical mission for researchers, engineers, and scientists to find ways to improve the long-term stability of SOEC under high current density. The long-term degradation reported for SOEC is more than twice that of similar cells running in the reverse mode, i.e. fuel cell mode. The degradation of an SOEC describes the irreversible increase of interfacial resistance during cell operation. According to the different degradation mechanisms of SOECs, there are generally three types of degradations: degradations that rise from chemical and electrochemical reactions, degradations that resulted from structural defects, and

degradations caused by thermal mechanical failures¹⁵. Among the three groups, the chemical and electrochemical degradation has been of great interest since the degradation caused can be extreme severe and is much more difficult to deal with¹⁴. A recent study shows that by operating an SOEC in a reversible electrolysis-fuel cycling mode, i.e. like a rechargeable battery, one is able to achieve long-term stability in the cell with negligible degradation¹⁴. While another study shows that under high current density, the degradation process becomes faster under the reversible cycling mode¹⁶. A possible explanation, by the authors, for the faster degradation process under high current density is that the polarization degradation is associated with the resistance that lies in YSZ grain boundaries. A large scale electricity storage strategy was proposed utilizing the reversible SOEC idea¹⁷. This leads to the promising widespread usage of SOEC to store energy and to utilize renewable energy in the future.

Although the working principles of SOEC are quite clean, the actual reaction zones during cell operation are highly dynamic. The changes that take place at these reaction zones are very complicate and can have either positive or negative effects on the performance. For example, the accumulation of impurities, segregation of inactive or active ions, reactions at interfaces, and phase transitions, all these changes have complicate effects on the performance. To increase the performance of SOEC and make it more promising as the future energy storage solution, it is essential to fully understand the ionic and electronic transportation properties in the related materials. As the mainly conducting ions in SOECs are oxygen ions, oxygen ion related properties of related materials are of the focus in this study.

1.2 Objectives and Scope

As the anode is where oxygen ions lose their electrons, high mixed conducting property is required for an eligible anode material. Oxides with perovskite structure are intensely studied and lanthanum strontium cobalt ferrite (LSCF) is widely used nowadays. The electrolyte material is usually chosen to be yttria stabilized zirconia (YSZ), which

demonstrates good ion conducting property under a wide range of oxygen partial pressure and demonstrates good mechanical and thermal stability under high temperature.

In practice the electrolyte is in the form of a dense layer. Different from a single crystal structure, the thin film structure allows for more defects in the structure. One particular example of such defects is the grain boundary, which usually dominates the properties of a material in a thin film structure. Since the oxygen conducting property of the electrolyte is of extreme importance to the cell performance, we are thus interested in the oxygen conducting properties in YSZ and in the grain boundary area of YSZ.

LSCF and YSZ are both good selections on their own. However, under working temperature, LSCF reacts with YSZ, generating an insulating phase, SrZrO_3 , which further influences the performance and stability of the cell. An interlayer of gadolinium doped ceria (GDC) has to be associated between the anode and the electrolyte material to block the chemical reaction. As the reaction happens between YSZ and Sr^{2+} ions, this interlayer has to block the diffusion of Sr^{2+} ions to effectively block the reaction. Because of the poor sintering properties of GDC, the interlayer cannot be too thick. It is thus of our interest to find the minimum thickness requirement for this GDC interlayer.

One extreme severe degradation mechanism in SOEC is the high internal oxygen pressure at the interface between electrolyte and the anode. The internal oxygen pressure built at the interface between anode and electrolyte materials can be extremely high that no practical strengthening or toughening can prevent the degradation. Although recent studies show that this high internal pressure can be eliminated by operating in a low current density reverse cycling mode¹⁴, it is not yet confirmed whether the relief of the high pressure occurs before or after the structural deterioration has started¹⁸. If the relief happens after the nano/micro-cracks have begun to form, it means that the cracks are sintered back together during the fuel cell mode. Anyway, the nature remains to be discovered, and seems to be dependent on the details of the interface of a cell. In order to understand the degradation mechanism and achieve long-term stability, it is essential to fully understand the ionic and electronic transportation properties of the anode and electrolyte materials. Since the electric

and ionic conducting properties of LSCF have been intensely studied, the additional buffer layer of GDC will be the focus of for this part. Also, the oxygen vacancy in GDC, which determines GDC's diffusion properties, matters. If one can find a way to relate the GDC layer's thickness with its oxygen vacancy concentration, it would be very helpful for experimental device makers to estimate the interlayer's performance by a simple measurement of the thickness.

Figure 1.3 Components of SOEC and key issues associated with them

Figure 1.3 shows the schematic diagram of a SOEC cell, including key components and issues associated with each component. In summary, the objectives of this thesis are to investigate the grain boundary effects on oxygen conducting in YSZ, to find an optimized thickness for the GDC buffer layer to effectively block the diffusion of Sr^{2+} and keep good O^{2-} diffusion property between the electrolyte and the anode, to investigate GDC thin layer's electric transportation properties, and to find a way to relate the GDC interlayer's thickness with its oxygen diffusion performance.

1.3 Dissertation Overview

Chapter 1 gives a general introduction to the motivations of this project, describes the detailed objectives of this project, and summarized the major findings. An overview of the thesis is given.

Chapter 2 presents a detailed literature review on the background and degradation mechanisms of SOEC, the electrolyte and anode materials, oxygen diffusion properties in YSZ, the YSZ LSCF reaction, oxygen diffusion properties in GDC, defect and other properties in CeO_x , the material that is closely related with GDC.

Chapter 3 introduces the computational methodologies used in the calculations of this thesis. The main methods are the interatomic potential methods used in molecular dynamics, the quantum mechanics used in *ab initio* calculations, and the elastic equations used when analyzing the thickness dependent behaviors in a laminated structure. A brief description of the computing packages is also provided in this chapter.

In chapter 4, several molecular models of YSZ single crystal and grain boundary structures are built. Based on molecular dynamics simulations using these models, the detailed effects of the existence of grain boundary is presented and discussed. Oxygen ion migration mechanisms in YSZ are calculated and discussed.

Chapter 5 starts with a simple diffusion model of O^{2-} and Sr^{2+} ions in GDC, giving estimations on the minimum required thickness of GDC to block the diffusion of Sr^{2+} ions from one end to the other. A simplified laminates structure consisting layers of CeO_x is proposed as a first approximation of the GDC thin layer. The thickness dependent behaviors analyzed based on this model. Two other approaches to analyze the laminated model are described and discussed.

Chapter 6 focuses on the electronic properties of GDC. Band structures of CeO_2 , GDC, and thin layer GDC are calculated and discussed. To help improve the understanding of

electrochemical catalytic properties of CeO_x , the workfunctions of different CeO_2 surfaces are calculated and discussed.

Chapter 7 gives a general discussion of my work in the last four years. Possible future work is also presented in this chapter.

1.4 Findings and Outcomes

By running molecular dynamics simulations with well-tested interatomic potential parameters for the YSZ system, we confirm the experimental conclusion that YSZ with 8-10% Y_2O_3 doped has the highest oxygen diffusion coefficient under working temperature. By comparing the oxygen diffusion coefficients in and out of grain boundary area of YSZ, we find that the existence of grain boundary hinders the diffusion of oxygen ions, which agrees with both previous experimental and theoretical results. With further investigations into the oxygen ion diffusion behavior inside grain boundary area, we find that the diffusion of oxygen ions is more hindered across the grain boundary interface than along it. Hence, when making the device, grain boundaries perpendicular to the ion conducting direction shall be avoided, if possible, to allow for higher performance.

By comparing the oxygen ion migration energies in the zirconia lattice, we confirm the intuitive conclusion that oxygen ions tend to migrate to their nearest vacancy sites. The probabilities for oxygen ions to choose between different migration paths are presented based on the migration barrier energies. The influences of different cations along the migration path are also investigated. Migration paths with two Y^{3+} ions along it have the highest barrier, while paths with two Zr^{4+} ions at each side have the lowest barrier. This result helps explain the non-monotonic relationship between the doping concentration and oxygen ion conducting property, i.e. YSZ with 8-10% doped Y_2O_3 has the highest oxygen ion diffusion coefficient.

Using a simple diffusion model of oxygen and strontium ions diffusing inside a GDC layer, we find the minimum layer thickness requirement for the GDC buffer layer to effectively block the reaction between anode LSCF and electrolyte YSZ. The minimum thickness is found to be around 10nm at lower temperature (700°C) and around 2μm at higher temperature (1000°C). The result helps provide useful information for researchers on the design of the GDC buffer used in SOECs. Based on a clean yet reasonable laminated CeO_x model, micromechanical analysis gives a relationship between the model's thickness and the lattice parameter of CeO_x . The relationship is compared with relationships that are derived from simple volumetric average and Madelung energy fitting. With additional data from experimental measurements, this result can be used to help SOEC device makers have a quick and reasonable estimation of the layer's oxygen vacancy concentration, and furthermore the ionic conducting property, based on the layer thickness.

The band structures of CeO_x , 20% doped GDC, and thin layer of 20% doped GDC are calculated, showing that doping of gadolinium significantly decreases the band gap of bulk CeO_2 , and that the thin film structure increases the band gap by a considerable amount. Effects of oxygen vacancy on $CeO_2(111)$ are investigated by analyzing the DOS and band structure for $CeO_2(111)$ perfect and defect surfaces. We find that the creation of oxygen vacancy decreases the band gap of $CeO_2(111)$ surface. The workfunction of $CeO_2(111)$ surface decreases a lot with the existence of neutral oxygen vacancy as it's easier to move electrons out of the surface with remaining electrons.

Chapter 2

Literature Review

Over the past decades, with the fast increasing consumption of fossil fuel energy all over the world, it has become a global challenge to deduce the emission of CO₂ and to increase the share of renewable energy in total energy consumption. The co-electrolysis of CO₂ and H₂O, collected from flue gas, in solid oxide electrolyser cells (SOECs) is a promising scalable way towards the deduction of CO₂ emission and the storage of energy. However, the commercial usage of SOECs has been hindered for many years due to the long-term stability problem. This chapter reviews the background and working principles of solid oxide electrolyser cells and the materials used in each component of solid oxide electrolyser cells. Special attention is paid to the electrolyte and anode materials, which suffer from severe degradation problem that stops SOECs from being widely used.

2.1 Solid Oxide Electrolyser Cell

Solid oxide electrolyser cell (SOEC) is a device that converts steam water and carbon dioxide into hydrogen and carbon monoxide. It is regarded as a promising candidate technology for securing sustainable development for the future⁹. Its good scalability, simply achieved by assembling different SOECs into stacks, makes the technology very flexible and can be applied to a wide range of areas¹⁸.

2.1.1 Electrolysis of Water

The history of water electrolysis dates back to the 1800s, when Nicholson and Carlisle discovered the splitting of water by electric. The process can be written as

Nowadays, after more than two centuries of development in science and technology, the water splitting technologies can be classified into several groups: biological approaches^{19,20}, thermolysis²¹, photoelectrolysis²², and thermochemical processes²³. Currently, most of the world's hydrogen is produced through methane reforming²⁴ due to price and scalability. However, as the demand on energy grows dramatically over the last a few decades, new technologies for hydrogen generation have become the spotlight. The main interest at present for future hydrogen generation is alkaline, polymer exchange membrane, and solid oxide electrolyser cell. Among these new technologies, SOEC is the least developed technology due to its high operating temperature and poor long-term stability. Recently, there has been a significant growth of research activity for electrolysis of H_2O ^{11,12,25-33}, CO_2 ^{27,32,34-36}, and CO_2 / H_2O ^{10,13,37-41} mixtures for fuel production purposes, using SOECs.

2.1.2 Principle and Components of SOEC

A solid oxide electrolyser cell works by converting the fed steam and carbon dioxide into hydrogen and carbon monoxide, which can be further converted into synfuel catalytically. This procedure effectively turns electricity into chemical energy, providing an elegant way for energy storage.

2.1.2.1 Working Principles

The working principles and main components of an SOEC are shown in **Figure 2.1**. The carbon dioxide and steam get reduced at the cathode, or the fuel electrode, turning into hydrogen and carbon monoxide gases. The remaining oxygen ions pass through the electrolyte and turn into oxygen gas at the anode, or the so-called O₂ / air electrode, releasing electrons back in to the circuit. SOECs consist of three main components, as illustrated in **Figure 2.1**: two porous electrodes, the cathode (fuel electrode, where CO₂ and H₂O gases are fed) and the anode (O₂ / air electrode, where oxygen gases are released), with a dense electrolyte, which blocks the conduction of electrons but demonstrates high ionic conductivity. The typical thicknesses of components in an SOEC are 10-20 µm on a 300 µm layer support, which can be either the electrolyte or an electrode^{15,25}. The simplified electrode reactions are:

at the cathode (fuel electrode),

at the anode (O₂ / air electrode),

The typical working temperature for an SOEC is in the range of 450-1000°C at atmospheric or elevated pressures²⁴. While the high operating temperature helps increase the efficiency of SOECs, it places significant constraints on the electrode and electrolyte materials. To better understand the constraints on materials for each component, one has to understand the electrochemical reaction mechanisms of SOEC.

Figure 2.1 Working principle of SOEC.

2.1.2.2 Electrochemical reaction mechanisms

As **Figure 2.2** shows, the interfaces where the reactions take place is triple phase boundary (TPB), which is a confined spatial region where the electrolyte, which can be treated as the source of oxygen ions, the catalyst particles, from which the electrons are coming, and the gas phases are interacting⁴². Larger TPB's active area leads to higher kinetic performance of the cell.

To achieve a stable and high performance, the materials for each component have to satisfy certain requirements:

- chemical and microstructural stability under the operating conditions of an SOEC, i.e. stability under certain range of partial pressure and temperature
- thermal stability under operating temperature
- no reactions between different component materials

Figure 2.2 The schematic plot of triple phase boundary (TPB) of SOEC. (Adapted from Ref¹⁵ with permissions).

The electrolyte materials have to additionally satisfy the following criteria:

- High ionic conductivity to reduce the polarization loss
- No electronic conductivity to prevent current leakage

The electrodes have to additionally satisfy the following requirements:

- Fine electrocatalytic property
- Sufficient ionic conductivity
- Electronic conductivity that is as high as possible
- Sufficient porosity to promote gas transportation

2.1.2.3 The O₂ / Air electrode / Anode

The materials for air electrode of SOECs generally have a perovskite or related structure, i.e. $ABO_{3-\delta}$. The A site is usually taken by a lanthanide ion (La^{3+} , Pr^{3+} , Sm^{3+} , Gd^{3+} , etc.). Di-valent alkali earth ions (Ca^{2+} , Sr^{2+} , Ba^{2+}) are often doped into the A site to achieve both high ionic and high electronic conductivities. Usually, the B site is occupied by one or more transition metal ions (Fe, Co, Mn, Ni, each can be either 3+ or 4+ ion)²⁵. For most perovskites, the polarization resistance is determined by the oxygen surface exchange reaction⁴³, where the rate determining step involves oxygen molecule and oxygen vacancies⁴⁴.

Lanthanum strontium manganite (LSM) is the first material to be commercially used in the air electrode of solid oxide fuel cell, which is effectively an SOEC operating in the reverse mode. LSM is selected as the electrode material because of its high electronic conductivity, its compatibility of thermal expansion behavior with the electrolyte material YSZ, which ensures thermal stability under high temperature, and low reactivity with YSZ, which enhances the cell's lifetime. However, the poor ionic conductivity of LSM limits the active area of TPB. To overcome such drawback of LSM, electrodes with high mixed ion-electron conductivity have been developed, among which lanthanum strontium cobalt ferrite (LSCF) stands out⁴⁵.

2.1.2.4 The Electrolyte

The electrolyte transports oxygen ions from fuel electrode to anode electrode and prevents current leakage at the meantime. It contributes significantly to the overall resistivity⁴⁶. Common electrolyte materials are stabilized zirconia, which is zirconia with different doping oxides, e.g. Y_2O_3 , CaO , MgO , and Sc_2O_3 , aiming to enhance its high temperature stability. While the highest oxygen conductivity is obtained by doping scandium, the most widely used material for electrolyte is yttria stabilized zirconia (YSZ) with 3-10% yttria with conductivity in the range of 0.1 and 0.18 S/cm at 1000°C and in the range of 0.03 and 0.05 S/cm at 800°C^{47,48}. As reviewed by Laguna et al.⁴⁵, apart from YSZ, there are three other ceramic materials, which have been tested under the operating conditions of SOECs,

which are Scandia doped zirconia, Gd_2O_3 / Sm_2O_3 doped ceria, and $La_{1-x}Sr_xGa_{1-y}Mg_yO_{2.85}$ (LSGM). The superoxide ion conductivity is reported to be five times higher than the value of YSZ for LSGM.

2.1.2.5 The Fuel Electrode / Cathode

The typical fuel electrode consists of a porous composite of Ni and stabilized zirconia, the so-called “cermet”, which provides TPB for the electrochemical reaction to occur. Nickel here acts as a high electronic conductor and an excellent catalyst for the splitting of water. The porous structure is of critical importance since it provides the active area of TPB and the volume percentage and pore size affect the gas flow during cell operation³³. The mechanism of the reduction of carbon dioxide and water steam and the nature of the rate determining step is not yet clear, with different mechanisms such as adsorption or desorption, surface diffusion, and charge-transfer reactions suggested⁴⁹.

2.1.3 Challenges

The insufficient long-term stability of SOEC has hindered the widespread of SOEC for a long time, and is regarded as the most challenging problem in SOEC. The degradation of SOEC is usually twice higher than that of SOFC (solid oxide fuel cell) as reported by Schefold et al.⁵⁰. The degradation of SOEC has different mechanisms, such as fuel electrode poisoning by gaseous impurities⁵¹, extreme high internal oxygen pressure at the interface between electrolyte and air electrode⁹.

A recent study by Garves et al. showed that the degradation resulting from the internal high pressure at the interface between electrolyte and air electrode, which was thought to be irreducible, could be eliminated by operating the cell in a reversible cycling mode like a rechargeable battery¹⁴. However, the degradation elimination achieved in this study is at low current density ($1.0 A \cdot cm^{-2}$) with cycles of very short periods of electrolysis and fuel cell operation, which is not practical for most storage application scenarios. Barnett et al. showed that under high current density, the degradation process became faster under the reversible cycling mode¹⁶. A possible explanation, by the authors, for the faster degradation

process under high current density is that the polarization degradation is associated with the resistance that lies in YSZ grain boundaries.

Similar to the problems that solid oxide fuel cell (SOFC) faces, a critical issue in SOEC is from the impurities in the fed-in gases, which can poison the air electrode. Typical impurities include Cr, which is released from metallic interconnects or other components⁵². Egger et al. investigated the influence of chromium to $La_2NiO_{4+\delta}$ (LNO), a potential anode material for high temperature SOEC, under 800°C⁵³. Significant increase in area specific resistance (0.22 to 1.0 $\Omega \cdot cm^2$, a 350% increase) was observed. The degradation in LNO anode probably results from the poor contact between electrode and electrolyte.

2.2 Yttria Stabilized Zirconia

Yttria stabilized zirconia (YSZ), a fluorite-type structured ceramic, has been widely used in solid oxide electrolyser / fuel cells as electrolyte for a long time because of its high ionic conductivity and fine stability, both thermally and mechanically.

2.2.1 Structure and Properties

YSZ is a fluorite-type ceramic based on zirconium oxide (ZrO_2). Oxygen vacancies are introduced by replacing zirconia ions in the lattice with doped yttrium ions. The doping not only introduces oxygen vacancies to allow to ionic conductivity, but also stabilizes the structure of ZrO_2 . **Figure 2.3** illustrates the doping idea of YSZ.

Figure 2.3 Doping of Y_2O_3 into pure ZrO_2 . One Y^{3+} ion replaces one Zr^{4+} ion and three O^{2-} ions replace four O^{2-} ions, creating some oxygen vacancies. (Figure retrieved Jul 20, 2016, from Ref⁶⁴)

Pure zirconium dioxide has two phase transformations at about 1273K and 2643K. As temperature rises, it transforms from monoclinic phase, which is stable at room temperature, to tetragonal phase and then to cubic phase at the two separate temperatures. However, with Y_2O_3 (namely yttria) doped in ZrO_2 (commonly called zirconia) the cubic structure can remain stable at a much wider range of temperature. Hence comes the name yttria-stabilized zirconia.

While YSZ has good ionic conductivity, it is not the one with the highest ionic conductivity among many candidates. For example, as shown in **Figure 2.4**, GDC, SNDC ($Sm_xNd_xCe_{1-2x}O_{2-\delta}$), ESB ($(Er_2O_3)_x(Bi_2O_3)_{1-x}$), and DWSB ($(Dy_2O_3)_x(WO_3)_y(Bi_2O_3)_{1-x-y}$) all have higher ionic conductivity than YSZ. We choose to explore oxygen diffusion behavior only in YSZ due to economical and stability reasons²⁴. The reason of not exploring GDC is that GDC is known to leak current under high oxygen partial pressure, which is typical in SOEC working condition, making it unqualified as an electrolyte material for SOEC. Other electrolytes are not chosen due to economic reasons as the usage of highly priced elements (Nd, Er, and Dy) are not practical for large scale

commercial applications. The chemical and mechanical stability of YSZ, together with its economic price, make it the electrolyte candidate of our interest.

Figure 2.4 Ionic conductivity of different electrolyte materials. The chemical composition for each material is: YSZ: $\text{Y}_{0.16}\text{Zr}_{0.92}\text{O}_{2.08}$, GDC: $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$, SNDC: $\text{Sm}_{0.075}\text{Nd}_{0.075}\text{Ce}_{0.85}\text{O}_{2-\delta}$, ESB: $\text{Er}_{0.4}\text{Bi}_{1.6}\text{O}_3$, and DWSB: $\text{Dy}_{0.08}\text{W}_{0.04}\text{Bi}_{0.88}\text{O}_{1.56}$. (Adapted from Ref²⁴ with permissions).

Figure 2.4 shows a comparison of ionic conductivity of a variety of solid oxide electrolytes. Extensive research has been conducted towards low temperature SOEC with high ionic conductivity materials⁵⁵⁻⁵⁷.

The ionic conductivity of YSZ is known to exhibit a maximum at a doping concentration of 8-10mol%⁵⁸, beyond which the conductivity decreases with increasing Y_2O_3 concentrations. To determine the nature of such behavior, the oxygen vacancy distribution in YSZ was investigated. Roth et al. studied the distribution by Extended X-ray absorption fine structure (EXAFS) and found that oxygen vacancies prefer to bond to Y ions⁵⁹.

Molecular dynamics simulation by Yamamura et al showed that oxygen vacancies tended to be trapped at the second nearest neighbor position of Y ions in YSZ and that the mobility of oxygen vacancies decreased as the number of Y ions at the very position increased⁶⁰. The competition between the increasing number of oxygen vacancies and the decreasing of vacancy mobility was thought to be responsible for the maximum conductivity at 8-10mol%.

YSZ demonstrates good thermal stability under high temperature. Ogawa et al. measured the thermal diffusivity of 3% doped YSZ before and after heat treatment at various temperatures⁶¹. The results showed no difference between the before and after thermal diffusivities for temperatures at 1000°C or lower. The low thermal conductivity also make YSZ a favorable material for thermal barrier coatings⁵⁸.

2.2.2 Limitations

While YSZ is widely used as electrolyte in SOECs, there are certain aspects related with YSZ that need to be improved if one is to using SOEC commercially. To reduce the operating temperature of SOECs, it is critical to find electrolyte materials that have high ionic conductivities. The ionic conductivity of YSZ remains yet to be increased significantly to help reduce the currently high operating temperature. Santamaria et al. observed up to eight orders of magnitude increase of ionic conductivity of YSZ in ultrathin films^{62,63}. This enhancement, as authors explains, is often attributed to the epitaxial strain and suitable heterogeneous interfaces in the ultrathin YSZ/STO(SrTiO₃) heterostructures.

To decrease the polarization loss from electrolyte YSZ, ultrathin film of dense YSZ is used in electrode supported SOECs⁶⁴. In the thin film structure, the existence of grain boundaries has critical influences on the ionic conductivity of YSZ. Nakagawa et al. were the first to detect the blocking of oxygen diffusion across the interface of a single grain boundary in YSZ⁶⁵. A symmetric tilt $\Sigma 5$ grain boundary was built and the oxygen diffusion behavior was measured by secondary ion mass spectrometry (SIMS). **Figure 2.5** is the high resolution TEM image of the $\Sigma 5$ grain boundary they synthesised. Experimental results in

YSZ with an average grain size of 50nm by Martin et al. showed that the grain boundaries had deleterious effect on the overall oxygen transport⁶⁶. While decreased ionic conductivity is reported in some studies⁶⁷⁻⁷⁰, there are opposite reports⁷¹⁻⁷⁵.

Figure 2.5 (a) HRTEM image of the $\Sigma 5$ grain boundary; (b) the zoomed-in image of the grain boundary; (c) the schematic structure model for $\Sigma 5$ boundary. (Reprinted from Ref⁶⁵ with permissions.)

What remains largely unexplored is to manipulate the resistivity of grain boundaries in such thin film structures. Kim et al. showed that the resistivity of grain boundaries near the film-substrate interface was almost entirely eliminated in their experiments, suggesting that grain boundary “design” could be an attractive way of obtaining high ionic conductivity in YSZ⁷⁶.

Another limitation on YSZ is that under SOEC operation temperature, which is typically in the range of 600-1000°C, the reaction between YSZ and the electrode material LSCF generates an insulating layer at the interface, which is one of the degradation mechanisms

that have been found⁷⁷⁻⁸¹. A buffer layer of gadolinium doped ceria (GDC) is usually used to block this reaction^{79,82,83}.

2.2.3 Modeling Study in YSZ System

There has been extensive research on theoretical modeling in the stabilized zirconia system due to its wide application in solid oxide cells and its complicated nature. As the reaction area is usually at nanoscale or microscale, which makes it hard to observe directly in experiments, theoretical modeling acts as a useful tool for understanding the nature of reaction landscape change or electrochemical reactions at atomic scale. As it's the nanoscale / microscale reactions inside or on the surface of YSZ that attracts researchers the most, molecular dynamics and other theoretical approaches are widely used to study various properties in YSZ like the oxygen ion diffusion property^{60,84-94}, crystal structure^{85,89,94-96}, grain boundary structure^{92,97-99}, lattice vibration and specific heat capacity⁹⁵.

In the *ab initio* study by Parrinello et al., they found that only half of the total vacancy configurations in the 93-atom system they studied were locally stable, which might significantly affect the ionic conductivity of bulk YSZ⁸⁴. Murthy et al. calculated the oxygen ion diffusion coefficient from the mean square displacement (MSD) of oxygen ions using molecular dynamics and found the values to be in good agreement with experimental results⁹³. Meléndez et al. pointed the possibility that segregated yttrium were located at grain boundaries in YSZ using molecular dynamics simulations⁹⁸. They also did a systematic investigation on the effects of various grain boundary structures on oxygen diffusion properties, pointing out that oxygen diffusion in grain boundaries is generally slower than that in YSZ bulk⁹⁹. Atak et al. found composition dependence of heat capacity which showed a maximum at 10mol%, which matched well with experimental results⁹⁵. Lee et al. found that due to lower vacancy formation energy at grain boundary area, the grain boundary interface has high concentration of oxygen vacancy, which could provide explanation to the dopant segregation in YSZ⁹⁷.

2.3 Gadolinium Doped Ceria

Extensive studies have been carried out regarding gadolinium doped ceria (GDC), which is an alternative to YSZ¹⁰⁰⁻¹⁰³. However, GDC is known to be reduced and produce electronic conductivity at low oxygen partial pressures¹⁰⁴, which leads to current leakage in SOECs.

In GDC, Oxygen vacancies are introduced by doping of Gd into the CeO_2 lattice. For every two Gd ions doped, one oxygen vacancy is created to keep charge neutral, thus giving the chemical formula $Ce_{1-x}Gd_xO_{2-x/2}$. The cubic CeO_2 lattice is shown in **Figure 2.6**.

Figure 2.6 Lattice structure of CeO_2 . Red balls – oxygen atoms; Blue balls – cerium atoms.

2.3.1 Limitations

The limitations of GDC are mainly related to the electrical and ionic conductivity of GDC. Doping improves the ionic conductivity of ceria to some extent. However, the interactions between dopants and vacancies may form associates which decrease the mobility of vacancies. Extensive studies have been conducted seeking to improve the ionic conductivity of GDC and to solve the current leakage issue under low oxygen partial pressure, and to seek for a clear understanding of the physics behind various factors and the ionic conductivity. Xia et al. measured the cell parameters and electrical conductivities of GDC with various doping concentrations systematically and found a linear relationship between lattice parameter and doping concentration¹⁰⁵. Hayashi et al. measured the thermal expansion coefficients of both CeO₂ and GDC and found increase in the coefficient with increasing doping concentration, which could be attributed to the weakening binding energy due to the increase of oxygen vacancy¹⁰⁶. Wang and Dokiya et al. measured the electrical and ionic conductivity of GDC v.s. temperature and oxygen partial pressure, and found an increase of electrical conductivity with decreasing oxygen partial pressure; they also found that the activation energy of ionic mobility is higher in 20mol% doped GDC than that of 10mol% one¹⁰⁷. Different studies report different optimal concentrations for maximum ionic conductivity, such as $Ce_{0.9}Gd_{0.1}O_{2-x}$ ^{105,108}, $Ce_{0.85}Gd_{0.15}O_{2-x}$ ¹⁰⁹⁻¹¹², and $Ce_{0.8}Gd_{0.2}O_{2-x}$ ¹¹³⁻¹¹⁷.

2.3.2 Modeling Study in GDC System

As the state of the art method to investigate materials properties in atomic scale, computer modeling approach has been widely used to study various properties in GDC, like the lattice parameters^{105,118,119}, electrical and ionic conductivity¹¹⁸⁻¹²², and doping and defect properties^{119,121}. Andersson et al. investigated the behavior of ionic conductivity of ceria with various doping elements by using static energy barriers calculated with density functional theory (DFT)¹²¹. Dholabhai et al. used 3D Kinetic Lattice Monte Carlo (KLMC) to study the diffusion coefficient in doped ceria and predicted a maximum ionic conductivity at doping concentration around 25-25 mol % of Gd¹¹⁸. Burbano et al. investigated co-doping effects with molecular dynamics simulations assisted with their

newly developed potential parameters, and found no enhancement of ionic conductivity of co-doping¹²². The agreement among the results of different theoretical works and experiment is rather poor, indicating the need for more insights into the nature of oxygen diffusion in doped ceria.

2.4 Cerium Oxide

Despite the wide usage of doped ceria, cerium dioxide itself is a useful material in many areas, such as catalytic water-gas shift reaction¹²³⁻¹²⁷, dissociation of water¹²⁸⁻¹³², catalytic oxidation of carbon monoxide^{127,133,134}, reduction of carbon dioxide^{132,135}, other catalytic reactions¹³⁶⁻¹³⁸, and biological systems¹³⁹⁻¹⁴⁵.

The water-gas shift reaction (WGS) ($CO + H_2O \rightarrow CO_2 + H_2$) is critical to get clean hydrogen instead of using fossil fuels. Although CeO_2 itself is a very poor catalyst for the WGS reaction, its derivatives have been proved to be good catalysts to the same reaction. Extensive studies have been carried out on the catalytic properties of CeO_2 in the WGS reaction. Flytzani-Stephanopoulos et al. reported the excellent catalytic property of Au / Cu supported on nanocrystalline CeO_2 in the WGS reaction¹⁴⁶. Rodriguez et al. discovered that the high performance of Au- CeO_2 catalyst in WGS relies excessively on the direct participation of the interface between the nanoparticle and the substrate¹²³. Graciani et al. took DFT calculations in the CeO_x -metal interfaces and compared the behavior of this system with various metals, expecting the CeO_x -Ag(111) to demonstrate a high activity similar with CeO_x -Cu(111) and CeO_x -Au(111)¹²⁶.

Haile and Steinfeld et al. proposed to use a solar-driven thermochemical cycle for dissociating water and carbon dioxide using nonstoichiometric ceria¹³². Huang et al. studied the interaction of atomic hydrogen and water with reduced and unreduced $CeO_2(111)$ surface, and found the process is controlled by oxygen vacancy concentration in $CeO_2(111)$ surface¹²⁹. Cheung et al. proposed a way to build up the catalytic activity of cerium oxide nanostructure by engineering high density of oxygen vacancy defects without dopants¹⁴⁷.

There are many studies focused on using computation simulation methods to uncover the details on the catalytic properties of ceria. Woo and Hermansson et al. used *ab initio* methods to investigate the atomic and electronic structure of reduced and unreduced CeO_2 surfaces, discovered the relationship between formation energy, location preference of oxygen vacancies with different surfaces of CeO_2 (reduced and unreduced)¹⁴⁸. A DFT+U approach was used by Sun et al. to investigate the interaction of water molecule with the reduced and unreduced ceria surface¹²⁸. Hansen and Wolverton also carried out DFT investigation on the water dissociation reaction on reduced ceria surface, and suggested substitutional doping with a cation to improve the decomposition of hydroxyls into hydrogen¹³⁰.

In summary, although extensive studies have been conducted in different materials and components in SOEC/SOFC, the nature of oxygen diffusion behavior in YSZ remains unclear and the agreement among different theoretical studies on the properties of GDC is rather poor. Also, there lack theoretical studies focusing on GDC as the buffering layer. Hence, in this study, we start with exploring details of oxygen diffusion behavior in YSZ and focus on the properties of GDC as an interlayer in SOEC.

Chapter 3

Methodology

Over the past decades, with the fast development of high performance computing hardware and software, computer modeling approach, which is closely integrated with experimental approach, has become a powerful and reliable tool that helps researchers gain insights and make predictions in science, especially physics, chemistry, and biology. Generally, the techniques used in computer modeling can be categorized into two types: methods which define interatomic interactions by using force fields, i.e. parameterized interatomic potentials; and methods which are based on ab initio calculations by solving Schrödinger equation with some level of approximation. This two kinds of methods can be combined and applied to one same system with focuses on different parts of the system. This chapter describes the detailed computational principles, methods, and models used in this dissertation. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is chosen to investigate atomic diffusion properties in YSZ using interatomic potentials. GULP is chosen to investigate oxygen migration properties in YSZ by using interatomic force fields. VASP (Vienna Ab Initio Simulation Program) is used to calculate accurate surface properties in ceria. In addition to these computational software packages, VESTA, a 3D visualization program, is used to calculate Madelung Energy by using Fourier method.

3.1 Interatomic Potential Methods

For strong ionic systems like YSZ, interactions between atoms are usually simplified into two-body interactions only. Together with shell model, which models ionic polarization, these methods successfully describe the behavior in solid ionic systems with satisfactory results and speed. Different from *ab initio* calculations, which usually involve solving of large matrices, classical simulations with potential functions require much less calculations and can be easily scaled up to millions of atoms. Therefore, interatomic potential methods have been chosen in the research of this dissertation as the main method of large scale atomic simulations.

3.1.1 Interatomic Potentials

The potential energy of a system whose interaction is described by potential function can be expanded by number of interacting atoms, suppose there are N atoms in the system:

$$U(r_1, r_2, \dots, r_N) = \sum_i U_1(r_i) + \sum_{i,j} U_2(r_i, r_j) + \sum_{i,j,k} U_3(r_i, r_j, r_k) + \dots \quad (3.1)$$

Here, $r_1, r_2, \dots, r_N$ are the coordinates of all atoms; U_1 is one-body term, which typically results from external field; U_2 is two-body term, which represents pair-pair interaction in the system and depends on only the two atoms in consideration; U_3 is three-body term, which needs to be considered when pair interactions are influenced by a third atom; higher terms, such as U_4 or even U_5 may arise when interaction becomes more complicated.

Based on **Equation 3.1**, we can divide interatomic potentials into two categories: pairwise potentials / pair potentials and many-body potentials which takes interactions with more than two atoms into account. Pair potentials are widely applied in van der Waals interactions between atoms and particle simulations which treat atoms as material non-specific particles and focus on general effects. Many-body potentials, on the other hand, are usually used in systems where pair potentials are limited, such as angular dependent systems (potential energy depends on bond angle) and metallic systems.

The following parts in this chapter will focus on principles in pair potentials only since YSZ system is an ionic system which can be described satisfactorily by pair potentials. In addition, there are no external field or boundary conditions which raise one-body term in the system in interest. Thus the potential function is approximated as

$$U(r_1, r_2, \dots, r_N) = \sum_{i,j} U_2(r_i, r_j) \quad (3.2)$$

3.1.1.1 Long Range Interactions

The electrostatic energy, defined by Coulombic interaction, is determined by atom charges and interatomic distances in an ionic system.

$$U(r_{ij}) = \frac{Z_i Z_j}{r_{ij}} \quad (3.3)$$

where Z_i and Z_j are the charges of atom i and atom j , and r_{ij} is the interatomic distance between the two atoms. As **Equation 3.3** shows, the electrostatic energy is inversely proportional to the interatomic distance. However, the fact that the number of ions involved in Coulombic interaction increases by $4\pi r^2$ (the area of a sphere) makes it difficult to calculate the sum of electrostatic energy given by **Equation 3.3**. The sum itself decays slower than the number of ions involved for summation, leading to the difficulty of convergence. Thus, Ewald summation, presented by Paul Peter Ewald in 1921, has been widely used in the summation of Coulombic energy^{149,150}.

In Ewald summation, which enables rapid convergence of energy in periodic system, the electrostatic potential is rewritten as the sum of two terms

$$\mathbf{U}(\mathbf{r}) = \mathbf{U}_{sr}(\mathbf{r}) + \mathbf{U}_{lr}(\mathbf{r}) \quad (3.4)$$

Here $U_{sr}(r)$ is short-range contribution which is calculated in real space and $U_{lr}(r)$ is long-range contribution which can be evaluated in Fourier space. The two terms come from adding two groups of Gaussian distributed charges into the original charge lattice. The process is described by the following equation:

$$Lattice_a = Lattice_b + Lattice_c \quad (3.5)$$

where $Lattice_a$ is the original charge lattice (**Figure 3.1-a**), $Lattice_b$ differs a little from $Lattice_a$: for each point charge, a surrounding Gaussian distributed charge is added, as shown in **Figure 3.1-b**, $Lattice_c$, as shown in **Figure 3.1-c**, is composed by a group of Gaussian distributed charges used to compensation the additional charge introduced in $Lattice_b$.

Figure 3.1 Charge lattices used in Ewald summation: (a) original lattice of point charges only; (b) point charges surrounded by opposite signed Gaussian distributed charges; (c) lattice with only Gaussian distributed charges to neutralize charge introduced in (b).

In $Lattice_b$, the Gaussian charges look just like point charges over a large enough distance. It will cancel with the point charge at the same position in remote distance. This kind of interactions, along with the self-interaction inside each Gaussian charge distribution, account for the short-range term in **Equation 3.4**, and can converge rapidly in real space. To obtain the electrostatic energy of the original point charge lattice, electrostatic energy

in $Lattice_c$ has to be added to that of $Lattice_b$. The electrostatic energy in $Lattice_c$ can be easily calculated by using reciprocal space. The convergence speed of the two terms in **Equation 3.4** is determined by the width of the Gaussian distributions, which can be adjusted to achieve optimized time cost.

3.1.1.2 Short Range Interactions

While the idea of long range Coulomb interaction is not complicate, the principles behind short range interactions between atoms are more complex. When two atoms are at a relatively large distance, they will have attractive interaction, called van der Waals interaction, with each other. The van der Waals interaction comes from the formation of immediate dipoles between two atoms' electron clouds^{151,152}. However, when the two atoms are too close, the overlap of electron clouds leads to strong repulsive forces. This repulsive interaction arises partly from the positive charged nuclei. Besides the simple coulombic repulsion, this repulsion interaction has a quantum mechanical character rooted in the **Pauli exclusion principle**, which states that no two electrons can have the same energy state. As the two atoms getting closer, the overlap of electron clouds increases, forcing electrons to occupy higher energy states due to the Pauli exclusion principle. Since electrons tend to occupy lowest energy states when they can, the new set of energy states formed in the two atom composite have higher energy. It requires energy to reach the new state. This requirement is expressed as a repulsion between the two atoms. **Figure 3.2** shows the typical shape of short range interactions between atoms along with the attractive and repulsive components.

Figure 3.2 Short range interaction energy together with its repulsive component and attractive component as a function of interatomic distance r .

The simplest short range interaction potential is hard / soft sphere potential, which is useful in theoretical investigation of some idealized problems while is not used in any practical problems. They are written in the form that

$$U_{hard}(r_{ij}) = \begin{cases} \infty & \text{for } r_{ij} \leq r_0 \\ 0 & \text{for } r_{ij} > r_0 \end{cases} \quad (3.6)$$

$$U_{soft}(r_{ij}) = \left(\frac{r_{ij}}{r_0}\right)^{-n} \quad (3.7)$$

where r_{ij} is the interatomic distance and r_0 is the sphere radius.

The Lennard-Jones interatomic potential, or 6-12 potential, proposed by John Lennard-Jones in 1924, is widely used to investigate general effects rather than material specific properties¹⁵³. It has two terms, a r^{-12} term which stands for the repulsive interaction and a r^{-6} term which represents the attractive term.

$$U_{LJ}(r_{ij}) = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right) \quad (3.8)$$

where r_{ij} is the interatomic distance and σ and ϵ are potential parameters.

Similar to Lennard-Jones potential, P. M. Morse proposed Morse potential, which is more suitable for systems where attractive interaction comes from the formation of chemical bonds¹⁵⁴. It is widely used in metal systems that have hcp and fcc structures. The Morse potential is written as

$$U_{Morse} = \epsilon \left(e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)} \right) \quad (3.9)$$

similarly, r_{ij} is the interatomic distance; ϵ and α are potential parameters.

For atoms that are not directly bonded, Richard Buckingham proposed a formula, the Buckingham potential, in 1938 to describe the Pauli repulsion energy and van der Waals energy in such system¹⁵⁵. The Buckingham potential is a simplification of the Lennard-Jones potential by replacing the r^{-12} term with an exponential function of r .

$$U_{Buckingham}(r_{ij}) = A_{ij} e^{-\frac{r_{ij}}{\rho}} - \frac{C_{ij}}{r_{ij}^6} \quad (3.10)$$

where r_{ij} is the interatomic distance and A, ρ , and C are fitted potential parameters. The Buckingham potential is the most commonly used potential in ionic and semi-ionic solid systems.

In this work, we also choose use the Buckingham potential in our system of interest because of its proven success in such systems. Now, with the long range and short range interaction combined together, we have the potential energy for the whole system written as

$$U(r_{ij}) = \sum_{ij} \left(\frac{q_i q_j}{r_{ij}} + A_{ij} e^{-\frac{r_{ij}}{\rho}} - \frac{C_{ij}}{r_{ij}^6} \right) \quad (3.11)$$

3.1.2 Shell Model

Until now, we are treating the ions and atoms as point charges. However, in practice, charges from ions and defects will polarize their nearby ions, i.e. polarization. Polarization of atoms are due to the deformation of electron cloud caused by external electric field. With the presence of other ions or defects, the electron clouds are polarized to lower total energy of the system. For this reason, rigid ion models that treat ions and atoms as single point charges tend to overestimate the total energy of a system. This effect can be tolerated in large scale molecular dynamics simulations, where the mean square displacements of ions are of concern. However, if we are to calculate properties that are sensitive to energy values, such as surface energy or defect formation energies, the effects have to be well included. To avoid such overestimation, shell model is introduced into the interaction model.

The shell model, proposed by Dick and Overhauser in 1958, provides a simple way to exceed the limitation of rigid ion models by including the effects from polarization approximately in a potential method¹⁵⁵. It can be implemented efficiently in classical molecular dynamics simulation. **Figure 3.3** shows a schematic illustration of shell model.

Figure 3.3 Shell model showing a core and a shell connected by an imaginary spring. Both the core part and the shell part are treated as point entities.

In shell model, the ion, with total charge Z , is treated as two indirectly connected parts: the core and the shell. Instead of treating the ion as a point charge, the total charge Z is split between the core (of charge $Z - Y$) and the shell (of charge Y). The core and shell are connected by an imaginary spring, leading to the harmonic interaction between the core and the shell:

$$E_{cs}(r) = \frac{1}{2}k_{cs}r^2 \quad (3.12)$$

Short-range forces defined by potential parameters act only on the shells, while Coulomb forces act on both shells and cores. In this way, the shells are allowed to be polarized by the electric and potential fields resulting from surrounding ions, making it possible for an ion's local environment to affect its charge distribution. If a three-body interaction potential is included in shell model, the effects of partial covalence bond can be approximately included. The three body term is written in a form of a harmonic potential as a function of bond angle:

$$E_{3b}(\theta) = \frac{1}{2}k_{3b}(\theta - \theta_0)^2 \quad (3.13)$$

where θ_0 is the equilibrium bond angle, and k_{3b} is the bending force constant.

3.1.3 Potential Parameters

Potential parameters are usually determined either by fitting to experimental data or the results of *ab initio* calculations. In this dissertation, the potential parameters used for molecular dynamics and defect simulations of the YSZ system are taken directly from previous literatures^{156,157}. The parameters have been proven to be reasonable and well tested in this system. The Buckingham potential parameters are listed in **Table 3.1** (a). To account for the ion polarization effects, oxygen ions and zirconium ions are treated with shell model. The shell model related parameters are listed in **Table 3.1** (b).

Table 3.1 Potential parameters in YSZ system

(a) Buckingham potential parameters

Pair Interaction	$A_{ij}(eV)$	$\rho(\text{\AA})$	$C_{ij}(eV \cdot \text{\AA}^6)$
$O^{2-} - O^{2-}$	22764.0	0.149	27.879
$Zr^{4+} - O^{2-}$	985.86	0.376	0.0
$Y^{3+} - O^{2-}$	1345.1	0.3491	0.0

(b) Shell model

Ion Species	$Y(e)$	$k(eV \cdot \text{\AA}^{-2})$
O^{2-}	-2.077	27.290
Zr^{4+}	1.35	169.617

3.1.4 Modeling of Point Defects

Oxygen vacancy plays a critical role in the YSZ system. To model the existence of point defects in lattice, there are generally two ways. One is to use a periodic super lattice large enough to approximate the defect concentrations, i.e. create vacancy or other defects in a large super lattice and apply periodic boundary conditions to that super lattice. Another one is to use the Mott-Littleton method, which will be described in details in the following paragraphs.

The super lattice approach utilizes a relatively large super cell with 3D periodic boundary conditions applied to calculate the defect formation energy in a system¹⁵⁸. With 3D periodic boundary conditions applied, the system consist with the super lattice repeated infinitely in three lattice directions. By varying the size of the super lattice, one is able to model different defect concentrations of that system. To calculate the defect formation energy in such model, the total energy of prefect lattice is used as a reference. For example, the defect formation energy of a single vacancy in CeO_2 lattice can be calculated using a super cell with chemical formula $Ce_{12}O_{24}$.

$$E(\text{Oxygen Vacancy}) = E(Ce_{12}O_{23}) - E(Ce_{12}O_{24}) + E(O) \quad (3.14)$$

depend on the vacancy formation details, the last term $E(O)$ can either be the energy of a single oxygen atom or half the energy of oxygen gas.

The Mott-Littleton method simplifies the defect model by dividing the crystal that surrounds the defect into two spherical regions and one region outside the larger sphere, i.e. region 1, region 2a, and region 2b, as shown in **Figure 3.4**¹⁵⁹. When there are more than one defects, the defect center, which is the weighted averaged coordinates of all point defects, is used. The size of these regions are usually determined by their radiuses or the number of ions they contain. During defect calculations, ions in region 1, typically with number of 100-300, are assumed to be heavily influenced by the defect. Thus the ions are relaxed explicitly. While ions in region 2 are assumed to be only slightly perturbed and can be approximated in some way. To be specific, region 2a ions are usually assumed to be constrained in harmonic wells, while ions in region 2b, which are again less perturbed by the defect, are dealt with a quasi-continuum approximation.

Figure 3.4 Regions of crystal divided by Mott-Littleton method. Regions are divided according to their distances to defect center.

Under such schema, the total energy of the system can be written as:

$$U_{tot}(x, \xi) = U_{11}(x) + U_{12}(x, \xi) + U_{22}(\xi) \quad (3.15)$$

where $U_{11}(x)$ stands for the total energy of region 1 which depends only on x , $U_{22}(\xi)$ stands for the total energy of region 2a and region 2b and depends only on the displacements, ξ , of ions in region 2, and $U_{12}(x, \xi)$ is the interaction energy between the two regions. Region 2a and region 2b are not distinguished in this stage, and are discussed in further approximations.

3.1.5 Transition State Search

In theoretical chemistry and condensed matter physics, one common yet important problem is to determine the minimum energy path of a chemical reaction. Such path is defined as the lowest potential energy path from one stable state to another, such as the process of defect migration in a lattice and gas molecule adsorption on a surface. Within all configurations along the path, the one with the highest potential energy is called the saddle point configuration (i.e. transition state), and hence the energy saddle point energy. This energy gives the activation energy barrier, and can be used to estimate the transition rate within the transition state theory.

There are several classes of methods in searching for transition states. One is to start from the initial configuration, local minimum, and follow a lowest ascent path in a stepwise manner. This method does not necessarily lead to saddle points and is computational inefficient due to its sequential nature. Other methods start with two local minimums, the initial configuration and final configuration. One example of such kind of methods is the “drag” method, in which some of the coordinates are used to define a progress variable. At each step, this variable is changed and other degrees of freedom are changed in a following energy minimization. This method works well in simple systems. However, it fails in many circumstances, the path found may be discontinuous, the results depend on the direction of drag, etc.

The currently most powerful methods are the “chain of images” methods. In such methods, a series of configurations (or, images) of the system is generated, usually by linear interpolation, between the initial and final states, and all configurations are optimized simultaneously in some concerted way. These images are connected with springs to trace the minimum energy path. For plain elastic band method, one of such methods, the objective function is written as

$$U^{chain}(x_1, \dots, x_{n-1}) = \sum_{i=0}^n U(x_i) + \sum_{i=1}^n \frac{k_i}{2} (x_i - x_{i-1})^2 \quad (3.16)$$

where x_i is the coordinates of i th image, $U(x_i)$ is the potential energy of i th image, k_i is the elastic constant of the spring that connects i th and $(i - 1)$ th image. Although this method can give good indication of the location of the saddle point, it usually fails to find the minimum energy path and to give good estimation of saddle point energy.

The Nudged Elastic Band (NEB) method¹⁶⁰⁻¹⁶², based on the plain elastic band method, greatly improves the convergence problem in plain elastic band method. **Figure 3.5** shows the two main problems, cutting corner and sliding down, related with plain elastic band method.

When the elastic band is too hard, the path generated by band will cut the corner and miss the saddle point, as **Figure 3.5-a** shows. Such behavior is called cutting corner. When the elastic band is too soft, the images tend to slide down to initial and final local minimums, resulting poor resolution around saddle point, as **Figure 3.5-b** shows. This behavior is called sliding down.

Figure 3.5 A sample of contour of a potential energy surface. (a) Cutting corner: blue dots connected by red dashed line: a plain elastic band with large spring; solid red line across contour lines: the minimum energy path. (b) Sliding down: blue dots connected by red dashed line: a plain elastic band with small spring; the minimum energy path is shown using a solid red line.

The problem of the cutting corner results from the perpendicular component of the spring force to the direction of the path. Forces in this direction tend to pull images away from the minimum energy path, making it unable to locate the saddle point. The sliding down problem comes from the component of the potential force (force on image by the potential surface) which is in the same direction with the path. The distance between images are uneven as a result of spring force balancing the parallel component of the potential force.

To solve this problem, Nudged Elastic Band (NEB) method is used. NEB can convergence to the minimum energy path efficiently when enough number of images are used. The NEB method carries out the elastic band minimization by taking the parallel component of potential force and the perpendicular component of spring force out of consideration. The force on image i then becomes:

$$F_i^0 = -\nabla U(x_i)_\perp + F_i^s \cdot \hat{\tau}_\parallel \hat{\tau}_\parallel \quad (3.17)$$

where $\hat{\tau}_{\parallel}$ is the unit tangent to the path and $\nabla U(x_i)_{\perp} = \nabla U(x_i) - \nabla U(x_i)\hat{\tau}_{\parallel}\hat{\tau}_{\parallel}$ is the perpendicular component of the potential force. This process of projection is called “nudging”, thus coming the name “Nudged Elastic Band”. The advantage of NEB is that the relaxation of images and the distribution of images along the path are decoupled, which ensures the convergence to the minimum energy path.

3.2 Molecular Dynamics

One of the principle tools in theoretical chemistry, physics, and biology is molecular dynamics simulations (MD). It involves solving the classical many-body problem in the concerned system at atomistic level. With no other competent tools and methods, MD has proved itself to be an essential part in both pure and applied research. Although the simplest form of MD, which deals with only structureless particles, hardly goes beyond Newton’s second law, the theoretical basis of MD involves more than Newton laws. For example, for systems with rigid molecules, Euler equations are required; for molecules, which have structural constraints, the Lagrange approach is required; for equilibrium system, the ensembles of statistical mechanics are required. While MD is widely used and well tested, it pays little heed to the two most prominent developments in physics in the 20th century – quantum mechanics and relativity. In particular, relativity proscribes information to transfer at a speed higher than the speed of light, while MD assumes infinite propagate speed for all interactions. Quantum mechanics has the uncertainty principle as its basic results, while MD requires accurate and complete information of each atom at all times. Due to the nature of MD simulations, MD deals with systems where the relativistic effects can be ignored and where quantum effects can be incorporated as semi-classical corrections.

3.2.1 Mean Square Displacement

Mean square displacement (MSD) is an observable in statistical mechanics which measures the deviation over time between the position of a particle and some reference position. It is defined as

$$MSD = \frac{1}{T} \sum_{t=1}^T (x_t - x_0)^2 \quad (3.18)$$

where T is the interested time period, x_0 is the reference position, and x_t is the position of particle at time t . As an observable that describes the displacement over time, MSD contains information on the diffusion coefficient D as the Einstein relation suggests:

$$MSD = A + 6Dt \quad (3.19)$$

where D is the diffusion coefficient, t is the diffusion time, 6 is the parameter for three-dimensional system, and it becomes 4 for two-dimensional system and 2 for one-dimensional system. This expression was first derived by Albert Einstein in his Ph.D. dissertation in 1905. It relates the diffusion coefficient D with the mean square displacement of molecular migration, thus creating a link between the macroscopic transportation property and microscopic movement in a system. In this thesis, this relation is used to calculate the diffusion coefficient as the following equation denotes.

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{MSD}{t} \quad (3.20)$$

3.2.2 Activation Energy

When oxygen vacancies are migrating inside solid lattices, it is actually oxygen ions “jumping” from one site to another. This “jumping” event usually requires enough external thermal energy to be provided. The energy required is called the activation energy, as **Figure 3.6** shows.

Figure 3.6 Schematic plot of ion migration and activation energy

For reactions that are temperature dependent, the Arrhenius equation describes the temperature dependence of reaction rates. The formation of vacancy and ion migration are both reactions that can be described by the Arrhenius equation. To realize a successful migration, there has to be a vacancy in the adjacent sites and there has to be enough thermal energy to activate it. According to the Arrhenius equation, the probability of finding a vacancy in adjacent sites is

$$P_v = A_v e^{-\frac{E_v}{k_b T}} \quad (3.21)$$

The probability of thermal fluctuation to overcome the migration barrier is

$$P_m = A_m e^{-\frac{E_m}{k_b T}} \quad (3.22)$$

Thus, the diffusion coefficient can be estimated as

$$D = A_v A_m e^{-\frac{E_v + E_m}{k_b T}} = D_0 e^{-\frac{E_d}{k_b T}} \quad (3.23)$$

where A_v , A_m , and D_0 are coefficients; E_v , E_m , and E_d are activation energies for the formation, migration, and diffusion of vacancies, respectively; The above Arrhenius equation for diffusion can be rewritten as

$$\ln D = \ln D_0 - \frac{E_d}{k_b T} \quad (3.24)$$

Thus the activation energy E_d is proportional to the absolute value of the slope of plot $\ln D$ v.s. $\frac{1}{T}$.

3.3 Quantum Mechanics

Different from force field method, quantum mechanics, one of the most important tools of physics developed in the 20th century, deals with interactions between electrons and nucleus from the very beginning with the help of Schrödinger equation. As the computation power grows rapidly in the last few decades, it is now possible to solve complex quantum mechanics problems with up to around 100 atoms or more numerically.

3.3.1 Born-Oppenheimer Approximation

In 1926, Erwin Schrödinger proposed the Schrödinger equation which describes how the wavefunction of a system changes over time. Since it is extremely difficult to solve the time dependent Schrödinger equation for most systems, most quantum mechanical approaches treat the systems by solving the time-independent Schrödinger equation with certain approximations. The time-independent Schrödinger equation can be written as

$$\hat{H}\Psi = E\Psi \quad (3.25)$$

where $\hat{H}$ is the Hamiltonian operator, which have different forms depending on the system; Ψ is the wave function, which contains all information of the system; E is the energy of state. This equation states that the wave function Ψ is a stationary state if the result of

acting the Hamiltonian operation on the same wave function is proportional to Ψ itself. The energy of this state is E , which is the proportionality constant.

The non-relativistic time-independent Schrödinger equation in atomistic systems is¹⁶³

$$\left[-\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \right] \Psi = E \Psi \quad (3.26)$$

where Ψ and E have previous meanings; i and j are indexes for the N electrons; A and B are indexes for the M nuclei; M_A is the mass of nucleus A ; Z_A is the atomic number of nucleus A ; r_{iA} , r_{ij} , and R_{AB} are the distances for pairs of electron-nucleus, electron-electron, and nucleus-nucleus. The terms in above equation represent: the kinetic energy of electrons (1st term) and nuclei (2nd term), the interaction between electron and nucleus (3rd term), the interaction between electron and electron (4th term), and the interaction between nucleus and nucleus (5th term). For one electron system, the equation can be solved exactly. However, for many electron systems, extra approximations are needed to get a solution for this equation.

One especially practical approximation is the Born-Oppenheimer approximation¹⁶⁴, or the adiabatic approximation. Based on the fact that the nuclei are much heavier than electrons and that the electrons move much faster than the nuclei, the Born-Oppenheimer approximation assumes that the motion of atomic nuclei and electrons can be separated. Under this assumption, the problem is reduced to the problem of solving the equation of electrons only.

$$\left[-\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \right] \Psi = E \Psi \quad (3.27)$$

where the terms have similar meanings to those in the previous equation. Further simplifications, the Hartree-Fock theory and Density Functional Theory, can be used to allow efficient calculations for most systems.

3.3.2 Hartree-Fock Method

The Hartree-Fock method treats many body problem with a one body picture. The electrons are treated as occupying single particle orbitals making up the wavefunction. The effects of the presence of other electrons are indirectly taken into account by making use of an effective potential, giving Hamiltonian in the form of

$$H = -\sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N V_{ext}(r_i) + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = T + V_{bkg} + V_{ee} \quad (3.28)$$

where the three terms are, in the order they appear, the kinetics, the background potential, and electron-electron interaction.

The Hartree-Fock method assumes that the ground state wavefunction can be approximated by a Slater determinant made up of one spin orbital per electron¹⁶⁵⁻¹⁶⁷. For an N-electron system, the wavefunction is

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(r_1) & \varphi_2(r_1) & \cdots & \varphi_N(r_1) \\ \varphi_1(r_2) & \varphi_2(r_2) & \cdots & \varphi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(r_N) & \varphi_2(r_N) & \cdots & \varphi_N(r_N) \end{vmatrix} \quad (3.29)$$

where r_i is the spin and spatial coordinates of electrons. This forms correctly demonstrates the antisymmetric nature of the wavefunction: the wavefunction changes its sign when two electrons are exchanged. This principle results from Pauli exclusion principle, which says that no two electrons can have the same energy state.

The ground state energy is given by,

$$\begin{aligned}
E = \langle \Psi | H | \Psi \rangle &= \sum_{i=1}^N \int \varphi_i^*(r) \left(-\frac{1}{2} \nabla^2 + V_{ext}(r_i) \right) \varphi_i(r) dr \\
&+ \frac{1}{2} \sum_{i,j} \int \frac{|\varphi_i(r)|^2 |\varphi_j(r')|^2}{|r - r'|} dr dr' \\
&- \frac{1}{2} \sum_{i,j} \int \frac{\varphi_i(r) \varphi_j^*(r) \varphi_j(r') \varphi_i^*(r')}{|r - r'|} dr dr'
\end{aligned} \tag{3.30}$$

The Hartree-Fock equations are obtained by taking variations with respect to each $\varphi_i(r)$, giving

$$\begin{aligned}
&\left(-\frac{1}{2} \nabla^2 + V_{ext}(r) + \sum_j \int \frac{|\varphi_j(r')|^2}{|r - r'|} dr' \right) \varphi_i(r) - \sum_j \int \frac{\varphi_j^*(r') \varphi_i(r')}{|r - r'|} dr' \varphi_j(r) \\
&= \epsilon_i \varphi_i(r)
\end{aligned} \tag{3.31}$$

or, in a concise form

$$[h(r) + \sum_j \mathcal{J}_j(r) - \sum_j \mathcal{K}_j(r)] \varphi_i(r) = \epsilon_i \varphi_i(r) \tag{3.32}$$

$$h(r) = -\frac{1}{2} \nabla^2 + V_{ext}(r) \tag{3.33}$$

$$\mathcal{J}_j(r) = \int \frac{|\varphi_j(r')|^2}{|r - r'|} dr' \tag{3.34}$$

$$\mathcal{K}_j(r) \varphi_i(r) = \int \frac{\varphi_j^*(r') \varphi_i(r')}{|r - r'|} dr' \varphi_j(r) \tag{3.35}$$

Here, $h(r)$ is the kinetics term and background potential term; $\mathcal{J}_j(r)$ is the classical Coulomb interaction of electron I from electron j; $\mathcal{K}_j(r)$, which results from the antisymmetric principle of the Slater determinant, doesn't have a classical equivalence and is called exchange interaction. The operator $h(r) + \sum_j \mathcal{J}_j(r) - \sum_j \mathcal{K}_j(r)$ is called the Fock operator.

The numerical approach used to solve the Hartree-Fock equations is to solve it in an iterative way: to begin with, an initial guess of the orbitals is used to construct the Fock

operator. By solving the Hartree-Fock equations using this Fock operator, one is able to obtain new orbitals from the equations. Thus a new Fock operator is constructed from the new set of orbitals. This process is repeated until the convergence condition is satisfied. With the resulting converged orbitals, one is able to get the wavefunction in the form of the Slater determinant, and thus all the other physical properties of the system.

As the Slater determinant is a product of imagination, there is no guarantee that it will satisfy all the properties of the exact wavefunction. In particular, as the electron interactions are represented indirectly through the mean field, electron correlation, the effects arise from electrons with opposite signs, are completely neglected. This neglect can lead to significant deviations from experimental results. Many approaches, called post-Hartree-Fock methods, have been proposed to include electron correlation into the wavefunction.

3.3.3 Density Functional Theory

While many powerful methods have been developed to solve the Schrödinger equation for many-body system, the huge computational complexity simply makes it impossible to apply these methods on large and complex systems. Density Functional Theory (DFT) approaches the problem by using functionals of the spatially dependent electron density, providing a much more adaptable alternative. DFT realizes that “nonrelativistic Coulomb systems differ only by their potential $V(r)$, and supplies a prescription for dealing with the universal operators T and U once and for all”¹⁶⁸. It further provides a systematic way to map many-body problem into a single-body problem, by treating the spatially dependent electron density as the key variable.

3.3.3.1 The Hohenberg-Kohn Theorem

The two ingeniously simple Hohenberg-Kohn (HK) theorems, put forward and proven by Hohenberg and Kohn in 1964, lays the foundations of DFT¹⁶⁹.

Theorem I: *For any system of interacting particles in an external potential $V_{ext}(r)$, the density $n(r)$ is uniquely determined, i.e. the external potential $V_{ext}(r)$ is a unique functional of the density.*

Since $V_{ext}(r)$ determines the Hamiltonian operator $\hat{H}$, this theorem implies that the ground state wavefunction Ψ is also a unique functional of the density $n(r)$. Furthermore, all observables of this system can be calculated once the density $n(r)$ is known.

Theorem II: *A universal functional for the energy $E[n(r)]$ can be defined in terms of the density, the exact ground state is the global minimum value of this functional.*

This theorem makes it possible to obtain the orbitals that lead to the ground state energy, by minimizing the total energy with respect to the orbitals. This procedure leads to the Kohn-Sham Equations.

3.3.3.2 Kohn-Sham Equations

For N-electron systems, the universal functional in **Theorem II** can be written as the sum of kinetic energy and interaction energy,

$$E[n] = T[n] + U[n] \quad (3.36)$$

Taking exchange correlation into consideration, the kinetic energy and interaction energy can be split into two terms, respectively.

$$T[n] = T_s[n] + T_c[n] \quad (3.37)$$

$$U[n] = U_H[n] + U_c[n] \quad (3.38)$$

where $T_s[n]$ and $T_c[n]$ are the kinetic energies rise from single particle and correlation, the subscript s and c represent ‘single-particle’ and ‘correlation’; similarly, $U_c[n]$ is the interaction energy rises from correlation; $U_H[n]$ is the so-called Hartree energy, the electrostatic interaction energy of the charge distribution $n(r)$

$$U_H[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r-r'|} \quad (3.39)$$

Notice here that $T_s[n]$ is not a direct functional of $n(r)$, but it can be expressed in terms of the single particle orbitals $\varphi_i(r)$ of a non-interacting system with density $n(r)$,

$$T_s[n] = -\frac{1}{2} \sum_{i=1}^N \int d^3r \varphi_i^*(r) \nabla^2 \varphi_i(r) \quad (3.40)$$

This expression is not an explicit functional of density, but an explicit functional of orbital. However as $\varphi_i(r)$ is density functional, $T_s[n]$ is an implicit functional of density, i.e. $T_s[n] = T_s[\{\varphi_i[n]\}]$.

Thus the exact energy functional can be rewritten as

$$E[n] = T[n] + U[n] + V[n] = T_s[\{\varphi_i[n]\}] + U_H[n] + E_{xc}[n] + V[n] \quad (3.41)$$

where the functional $E_{xc}[n]$, which contains the differences $T[n] - T_s[n]$ and $U[n] - U_H[n]$ by definition, is called the exchange-correlation (xc) energy. The exchange-correlation energy can be split into two terms, i.e. $E_{xc} = E_x + E_c$, where E_x is due to the Pauli exclusion principle, i.e. exchange energy, and E_c is due to correlations, i.e. correlation energy. The exchange energy can be expressed as the functional of single-particle orbitals as

$$E_x[\{\varphi_i[n]\}] = -\frac{1}{2} \sum_{jk} \int d^3r \int d^3r' \frac{\varphi_j^*(r) \varphi_k^*(r') \varphi_j(r') \varphi_k(r)}{|r-r'|} \quad (3.42)$$

This term is known as the Fock term, which has no exact expression in terms of density till now.

The following derivation of the Kohn-Sham equations becomes straightforward. The ground state is obtained by minimizing $E[n]$, notice here $T_s[n]$ cannot be minimized directly since it is not an explicit functional of $n(r)$.

$$0 = \frac{\delta E[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + \frac{\delta V[n]}{\delta n(r)} + \frac{\delta U_H[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + v(r) + v_H(r) + v_{xc}(r) \quad (3.43)$$

where $\frac{\delta V[n]}{\delta n(r)} = v(r)$ is the external potential; $\frac{\delta U_H[n]}{\delta n(r)} = v_H(r)$ is the Hartree potential; $\frac{\delta E_{xc}[n]}{\delta n(r)} = v_{xc}(r)$ can be calculated as long as an approximation is chosen for $E_{xc}[n]$.

Now consider a system of non-interacting particles in a potential v_s , the minimization is simple and is shown as

$$0 = \frac{\delta E_s[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + \frac{\delta V_s[n]}{\delta n(r)} = \frac{\delta T_s[n]}{\delta n(r)} + v_s(r) \quad (3.44)$$

The density solved from this equation is denoted as $n_s(r)$.

Comparing the two equations, we realize that by choosing

$$v_s(r) = v(r) + v_H(r) + v_{xc}(r) \quad (3.45)$$

we have $n_s(r) \equiv n(r)$. That is to say, one is able to calculate the density of an interacting system with potential $v(r)$ by solving the equations of a non-interacting system with potential $v_s(r)$.

The corresponding Schrödinger equation for this non-interacting system,

$$\left[-\frac{1}{2} \nabla^2 + v_s(r) \right] \varphi_i(r) = \epsilon_i \varphi_i(r) \quad (3.46)$$

gives orbitals that replicate the density $n(r)$ of the interacting system,

$$n(r) \equiv n_s(r) = \sum_{i=1}^N f_i |\varphi_i(r)|^2 \quad (3.47)$$

where f_i is the occupation of the i th orbital.

The three equations are called the Kohn-Sham (KS) equations. The KS equations can be solved in an iterative manner by assuming an initial density, calculating $v_s(r)$ from the guessed density, obtaining a new density from the equation, until convergence. The equations are exact except we have to propose approximation for the exchange correlation functional $E_{xc}[n]$.

3.3.4 Exchange-Correlation Functionals

As we've seen in the previous section, to solve the KS equations, one has to generate approximations of the exchange correlation functionals. Many different functionals have been proposed. The local density approximation (LDA) and the generalized gradient approximation (GGA) are two important levels of approximations and are used in the calculations of this thesis.

3.3.4.1 Local Density Approximation

Local density approximation (LDA) assumes that the charge density varies gently enough in the atom, so that the electronic systems, inhomogeneous in practical, can be treated as locally homogeneous systems¹⁷⁰. Hence, the exchange-correlation functional in LDA can be written as the integration of the local exchange-correlation functional $\epsilon_{xc}(n(r))$, which is the functional standing for the exchange-correlation energy at r in a uniform system,

$$E_{xc}^{LDA}[n(r)] = \int d^3r n(r) \epsilon_{xc}(n(r)) \quad (3.48)$$

$\epsilon_{xc}(n(r))$ can be divided into two components, the exchange term ϵ_x and the correlation term ϵ_c . The per-volume exchange energy of the homogeneous electron gas is known exactly,

$$\epsilon_x(n) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n^{\frac{4}{3}} \quad (3.49)$$

Highly accurate correlation energy term is available from quantum Monte Carlo simulations by Ceperley and Alder¹⁷¹.

LDA has been applied in, for example calculations of band structures and total energies in solid state physics for decades. Although LDA is reasonable and practical for many systems, the exchange energy is usually underestimated by a percentage of ~10% comparing with the result from Hatree-Fock method, and the correlation energy is usually overestimated by a percentage of ~200%, leading to an overestimation of bond length thus less popularity in quantum chemistry.

3.3.4.2 Generalized Gradient Approximation

In LDA, one's knowledge about the density is limited to the local density at point r . In any real system, the density is spatially inhomogeneous. It's apparently useful to take the rate of variation of $n(r)$ into account when dealing with real systems. Generalized-gradient approximations (GGAs) was proposed by using general functions of $n(r)$ and $\nabla n(r)$, in the form of

$$E_{xc}^{GGA}[n] = \int d^3r f(n(r), \nabla n(r)) \quad (3.50)$$

Different GGAs have different choices in the function $f(n, \nabla n)$. The GGA used in this study is PW91, which was developed by Perdew and Wang in 1991^{172,173}. As Perdew states, PW91 is “based on real-space cutoff of the spurious long-range components of the second-order gradient expansion for the exchange-correlation hole”¹⁷³. Typically, as calculations show, the PW91 functional reduces the error in exchange energy to 1% comparing with the 10% error in LDA and reduces the correlation energy error to 10% from the 100% error in LDA¹⁷⁴. It provides highly accurate total energies and atomization energies compared with LDA. In this thesis, the PW91 functional is used to describe the exchange-correlation energy.

3.3.5 DFT+U Theory

The results of a Kohn-Sham equation would be exact if the exact exchange-correlation function, which is unknown unfortunately, could be used. Since LDAs and GGAs are both approximations for the exchange-correlation functional, we expect some extent of error to along with the usage of such approximations. Taking the system of a single H atom as an example, since there exists only one electron in this system, the electron cannot interact with itself through the Coulomb interaction. The contribution of Coulomb interaction should be zero for such system, which is not true for neither LDAs nor GGAs. Such kind of error that results from non-vanishing self-interaction is called self-interaction error (SIE).

The self-interaction error is significant for $3d$ and $4f$ electrons, which, due to strong on-site Coulomb interactions, are localized to atomic-like orbitals. For example, the LDAs and GGAs incorrectly predict the ground state of atomic Ni to have the configuration $3d^9 4s^1$ instead of the correct configuration $3d^8 4s^2$. Another situation is the underestimation of band gaps in transition metals by LDAs and GGAs. To improve the description of DFT on such systems, the DFT+U method was proposed.

In the semi-empirical band structure calculation methods, the generalized Hubbard model, named after John Hubbard, is a simple model of interacting particle in lattice, with only two terms, one kinetic term allowing for particle hopping between lattice sites, and one potential term for the on-site interaction¹⁷⁵. Inspired by the Hubbard model, an orbital occupation dependent energy correction term (Hubbard-like term) to the DFT functional can be added to exclusively improve the electron-electron description of the $3d$ electrons. This leads to the formulation of the DFT+U theory. The strength of the on-site interactions is usually described by parameters U (on site Coulomb) and J (on site exchange). The value of U and J are usually obtained using semi-empirical methods.

The DFT+U correction can be introduced to calculations in different ways. The two main implementations are the one proposed by Liechtenstein et al., where U and J are independent corrections in the calculations, and the one by Anasimov et al., in which only

the difference between U and J , i.e. $U_{eff} = U - J$, determines the Coulomb interaction, neglecting any higher multi-polar terms^{176,177}. The latter one is the one that is used in this thesis. The total energy function of DFT+U theory thus can be written as

$$E^{DFT+U}[n(r), f_s] = E^{DFT}[n(r)] + E^U[f_s; U_{eff}] \quad (3.51)$$

where f_s is the occupation numbers of a particular shell of orbitals. In solid state systems, the DFT+U theory has been proven to be successful, especially when dealing with transition metal systems.

3.3.6 Pseudopotentials and Projector Augmented Wave Method

Since the valence electrons have much greater influence on the system properties than core electrons in most systems, approximations and optimizations can be applied to lower the computation complexity. The approximation of pseudopotential approach assumes that only the outer shell electrons, i.e. valence electrons, need to be considered carefully in the interaction between atoms, and that the system can be replicated by replacing the potential of the nucleus and core electrons with an effective potential. The potential is supposed to only act on the valence electrons. The benefit of pseudopotential model is that the resulting wavefunction is smoother than the original wavefunction which oscillates rapidly. Such behavior is due to the large attractive potential of the nucleus. As a result, the number of basis functions that are needed in the calculation can be significantly diminished while keeping satisfactory level of accuracy¹⁷⁸. **Figure 3.7** shows a schematic comparison between actual wavefunction and the pseudopotential resulting wavefunction.

Figure 3.7 Schematic comparison between pseudopotential and actual nuclear potential and comparison between pseudopotential wave function and real wave function (Figure retrieved Jul 20, 2016, from Wikipedia¹⁷⁹).

The method that the augmented wave methods uses is to split the wave function into different parts. By dividing the space using atom-centered spheres, different expansions are used in and outside the spheres: in the spheres, partial-wave expansions are used; outside the spheres, envelope functions are used. At the boundary spheres, the envelop function and the partial-wave expansions are matched with each other involving both their

values and derivatives. To allow for greater computational efficiency, the envelop function is usually expanded into plane waves.

The projector augmented wave (PAW) method, different from augmented wave methods, which determines the coefficients from the value and derivative of the pseudopotential wave function at boundary sphere, uses a more general principle to determine the coefficients¹⁸⁰. This principle is called the principle of projector augmentation. It has been shown by the authors of PAW that, linear augmented plane wave method (LAPW) can be treated as a special case of the PAW method¹⁸¹. The PAW method transforms the physically relevant all-electron wavefunctions into computationally convenient pseudo wavefunctions. If we denote all pseudopotential representation related quantities with a tilde, with the transformation $\mathcal{T}$ from pseudopotential wavefunctions to the all-electron wavefunctions, the physical observables, or the expectation $\langle A \rangle$ of some operator A , can be obtained either directly by $\langle \Psi | A | \Psi \rangle$ after the transformation $\Psi = \mathcal{T} \tilde{\Psi}$, or by using $\langle \tilde{\Psi} | \tilde{A} | \tilde{\Psi} \rangle$ with $\tilde{A} = \mathcal{T}^T A \mathcal{T}$. Similarly, the total energy can be evaluated directly as a functional of the pseudopotential wavefunctions,

$$\frac{\partial E[\mathcal{T} \tilde{\Psi}]}{\partial \tilde{\Psi}} = \epsilon \mathcal{T}^T \mathcal{T} \tilde{\Psi} \quad (3.52)$$

In PAW, the transformation is written in the form

$$\mathcal{T} = 1 + \sum_R \mathcal{T}_R \quad (3.53)$$

where the local, atom-centered term $\mathcal{T}_R$ acts only inside the augmentation region surrounding the atom and is determined by using the target functions ϕ_i and initial functions $\tilde{\phi}_i$ of the transformation $\mathcal{T}$, i.e. $\phi_i = (1 + \mathcal{T}_R) \tilde{\phi}_i$.

The formalism of PAW method states that, with some augmentation region enclosing the atom denotes as Ω_R , a set of auxiliary functions $\tilde{\phi}_i$ introduced to link, in the augmentation region, the expansion of all-electron wavefunctions and that of pseudopotential wavefunctions, the pseudopotential wavefunction and the all-electron wavefunction are

identical outside the augmentation region Ω_R . Within the augmentation region Ω_R , we have the pseudopotential wavefunction expanded with respect to pseudopotential partial waves

$$\tilde{\Psi} = \sum_i c_i \tilde{\phi}_i, \text{ within } \Omega_R \quad (3.54)$$

Since $\phi_i = \mathcal{T} \tilde{\phi}_i$, the corresponding all-electron wave function can be expanded with respect to the all-electron partial waves

$$\Psi = \mathcal{T} \tilde{\Psi} = \sum_i c_i \phi_i, \text{ within } \Omega_R \quad (3.55)$$

As the coefficients c_i are identical for both equations, the all-electron wavefunction can be written as

$$\Psi = \tilde{\Psi} - \sum_i c_i \tilde{\phi}_i + \sum_i c_i \phi_i \quad (3.56)$$

with the coefficients determined by

$$c_i = \langle \tilde{p}_i | \tilde{\Psi} \rangle \quad (3.57)$$

where p_i is some fixed functions called projector functions, which must satisfy the condition that

$$\sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i| = 1, \text{ within } \Omega_R \quad (3.58)$$

since $\sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i| \tilde{\Psi}$ should equal $\tilde{\Psi}$ itself, which implies that $\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}$.

In summary, using the transformation

$$\mathcal{T} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i| \quad (3.59)$$

the all-electron wavefunction can be obtained from the pseudopotential wavefunction by

$$|\Psi\rangle = |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi} \rangle \quad (3.60)$$

Under this transformation, the calculations for integrals are significantly reduced as only smooth functions and localized integrals are involved. PAW handles the all-electron wavefunctions, with core states frozen at the atomic solutions, thus has great advantage over pseudopotentials in full charge and spin density calculations. The PAW method is used in the calculations of this thesis to allow for higher computational accuracy and efficiency¹⁸².

3.4 Theory of Elasticity

The ability of solid materials to resume its shape after deformation, i.e. change in shape and volume, under external force is called elasticity. The theory of mechanics of solid bodies, which are treated as continuous media, is the theory of elasticity. Perfect elasticity is an approximation of the real world, but is of great use in mechanics and engineering.

3.4.1 Deformations by Finite Displacements

The mathematical description of deformation is defined by the coordinates of a deformed body, before and after the deformation. If we denote the coordinate of any point in the body using a radius vector $\mathbf{r}$ (with three components $x_1 = x$, $x_2 = y$, $x_3 = z$), when the body is deformed, every point is somehow displaced. For example, a point with coordinate $\mathbf{r}$ before the deformation will have a different $\mathbf{r}'$ after deformation. The displacement of this point is given by $\mathbf{r} - \mathbf{r}'$ and is denoted as $\mathbf{u}$, the displacement vector,

$$u_i = x'_i - x_i \quad (3.61)$$

The entire deformation would be known if the displacement vector $\mathbf{u}$ is a known function of coordinates x_i .

Consider two points closely located to each other, the radius vector joining them is dx_i before deformation, and dx'_i after deformation, where $dx'_i = dx_i + du_i$. The distance between the points before and after deformation is dl and dl' , and satisfies the relation

$$dl'^2 = dl^2 + 2 \sum_{i,k} u_{ik} dx_i dx_k \quad (3.62)$$

$$u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} + \sum_l \frac{\partial u_l}{\partial x_i} \frac{\partial u_l}{\partial x_k} \right) \quad (3.63)$$

The tensor u_{ik} is called the strain tensor. From definition, the strain tensor is symmetrical, i.e. $u_{ik} = u_{ki}$.

For small deformations, while the displacement vector u may be very large, all the components of the strain tensor are small because they are giving relative changes in the length of the body. Therefore, in the definition of the strain tensor, the last term, which is of the second order of smallness, can be neglected, giving the strain tensor for small deformations as

$$u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \quad (3.64)$$

The strain tensor for spherical coordinates, r , θ , and ϕ are given as follows:

$$\begin{aligned} u_{rr} &= \frac{\partial u_r}{\partial r}, u_{\theta\theta} = \frac{1}{r} \frac{\partial u_\theta}{\partial \theta} + \frac{u_r}{r}, u_{\phi\phi} = \frac{1}{r \sin \theta} \frac{\partial u_\phi}{\partial \phi} + \frac{u_\theta}{r} \cot \theta + \frac{u_r}{r} \\ 2u_{\theta\phi} &= \frac{1}{r} \left(\frac{\partial u_\phi}{\partial \theta} - u_\phi \cot \theta \right) + \frac{1}{r \sin \theta} \frac{\partial u_\theta}{\partial \phi} \\ 2u_{r\theta} &= \frac{\partial u_\theta}{\partial r} - \frac{u_\theta}{r} + \frac{1}{r} \frac{\partial u_r}{\partial \theta} \\ 2u_{\phi r} &= \frac{1}{r \sin \theta} \frac{\partial u_r}{\partial \phi} + \frac{\partial u_\phi}{\partial r} - \frac{u_\phi}{r} \end{aligned} \quad (3.65)$$

For cylindrical coordinates, r , ϕ , and z , the strain tensor is,

$$\begin{aligned}
u_{rr} &= \frac{\partial u_r}{\partial r}, u_{\phi\phi} = \frac{1}{r} \frac{\partial u_\phi}{\partial \phi} + \frac{u_r}{r}, u_{zz} = \frac{\partial u_z}{\partial z} \\
2u_{\phi z} &= \frac{1}{r} \frac{\partial u_z}{\partial \phi} + \frac{\partial u_\phi}{\partial z}, 2u_{rz} = \frac{\partial u_r}{\partial z} + \frac{\partial u_z}{\partial r} \\
2u_{r\phi} &= \frac{\partial u_\phi}{\partial r} - \frac{u_\phi}{r} + \frac{1}{r} \frac{\partial u_r}{\partial \phi}
\end{aligned}
\tag{ 3.66 }$$

When there are deformations, there are internal forces, the so-called internal stresses. The internal stresses are due to molecular forces, which have a very short range of actions. This short range nature suggests that any forces exerted on some part of the body by its surrounding parts act only on the surface of that part. Take the total force on some portion of the body as example. The total force can be summed over the total volume, i.e. written as $\int F dV$, where F is the force in unit volume. Since forces on different parts inside the portion will cancel with each other, leaving only surface parts of those forces, the total force is the integral over the surface. This property holds true for all three components for the forces, i.e. $\int F_i dV, i = 1, 2, 3$. Since we have a force which is a vector, and its integral over any volume can be written as an integral over a surface, the vector F_i has to be the divergence of a tensor of rank two, i.e. in the form of

$$F_i = \sum_k \frac{\partial \sigma_{ik}}{\partial x_k} \tag{ 3.67 }$$

Hence, we have

$$\int F_i dV = \int \sum_k \frac{\partial \sigma_{ik}}{\partial x_k} dV = \oint \sum_k \sigma_{ik} df_k \tag{ 3.68 }$$

where df_i are the components of the surface element vector df , directed along the outward normal.

The tensor σ_{ik} is called the stress tensor. With some further analysis, it is easy to find that the stress tensor is symmetrical, i.e. $\sigma_{ik} = \sigma_{ki}$.

The relationship between stress tensor and strain tensor in homogeneous deformation is

$$\sigma_{ik} = \frac{E}{1+\sigma} \left(u_{ik} + \frac{\sigma}{1-2\sigma} \sum_l u_{ll} \delta_{ik} \right) \quad (3.69)$$

$$u_{ik} = \frac{(1+\sigma)\sigma_{ik} - \sigma \sum_l \sigma_{ll} \delta_{ik}}{E} \quad (3.70)$$

where E is Young's modulus, and σ is the Poisson's ratio, which is the ratio of the transverse compression to the longitudinal extension.

$$E = \frac{9K\mu}{3K+\mu}, \sigma = \frac{1}{2} \frac{3K-2\mu}{3K+\mu} \quad (3.71)$$

where K is the modulus of hydrostatic compression (in short the modulus of compression) and μ is the modulus of rigidity.

3.4.2 Elastic Equilibrium Equations

When the body is at elastic equilibrium, the internal stresses of every unit volume must balance with each other. That is to say, all the components of the forces per volume must be zero. Hence, the equations of equilibrium for a deformed body are

$$F_i = \sum_k \frac{\partial \sigma_{ik}}{\partial x_k} = 0, i = 1, 2, 3 \quad (3.72)$$

For isotropic solid bodies, as stated in previous section,

$$\sum_k \frac{\partial \sigma_{ik}}{\partial x_k} = \sum_l \frac{E\sigma}{(1+\sigma)(1-2\sigma)} \frac{\partial u_{ll}}{\partial x_i} + \sum_k \frac{E}{1+\sigma} \frac{\partial u_{ik}}{\partial x_k} \quad (3.73)$$

Recall that

$$u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \quad (3.74)$$

We obtain the equations for equilibrium in the form

$$\frac{E}{2(1+\sigma)} \frac{\partial^2 u_i}{\partial x_k^2} + \frac{E}{2(1+\sigma)(1-2\sigma)} \sum_l \frac{\partial^2 u_l}{\partial x_i \partial x_l} = 0 \quad (3.75)$$

or, in a cleaner form

$$\nabla^2 u + \frac{1}{1-2\sigma} \nabla(\nabla \cdot u) = 0 \quad (3.76)$$

remember that

$$\nabla^2 u = \nabla(\nabla \cdot u) - \nabla \times (\nabla \times u) \quad (3.77)$$

the equilibrium equation can also be written as

$$2(1-\sigma)\nabla(\nabla \cdot u) - (1-2\sigma)\nabla \times (\nabla \times u) = 0 \quad (3.78)$$

3.4.3 Solutions for Simple Systems

The equations of equilibrium have wide applications in different systems. Knowing the solutions for some common systems will benefit us a lot when dealing with real world problems.

3.4.2.1 Deformation of a Hollow Sphere

For a hollow sphere of internal and external radii R_1 and R_2 with inside and outside pressure p_1 and p_2 , the deformation can be determined by the following procedure.

With a properly set spherical coordinate, the displacement vector is u is everywhere radial, and is the function of r along. Thus we have $\nabla \times u = 0$, leading to

$$\nabla(\nabla \cdot u) = 0 \quad (3.79)$$

according to the equation of equilibrium. Hence

$$\nabla \cdot u = \frac{1}{r^2} \frac{d(r^2 u)}{dr} \equiv \text{const} \equiv 3a \quad (3.80)$$

giving

$$u = ar + \frac{b}{r^2} \quad (3.81)$$

$$u_{rr} = a - \frac{2b}{r^3}, u_{\theta\theta} = u_{\phi\phi} = a + \frac{b}{r^3} \quad (3.82)$$

The radial stress is

$$\sigma_{rr} = \frac{E[(1-\sigma)u_{rr} + 2\sigma u_{\theta\theta}]}{(1+\sigma)(1-2\sigma)} = \frac{E}{1-2\sigma}a - \frac{2E}{1+\sigma}\frac{b}{r^3} \quad (3.83)$$

By applying the boundary conditions,

$$\sigma_{rr}(r = R_1) = -p_1, \sigma_{rr}(r = R_2) = -p_2 \quad (3.84)$$

we can obtain the value of the coefficients a and b :

$$a = \frac{p_1 R_1^3 - p_2 R_2^3}{R_2^3 - R_1^3} \frac{1-2\sigma}{E}, b = \frac{R_1^3 R_2^3 (p_1 - p_2)}{R_2^3 - R_1^3} \frac{1+\sigma}{2E} \quad (3.85)$$

3.4.2.2 Deformation of a Cylindrical Pipe

Similar to the hollow sphere problem is the problem in a cylindrical pipe system. The cylindrical pipe, with internal and external radii R_1 and R_2 , bears a pressure p inside and no pressure outside.

With a properly set cylindrical coordinate, which has the z -axis along the axis of the pipe, the deformation is all radial, and is a function of r along. As the sphere problem in the previous section, we have

$$\nabla \cdot u = \frac{1}{r} \frac{d(ru)}{dr} \equiv \text{const} \equiv 2a \quad (3.86)$$

leading to,

$$u = ar + \frac{b}{r} \quad (3.87)$$

Hence, we have

$$u_{rr} = a - \frac{b}{r^2}, u_{\phi\phi} = a + \frac{b}{r^2} \quad (3.88)$$

With the boundary conditions

$$\sigma_{rr}(r = R_1) = -p, \sigma_{rr}(r = R_2) = 0 \quad (3.89)$$

we are able to obtain the coefficients

$$a = \frac{p_1 R_1^2}{R_2^2 - R_1^2} \frac{(1+\sigma)(1-2\sigma)}{E}, b = \frac{p R_1^2 R_2^2}{R_2^2 - R_1^2} \frac{1+\sigma}{E} \quad (3.90)$$

3.5 Code Packages

As mentioned at the beginning of this chapter, physics and chemistry research have benefitted a lot from the rapid development of computer technology. Those methodologies that are introduced earlier this chapter also have great influence on the development and improvement of theories. However, without any doubt, it would be a huge waste in both time and human resource for everyone to implement those methods all by oneself. Fortunately, we've got plenty number of open source or commercial packages with almost all the methods implemented to help with daily research. The following will be a brief introduction on the code packages that are used in the study of this thesis.

3.5.1 LAMMPS

The code package used for the molecular dynamics simulation calculations is the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), URL <http://lammps.sandia.gov>, a classical molecular dynamics code written in C++ from Sandia National Laboratories¹⁸³. LAMMPS is open source and is distributed under the GPL license. As the official website of LAMMPS says, "LAMMPS has potentials for soft materials

(biomolecules, polymers) and solid-state materials (metals, semiconductors) and coarse-grained or mesoscopic systems. It can be used to model atoms or, more generically, as a parallel particle simulator at the atomic, meso, or continuum scale¹⁸⁴.” As a molecular dynamics simulator, LAMMPS is able to deal with systems from only a few particles up to millions or billions of particles, exhibiting excellent performance and scalability.

3.5.2 GULP

The code used for migration energy calculation, including transition state search using NEB, is GULP, “a program for performing a variety of types of simulation on materials using boundary conditions of 0-D (molecules and clusters), 1-D (polymers), 2-D (surfaces, slabs and grain boundaries), or 3-D (periodic solids). The focus of the code is on analytical solutions, through the use of lattice dynamics, where possible, rather than on molecular dynamics.”¹⁴⁹ GULP has been built with supporting for many force fields, including but not limited to the shell model for ionic materials, molecular mechanics for organic systems, and embedded atom model (EAM) for metals. GULP is free for academic use and is available on the web.

3.5.3 VASP

The Vienna Ab-initio Simulation Package (VASP) is a density functional code package for performing *ab initio* quantum mechanical molecular dynamics, electronic structure calculations, and other atomic scale materials modellings^{182,185-187}. While not dealing with the original Schrödinger equation directly, VASP implements approximations to the many-body Schrödinger equation, either by DFT or by Hartree-Fock theory. Hybrid functionals, which mixes the DFT theory with the HF theory, are also available in VASP.

3.5.4 VESTA

Visualization for Electronic and Structural Analysis (VESTA) is a 3D visualization program for many data and systems, such as structural models, electron / nuclear densities, and crystal morphologies. Besides visualization, VESTA is capable of a variety of

calculations, for example the electron / nuclear density from structure parameters, the Patterson-function densities from structure parameters or volumetric data, and the Madelung energy by using external program MADEL. In the study of this thesis, VESTA is used to visualize many of the structures and to calculate the Madelung energy.

Chapter 4

Grain Boundary Effects on Oxygen Diffusion in YSZ

In this chapter, the atomic models used in the simulation calculations of YSZ are briefly introduced. Lattice constants of single crystal YSZ and YSZ with grain boundary (GB) are observed using molecular dynamics simulation for different doping concentrations and temperatures. Mean square displacement graphs of oxygen ions in YSZ and YSZ with GB are analyzed from simulation results. From the mean square displacement, oxygen diffusion coefficient is calculated for each system. Oxygen diffusion coefficients are found to be lower in GB than in bulk area. By relating oxygen diffusion coefficient with corresponding temperature, the activation energy is obtained. Oxygen migration energies are also calculated in YSZ. The existence of yttria ions along the migration paths is found to raise up the migration energy of oxygen ions.

4.1 Atomic Model

The atomic models used for calculations in the stabilized zirconia system are the single crystal and bicrystals of YSZ, used for molecular dynamics simulations, and the defect lattices, used for calculations of oxygen ion migration energy.

4.1.1 YSZ Single and Bicrystal

Two groups of YSZ simulation models are used. One is the single crystal YSZ, the other one is grain boundary bicrystal YSZ. **Figure 4.1** shows the atomic model of single crystal ZrO_2 that is used to generate structure of bulk YSZ which is then used in the calculations.

Figure 4.1 The atomic model of bulk ZrO_2 , used to generate the structure for bulk YSZ. Blue ball – zirconia ion, red ball – oxygen ion. Based on this structure, some zirconia ions will be replaced randomly with oxygen ions removed randomly to give the structure of YSZ.

The lattice parameter of ZrO_2 used to build the structure in **Figure 4.1** is $5.12\text{\AA}$. The bulk model has a size of $20.48\text{\AA} \times 25.60\text{\AA} \times 66.56\text{\AA}$. The structures of YSZ are generated by randomly replacing Zr ions with Y ions and removing oxygen ions randomly for every two Zr ions replaced. By changing the number of ions replaced, different structures corresponding to YSZ with different doping concentrations are created. YSZ with doping concentration of 4mol%, 6mol%, 8mol%, 19mol%, 15mol%, and 20mol% are studied.

According to reported experimental structures, two types of grain boundaries are studied in this thesis – $\Sigma 5(310)$ and $\Sigma 13(510)$ GB structures^{65,188}. Thus, two kinds of YSZ grain

boundary models, namely $\Sigma 5(310)$ and $\Sigma 13(510)$ model, are built. In each model, two symmetric tilt grain boundaries are built in one unit structure. In each kind of grain boundary model, different configurations with different yttrium doping concentrations are created to investigate the influences of yttrium concentration on oxygen diffusivity. The concentrations of Y_2O_3 used are 4%, 6%, 8%, 10%, 15%, and 20%. The progress of constructing a grain boundary structure is described detailed in **Figure 4.2**: two mirror surfaces are cleaved and then combined together; the generated structure was then shift by 25% of the lattice constant along the orientation which is perpendicular to the grain boundary surface to keep the continuous property of the edge. The final structure is then used in the simulation with periodical boundary conditions in all three directions applied.

As **Figure 4.3** shows, the simulation box of $\Sigma 5(310)$ grain boundary structure has a size of $20.48\text{\AA} \times 24.29\text{\AA} \times 64.76\text{\AA}$, with the longer dimension perpendicular to the interface of the grain boundary. The lateral shifting in lattice produces two identical $\Sigma 5$ grain boundaries; the separation between them is $32.88\text{\AA}$, a distance which is considered large enough to neglect electrostatic mutual interactions. The structure presented in **Figure 4.3** is the grain boundary structure for zirconia lattice, Y ions will be doped into the system by randomly replacing Zr ions and deleting oxygen ions later. For every two Zr ions replaced by Y, one oxygen ion is removed to keep charge neutral.

The $\Sigma 13$ is a (510) boundary, as **Figure 4.4** shows. The simulation box has a size of $20.48\text{\AA} \times 26.11\text{\AA} \times 104.43\text{\AA}$, with the longer dimension perpendicular to the GB plane, similarly. Distance between the two identical GBs in $\Sigma 13$ is $52.22\text{\AA}$. Both grain boundary structures are then applied with three-dimensional periodical boundary conditions during the simulation.

Figure 4.2 The construction of the simulated grain boundary. Firstly, grain boundary surface is cleaved from the cubic crystal of YSZ (a, b, and c). Then another mirror surface is cleaved and combined together with the first one, creating a structure containing grain boundary structure both at the middle and at the edge of the unit (d and e). The generated structure is then shifted along the orientation that perpendicular to the grain boundary surface for 25% of the corresponding lattice constant (f). The final structure is then applied with periodical boundary conditions in all three directions during the simulations (g).

Figure 4.3 Atomic model of zirconia $\Sigma 5(310)$ GB structure. Red ball – oxygen ion, blue ball – zirconia ion. Ions are grouped into different groups, bulk and GB area, by their position as labeled. Based on this structure, some zirconia ions will be replaced randomly with oxygen ions removed randomly to give the structure of YSZ.

Figure 4.4 Atomic model of zirconia $\Sigma 13(510)$ GB structure. Red ball – oxygen ion, blue ball – zirconia ion. Ions are grouped into different groups, bulk and GB area, by their position as labeled. Based on this structure, some zirconia ions will be replaced randomly with oxygen ions removed randomly to give the structure of YSZ.

Two regions are distinguished in each GB model. All ions within one CSL lattice length at each side of the GB plane are defined as “grain boundary ions”, and all other ions are

considered as “bulk ions”. When calculating GB oxygen diffusion coefficients, only ions that belong to “grain boundary ions” are considered. The two regions are labeled in **Figure 4.3** and **Figure 4.4**.

The energy of each initial configuration is minimized using the conjugate gradient (CG) method. MD simulations are performed under NPT ensemble, which ensures constant pressure, temperature, and particle number during simulation. The pressure and temperature are adjusted every 100 time steps using Nose-Hoover thermostat¹⁸⁹⁻¹⁹¹ and Parrinello-Rahman barostat¹⁹². The pressure is set to 0.1MPa, with various temperatures. The time step is set to 1 fs, with total simulation time up to 500 ps, which is 5×10^5 steps.

4.1.2 Atomic Model for Migration Energy Calculation

A $2 \times 2 \times 2$ super-cell of ZrO_2 is used to simulate the migration behavior of oxygen ions in YSZ lattice. The structure of the super-cell is shown in **Figure 4.5**. Before simulation, six Zr^{4+} ions in the super-cell were replaced with Y^{3+} ions and three O^{2-} ions were removed to reach charge neutral, creating the structure of YSZ with yttrium concentration of 9%.

Figure 4.5 $2 \times 2 \times 2$ supercell of ZrO_2 used to create 9mol% YSZ

Figure 4.6 Three possible pathways of oxygen migration in YSZ – pathway 1: oxygen vacancy migrates to the nearest oxygen site; pathway 2: oxygen vacancy migrates to the second nearest oxygen site; pathway 3: oxygen vacancy migrates to the diagonal site of the oxygen cube. Blue ball indicates Zr^{4+} , red ball indicates O^{2-} , and yellow ball indicates oxygen vacancy.

Three possible pathways of oxygen migration have been investigated as **Figure 4.6** shows. Oxygen ion may migrate to the nearest oxygen site along path 1, to the second nearest oxygen site along path 2, and to the diagonal site of the oxygen cube along path 3.

In migration along path 1, oxygen ion travels across the edge of the cation tetrahedral. The migration behavior of oxygen ions across different kinds of cation tetrahedral edges, Y-Y edge, Y-Zr edge, and Zr-Zr edge, has been investigated. **Figure 4.7** shows the schematic illustration of the model used here.

Figure 4.7 Atomic model used to investigate the influence of side cations along migration path to migration energy of oxygen ions. Blue balls – zirconia ion, red balls – oxygen ion, blue line – tetragonal edge across migration path, white line – migration path. The cations at each end of the blue line can be either Y^{3+} or Zr^{4+} during simulations.

4.2 Lattice Constant of YSZ

Lattice constants for different structures and calculations are observed according to the final structures after performing molecular dynamics simulations. The result shows good agreement with the previous published lattice constants. The results for single crystal YSZ and YSZ with grain boundary structure under different yttrium concentrations and temperatures are shown in **Figure 4.8** and **Figure 4.9**.

Figure 4.8 Lattice constant of YSZ single crystal with different doping concentrations under different temperatures (“4y” indicates 4mol% doped YSZ)

Figure 4.9 Lattice constant of YSZ models with $\Sigma 5$ GB under different doping concentrations and different temperatures (“4y” indicates 4mol% doped YSZ)

The lattice constant shows a clear linear dependency on temperature. As the concentration of doped yttria increases, the lattice constant increases, which is reasonable since the radius of yttria ions is larger than that of zirconia ions. The lattice constant is also raised up by the existence of grain boundary, as grain boundaries introduce extra space at the interface.

4.3 Mean Square Displacement of Oxygen Ions

Mean square displacement (MSD) for oxygen ions during the simulation process has been calculated for each run as a function of simulation time. As stated in methodology chapter, a MSD graph with a larger slope corresponds to a diffusion which is easier to occur. The MSD behaviors in YSZ with different yttrium concentrations under different temperatures are very similar; thus only the results with 8YSZ at 2000K are listed below as a representation. In the bulk material of 8YSZ, i.e. single crystal 8YSZ, MSD along three directions and the total MSD are calculated as shown in **Figure 4.11**.

Figure 4.10 MSD (Mean square displacement) along x, y, and z and total MSD in 8YSZ single crystal at 2000K.

As **Figure 4.10** shows, the diffusion of oxygen ions along x and y directions are slightly easier than the diffusion along the z direction in YSZ single crystal. The MSD graphs in YSZ models with GB (**Figure 4.11** and **Figure 4.12**) indicate this preference, too.

Figure 4.11 MSD (Mean square displacement) along x, y, and z and total MSD in 8YSZ $\Sigma 5$ grain boundary area at 2000K.

Figure 4.12 MSD (Mean square displacement) along x, y, and z and total MSD in 8YSZ $\Sigma 13$ grain boundary area at 2000K.

The MSD in the YSZ models with grain boundary structure are also calculated. Fig.14. gives the comparison between the overall MSD in $\Sigma 5$, $\Sigma 13$ grain boundary structure and the MSD in single crystal YSZ.

Figure 4.13 Overall MSD (Mean square displacement) in $\Sigma 5$ and $\Sigma 13$ GB structure in comparison with MSD in 8YSZ single crystal

We can see that with the presence of grain boundary, the MSD of oxygen, namely the diffusion of oxygen ion, will have some decrease, which means that the existence of GB may obstruct the diffusion of oxygen in YSZ.

To see it more clearly, the MSD comparison between single crystal YSZ and MSD in GB area is shown in **Figure 4.14**:

Figure 4.14 GB area MSD (Mean square displacement) in $\Sigma 5$ and $\Sigma 13$ GB structure in comparison with MSD in 8YSZ single crystal

The difference between MSD in YSZ single crystal and GB area is obvious, indicating the obstruction that GB has on the diffusion of oxygen, which is in good agreement with previous experimental and theoretical research results.

4.4 Oxygen Diffusion Coefficient

Oxygen diffusion coefficients have been calculated using MSD. The calculated oxygen diffusion coefficients are listed in **Table 4.1** and then graphed in **Figure 4.15** to **Figure 4.18**.

Table 4.1 Oxygen diffusion coefficients calculated in YSZ single crystal and GB models. The data for GB models are diffusion coefficients in GB area.

YSZ Model	Temperature (K)	Diffusion Coefficient ($10^{-9}\text{m}^2/\text{s}$)					
		4Y	6Y	8Y	10Y	15Y	20Y
Single Crystal	1500	0.1255	0.1332	0.1209	0.1095	0.0586	0.0229
	1800	0.2158	0.2266	0.2134	0.2061	0.1465	0.0734
	2000	0.2718	0.3015	0.3000	0.3207	0.2461	0.1426
	2500	0.4315	0.5135	0.5712	0.5976	0.5408	0.4016
	3000	0.6369	0.8167	0.9341	1.0541	1.0425	0.9947
YSZ with $\Sigma 5$ GB	1500	0.0507	0.0550	0.0603	0.0542	0.0313	0.0221
	1800	0.1094	0.1430	0.1282	0.1289	0.0947	0.0537
	2000	0.1601	0.2069	0.2072	0.2094	0.1517	0.1141
	2500	0.3732	0.4924	0.4977	0.5502	0.4905	0.3836
	3000	0.7279	1.0132	0.9496	1.0457	1.0338	0.9157
YSZ with $\Sigma 13$ GB	1500	0.047	0.0489	0.515	0.451	0.0308	0.0136
	1800	0.1080	0.1157	0.1251	0.1112	0.0818	0.0435
	2000	0.1577	0.1891	0.2072	0.1787	0.1571	0.0916
	2500	0.3772	0.4470	0.5210	0.5049	0.4963	0.3722
	3000	0.7957	0.9144	0.9978	1.0822	1.0444	0.9629

Figure 4.15 Oxygen diffusion coefficients in YSZ single crystal model with different yttrium concentrations.

Figure 4.16 Oxygen diffusion coefficients in YSZ $\Sigma 13$ GB model with different yttrium concentrations.

Figure 4.17 Oxygen diffusion coefficients in YSZ $\Sigma 5$ GB model with different yttrium concentrations.

Figure 4.18 Comparison of oxygen diffusion coefficients in 10YSZ model between $\Sigma 13$ GB area, bulk area, and YSZ single crystal.

The result of oxygen diffusion coefficient at 2000K in single crystal YSZ ($3.0 \times 10^{-10} \text{m}^2/\text{s}$) is in good agreement with the result of $3.0 \times 10^{-10} \text{m}^2/\text{s}$ in previous research as a benchmark.

As shown in **Table 4.1** and **Figure 4.15** to **Figure 4.18**, the oxygen diffusion coefficients are larger in single crystal YSZ and smaller in GB area. At low temperatures, this kind of obstruction is very significant: D_{GB} is less than half of single crystal YSZ D_{SC} at 1500K. When temperature goes higher, the difference between D_{SC} and D_{GB} becomes smaller and eventually disappears, indicating that the obstruction that GB has on oxygen diffusion becomes less and less important as the ion mobility become higher and higher with the increase of temperature. At about 3000K, D_{SC} becomes slightly larger than D_{Bulk} , this is interesting and further simulations are needed for a deep investigation into this phenomenon.

4.6 Hopping Events

To better analyze the nature of oxygen diffusion behavior in YSZ, hopping events are counted during the simulation, as Figure X.X and Figure X.X shows. A hopping event is defined as an oxygen ion jumping from its current site to nearby sites in one timestep. The events are counted in the beginning 10ps of the 500ps simulation.

Figure 4.19 shows the hopping distance distribution of oxygen ions in YSZ (GB310 of 8% doped YSZ under 2000K). The peaks of this distribution graph represent common hopping distances of oxygen ions. Denoting the nearest distance between oxygen ions as a , these peaks represent the first nearest oxygen sites (a), the second nearest sites ($\sqrt{2}a$), the third nearest sites ($\sqrt{3}a$), and so on ($2a$, $\sqrt{5}a$, and $3a$), which is as expected.

Figure 4.19 Oxygen ion hopping distance distribution in $\Sigma 5(310)$ 8%-doped YSZ under 2000K

Figure 4.20 shows the hopping events distribution along x -axis, along which two grain boundaries are built in the structure at $x = 16\text{\AA}$ and $x = 48\text{\AA}$. It is clear that there are two “valleys” around the points where the grain boundaries are located, indicating that oxygen ions hopping events are less likely to occur in those areas, leading to smaller oxygen ion diffusion coefficients in grain boundary area. The qualitative results given by hopping events agree with the quantitative results given by calculation of diffusion coefficients from mean square displacements.

Figure 4.20 Oxygen ions hopping count distribution along x -axis in $\Sigma 5(310)$ 8%-doped YSZ under 2000K. Two grain boundaries are located at $x = 16\text{\AA}$ and $x = 48\text{\AA}$.

In summary, investigation into the distribution of oxygen ion hopping events provides important insights into the nature of oxygen ion diffusion behavior in YSZ, i.e. oxygen ions tend to hop more in non-grain-boundary areas rather than in grain boundary areas.

4.7 Activation Energy

The Arrhenius plot of diffusion coefficients of 10YSZ with $\Sigma 13$ GB is shown in **Figure 4.21**. According to Equation 6, the absolute value of the plot slope is proportional to the activation energy of oxygen diffusivity. The activation energy for oxygen diffuse in GB area is larger than that in YSZ single crystal. This again draws to the conclusion that the existence of GB obstructs the diffusion of oxygen ions in YSZ.

Figure 4.21 Arrhenius plot of oxygen diffusion in 10% YSZ single crystal and $\Sigma 13(510)$ grain boundary area.

Activation energies are calculated according to Arrhenius plot and are presented in **Table 4.2**. The activation energy in single crystal YSZ is slightly larger than the oxygen migration energy calculated in the next section, which is reasonable since the migration energy doesn't take into account the availability of oxygen vacancy at target site. The value shall be increased as the number of oxygen vacancies is limited.

Table 4.2 Activation energies of 10%-doped YSZ single crystal and bicrystal (GB area and bulk area)

	$\Sigma 13(510)$	Single Crystal
Activation Energy (eV)	0.822	0.583

As shown in **Table 4.2**, the activation energy in grain boundary area is significantly larger than that of single crystal area. It helps explain why oxygen diffusion coefficients are lower in GB area and why less hopping events occurs in the grain boundary area.

4.8 Oxygen Migration Energy

Migration energies for oxygen ion are calculated in the lattices described in previous section. As described in the previous section, the doping concentration of this model is 9mol%. The migration energy and probability for different migration paths, indicated in **Figure 4.6**, are listed in **Table 4.3**.

Table 4.3 Oxygen ion migration energy and probability along different paths in 9YSZ

Migration Path	Path 1	Path 2	Path 3
Migration Energy (eV)	0.484	3.419	7.951
Probability (%)	94.90	5.05	0.05

As the results show, it's easier for oxygen ions to migrate to vacancies at the nearest sites, and as the distance between vacancy and oxygen ion increases, the migration energy increases, which is in agreement with the intuitive result. By using the exponential relationship between migrate probability and migration energy, we can have an estimation of the probabilities for oxygen ion to migrate along different paths. The probability for path i is calculate by the following equations,

$$P_i = \frac{Ae^{-bE_i}}{\sum_j Ae^{-bE_j}} = \frac{e^{-E_i}}{\sum_j e^{-E_j}} \quad (4.1)$$

The calculated probabilities are presented in **Table 4.3**, showing that oxygen ions tend to migrate through the shortest path with a probability of 94.49%, and migrate along the longest path with a probability of only 0.05%.

Particularly, the cation effects along the shortest migration path are studied. By changing the elements along the migration path, the migration energies with various ions along the shortest path are calculated, **Table 4.4**.

Table 4.4 Migration energy and probability of oxygen migrating to nearest vacancy site, with various cations along the path.

Ions	Zr-Zr	Zr-Y	Y-Y
Migration Energy (eV)	0.484	2.218	3.573
Probability (%)	81.82	14.45	3.73

The result shows clear preference for oxygen ions to migrate in a path with two zirconia ions at the sides over the path that has two yttria ions at the sides. Even introducing of a single yttria ion along the path significantly raises up the migration energy, thus decreasing the probability of oxygen ions going along that path. The negative effects of yttria ions on the migration energy, together with the fact that the number of oxygen vacancies increases as the doping concentration of YSZ increases, may be responsible for the maximum ionic conductivity at 8-10mol% YSZ.

Chapter 5

Gadolinium-doped-Ceria as an Interlayer – Effects and Properties

In SOECs, to block the undesired chemical reactions between the electrolyte material yttria-stabilized zirconia (YSZ) and electrode material lanthanum strontium cobalt ferrite (LSCF), gadolinium-doped ceria (GDC) is used as an interlayer material between YSZ and LSCF. In order to effectively block the reactions, the minimal thickness requirements of this interlayer under different working temperatures are calculated based on a two-sided diffusion model. The minimal thickness is found to be $\sim 10\text{nm}$ and $\sim 22\mu\text{m}$ under 700°C and 1000°C , respectively. To help better understand the lattice expansion properties in layered GDC, a laminated CeO_x model was proposed, with the relationship between CeO_x lattice parameter and layer thickness derived using this model.

5.1 Theoretical Models

Two models are proposed to describe the ion diffusion and lattice expansion behavior in GDC and in reduced ceria (CeO_2).

5.1.1 Diffusion Model

To calculate the minimum thickness of GDC interlayer which is used to block the reaction between electrolyte YSZ and anode LSCF, a simple diffusion model is proposed, as shown in **Figure 5.1**.

Figure 5.1 Diffusion model for O^{2-} and Sr^{2+} diffusion in GDC. Colored slabs illustrate different components (red – YSZ electrolyte, yellow – GDC interlayer with thickness d , blue – LSCF anode), solid arrows indicate the diffusion direction for oxygen ions (red arrow) and strontium ions (blue arrow), the dash lines inside GDC interlayer represent the relative ion concentration distribution of O^{2-} and Sr^{2+} .

The model simplifies the three components – YSZ electrolyte, GDC interlayer (with thickness d), and LSCF anode – into three colored slabs. The concentration of oxygen ions in YSZ and the concentration of strontium ions in LSCF are assumed to be constant, denoted as $C_{O,0}$ and $C_{Sr,0}$, respectively. The relative ion concentrations inside GDC layer

are denoted as $C_{O,x}$ and $C_{Sr,x}$ for oxygen ions and strontium ions, respectively. Here, the relative concentration is defined as

$$C_{O,x} = \frac{C'_{O,x}}{C_{O,0}}, C_{Sr,x} = \frac{C'_{Sr,x}}{C_{Sr,0}} \quad (5.1)$$

where x is the distance between position of interest and the ion source boundary (LSCF or YSZ), $C'_{O,x}$ is the actual concentration value of oxygen ions in GDC at distance x to YSZ, $C'_{Sr,x}$ is the actual concentration value of strontium ions in GDC at distance x to LSCF. By assuming $C_{O,0}$ and $C_{Sr,0}$ to be 1 at YSZ and LSCF source, the meaning of relative concentration becomes clean and clear when analyzing the effects.

This model describes the influence of GDC layer to the diffusion of oxygen ions and strontium ions in SOEC, and can help figure out the minimum thickness of GDC required to effectively block the diffusion of Sr^{2+} ions, while not effecting the oxygen concentration difference across the layer significantly.

5.1.2 Laminated CeO_x Model

To describe the lattice expansion properties in GDC, a simplified laminated CeO_x model is used here as an approximated approach. Since oxygen vacancy is of the most concern in cerium oxide system, CeO_x is used instead of GDC to keep simplification. Considering the spatial distribution of Ce^{3+}/Ce^{4+} ions, a laminated model consists of a layer of CeO_2 covered with thin top and bottom layers of $CeO_{1.5}$ is used. The model is illustrated in **Figure 5.2**. Additional elastic analysis is applied to the system based on this simple yet reasonable model. More details about the elastic analysis are described in **Section 5.3**.

Figure 5.2 Laminated model of CeO_x . The structure consists of three layers of cerium oxide, one middle layer of CeO_2 with thickness d , and two layers of $\text{CeO}_{1.5}$ with thickness h attached to the top and bottom of the middle layer.

5.1.3 Atomic Model used for Madelung Energy Calculation

To calculate the Madelung energy of CeO_2 thin layers, slabs of $\text{CeO}_2(111)$ surface with different thicknesses are built as shown in **Figure 5.3**. The initial structures are first relaxed using VASP and then used to calculate Madelung energy. The calculation of Madelung energy is done using VESTA. A total of five configurations are considered, as Figure 5.3 demonstrates – from single three-atom layer to five layers of three-atom layer of CeO_2 . The structures are applied with 3D periodical conditions during calculations. The vacuum slabs between atom layers in z-axis direction are large enough to ignore the interaction effects result from other slabs.

Figure 5.3 Atomic models of CeO_2 slabs used for Madelung energy calculation. Red ball – oxygen ion, yellow ball – cerium ion, a-e are $\text{CeO}_2(111)$ surface slabs with different thicknesses.

5.2 Minimal Thickness Requirement of GDC Interlayer

As the interlayer material in SOECs, the thickness of GDC affects the cell performance considerably. On one hand, a layer with large thickness will probably decrease the overall cell performance. It may influence the diffusion of oxygen ions from YSZ to LSCF; and GDC is known to have poor sintering properties. On the other hand, a thin layer of GDC may not be able to effectively block the diffusion of Sr^{3+} ions between electrolyte and anode, thus generating insulating SrZrO_3 phase in the cell, leading to poor cell performance over time. To effectively block the undesired reactions, maintain good oxygen ion diffusion property, and keep the influence of GDC's poor sintering properties as low as possible, a requirement on the minimal thickness of GDC layer should be presented when designing SOEC devices.

The Fick's law of diffusion gives the solution to diffusion in one dimension system with constant concentration at boundary as,

$$C(x, t) = C_0 \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (5.2)$$

Where C_0 is the concentration at boundary, $\operatorname{erf}()$ is the Gauss error function, x is the distance to boundary, D is diffusion coefficient, and t is diffusion time.

By applying Fick's law of diffusion in the diffusion model described in previous section, using published diffusion coefficients of oxygen ion and strontium ion^{107,193}, the distribution of oxygen ion and strontium ion inside GDC after working for certain period can be calculated under different working temperatures. The diffusion coefficients used here are listed in **Table 5.1**.

As stated in previous section, here we assume the oxygen ion and strontium ion concentration to be 1.0 at GDC boundaries. **Figure 5.4(a)** and **Figure 5.4(b)** shows the relative oxygen / strontium ion concentration (with respect to boundary concentration) distribution inside GDC after operating for 100 hours under 700°C.

Table 5.1 Diffusion coefficient of O^{2-} and Sr^{2+} in GDC under different temperatures

Temperature (°C)	Diffusion Coefficient (cm^2/s)	
	O^{2-}	Sr^{2+}
700	2.76×10^{-10}	7.25×10^{-21}
1000	2.42×10^{-8}	7.36×10^{-16}

Figure 5.4 Relative concentration distribution of oxygen and strontium ions in GDC after working for 100 hours under 700°C, a – oxygen ion, b – strontium ion.

The diffusion length for oxygen ion and strontium ion under 700°C for 100 hours are 199 μ m and 1.09 nm, separately. At the depth of diffusion length, the concentrations of ions are 15.73% that of the concentrations at GDC boundary. Since the diffusion length of oxygen ion is notably larger than that of strontium ion, a layer of GDC with 3nm thickness will effective block the diffusion of strontium ions while hardly influence the diffusion of

oxygen ions. **Figure 5.5** plots the relative concentration of each two ions together after operating for 100 hours under 700°C.

Figure 5.5 Relative concentration distribution of oxygen and strontium ions in 3nm-thick GDC after operating for 100 hours under 700°C.

As **Figure 5.5** shows, a GDC layer with 3nm thickness is thick enough to block Sr²⁺ diffusion between LSCF and YSZ. Meanwhile, the 3nm-thick GDC hardly influenced the diffusion of O²⁻. As the working time may be longer than 100 hours in practice, a thickness around 10nm will be a better choice at such temperature.

Another operating temperature, 1000°C, is considered, too. Since strontium ion has remarkably larger diffusion coefficient in GDC at 1000°C than 700°C, the thickness required to block strontium diffusion is expected to be significantly larger. Similarly, the relative concentration distribution of O²⁻ and Sr²⁺ ions inside GDC after operating under 1000°C for 100 hours is shown in **Figure 5.6(a)** and **Figure 5.6(b)**.

Figure 5.6 Relative concentration distribution of oxygen and strontium ions in GDC after working for 100 hours under 1000°C, a – oxygen ion, b – strontium ion.

Figure 5.7 Relative concentration distribution of oxygen and strontium ions in 800nm-thick GDC after operating for 100 hours under 1000°C.

The diffusion lengths for O^{2-} and Sr^{2+} are 1860 μm and 325.6 nm separately. As a result, thickness of 2 μm is chose to block the diffusion of Sr^{2+} ions from LSCF to YSZ. The result of applying a GDC layer with 2 μm thickness under such condition is plotted in **Figure 5.8**, showing that the oxygen diffusion is hardly affected by the existence of GDC while the diffusion of strontium ions across GDC is effectively prevented.

Figure 5.8 Relative concentration distribution of oxygen and strontium ions in 2μm-thick GDC after operating for 100 hours under 1000°C.

5.3 Preference of Oxygen Vacancy on CeO₂ surface

The formation energy of different kinds of oxygen vacancies on CeO₂(111) surface are calculated. The energies are calculated using the following equation:

$$E(\text{Vacancy}) = E(\text{Ce}_{12}\text{O}_{23}) + E(M) - E(\text{Ce}_{12}\text{O}_{24}) \quad (5.3)$$

Here, $E(M)$ represents the energy of oxygen atom and oxygen ion with different charges, i.e. O , O^- , and O^{2-} , where the corresponding vacancy species are V_O , $V_{\dot{O}}$, and $V_{\ddot{O}}$ and the corresponding cerium types are Ce , Ce^+ , and Ce^{2+} . The values of $E(O^-)$ and $E(O^{2-})$ are determined by subtracting first and second ionization energy of oxygen atom from the energy of oxygen atom. The calculated energies are listed in **Table 5.2**.

Table 5.2 Formation energy of oxygen vacancies on $\text{CeO}_2(111)$ surface and in bulk CeO_2

Vacancy Species	Formation Energy (eV)
$V_{O,bulk}$	3.98
$V_{O,surf}$	2.63
$V_{\dot{O},surf}$	1.17
$V_{\dot{O},surf}$	4.97

As we can see from **Table 5.2**, the formation energy of oxygen vacancy on the surface is significantly less than that in bulk CeO_2 . And on the surface, the formation energy of $V_{\dot{O}}$ is lowest compared with other species, meaning that oxygen ions on surface are easiest to get lost in the form of O^- , leaving a 3+ cerium ion on the surface. Thus it is reasonable to argue that on the surface, $V_{\dot{O}}$ is the dominate vacancy rather than the other two vacancy species. This result is compatible with experimental measurements where the composition of surface cerium oxide is mainly $\text{CeO}_{1.5}$.

5.4 Micro-mechanical Model of Laminated CeO_x

As the size of GDC layer decreases, its lattice parameter changes, similar to the case of CeO_x nanoparticle¹⁹⁴⁻¹⁹⁶. To describe the behavior of this phenomenon, we propose a simplified model as described in previous section. By using three layers of CeO_x , i.e. two symmetric $\text{CeO}_{1.5}$ surface layers covered on the top and bottom of a centered CeO_2 layer, this model represents an approximation to the real spatial distribution of oxygen vacancy in CeO_x . Considering the dominance of oxygen vacancy on the oxygen conducting property of GDC and the success of similar model in nanoparticle system, this model is a reasonable first approximation.

To analyze lattice dependence on layer thickness, micro-mechanical analysis is applied to this model. We take a uniform layer of CeO_2 with thickness of $d + 2h$, lateral size of $2R_M$,

lattice parameter of a_0 , and use Eshelby's hypothetical cutting-transformation-rejoining operations to estimate the elastic strain generated by surface oxygen loss. In this imaginary operation, two layers of CeO_2 with thickness h are removed from the reference layer's top and bottom surfaces. Their compositions are then changed to $CeO_{1.5}$ by uniformly creating oxygen vacancies in the two layers. The creation of oxygen vacancies causes the lattice parameter to increase to a_1 in the two layers, thus increasing the layers' lateral size from $2R_M$ to $2R_T$, respectively. The two surface layers and the remaining middle layer are then rejoined and matched together with external surface tractions applied, i.e. the three layers are compressed and stretched to the same lateral size. By removing external surface traction, these layers, either compressed or stretched, are then allowed to have elastic deformation until internal stresses are balanced, resulting a final lateral size $2R_F$ for all three layers. This imaginary process is shown in **Figure 5.9**.

Figure 5.9 Imaginary cutting-transformation-rejoining procedure. **a** – a single slab of CeO_2 with thickness of $d+2h$; **b** – the top and bottom of the slab in **a** are changed into $CeO_{1.5}$, with corresponding change in lattice size and lateral size, giving radius R_T , R_M , and $R_B = R_T$, where the subscripts means top, middle, and bottom, respectively; **c** – the three layers in **b** are stretched and joined together with radius R_{Join} ; **d** – the layers are allowed to relax and reach equilibrium, reaching a final radius R_F , where the subscript F means final.

By considering the system in cylindrical coordinates, we have the following elastic equilibrium equations:

$$\mathbf{u} = \mathbf{A}\mathbf{r} \quad (5.4)$$

$$\mathbf{u}_T(\mathbf{r} = \mathbf{R}_T) = \mathbf{A}_T \mathbf{R}_T = \mathbf{R}_F - \mathbf{R}_T \quad (5.5)$$

$$\mathbf{u}_M(\mathbf{r} = \mathbf{R}_M) = \mathbf{A}_M \mathbf{R}_M = \mathbf{R}_F - \mathbf{R}_M \quad (5.6)$$

Here, u is the elastic strain of a one dimensional system, u_T is the elastic strain of top and bottom layer, u_M is the elastic strain of middle layer; A_T is the coefficient of top and bottom layer, A_M is the coefficient of middle layer. From the equations above, we can write A_T and A_M as a function of radius:

$$\mathbf{A}_T = \frac{\mathbf{R}_F - \mathbf{R}_T}{\mathbf{R}_T} \quad (5.7)$$

$$\mathbf{A}_M = \frac{\mathbf{R}_F - \mathbf{R}_M}{\mathbf{R}_M} \quad (5.8)$$

The strain energy density for a one dimensional system is:

$$\mathbf{U} = \frac{4(3K+\mu)}{3} \mathbf{A}^2 \quad (5.9)$$

Hence, with A_T and A_M inserted, the average strain energy density in this laminated system is:

$$\mathbf{U}(\mathbf{R}_F) = \left(\frac{2h\beta_T}{\mathbf{R}_T^2} + \frac{d\beta_M}{\mathbf{R}_M^2} \right) \mathbf{R}_F^2 - \left(\frac{4h\beta_T}{\mathbf{R}_T} - \frac{2d\beta_M}{\mathbf{R}_M} \right) \mathbf{R}_F + (d\beta_M + 2h\beta_T) \quad (5.10)$$

$$\frac{\Delta a_0}{a_0} = \frac{\mathbf{R}_F - \mathbf{R}_M}{\mathbf{R}_M}, \frac{\Delta a_1}{a_1} = \frac{\mathbf{R}_F - \mathbf{R}_T}{\mathbf{R}_T} \quad (5.11)$$

$$\beta_T = 3K_T + \mu_T, \beta_M = 3K_M + \mu_M \quad (5.12)$$

where $2R_T$ and $2R_M$ are the lateral size of top / bottom $CeO_{1.5}$ surface layers and CeO_2 middle layer, K_T and μ_T are the bulk and shear modulus of top / bottom $CeO_{1.5}$ surface layers, K_M and μ_M are the bulk and shear modulus of middle CeO_2 layer.

By minimizing $U(R_F)$ as a function of R_F , we derived the equilibrium lateral size of this system as a function of initial sizes of $CeO_{1.5}$ and CeO_2 layers:

$$R_F = \frac{\frac{R_M + \frac{d}{2h} \frac{\beta_M}{\beta_T}}{\frac{R_M}{R_T} + \frac{d}{2h} \frac{\beta_M}{\beta_T}} R_M \quad (5.13)$$

Thus the averaged lattice strain for the $CeO_{1.5} - CeO_2 - CeO_{1.5}$ laminated system as a reference of a_0 , the lattice parameter of CeO_2 , was:

$$\begin{aligned} \left\langle \frac{\Delta a}{a} \right\rangle &= \frac{2h \times \left[\left(1 + \frac{\Delta a_1}{a_1} \right) \times a_1 - a_0 \right] + d \times \frac{\Delta a_0}{a_0}}{d + 2h} \\ &= \frac{\frac{2h}{d} \frac{\beta_T}{\beta_M} \left(\frac{R_T}{R_M} - 1 \right)}{\left(\frac{R_T}{R_M} \right)^2 + \frac{2h}{d} \frac{\beta_T}{\beta_M}} = \frac{\frac{2h}{d} \frac{\beta_T}{\beta_M} \left(\frac{a_1}{a_0} - 1 \right)}{\left(\frac{a_1}{a_0} \right)^2 + \frac{2h}{d} \frac{\beta_T}{\beta_M}} \end{aligned} \quad (5.14)$$

5.4.1 Lattice Parameter as a Function of Layer Thickness in Laminated CeO_x

With the above equation in hand, the relationship between lattice strain and layer thickness becomes clear. By inserting parameter values for h , $\frac{\beta_T}{\beta_M}$, and $\frac{a_1}{a_0}$, we will be able to have a quantitative relationship between averaged lattice parameter and layer thickness for the $CeO_{1.5} - CeO_2 - CeO_{1.5}$ laminated model. The parameters we used from experimental results and previous study results were $a_0 = 5.41 \text{Å}$ for CeO_2 , $a_1 = 5.61 \text{Å}$ for $CeO_{1.5}$, where a_1 is the lattice parameter of $CeO_{1.5}$ with an average (disordered) fluorite structure, and $\frac{\beta_T}{\beta_M} = 1.68$. The averaged lattice strain as a function of layer thickness was achieved by inserting experimental values above:

$$\left\langle \frac{\Delta a}{a} \right\rangle = \frac{0.074h}{1.8066d + 2h} \quad (5.15)$$

To have an intuitive impression on the relationship between lattice parameter and layer thickness, we further assume that the surface $CeO_{1.5}$ layer thickness is constant, with a thickness around two layers of $CeO_{1.5}$, i.e. $15\text{\AA}$. The resulting relationship is plotted in **Figure 5.10** using black line. To make a comparison, the volume-weighted lattice parameter, which averages the lattice parameter of CeO_2 and $CeO_{1.5}$ by their layer thickness, is plotted in **Figure 5.10** using red line. Apparently, the relationship can be more accurate if experimental results of $\frac{2h}{d}$ can be fitted as a function of d .

Figure 5.10 Lattice expansion as a function of layer thickness in CeO_x laminated model – a comparison between micro-mechanical model, volume average, and Madelung approach.

5.4.2 Madelung Model Approach in Laminated CeO_x

Another approach of estimating the relationship between lattice parameter and layer thickness is the Madelung Model Approach inspired by the model by Vasili et al.¹⁹⁵.

In bulk CeO_2 , the volume energy per formula unit is usually represented as

$$E_V = \frac{BV_0}{2} \left(\frac{V}{V_0} - 1 \right)^2 + E_0 \quad (5.16)$$

Where B is the bulk modulus, E_0 is the volume energy when lattice is at equilibrium, $V_0 = \frac{a_0^3}{4}$ is the filling volume of each CeO_2 formula at equilibrium, and V is the current filling volume of each CeO_2 formula.

The Madelung energy of bulk CeO_2 , which has fluorite (CaF_2) structure is

$$E_{Mad} = -N\beta_{bulk} \frac{e^2}{a} \quad (5.17)$$

$$\beta_{bulk} = \frac{Mz_i z_j}{r_0} \quad (5.18)$$

Where N is the number of CeO_2 formula, a is the lattice parameter, M is the Madelung constant, which is 2.52 for CaF_2 crystal structure. β_{bulk} is a coefficient calculated from Madelung constant, and ion charges are $z_i = 2, z_j = 4$ and the nearest neighbor distance r_0 is $\frac{\sqrt{3}}{4}a_0$.

To calculate the surface Madelung energy, another coefficient $\beta_{surface}$ and the layer thickness d are introduced into the equation, giving

$$E_{Mad} = N(-\beta_{bulk} + \frac{\beta_{surface}}{d}) \frac{e^2}{a} \quad (5.19)$$

To determine the value of $\beta_{surface}$, we've calculated the Madelung energies of a series of CeO_2 layers with different thicknesses. The energy and thickness values are then fitted according to the above equation with $\beta_{bulk} = 46.55$. The calculated and fitted results are plotted in **Figure 5.11**. The fitted value of $\beta_{surface}$ is 0.993nm.

Figure 5.11 Calculated and fitted value of Madelung energy for CeO₂ thin layers

After taking the surface contribution into Madelung energy, the total energy per *Ce* atom can be written as

$$\frac{E_{tot}}{N} = \frac{BV_0}{2} \left(\frac{a^3}{a_0^3} - 1 \right)^2 + \frac{\beta_{surface}}{d} \frac{e^2}{a} + E_0 \quad (5.20)$$

In the above equation, the first term is volume contribution, which includes Madelung energy in the bulk part; the second term is surface Madelung energy contribution, which can be treated as surface Coulomb energy; the third term is the energy when lattice is at equilibrium. By minimizing the total energy and omitting $o(\frac{\delta a^2}{a_0})$ terms, we have

$$\frac{\delta a}{a_0} = \frac{1}{9BV_0} \frac{e^2}{a_0} \frac{\beta_{surface}}{d} = \frac{\alpha}{d} \quad (5.21)$$

The bulk modulus $B = 230 \pm 10 \text{ GPa}$ is taken from previously published work. With $a_0 = 5.409 \text{ \AA}$, we have

$$\frac{\delta a}{a_0} = \frac{0.052 \text{ \AA}}{d} \quad (5.22)$$

This relationship is plotted in **Figure 5.10** using blue line. As a reference, the lattice parameter by using simple volume average is plotted in **Figure 5.9** in red line. It's obvious that this method notably underestimates the lattice parameter comparing with other

methods. To have a better comparison, the lattice change obtained by applying micro-mechanical analysis is

$$\frac{\delta a}{a_0} = \frac{0.614\text{\AA}}{a-13.39\text{\AA}} \quad (5.23)$$

The Madelung approach only accounts for about 8.5% of the lattice change in laminated CeO_x system. The missing parts might be assigned to the formation of point defects.

Chapter 6

Electronic Structure of CeO_x

GDC shows electronic conductivity under low oxygen partial pressures, which is related to the reduction of cerium ions. Hence it's necessary to look into the electronic structure of GDC and CeO_x to help better utilize this material. In this chapter, we present the band structure of bulk ceria (CeO_2), GDC, and thin film GDC. The doping of gadolinium ions into ceria decreases the band gap of ceria a lot. The thin film structure raises up the band gap of GDC by a significant amount. The surface effects and vacancy effects on the electronic structure of ceria are also investigated. Density of states (DOS) and local density of states (LDOS) are calculated for $\text{CeO}_2(111)$ surface with and without the presence of oxygen vacancy. A decrease in band gap is observed with the presence of oxygen vacancy on $\text{CeO}_2(111)$ surface. Workfunctions for $\text{CeO}_2(111)$ surface are also calculated with and without oxygen vacancy. The existence of oxygen vacancy lowers the workfunction of the surface, making it easier to remove electrons from the surface.

6.1 Atomic Model

In order to study the electronic structure of doped ceria, three structures are built for the calculations of band structure. The structures are a) the CeO_2 single crystal lattice, b) the 20mol% gadolinium doped ceria, and c) thin film of 20mol% gadolinium doped ceria. These three structures are presented in **Figure 6.1(a)-(c)**.

Figure 6.1 Atomic structures of a. bulk CeO_2 , b. bulk GDC ($\text{Ce}_8\text{Gd}_{12}\text{O}_{19}$), and c. GDC thin film ($\text{Ce}_8\text{Gd}_{12}\text{O}_{19}$). White ball – cerium ion, red ball – oxygen ion, cyan ball – gadolinium ion.

The calculations were carried out using DFT with VASP¹⁸⁵⁻¹⁸⁷. The electron wave functions were described using the projector augmented wave (PAW) with cut off energy of 520 eV¹⁸². For integration within the Brillouin zone, specific K points were selected using a $4 \times 4 \times 4$ grid for bulk CeO_2 and bulk GDC, and $4 \times 4 \times 1$ for GDC thin film. The PW91 form of GGA exchange correlation potentials have been used with the GGA+U variants which are implemented in VASP. The U_{eff} used in DFT+U method is 3eV as tested by previous studies.

To study the surface properties, surface structure of $\text{CeO}_2(111)$ 2×2 lattice is built, one oxygen is then removed to create vacancy. The structures are shown in **Figure 6.2**. A similar slab of $\text{CeO}_2(110)$ surface is built to study the workfunction and DOS.

Figure 6.2 $\text{CeO}_2(111)$ surface structure. Red ball – oxygen ion, yellow ball – cerium ball, red ball marked with yellow cross – oxygen vacancy.

Figure 6.3 $\text{CeO}_2(111)$ surface structure. Red ball – oxygen ion, yellow ball – cerium ball.

The periodically repeated slab structures used to here consist of two parts – three layer of CeO_2 three-atom layers and a vacuum slab with thickness of $15\text{\AA}$. Similar to calculations in bulk ceria and GDC, the calculations to calculate workfunctions DOS, and surface properties were carried out using DFT with VASP¹⁸⁵⁻¹⁸⁷. The electron wave functions were

described using the projector augmented wave (PAW) with cut off energy of 520 eV¹⁸². For integration within the Brillouin zone, specific K points were selected using a $4 \times 4 \times 1$ grid. The PW91 form of GGA exchange correlation potentials have been used with the GGA+U variants which are implemented in VASP. The U_{eff} used in DFT+U method is 3eV as tested by previous studies.

When calculating properties of defected surfaces, one oxygen ion, marked with yellow cross in **Figure 6.2**, on the surface is removed to create oxygen vacancy. DOS calculations are done for surfaces with and without defect; LDOS shows the local DOS for each layer in **Figure 6.2**.

6.2 Electronic Structure of GDC

The lattice parameter, bulk modulus, and band gap of bulk ceria from DFT calculations are listed in **Table 6.1**, together with the experimental results.

Table 6.1 Comparison between theoretical results and experimental results in ceria

Parameters	Theoretical	Experimental
a (Å)	5.48	5.41 ¹⁹⁷
Bulk Modulus (GPa)	179	204 – 236 ¹⁹⁸
Band Gap (eV)	2.06	3.0

The cell parameter given by this work, 5.48Å, is in good agreement with the parameter from experimental measurements, 5.41Å, with a mismatch of 1.3%. The agreement of bulk modulus between theoretical study and experimental is also good.

However, there is a significant difference in the value of band gap between the theoretical result of this thesis and the experimental results. The experimentally measured band gap for ceria is 3.0eV, while the value given by this work is 2.06eV, giving a 31% error. This is a well-known deficiency of DFT method in transition metal oxides, as stated in the

methodology chapter. Another theoretical study in the ceria system gives a band gap value of 2.5eV using LDA, which is close to the result of current study but still shows a significant mismatch compared with experimental values. As an aspect of benchmark, the comparison between the band structures of this work and previous theoretical study is presented in **Figure 6.4**.

Figure 6.4 Band structure of CeO_2 , left – this work, right – previous study¹⁹⁹.

To investigate the doping effects, a 20mol% doped GDC, i.e. $\text{Ce}_8\text{Gd}_2\text{O}_{19}$, structure is used. A GDC thin film structure of thickness 4.56nm is also built to investigate the structure effects on band structure. The band structures of the two structure are presented in **Figure 6.5**.

Figure 6.5 Band structures of bulk $\text{Ce}_8\text{Gd}_2\text{O}_{19}$ (left) and thin film $\text{Ce}_8\text{Gd}_2\text{O}_{19}$ (right).

The band gap values for GDC and GDC thin film are 0.81 eV and 1.14 eV, respectively. A significant decrease in band gap is resulted from the doping of Gd ions. The low band gap is then raised up by the thin film structure by a value of 0.33 eV.

To compare with the results of CeO_2 and GDC, the band structures of ZrO_2 and YSZ are also investigated, as shown in **Figure 6.6**.

Figure 6.6 Band structures of a.) ZrO_2 and b.) $\text{Zr}_8\text{Y}_2\text{O}_{19}$

Different from CeO_2 and GDC, the band gap of ZrO_2 increased from 3.07 eV to 3.54 eV rather than the other way round. This explains the advantage of YSZ over GDC as electrolyte material due to current leakage problem of GDC. The smaller band gap of GDC makes it more likely to leak current under working temperature while the increased band

gap of YSZ makes it excellent electrolyte material with no electronic conductivity under working condition.

6.3 Electronic Structure and Work Function of $\text{CeO}_2(111)$ surface

As GDC shows electronic conductivity under low oxygen partial pressure, which is due to the reduction of cerium ions, and CeO_2 shows catalytic properties in some systems, it is of our interest to investigate the effects of oxygen vacancies, which is related to the reduction of cerium ions, on the electronic structure and work function of $\text{CeO}_2(111)$ surface.

The $\text{CeO}_2(111)$ surface is studied in this work. **Figure 6.7** shows the workfunction of $\text{CeO}_2(111)$ surface with or without oxygen vacancy. The workfunction of $\text{CeO}_2(111)$ surface is 6.03 eV, and the workfunction of $\text{CeO}_2(111)$ surface with oxygen vacancy is 4.98 eV. The difference is significant and reasonable, as the removal of one oxygen atom leaves two un-bonded ions in the surface, which makes it easier to remove one electron from it.

The workfunction for $\text{CeO}_2(110)$ surface is also calculated, giving a value of 4.52 eV, which is significantly lower than that of $\text{CeO}_2(111)$ surface and shown in **Figure 6.8**. The value of workfunction indicates the hardness to remove one electron from the surface, thus to some extent indicating how strong a molecule, such as CO_2 and CO, can be bound to the surface. This indication of binding energy helps further determine the catalytic properties. For nanoparticles, such as Au, on CeO_2 surfaces, the interface between substrate and nanoparticle plays an important role in the reactions that are activated by this supported structure. Hence, the binding energy of reaction molecule on CeO_2 substrate surfaces is a critical indicator of its catalytic performance.

Figure 6.7 Work function of $\text{CeO}_2(111)$ surface (left) and $\text{CeO}_2(111)$ defect surface (right). White ball – cerium ion, red ball – oxygen ion, blue circle – oxygen vacancy.

Figure 6.8 Workfunction of $\text{CeO}_2(110)$ surface

The DOS is calculated for bulk CeO_2 , $\text{CeO}_2(111)$ surface, $\text{CeO}_2(110)$ surface, and $\text{CeO}_2(111)$ surface with oxygen vacancy. The results for bulk and (111) and (110) surfaces are shown in **Figure 6.9** and **Figure 6.10**. We can see that the DOS of $\text{CeO}_2(111)$ surface is very close to that of bulk CeO_2 , including the large gap between O 2p and Ce 5d states. However, the creation of oxygen vacancy introduces some impurity states and decreases the band gap both between the O 2p and Ce 4f states and between the O 2p and Ce 5d states.

Figure 6.9 DOS of for bulk CeO_2 (black dashed line), $\text{CeO}_2(111)$ surface (blue line), and $\text{CeO}_2(111)$ surface with oxygen vacancy (red line).

Different from the DOS of (111) surface, the DOS of (110) shows slightly difference to the DOS of bulk ceria, indicating more significant surface effects. **Figure 6.11** shows the comparison between DOS of bulk ceria and the total and LDOS of $\text{CeO}_2(110)$ surface. As **Figure 6.11** shows, the deviation in DOS results from the DOS in first and third layer, which are the terminating layers in calculations, showing the effects of surface.

Figure 6.10 DOS comparison between $\text{CeO}_2(110)$ surface (green solid line) and bulk ceria (black dashed line)

To further confirm that the change in DOS in defected (111) surface comes from the introducing of oxygen vacancy, LDOS plots for $\text{CeO}_2(111)$ surface and $\text{CeO}_2(111)$ defect surface are calculated and compared in **Figure 6.12**. As the results show, the LDOS plots of second and third layer in $\text{CeO}_2(111)$ surface are very close to the DOS of bulk ceria. However, the LDOS of the first layer of $\text{CeO}_2(111)$ surface is apparently different from that of bulk CeO_2 . Meanwhile, by comparing the LDOS for each layer with and without an oxygen vacancy, the difference is only significant in the first layer, where the oxygen vacancy locates. Hence, the difference in DOS between defect and perfect $\text{CeO}_2(111)$ surfaces does come from the presence of oxygen vacancy.

Figure 6.11 Comparison between DOS of bulk ceria and total DOS and LDOS of $\text{CeO}_2(110)$ surface

Figure 6.12 LDOS of $\text{CeO}_2(111)$ surface (a, blue line), and $\text{CeO}_2(111)$ surface with oxygen vacancy (b, red line). Total DOS for each surface and LDOS of each layer for each surface are shown.

Chapter 7

Discussion and Future Work

This chapter reviews the results of this thesis. Implications of the results and possible future work are discussed. The result of molecular dynamics simulations in YSZ confirms the fact that YSZ has a maximal ionic conductivity at 8-10mol% doping concentration, finds that the existence of grain boundary hinders the diffusion of oxygen ions in YSZ, and that the diffusion is more hindered across the GB interface than along it. Result of oxygen migration energy in YSZ shows that the migration of oxygen ions is significantly hindered by the presence of yttria ions, which, together with the fact that oxygen vacancies have positive effect on oxygen diffusion, helps explain the maximal ionic conductivity of YSZ at 8-10mol% doping concentration. By using a simple diffusion model, the minimal thickness requirement for the GDC interlayer is calculated to be $\sim 10\text{nm}$ and $\sim 2\mu\text{m}$ under $700\text{ }^{\circ}\text{C}$ and $1000\text{ }^{\circ}\text{C}$, respectively. The relationship between lattice parameter and layer thickness in CeO_x laminated structure is derived and compared with relationships from other methods. The result helps provide useful information for SOEC device makers in both the design and synthesis of SOEC components. The electronic structure as well as workfunction in GDC and ceria systems are investigated, providing helpful insights into the electronic conductivity mechanism of GDC. Possible ways to improve the results of this thesis and possible further follow-ups are proposed at the end of this chapter.

7.1 Discussion

Molecular dynamics simulations have been carried out in the YSZ system, in both single crystal YSZ and grain boundary YSZ structures. Two types of grain boundaries have been investigated, $\Sigma 5(310)$ and $\Sigma 13(510)$. The mean square displacement of oxygen ions in and out of grain boundaries areas are calculated. Diffusion coefficients are calculated based on the mean square displacements. The lattice parameter and diffusion coefficient of oxygen ion under 2000K in 8mol% YSZ show good agreement with previous studies. Mean square displacements show good linear behavior overtime, which is consistent with the Einstein equation. The existence of grain boundary hinders the diffusion of oxygen ions, giving MSD plots with smaller slopes and smaller values of diffusion coefficients. This result agrees with previous experimental and theoretical results, and indicates that in the preparation of SOEC electrolyte materials (i.e. YSZ), grain boundaries shall be avoided if possible to improve the ionic conductivity of YSZ electrolyte. Hopping events of oxygen ions are analyzed in single crystal YSZ and bicrystal YSZ, oxygen ions are found to hop less in GB area than in bulk area, supporting the conclusion that grain boundary has negative effects on oxygen ion diffusion.

The activation energy for oxygen ion mobility has been calculated for bulk and GB YSZ, giving results supporting the same conclusion that the existence of GB makes it more difficult for oxygen ions to move around in the lattice. Migration energy of oxygen ions has been calculated, with the influences of cations along the migration path considered. The result shows that yttrium ions along the migration path makes it significantly more difficult for oxygen ion to hop to a nearby vacancy site. The migration energy of oxygen ion is slightly lower than the activation energy calculated from Arrhenius plot, which is reasonable since the migration energy calculation does not take into account the availability of oxygen vacancies in the target site. This result, together with the fact that the concentration of oxygen vacancy increases as the number of yttrium ions increases, helps explain the maximum ionic conductivity at 8-10mol% YSZ.

By further analyzing the directional MSD in grain boundary area, we find that the diffusion of oxygen ion in YSZ is more severely hindered moving across the GB interface than moving along the GB interface. Such behavior suggests that in the preparation of YSZ as electrolyte for SOEC, the grain boundary interfaces, if not avoidable, shall be aligned parallel to the ionic conducting direction to help improve the ionic conductivity of YSZ. In summary, the results of this work explain the maximum ionic conductivity in YSZ, confirm the negative effects of GB to the ionic conductivity of YSZ, and provide useful information for researchers on the synthesis of YSZ as an electrolyte material.

A simplified diffusion model is used to help simulate the influence of GDC interlayer on the oxygen and strontium ion diffusion behavior. By using diffusion coefficients of oxygen and strontium ions in GDC under different temperatures, we find the minimal thickness requirement of this GDC interlayer. The minimal thicknesses required to effectively block the diffusion of strontium ions are found to be $\sim 10\text{nm}$ and $\sim 2\mu\text{m}$ under 700°C and 1000°C , respectively. Under the thicknesses we find, the diffusion of strontium ions is effectively suppressed under long working hours, while the diffusion of oxygen ions is hardly influenced. The estimation of minimal thickness required helps provide guidance for researchers when designing and synthesizing GDC interlayers for SOEC devices. A simplified laminate structure model is proposed to investigate the lattice expansion behavior in GDC thin film. The lattice expansion in the laminated model is found to be

$$\begin{aligned} \left\langle \frac{\Delta a}{a} \right\rangle &= \frac{2h \times \left[\left(1 + \frac{\Delta a_1}{a_1} \right) \times a_1 - a_0 \right] + d \times \frac{\Delta a_0}{a_0}}{d + 2h} \\ &= \frac{\frac{2h}{d} \frac{\beta_T}{\beta_M} \left(\frac{R_T}{R_M} - 1 \right)}{\left(\frac{R_T}{R_M} \right)^2 + \frac{2h}{d} \frac{\beta_T}{\beta_M}} = \frac{\frac{2h}{d} \frac{\beta_T}{\beta_M} \left(\frac{a_1}{a_0} - 1 \right)}{\left(\frac{a_1}{a_0} \right)^2 + \frac{2h}{d} \frac{\beta_T}{\beta_M}} \end{aligned} \quad (7.1)$$

By assuming the outer layer thickness to be constant value, i.e. $15\text{\AA}$, and inserting experimental values, the relation is simplified into

$$\left\langle \frac{\Delta a}{a} \right\rangle = \frac{0.074h}{1.8066d+2h} \quad (7.2)$$

The result can be further improved if the experimental measured $CeO_{1.5}$ thickness can be fitted as a function of overall thickness. The result has been compared with a simple volume average approach, and the result is close. The difference between the volume average approach and the micro-mechanical approach lies in the internal strain between different layers. Another comparison is made between the micro-mechanical approach and the Madelung energy approach, which gives the lattice expansion as

$$\frac{\delta a}{a_0} = \frac{0.052\text{\AA}}{d} \quad (7.3)$$

The disagreement between the micro-mechanical model and the Madelung energy model lies in the formation of oxygen vacancies which is not taken into consideration in the latter one.

The result of this model relates the lattice expansion, which acts as an estimation of oxygen vacancy concentration, with the layer thickness of CeO_x , which can be easily extended into the GDC case. This relationship has never been studied theoretically before. Hence the result of this model provides a new and useful tool for researchers to estimate the ionic conductivity of GDC layer simply by measuring the thickness of this layer.

The electronic structures of CeO_2 , GDC and thin film GDC are studied, showing that the doping of gadolinium ions significantly decreases the band gap of CeO_2 , and that a thin film structure increases the band gap a lot. This is different from what happens in ZrO_2 and YSZ, where the doping increases the band gap by 0.4eV, this helps YSZ to be considered as a better electrolyte material than GDC as YSZ shows no current leakage under working condition. The influence of oxygen vacancy on the electronic structure on $CeO_2(111)$ surface is also investigated. The existence of oxygen vacancy decreases the band gap of $CeO_2(111)$ surface. The results here help provide an explanation to the electronic conductivity of GDC under low oxygen partial pressure – giving that doping of

gadolinium ions already lowers the band gap of CeO_2 , under low oxygen partial pressure, oxygen vacancies are easier to form in GDC, which further decreases the band gap, leading to some extent of electronic conductivity.

In summary, the main results of this work help explain the maximum ionic conductivity in YSZ, provide useful advices and information for the designing and synthesizing of SOEC components, arm the researchers with a simple tool to estimate the ionic conductivity of GDC interlayer, and help explain the electronic conductivity of GDC under low oxygen partial pressure.

7.2 Future Work

To have better and deeper insights into the reaction mechanisms in SOEC and to extend some of the conclusions of this thesis, there are several aspects that can be improved and extended in the future work of this thesis.

In the comparison of oxygen diffusion between YSZ bulk / single crystal structure and YSZ GB structures, we've only investigated two types of grain boundaries that have been synthesized in experiments. However, in practice, there are many kinds of grain boundaries in a YSZ thin film. To have a thoroughly understanding on the effects of grain boundaries, and to find preferred grain boundaries, more GB structures shall be investigated compared. With the performance and relationship of different GB structures in hand, it will help researchers make better decisions when designing and synthesizing SOEC devices.

As experimental results show that low resistance can be achieved at the interface between YSZ and the substrate STO, it is of great interest to investigate the interface effects. One promising approach is to study the strain, which is introduced by the existence of substrate, dependent behavior of ionic conductivity of YSZ using simulation methods. Properties like vacancy formation energy, oxygen ion mobility, migration energy, and ion hopping

behaviors are good examples to be studied to help provide better understanding in the effects of substrate.

In the simple diffusion model, which investigates oxygen ion and strontium ion diffusion behavior in GDC, the accuracy of the results depends totally on the accuracy of the diffusion coefficients used. Since we used experimental values of diffusion coefficients for oxygen and strontium ions, the impact of carrying out MD simulations in GDC system to calculate diffusion coefficients will be limited. However, it remains interesting to look in to the diffusion behavior in a more complex model, for example a YSZ-GDC-LSCF composite. Although, it requires significant efforts to setup benchmarks and simulations for such kind of complex models, it is an interesting start point for future works.

Regarding the micro-mechanical model that related lattice expansion with layer thickness in CeO_x laminated structures, the model can be improved by using the fitted relationship between $CeO_{1.5}$ layer thickness and overall layer thickness based on experimental results. More efforts shall be made to extend the model to GDC to provide more accurate prediction between the lattice expansion behavior and layer thickness in practical SOEC device synthesizing.

More CeO_2 surfaces shall be studied and the electrochemistry properties of CeO_2 shall be studied to provide more insights into the reaction mechanism at the electrolyte-electrode interface, which is of critical importance to the improvement of SOEC performance. Other common low index surfaces of CeO_2 are (110) and (100), further studies on the surface properties and catalytic properties of these surfaces shall be carried out.

Some interesting and critical problems that are not covered in this thesis are also worth investigating in future works, for example the strontium ion segregation problem in LSCF, the electro-catalytic properties of ceria and LSCF surfaces, the poisoning problem in SOEC, and so on. Theoretical modeling approach can be used to investigate these problems, providing helpful and critical insights into the nature of these problems.

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