Study on localized ion transportation phenomena in YSZ at high temperature

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NANYANG
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**STUDY ON LOCALIZED ION TRANSPORTATION
PHENOMENA IN YSZ AT HIGH TEMPERATURE**

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2016

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

2016

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.

05-08-2016

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Date

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Abstract

Yttria stabilized zirconia (YSZ) is a popular solid oxide electrolyte material for solid oxide fuel cell (SOFC) due to its high ionic conductivity and high stability properties at high operating temperature. Much of the research effort has been focused on lowering the operating temperature of SOFC for wider material selection and reduction on the thermal related damage when operating at high temperature. The drawbacks of reduction of operating temperature in SOFC include increase in the ionic resistivity of the electrolyte and decrease in reaction kinetic of the fuel cell compared to higher operating temperature. One of the strategy to reduce the ionic resistance of the electrolyte is through reduction of the electrolyte layer thickness. Thin film YSZ with thickness in the range of nm to μm can be used to improve the ionic conductance of the electrolyte layer.

There has been reports on variation of ionic conductivity in nanocrystalline structure of YSZ thin film where grain boundary in YSZ has played an important role in ionic transport of oxygen ions in YSZ electrolyte. Reported studies confirmed that diffusion of oxygen ion across the grain boundary is slower than in the bulk region. However, there is not much work on verifying the contribution of ionic transport parallel to the grain boundary in nano thin film YSZ. The hypothesis of this work is that the diffusion of atom in grain boundary region could be faster due to higher defect concentration. The aim of this work is to investigate on the existence of fast ionic conduction for oxygen ion diffusion along the grain boundary in YSZ electrolyte.

In this work, atomic force microscopy (AFM) conductive probe was used as working electrode for high temperature electrochemical studies of the thin film YSZ electrolyte while resolving the grain boundary feature of thin film YSZ. For

electrochemical characterization of the grain boundary of YSZ, electrochemical impedance spectroscopy (EIS) were applied to analyze the ionic conductivity of the thin film. High temperature beyond 500 °C is needed for EIS measurement with ionic resistance below 100 M Ω at contact radius of 100 nm, due to instrument limitation of 1 T Ω impedance measurement. Due to unavailable commercial AFM high temperature measurement beyond 250 °C, a MTS was designed and fabricated as a heating solution for thin film YSZ electrolyte to be compatible in conventional AFM setup. Pt-metal AFM probes were fabricated for better resistance towards thermal degradation when in contact with high temperature thin film surface. Characterization were performed for the MTS and Pt-metal tip.

Molecular dynamic (MD) simulations were used to understand and predict the behavior of oxygen ion transport YSZ with the presence of grain boundary. Two approaches were used which target at the local variation and regional variation of properties in YSZ simulation cell. The first approach calculates the number of oxygen vacancies and the oxygen ion jump rate at every possible oxygen lattice location. In the second approach, electric field was applied parallel to the grain boundary and the ionic transport of the oxygen ions at different regions were calculated.

As conclusion, the MD simulations results so far pointed toward blocking behavior of grain boundary in ionic conductivity in all direction. For local characterization of electrochemical properties using AFM, preliminary results have demonstrated the viability of such approach. In future, experimental works on local measurement of ionic conductivity of YSZ can be performed to support the prediction from the MD simulation.

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Abbreviations

AFM	Atomic force microscopy
ALD	Atomic layer deposition
BMB	Born-Mayer-Buckingham potential
CAFM	Conductive AFM
CAHT-AFM	Controlled atmosphere high temperature AFM
CE	Counter electrode
DC	Direct current
EELS	Electron energy loss spectroscopy
EIS	Electrochemical impedance spectroscopy
ESM	Electrochemical strain microscopy
FEM	Finite element method
FRA	Frequency response analyzer
GDC	Gadolinium doped ceria
KPFM	Kelvin probe force microscopy
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
LSCF	Lanthanum Strontium Cobalt Ferrite
LSGM	Strontium/magnesium doped lanthanum gallate
MC	Monte-Carlo simulation
MD	Molecular dynamic simulation
MTS	Micro-thermal stage
MSD	Mean square displacement
ORR	Oxygen reduction reaction
PECVD	Plasma enhanced chemical vapor deposition
PLD	Pulsed laser deposition
PR	Photoresist
PVD	Physical vapor deposition

RE	Reference electrode
RF	Radio frequency
S	Sense electrode
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
SPM	Scanning probe microscopy
TEM	Transmission electron microscopy
TPB	Triple phase boundary
WE	Working electrode
XRD	X-ray diffraction
YSZ	Yttria-stabilized zirconia

Chapter 1

Introduction

Thin film yttria-stabilized zirconia (YSZ) is a popular solid oxide electrolyte in solid oxide fuel cell (SOFC). In order to improve device maximum power density at lower operation temperature of SOFC, grain boundary diffusion of oxygen ion in YSZ has been studied intensively to reveal the role of grain boundary on ionic conductivity in the YSZ. There have been contradicting reports on the ionic conductivity of nanocrystalline YSZ thin film from previous experimental works. Two different approaches on study the ionic transport properties in the grain boundary structure of YSZ are suggested in this study, which aims to reveal the true nature of oxygen ion diffusion in the grain boundary of YSZ. This includes experimental work to locally reveal the electrochemical properties of the thin film and simulation work to predict and analyze the behavior of ions in the grain boundary structure.

1.1 Motivation

Solid oxide electrolyte such as yttria stabilized zirconia (YSZ), gadolinia doped ceria (GDC), and strontium/magnesium-doped lanthanum gallate (LSGM) are oxygen ion conductors at high temperature.¹ Oxygen ions in the oxide material are the charge carrier responsible for the ionic transport. For example, YSZ has ionic conductivity around 0.00448 Scm^{-1} at 600°C .² The oxygen ion conducting and electronic blocking properties allow the solid oxide material to be used in solid state electrochemical devices as electrolyte such as solid oxide fuel cell (SOFC), solid oxide electrolyzer and oxygen sensor.

SOFC is a type of fuel cell that uses solid oxide or ceramic material as electrolyte and operates at high temperatures, ranging from 500°C to 1000°C . SOFC has application in stationary power generation, combined heat and power system and auxiliary power unit, due to high conversion efficiency up to 60%.³ The application and potential of SOFC as an alternative efficient energy conversion device has led to significant of research into improving the device performance such as mechanical and chemical stability issues at high temperature, long term stability and reducing the cost of device. The research direction has been in reducing the operating temperature of the SOFC. High operating temperature lead to high reaction kinetics and increase in ionic conductivity, but the cost of operating at high temperature is higher, and often lead to degradation of the electrode and electrolyte due to diffusion of the impurities.⁴ A lower operating temperature on the other hand, allows lower temperature material to be used as component of the SOFC, such as metallic interconnects. The cyclability and long term operation of the SOFC will also be improved at lower operating temperature.

Figure 1-1: Simple schematic for planar design of anode-electrolyte-cathode of fuel cell

At lower temperature, there are more losses in terms of ionic conductivity of the solid electrolyte and the kinetics of the oxygen reduction reaction (ORR). These has prompted researchers in searching for alternative or solution for achieving high power density output SOFC at a reduced temperature, such as to substitute YSZ electrolyte with higher conductivity electrolyte material and using thin film electrolyte layer. In addition, microstructure and defect manipulation is another method of tailoring the properties of the solid oxide material. For example, in YSZ, yttria (Y_2O_3) is doped into zirconia (ZrO_2) to stabilize the cubic structure of the ZrO_2 at room temperature. The other microstructure that has been looked into is the grain size of the electrolyte. Polycrystalline YSZ has different ionic conductivity and electrochemical activity compared with single crystalline YSZ. It is known that grain boundary has blocking effect to the ionic transport compared to the grain region.⁵⁻⁸ Thin columnar YSZ film can be deposited via advanced thin film deposition technique such as sputtering, atomic layer deposition (ALD) and pulsed-laser deposition, where oxygen ion transport direction is parallel to the grain boundary.⁹ The transport of ions across grain boundary can be significantly reduced using such film. However, there is another concern on whether grain boundary parallel to the

ionic transport path provides fast transport pathway for oxygen ion. In general, grain boundary provides a path for fast atomic diffusion due to larger open space and higher concentration of defects. If grain boundary in YSZ possesses fast ionic conduction path for oxygen ions, the YSZ thin film can be modified to contains nanocrystalline size of grain which increase the density of the grain boundary at the interface. However, the effect of nanostructured thin film YSZ to the ionic conductivity and electrochemical activity of the YSZ has been a great debate among researcher while there is no general agreement has been made for the issue. In a closer inspection, there are variation of methods of sample characterization, but most of the characterization was done by ‘bulk-type’ measurement¹⁰, where the contribution of the grain structure is calculated from the assume width or thickness of the grain boundary and grain region with an averaged result from the microstructure.

To further understand the effect of microstructure to the ionic transport and/or ORR reaction, localized electrochemical studies would be much more valuable in providing the insight of the properties of the microstructure. Local measurement of the grain boundary region versus grain region of a thin film sample can resolve the difference in properties for these region. For example, using scanning probe microscopy (SPM) such as atomic force microscopy (AFM), the topography of the thin film sample can be resolved while the conductive probe can be functioned as nano-scale electrode to perform electrochemical measurement in the sample, as illustrated in **Figure 1-2**. However, not much work has been done in the abovementioned method. A detail work on local direct observation of ionic transport and reaction kinetics will certainly provide insight into the factor of grain structure to the performance of the SOFC, therefore enable us to further engineer and design a better performance solid electrolyte at low operating temperature. In this thesis, the work on local observation of ionic transport of YSZ at high temperature are explored.

Modelling and simulation work on ionic diffusion characteristic on grain boundary structure are performed to predict and understand the behavior of the enhancement or degradation of ionic transport in grain boundary structure of YSZ.

Figure 1-2: Schematic of concept for SPM measurement for resolving local microstructure and ionic conductivity in YSZ thin film

1.2 Objectives and Scope

The main objective of the work is to understand the effect of grain boundary toward the ionic transport and reaction kinetics of the SOFC. There are two approaches for this goal, which are

- 1) To perform in-situ high temperature localized electrochemical measurement for characterizing the properties of the microstructure. Conventional high temperature AFM measurement has temperature limitation around 250 °C which is insufficient for nano-scale probing of electrochemical impedance of solid oxide electrolyte system. Since there is no available commercial instrument capable of achieving higher operation temperature, the scope of

the work includes setting up instrumentation that allows higher operation temperature AFM electrochemical studies. Analysis and modeling of the electrochemical measurement results are required to resolve the properties of the electrochemical cell.

- 2) To understand ionic transport in microstructure through the use of modeling tools and simulation. From modeling and simulation, behavior of the ionic transport in grain boundary structure will be observed which is used to explain and support the finding from experimental results.

1.3 Dissertation Overview

This section gives an overview of the content for the following chapters in this dissertation.

Chapter 1 provides a brief introduction to the study of YSZ electrolyte as SOFC's electrolyte and the rationale for performing further research on grain boundary ionic transport in YSZ. The objective, goals and scope of the work is outlined in this chapter followed by the overview of the dissertation contents.

Chapter 2 reviews the literature concerning the YSZ electrolyte as ionic conductor in SOFC. The structure, characteristic and properties of YSZ will be discussed in this chapter. Effect of microstructure to the properties of YSZ electrolyte, such as density of grain boundary and defects will be reviewed. Aside from physical experiment on YSZ electrolyte, simulation such as molecular dynamic simulation (MD) on YSZ will be discussed. Experiments which use of conductive AFM in measurement of ionic properties of electrolyte will be reviewed.

Chapter 3 focuses on the various techniques available for investigating the effect of microstructure to the ionic property of thin film solid oxide electrolyte. This includes bulk-type of measurement technique, in-situ characterization and simulation technique. The different aspect of these technique will be discussed.

Chapter 4 elaborates on the approach for using AFM as tools for high temperature electrochemical measurement, which includes modification of heating methods and AFM probe design. The design, fabrication and characterization of micro-thermal stage (MTS) and fabrication process of the metal Pt AFM tip, which are necessary for the high temperature AFM measurement, will be discussed in this chapter. Electrochemical measurement results obtained from the experiment will be discussed.

Chapter 5 explains on two different approaches of studying grain boundary oxygen ion diffusion and transport using MD simulation. Simulation model and construction of grain boundary structure YSZ is discussed in the chapter. The analysis of oxygen vacancies distribution and oxygen ion transport for different location was carried out. The ionic conductivity of the bulk region and grain boundary region were calculated based on the ionic transport resulting from an applied electric field. Results of ionic transport in grain boundary structure is compared with other research work.

Chapter 6 draws together the conclusion of the thesis. The important findings from the experiments and modeling work are discussed, and implication from the results are explained.

1.4 Findings and Outcomes/Originality

This research led to several outcomes by:

1. Understanding the effect of grain boundary to the ionic conduction properties through MD simulation. Two different approaches used in MD simulation provides view of distribution of oxygen vacancies in the YSZ lattice, oxygen transport rate of the oxygen lattice with respect to the location in the YSZ simulation cell. With the information of the distribution of the oxygen vacancies, we have a stronger evidence on the mechanism that lead to behavior of ionic conduction in the grain boundary region. The ionic conductivity is directly calculated from the electric current caused by the displacement of oxygen ions when an electric field is applied onto the YSZ simulation cell, which is not explored by previous research. This further confirm the ionic conductivity of the grain boundary when the oxygen ion transport along the grain boundary, since the applied electric field can be imposed parallel to the grain boundary in the simulation cell.
2. Established working setup for electrochemical measurement using AFM at high operating temperature. Currently there is no commercial AFM which could heat up the sample to high temperature more than 250 °C in atmospheric condition as it would damage the AFM scanner. For solid oxide thin film characterization at temperature range of 600 °C using commercial AFM setup, we have designed and fabricated functional MTS as a solution for sample heating used in AFM setup. Characterization and testing of MTS for AFM measurement was successfully demonstrated. On the other hand, we have succeeded in fabrication of Pt-metal AFM probe for the use in high temperature electrochemical measurement for better resistance towards thermal degradation.

Chapter 2

Literature Review

YSZ is a popular ionic conductor used in SOFC due to its high ionic conductivity and chemical stability at high temperature. In order to reduce operating temperature of SOFC, different types of thin film fabricated YSZ has been experimented on. Due to difference in fabrication process and thermal history, the properties YSZ thin film fabricated from different process varies, such as the defect, microstructure, grain size, strain, density/porosity and dopant distribution. The apparent ionic conductivity enhancement due to reduction in thin film thickness has drawn interest in researcher in investigating if grain size effect or strain effect has significant factor in changing the ionic properties of the thin film. In addition, several molecular dynamic simulation works have been carried out for YSZ simulation cell to investigate the properties of YSZ under different scenario such as having different dopant cluster and distribution, grain boundary and strain level. Aside from this, novel experimental technique on scanning probe based in-situ ionic conductivity measurement has been proposed and demonstrated to resolve the properties of ionic material.

2.1 YSZ Electrolyte

YSZ is a high temperature ionic conductor, where oxygen ions are the charge carrier responsible for the charge transport. To further understand YSZ, we start our discussion on pure zirconia, without yttrium doping. The most common oxidation state of zirconium is 4, therefore zirconia is also known ZrO_2 . Nature occurring zirconia is monoclinic structure in room temperature, tetragonal at temperature between 1170 to 2370 °C and cubic at temperature beyond 2370 °C. Change in crystal structure during heating resulting in change in volume of the material, which causes crack during heating to high temperature.

Figure 2-1: Illustration of a unit cell for cubic fluorite structure of ZrO_2

Doping of yttria (Y_2O_3) into zirconia results in stable cubic phase of the material even at room temperature. The structure also known as yttria stabilized zirconia (YSZ). The actual structure of YSZ is also known as cubic fluorite structure. **Figure 2-1** illustrates the structure of a unit cell ZrO_2 in cubic fluorite structure, which has Zr^{4+} ions occupying the FCC site while O^{2-} ions occupying the tetrahedral site each formed by the 4 nearest neighbor of Zr^{4+} ions, forming a smaller unit of cubic lattice inside the Zr^{4+} ions. Yttrium ion has normal oxidation state of 3, and it is slightly bigger than Zr^{4+} ions in terms of ionic radii. Due to different oxidation state between Y^{3+} and Zr^{4+} , oxygen vacancies has to be created to compensate the

charge balance. For every $2Y^{3+}$ ions in the YSZ, one oxygen vacancy has to be created in order for the material to be charge neutral. In Kröger-Vink notation, the substitution of Y_2O_3 into ZrO_2 lattice can be written as followed,¹¹

Oxygen vacancies created are responsible for oxygen ion migration. Oxygen ion which migrate to the neighbor oxygen vacancies resulting in a net oxygen ion transport for the material.

2.1.1 Fabrication Methods of Thin Film YSZ

In this section we will be discussing on the fabrication methods of thin film YSZ typically reported in the research. Different fabrication process will result in different quality of YSZ in terms of microstructure, residue stress and defects. Therefore, in this section, we will briefly discuss the fabrication methods and the properties of the YSZ from each fabrication methods. A detail review on different types of fabrication method for SOFC layer can be found here.¹²

Single crystalline YSZ are usually fabricated through skull melting process. The block of single crystal YSZ is then cut and polished into desire orientation, size and shape. On the other hand, polycrystalline YSZ can be fabricated through different type of process. Conventional ceramic processing methods usually starts with YSZ powder or YSZ nano-particle, which is then sintered at high temperature for densification of the powder. Types of fabrication method which involve YSZ powder as starting material includes, tape casting, screen printing and pressing methods. High temperature sintering, usually above 1200 °C for long hours is required to achieve high quality and dense electrolyte film. Spark plasma sintering

is another method to sinter YSZ powder at a lower temperature, with reduced sintering time compared to conventional sintering technique.¹³

In addition to conventional ceramic processing technique, there are other fabrication process which involve coating of YSZ onto a substrate. This includes spray pyrolysis, pulse laser deposition, sputtering, sol-gel, chemical vapor deposition and ALD, which will be reviewed in the following paragraph.

Spray pyrolysis is one of the technique to fabricate thin film YSZ over a large area.¹⁴ Metallo-organic precursors which include Zr and Y metal are dissolved in volatile and highly combustible solvent such as methanol. The solution is then spray onto heated substrate, at temperature around 600 °C to form YSZ thin film. Different variant of the spray pyrolysis exists based on the aerosol forming methods and deposition atmosphere. Nanocrystalline and dense thin film YSZ can be deposited by controlling the deposition temperature and droplet size of the spray.

Pulsed laser deposition (PLD) is one of the method used to produce thin film YSZ sample.^{9,15-18} PLD is a physical vapor deposition technique where high energy laser pulse is used to ablate or vaporize target material to be deposited to the substrate. The advantages of using PLD technique is that the deposited thin film will have the same stoichiometry as the target material. Thin and dense thin film YSZ can be produced by PLD method, by varying deposition parameter, such as laser wavelength, pulse energy, pulse rate, oxygen pressure, deposition temperature and substrate-target distance. High quality YSZ thin film can be deposited at lower temperature, around 600 °C, without the need to anneal the thin film at higher temperature. Therefore, nanometer grain size, around 20 nm, can be preserved using PLD fabrication method.¹⁷

Sputtering is a process where high energy particle, usually Ar ion, bombard at the target substrate surface, causing material from the target to be sputter ejected to the sample substrate. There are a few types of sputtering of YSZ reported in the literature, namely direct current (DC) sputtering^{19,20}, RF sputtering²¹, magnetron sputtering²² and reactive sputtering²³. The sample substrate is usually heated to temperature around 500 to 700 °C during sputtering for crystalline growth of YSZ thin film. Room temperature deposited film usually has grain size less than 10 nm or in amorphous phase.²¹ Sputtering at relatively low temperature often results in columnar structure, which may have pin-holes between the gap of the column.²²

Spin coating or dip coating of polymeric precursor or sol-gel is another method of depositing thin film YSZ.^{24,25} Metal alkoxide which contains zirconium and yttrium is used as starting material. Polymerization reaction take place which convert the monomer into network of gel containing the metal alkoxide. Spin coating of the polymeric precursor can be performed to coat a thin uniform layer onto the substrate. To achieve higher thickness, multiple cycle of spin coating can be done after drying and heat treatment of the previous spin coated layer. Composite sols, which contains nano powder of YSZ crystal, colloidal sol (binder) and organic matter can be used instead to increase the thickness per coating.²⁶ The thin film is then crystallized by heating at high temperature, typically around 600 °C and above. Due to low temperature heat treatment process, the grain size of sol-gel fabricated thin film is usually in tens of nanometers. Larger grain growth can be achieved by heating the thin film to higher temperature.

Chemical vapor deposition method in depositing thin film YSZ layer has been reported in the literature.²⁷ Precursor which contains Zr and Y are mixed in desirable proportion in a solvent, before vaporized and carried into reaction chamber by a carrier gas. The substrate to be coated with YSZ thin film is heated up to

decomposition temperature of the Zr and Y precursor, usually in the range of 500 °C to 700 °C. Grain size around 100 nm can be achieved by CVD method.

ALD is another feasible method in depositing thin film YSZ layer.²⁸⁻³¹ ALD is pulsed form of chemical vapor deposition, where different reactants are separately introduced into the reacting chamber in sequences. Organometallic compound which contains the Zr and Y are used as precursor in ALD. Surface absorption of reactant species on substrate results in less than a single layer growth which conform to the substrate surface in each ALD cycle. 4:1 ratio of Zr precursor cycle to Y precursor cycle will result in Y dopant concentration close to 8YSZ.²⁹ The deposition temperature of ALD layer is usually less than 300 °C, thus nanometer range of grain size 2-4 nm can be achieved in as-deposited ALD YSZ.

2.2 Ionic Conductivity Properties of YSZ

Ionic conductivity (σ) of material is defined as the product of charge number (q), charge density (n) and ionic mobility (μ):

$$\sigma = nq\mu \quad (2)$$

Theoretically, if the amount of oxygen vacancies and oxygen ions are equal, this would result in highest ionic conductivity as every oxygen contribute to the conductance of electricity under applied electric field. However, in reality, dopant concentration is not independent from its ionic mobility. The maximum achievable ionic conductivity occurs at around 8mol% of Y_2O_3 , followed by sharp decrease in ionic conductivity as the dopant concentration increases. The maximum conductivity of YSZ occurs at Y_2O_3 doping concentration around 8-9 mol%, which is due to lower activation energy for ionic transport at such doping level rather than amount of

oxygen vacancies created.³² 8mol% yttria doped zirconia is also known as 8YSZ in the literature.

Mobility of oxygen vacancies is one of the key parameter in affecting the ionic conductivity. Diffusion of ions in the material can be related to mobility through Nernst-Einstein relation.

$$\mu = \frac{qD}{k_B T} \quad (3)$$

where D is the diffusivity of the material, k_B is the Boltzmann constant and T is the temperature. Diffusion is material transport process, which is the product of diffusivity and concentration gradient of the species. Empirically, diffusivity of species follows Arrhenius law, which has the following form,

$$D = D_0 e^{-\frac{E_A}{kT}} \quad (4)$$

where E_A is the activation energy, D_0 is known as the pre-exponential factor for the equation. In atomistic view, each oxygen ion transport process can be viewed as chemical reaction with an energy barrier to form the product (transport to the neighbor vacancy site). The energy barrier is known as activation energy.

Temperature plays a role in the ionic conductivity of the material, as it changes the ratio in the exponential term. However, a series of study on ionic conductivity of YSZ with temperature shows two slope of activation barrier at around 650 °C. This is contributed to the association effect of oxygen vacancies at lower temperature. At lower temperature, cluster of yttria ion and oxygen vacancies are formed which increase the activation barrier for oxygen ion to escape the cluster. At higher

temperature, the cluster of yttria ion and oxygen vacancies dissociate, which lead to lower energy barrier for migration.

2.2.1 Effect of Stress and Strain to YSZ Ionic Properties

Stress level in the thin film YSZ can affect the YSZ ionic properties. A study performed by Wakako Araki *et al.*³³ shows that tensile stress of 20 MPa improves around 10 to 20 % of ionic conductivity and compressive stress decrease 10 to 20 % of ionic conductivity in YSZ single crystal. The change in ionic conductivity is reversible with the stress load, and upon releasing the stress, the ionic conductivity returns to the original level. Note that the strain level is only about 0.025%, which is well in the elastic region.

Another study by Igor Kosacki *et al.*³⁴, which PLD deposited nanocrystalline thin film YSZ on Al₂O₃ single crystal substrate has showed that the interface of YSZ and Al₂O₃ greatly enhances the ionic conductivity at the interface to over 3 order magnitude. Micro lattice strain of about 22 % at the interface, without dislocation arrays may be a factor of greatly increase ionic conductivity.

2.2.2 Effect of Defects to YSZ Ionic Properties

Generally, most of the studies on YSZ properties focused on different defects on the sample. These include investigating the effect of different type and concentration of impurities in the material, effect of dislocation³⁵ and grain boundary effect, which is essentially a 2D defect. Other types of study include different operating condition such as effect of stress and strain to the ionic properties.

Single crystalline YSZ³⁶ and polycrystalline YSZ has been the subject of studies and research in characterizing the ionic properties of YSZ. Polycrystalline material consist of multiple grains with different orientation, where each grain is considered to be a single crystal. The intersection surface between two grains are called grain boundary. Polycrystalline material are common in the above mentioned fabrication process due to multiple nucleation site produced during thin film deposition or growth, while each of the nucleation site produce different grain orientation. A grain boundary is a 2D defects of the material, which is often tends to decrease the electrical conductivity and thermal conductivity of the material, while strengthening the mechanical properties of the material due to slip dislocation motion disruption.

The energy of the material with grain boundary is higher due to the fact that grain boundary is a 2D defect. Grain boundary migration occurs when there is a driving force to reduce the system energy, which eventually lead to grain growth. Besides that, excess volume created with the present of grain boundary is an important property of the grain boundary. The excess volume of the grain boundary is one of the link to the segregation of impurities in the material.

Grain size of the material can be controlled by varying the thin film YSZ fabrication process, such as temperature and time of the heat treatment process. Size of the grain can be characterized by different technique. Grain boundary is susceptible to grain boundary grooving after heat treatment to reduce the total energy of the surface. Grain boundary grooving produces trench at the grain boundary interface while produce slight bump away from the interface. For metal type of material, preferential etching of the grain boundary by the etchant can be performed to reveal the interface structure. For large grain size, optical microscope can be used to observe the grain after the sample is being polished and surface etched to reveal

the groove of the grain. For smaller grain size, SEM imaging is helpful to reveal the groove of the grain. For nano-sized grain, AFM characterization can be performed to reveal the microstructure of the grain. In addition, XRD can be used to estimate the grain size from Scherrer equation.

The contribution of grain boundary to ionic conductivity of YSZ has been a subject of discussion in the research. For single crystalline YSZ, electrochemical impedance spectroscopy (EIS) measurement shows a single arc which correspond to the bulk ionic conductivity³⁷, while for polycrystalline YSZ sample, 2 arc are visible for the frequency range, which are attributed to the bulk ionic conductivity and the grain boundary contribution. Brick-layer model is often used to model the contribution of the grain boundary to the measured ionic conductivity. In brick-boundary model, the individual grain is considered as the brick and the grain boundary is the outer layer which coat the bulk grain. **Figure 2-2a** illustrate the brick layer model with grain size of d_g and grain boundary width of δ_{gb} . The contribution of the grain boundary conductivity in this model can be separated into two parts, one of it is perpendicular to the flux of the oxygen ion migration path, and the other is parallel to the flux of the oxygen ion migration path. To model this, an equivalent circuit for the grain boundary model is proposed based on the brick-boundary model, as shown in **Figure 2-2b**. In this model circuit, parallel grain boundary resistance component ($R_{gb\parallel}C_{gb\parallel}$) is in parallel with the grain resistance ($R_{bulk}C_{bulk}$) for ionic conduction, while the perpendicular grain boundary resistance ($R_{gb\perp}C_{gb\perp}$) is in series with the formal two components. For nanocrystalline size YSZ sample and thin sample, the parallel grain boundary conductivity can be significant, which could change the overall ionic conductivity property of the YSZ. For large grain size YSZ and thick sample, the contribution of the parallel grain boundary ionic conductivity become less significant.

Figure 2-2: a) Illustration of brick layer model b) Equivalent circuit for nano-thin film YSZ

In a study by Makoto Aoki *et al.*³⁸, the solute segregation at the grain boundary has been investigated for different condition. In this study, the solute refers to Si impurities and Y dopant. The optimum amount of dopant for highest ionic conductivity is thought to be the minimum dopant required to stabilize the cubic phase.³⁹ Generally, the segregation of the solute is being account for the lower grain boundary ionic conductivity in YSZ. When the sample is annealed longer in the furnace, resulting in larger grain size and greater solute segregation at the grain boundary. Therefore, the smallest grain sample seem to have higher grain boundary ionic conductivity compared to the larger grain. Nevertheless, the grain boundary

conductivity value is still 2-3 order magnitude smaller than the bulk grain ionic conductivity. Note that the author used a simplify form of brick-layer model in analysis which do not include the effect of the parallel grain boundary contribution for the analysis. In another study by M. Hattori *et al.*⁴⁰ where the ionic conductivity of the sample after long annealing at temperature range from 700 °C to 1000 °C for 1000 hours is measured. The results from the study showed substantial ionic conductivity decrease for sample annealed at 1000 °C for 1000 hours. In addition, 9.5YSZ seem to be much stable in terms of degradation of performance compared to 8YSZ. Though from XRD, only cubic phase of YSZ is detected and no tetragonal phase of YSZ is detected after long annealing time, the Raman spectroscopy study indicated present of tetragonal phase, which is responsible for the degradation after long annealing time. From the comparison of stability between 9.5YSZ and 8YSZ, we can hypothesize that dopant segregation in 8YSZ grain boundary cause local depletion of Y dopant in bulk phase, which result in scattered of tetragonal phase formed in the matrix of cubic phase in the bulk, while 9.5YSZ has greater amount of dopant to begin with, therefore, less tetragonal phase in the bulk phase after long annealing time. X. Guo and J. Maier⁵ showed that addition of 0.4mol% of Al_2O_3 does not result in significant change in bulk ionic conductivity, but result in 462 % of increase in grain boundary resistivity, which is attributed to the grain boundary segregation of impurities.

Oxygen diffusion across bicrystal YSZ is a straight forward experiment in determining contribution of grain boundary to the oxygen ion diffusion. Oxygen isotope O^{18} is used as tracer which will be incorporated and diffuse into YSZ during the experiment. Using secondary ion mass spectroscopy (SIMS), the tracer profile along the diffusion path can be obtained. Grain boundary is found to be blocking for oxygen diffusion, even in the absent of impurities such as Si.^{7,8}

One of the study by Kazuya Otsuka *et al.*³⁵ managed to show slight increase (10%) in ionic conductivity by introducing dislocation structure in YSZ single crystal below 800 °C, which is attributed to rapid diffusion path, known as pipe diffusion. Dislocation in the single crystal was introduced by compression, with 1 % and 10 % strain level. Note that dopant segregation does not occur in this study, since single crystal YSZ is used as starting material, and the operation temperature does not result in segregation of the dopant. Therefore, blocking behaviour by dopant segregation is not observed in this case, while sample shows slight improvement in ionic conductivity due to rapid diffusion path.

The effect of nanocrystalline thin film YSZ to ionic conductivity is reviewed in the following paragraph. J. H. Joo *et al.*⁹ shows that columnar, nanocrystalline YSZ in the region 60-100 nm grain size has no significant difference compared to the bulk in terms of ionic conductivity. Measurement of across plane conductivity of YSZ thin film with 20 nm thickness does not show any improvement from bulk ionic conductivity.⁴¹

There are a few that report great amount of increase in ionic conductivity of nanocrystalline thin film YSZ compared with micro-crystalline YSZ⁴²⁻⁴⁴. In those report, heat treatment is performed at temperature less than 1000 °C to achieve nanocrystalline YSZ structure. However, there are a few points to note. First, the ionic conductivity measurement is performed by in-plane conductivity measurement, with a supporting substrate at the bottom of the thin film sample. Si wafer, Al₂O₃, MgO and fused silica are used as the substrate. For the work by Y.W. Zhang *et al.*⁴⁴, the specific grain boundary conductivity calculated was still a magnitude lower than the bulk region conductivity, while the overall ionic conductivity is one magnitude higher compared to other reported result. In the reported work by Igor Kosacki *et al.*⁴², the increase of overall ionic conductivity was attributed to reduce in activation

energy from 1.34 eV for polycrystalline YSZ to 1.19 eV for microcrystalline YSZ to 0.93 eV for nanocrystalline material. Note that the effect of grain boundary is not separately investigate. The dependence of conductivity toward oxygen partial pressure may point to possible electronic conduction in the YSZ thin film.² However, in later similar experiment by Christoph Peters *et al.*⁶, it is found that grain boundary ionic conductivity is 2 order of magnitude lower compared to bulk conductivity, while for nanocrystalline sample (5nm to 36nm), the smaller grain size sample has larger total resistance compared to larger grain size sample. Grain boundary conductivity is constant and independent with grain size from 232 nm to 782 nm. The author attributes the large increase in ionic conductivity in Koscaki's study with large micro-strain on the nanocrystalline sample. Similarly, dependence of ionic conductivity on thin film thickness on MgO substrate also points toward the role of substrate-interface rather than grain boundary effect.⁴⁵⁻⁴⁷ However, in another similar experiment which uses PLD deposited YSZ on MgO substrate, the author found that YSZ/MgO interface has no important role in the ionic conduction as the conductivity is independent of the film thickness.⁴⁸

Oxygen tracer diffusion experiments on nanocrystalline YSZ has also been investigated to elucidate the effect of grain boundary to ionic diffusion. Roger A. De Souza *et al.*⁴⁹ performed oxygen tracer diffusion experiment on 50 nm grain size dense YSZ sample. However, no evidence of fast diffusion along grain boundary is found, rather the result indicates grain boundary hinder oxygen transport. On the other hand, Grenor Knöner *et al.*⁵⁰ reported 3 order magnitude enhancement in grain boundary diffusion compared to single crystal YSZ in oxygen tracer experiment. The variability between two experiment results could arise from the micro-crack in the YSZ sample and effect of strain in the sample.⁴⁹

The controversial topic of the nanosize effect were also investigated by a few researchers. Hae-Ryoung Kim *et al.*⁵¹ investigate the possible sources of illusional nano-size effect due to in-plane ionic conductivity measurement of thin film. When thin film thickness greatly reduced, the substrate conductance may be comparable with the thin film. Higher temperature also changes the conductivity of the substrate material. In addition, the use of ceramic adhesive may also result in electronic leakage, which apparently has similar activation energy barrier characteristic with YSZ thin film. On the other hand, Jun Jiang and Joshua L. Hertz⁵² reviewed extensively on the reported ionic conductivity of YSZ thin films. They pointed to the possibility of value of strain which results in the variability of the reported ionic conductivity value, as residue stress has strong dependence on processing parameter and thermal history.

2.2.3 Effect of grain boundary to surface oxygen exchange

The effect of grain boundary to surface oxygen exchange plays an important role in the performance of SOFC. Higher surface oxygen exchange entails better ORR kinetics. Oxygen tracer experiment has been performed to understand preferential site for oxygen incorporation⁵³ and has showed that grain boundary region has preferential oxygen incorporation compared to grain region. By depositing less than 10 nm thick of ALD YSZ, high grain boundary structure can be achieved, which could enhance surface exchange kinetics up to 3 times compared with un-coated YSZ sample.⁵⁴

2.3 Molecular Dynamic Studies of YSZ Ionic Properties

The previous section discussed on investigation of YSZ ionic properties using different experiment methods. In this section, simulation method of investigating the properties of YSZ will be reviewed.

In general, grain boundary has deleterious effect on oxygen diffusion from MD simulation. Kai-Shiun Chang *et al.*¹¹ constructed dislocation type of grain boundary and found that the present of grain boundary has lower oxygen mean square displacement (MSD) compared to the sample with no grain boundary. MD simulation on symmetrical tilt grain boundary, $\Sigma 5(310)$ and $\Sigma 13(510)$ YSZ bicrystal also shows that the presence of grain boundary reduces the oxygen ion diffusion rate.^{55,56}

The distribution of the oxygen vacancies and Y dopant in the YSZ crystal plays an important role for the diffusion property of YSZ as discussed in the previous section. Tarancón *et al.*⁵⁷ study of local transport behavior in YSZ material using MD simulation. Different set of combination of environment, such as the location of yttrium dopant with respect to the oxygen ion migration pathway were tested out in the study. The energy landscape for oxygen vacancy migration for each combination of environment was calculated. The study shows that preferred oxygen vacancy migration pathway is the environment which has no yttrium dopant on the path of the migration. This suggest that segregation or higher density of yttrium dopant at certain location of the YSZ does not improve the ionic conductivity of the material. Another important study by Steven P. Miller⁵⁸ investigated the dopant clustering effect to the stability of YSZ cubic phase, and ionic conductivity material studied by applying e-field to the sample. Different distribution of Y dopant cluster simulation cells was investigated, and the results show that high dopant cluster will entrap large

number of vacancies, hence lowering the vacancy concentration at the Zr-rich site and cause destabilization to the cubic phase at the Zr-rich site to tetragonal phase. It is known that the tetragonal phase of zirconia has much lower ionic conductivity than the cubic phase zirconia, hence the sample with more tetragonal phase present in the structure would lead to lower ionic conductivity compared to fully stabilized YSZ sample. In another study by Eunseok Lee *et al.*⁵⁹, the author explored different dopant configuration and predict the optimum Y dopant configuration which would produce the lowest effective activation energy for oxygen diffusion. They found that by forming [100] Y-segregated lines at certain periodicity, the enhancement can be significant depending on the temperature. In doped ceria, similar results were observed as dopant segregation lead to degradation of the ionic conductor.⁶⁰

For MD simulation, oxygen ions and vacancy are mobile at the simulation temperature. Therefore, to find the distribution of the oxygen ions of the system, a sufficient MD simulation run can be performed for the system to reach the equilibrium state. However, cation diffusion during MD simulation is rather rare given the high cation vacancy formation enthalpy and diffusion activation barrier which range between 4.4 eV to 5.3 eV.⁶¹ The cation diffusion event is simply not happening for the time-scale of the MD simulation. There are a few methods to simulate the cation diffusion. One of the method is to reduce the overall potential of the system, or hyperdynamics, which rare event would become achievable in the simulation time-scale. In one of the study carried out by R.L. González-Romero *et al.*⁶¹, the interaction potentials are modulated to promote cation mobility within the lattice. Activation energy and diffusion coefficient can be calculated for the case of normal interaction potential by extrapolation method. In addition, Monte-Carlo technique can be used to swap the position of the cation to simulate dopant diffusion in reality. In a study performed by M. Kilo *et al.*,⁶² the cation diffusion is accelerated

by increasing the number of cation vacancies and perform the simulation at very high temperature, from more than 2500K to around 5000K.

Jihwan An *et al.*⁶³ study the oxygen ion and vacancy distribution behavior near a single grain boundary in YSZ. Using TEM, a symmetric tilt grain boundary of YSZ is imaged, and the concentration of oxygen ion and vacancy is recorded using EELS measurement. The results of the experiment show that the intensity of the oxygen ion drop at the grain boundary interface at around 1.0 nm from the grain boundary core center. Hybrid MC-MD simulation performed also support the experimental result qualitatively by having ionic density of oxygen ion lower than the bulk phase.

In a similar research work has been performed by Hark B. Lee *et al.*⁶⁴ where the dopant segregation effect was investigated in addition to oxygen ion concentration at the grain boundary. MC-MD hybrid simulation was performed to find out the likely Y dopant distribution pattern in region of grain boundary structure. The research work suggests that high concentration of oxygen vacancies formed at the grain boundary interface due to lower vacancy formation energy lead to dopant segregation profiles at the grain boundary. Aside from dopant segregation at grain boundary interface, the effect of surface to the dopant distribution was also investigated.⁶⁵ Y dopant has large variation of distribution at the surface compared to the bulk phase, with low Y dopant at the surface while peak at 2-3 sublayer into the crystal before return to normal level at the bulk phase. Oxygen ion or vacancies distribution also followed the similar pattern, where high oxygen vacancies at the surface, which then dropped to minimum at 2-3 sublayer into the crystal before return to the normal level. It can be reasoned that the dopant distribution and the oxygen vacancies distribution are correlated from these studies.

The previous section postulated on the contribution of strain to the greatly enhancement of ionic conductivity in thin film YSZ sample. There are also a few studies performed by simulation to verify the possibility of the described scenario. Wakako Araki *et al.*^{33,66-68} managed to show about 44 % of improvement in oxygen diffusion with 1.8 % of strain level in YSZ simulation cell.

The effect of substrate interface has also been investigated via MD simulation. Subramanian K. R. S. S. and Ramanathan S.⁶⁹ investigate the interfacial conductivity between YSZ films and MgO substrate. Simulated amorphization and recrystallization was used to recrystallize YSZ thin film on MgO substrate. The author found that interfacial conductivity could increase by 2 order of magnitude as YSZ thin film size decreases from 9 nm to 3 nm.

2.4 In-situ Investigation of SOFC Component

In this section we will briefly review on the use of SPM method to obtain electrochemical properties of material as well as the microstructure of the thin film surface.

AFM is a versatile tool for surface characterization. Sensitive control of force can reduce the potential damage to the sample surface during measurement. Conductive AFM can be used to measure the response of SOFC components, such as electrolyte and electrode. However, high temperature is usually needed in such measurement, since solid oxide electrolyte has low ionic conductivity at low temperature. High temperature AFM is challenging as heating induces thermal drift and noise to the system. There are a few methods to extends the maximum operation of AFM measurement. Measurement in vacuum condition is one of the solution to operate AFM at elevated temperature. Up to 750 °C of temperature can be used for

AFM measurement at high vacuum.⁷⁰ In addition, for ambient atmosphere, high temperature AFM measurement can be performed by reducing the heat transfer to the piezoelectric scanner of AFM, such as to reduce the size and power of the heater.⁷⁰ Controlled atmosphere high temperature SPM (CAHT-SPM) has been developed to study sample in different environment such as oxygen, hydrogen and nitrogen at temperature as high as 850 °C.^{71,72} This is made possible by having water cooled system between the furnace and scanner which reduce the heat transfer to the piezoelectric scanner. EIS measurement and conductivity measurement can be performed on the sample using the CAHT-SPM system.

Ionic and electronic impedance imaging by AFM have been conducted to study the conductivity of the various material, such as Au-Si₃N₄ interface, ZnO varister, Nafion, poly(ethylene oxide), CsHSO₄.⁷³⁻⁷⁶ Localized impedance can be resolved given the contact size of the AFM tip, which is in 10 to 100 nm radii. Small contact area results in high resolution of the image, but also increase the impedance significantly, up to GΩ range of impedance. Given the stray capacitance of the system, the meaningful measurable signal by the instrument is limited to lower frequency data. Different type of ionic and electronic measurement technique can be applied to the sample, such as impedance measurement, cyclic voltammetry and I-V measurement.

Besides application of conventional electrochemical technique to the sample, surface potential can also be measured using SPM technique. Kelvin probe force microscopy (KPFM) or surface potential microscopy is a non-contact mode of AFM which measure the surface potential of the sample during the scan. Jiaxin Zhu *et al.*⁷⁷ demonstrated direct probing of local surface potential gradient of YSZ electrolyte under 600 °C to calculate the ionic conductivity and activation energy of the conductivity.

The electrochemical activity (oxygen reduction/evolution) measured by electrochemical strain microscopy (ESM) method is pioneered by Kumar Amit *et al.*^{78,79} High electric bias is applied to the conductive SPM tip which is in static contact with the thin film surface. The electric bias activates the ORR/OER process, which results in generation or depletion of oxygen vacancies local to the contacting region. The small change in local volume by the generation or depletion of vacancies causes surface deformation which is then recorded. Large ESM signal infers high local electrochemical activity, and vice versa. The experiment showed that region around Pt nanoparticles has larger EMS signal compared with region far away from Pt nanoparticles.⁷⁹

2.5 Conclusion

Research direction and research interest of SOFC has been moving toward designing lower operating temperature fuel cell which has equally good performance as high temperature fuel cell. The losses resulted from operating at lower temperature are due to sluggish reaction kinetics and high ionic resistance of the solid oxide electrolyte. Ionic transport in YSZ is through oxygen vacancies transport mechanism which is a function of temperature and activation energy of migration. At lower temperature, association of vacancies complex decreases the ionic conductivity of the YSZ electrolyte, while at higher temperature, the vacancies complex is fully dissociated, freeing all the available oxygen vacancies.

Different fabrication process for thin film YSZ thin film results in different ionic conductivity properties for the electrolyte. Nanocrystalline grain size YSZ can be obtained for fabrication process at low temperature. Microcrystalline grain size thin film tends to have more dopant segregation issue due to high temperature heat treatment process.

Grain boundary in YSZ was observed to have blocking effect on the ionic transport of the oxygen vacancies from oxygen tracer experiment. However, there are variability in ionic conductivity reported in literature occurs for thin film YSZ, especially for nano-crystalline size of thin film YSZ. Effect of substrate, strain and current leakage may be one of the reason on disagreement between various report.

Various simulation works has been performed to understand the behavior of YSZ, such as dopant distribution, preferential oxygen migration path and oxygen diffusion in the presence of grain boundary structure. In summary, the presence of dilative strain improves the ionic conductivity while the presence of grain boundary deteriorates the ionic conductivity.

Various researcher has demonstrated possibility of in-situ type of investigation on electrochemical properties of solid oxide electrolyte using SPM for different type of samples at high temperature. Some engineering work need to be done to perform in-situ high temperature characterization on YSZ thin film since commercially available setup is not yet available.

Chapter 3

Experimental Methodology

Three experimental and simulation methods were described, namely electrochemical impedance spectroscopy (EIS), conductive atomic force spectroscopy (CAFM) and molecular dynamic (MD) simulation. EIS is a powerful technique in resolving electrochemical response at different frequency range of perturbation signal. Randle's circuit and other circuit element can be used to describe the electrochemical response in the cell. High temperature CAFM allows measurement of topography of the sample as well as electrochemical probing of the sample surface at high temperature. Measurement of topography of the thin film YSZ surface and electrochemical properties using conductive AFM probe reveals the grain boundary structure of the thin film and local electrochemical properties of the sample surface. MD simulation which based on Newtonian mechanics is able to reveal the transport of oxygen ion in the electrolyte with time. By specifying interaction potential of the ionic species on YSZ, the trajectory of all the ions is calculated with time. YSZ Bicrystal is used to simulate grain boundary condition, while LAMMPS software is used to perform MD simulation.

3.1 Introduction

EIS⁸⁰ is one of the useful techniques in resolving the electrochemical behavior of the YSZ system. Understanding on the instrument and technique is required to correctly interpret the result of the measurement. A simple discussion on EIS will be presented in this chapter.

On the other hand, AFM is a technique used to resolve the surface properties of the sample. Topography are usually measured, but other properties of the sample such as conductivity, magnetic domain and adhesion force can be extracted from the interaction between the AFM probe and the sample surface. In this chapter, the principle of AFM and conductive AFM are explained.

Modeling of the diffusion and ionic conductivity of the solid oxide electrolyte can be performed in various way. In this research, MD simulation is used to study the ionic diffusion with the inclusion of grain boundary region. The principle of MD simulation will be briefly explained in this chapter.

3.2 Electrochemical Impedance Spectroscopy for Solid Oxide Material

Electrochemical measurement can be done either by controlling the applied voltage to the cell and measure the response current, or by controlling the current passing through the cell while measuring the response current. Instrument which controls the voltage applied is known as potentiostat while instrument which control the current passing through the cell is known as galvanostat. The same principle applies to the EIS instrument such as frequency response analyzer (FRA), where one can control the potential and measure the current response, or control the current and measure the potential response.

3.2.1 Principles of Electrochemical Impedance Spectroscopy

For EIS measurement in potentiostatic mode, sinusoidal voltage perturbation is generated for a range of frequency which is superimposed onto the set DC bias applied to the cell in testing. The frequency range that could be used depends on the FRA instrument specification, typically from a few MHz to μHz frequency, which is limited by the response frequency or bandwidth of the electronics. There is also limitation on the range of absolute impedance measured by the instrument. The accuracy of high impedance measurement is affected by the stray capacitance of the surrounding while very low impedance measurement is affected by the inductance of the wire in the connection.

For a standard electrochemical measurement, there are 4 connections (or more), which are the working electrode (WE), sense electrode (S), reference electrode (RE) and counter electrode (CE). The voltage is measured from sense to the reference electrode, while the current measured is provided from the working electrode to the counter electrode, as shown in **Figure 3-1**. In two electrodes connection, the working electrode and sense electrode are joined together while the reference and counter electrode are joined together.

The impedance is defined as the ratio of the Laplace transform of the voltage to the Laplace transform of the current signal. Since sinusoidal signal is used as the signal, it is equivalent to the ratio of the Fourier transform of the voltage signal to Fourier transform of the current signal. For an example of a capacitor element which the current is a product of capacitance (C) and rate of change of voltage, $i = C \frac{dV}{dt}$, the impedance of the capacitor under sinusoidal signal is $Z = 1/j\omega C$, where j is the imaginary number and ω is the angular frequency. For a resistor element, the impedance will be independent with frequency, $Z = R$. An RC element in parallel

would have the impedance similar to adding the two impedances of the element in parallel, which results in the following impedance

$$\frac{1}{Z} = \frac{1}{R} + j\omega C \quad (5)$$

Figure 3-1: Illustration of 4-probe setup where current flow from WE to CE, while voltage drop across distance d is measured by S and RE.

For an electrochemical cell, the reactions and process at electrochemical interface between electrode and electrolyte can be approximated with a series of circuit element when the applied voltage perturbation is small. The next section will describe on the electrochemical interface model and circuit element in the form of equivalent circuit element.

There are three conditions to be met for an accurate EIS measurement, which are 1) linearity, 2) causality and 3) stability. Since electrochemical process is non-linear toward applied bias, the applied perturbation signal should be small enough to approximate the linear current response from the cell. However, the applied signal should be also large enough to have acceptable signal-to-noise ratio. For the second condition, causality implies that the response signal should be only due to the applied

signal and not from other unwanted signal such as the line frequency. Unwanted signal could be picked up by the instrument when the applied signal is too small, resulting in measurement of the noise signal instead of the current response. The other possibility of measurement of unwanted signal is due to measurement at frequency close to the line frequency, or partials of the line frequency. The unwanted noise from the surrounding can be shielded using a Faraday cage connected to the ground of the instrument. In terms of stability, the measured signal should be stable with measurement time, while repeat measurement at the same frequency should result in the same measured response.

The work flow of EIS measurement and analysis are as follow. First, an adequate understanding of the electrochemical cell system is necessary for EIS analysis. Then, an equivalent circuit which could describe the electrochemical process for the cell is proposed. The measured impedance of the electrochemical cell is fitted with the proposed equivalent circuit element. Finally, the important parameter from the fitting obtained from the fitting of the impedance data to the equivalent circuit. The challenge of performing a meaningful EIS measurement lies in obtaining meaningful impedance data from the electrochemical cell and analysis of the impedance data. It is the responsibility of the researcher to come out with a suitable equivalent circuit and test the system to ensure the proposed reaction processes are indeed the actual process occurring in the electrochemical cell.

3.2.2 Equivalent Circuit Element for Solid Oxide Material System

The electrochemical cell can be approximated with certain equivalent circuit element, such as the double layer capacitance, charge transfer resistance, diffusion circuit element and electrolyte impedance. The following paragraph will briefly describe the on physical meaning of the element.

In general, electrochemical processes occur at the interface between electrode and electrolyte. Electrode is an electronic conductor while electrolyte is an ionic conductor. The interface between electrode and electrolyte forms an electrochemical double layer. The electrochemical double layer at the interface between electrode and electrolyte can be approximated as a capacitor element, C_{dl} . For electrochemical reaction such as oxidation or reduction reaction, the reaction kinetic can be approximated as linearly proportional to a small signal voltage. Therefore, charge transfer resistance, R_{ct} can be used to approximate the change in reaction rate with change in applied voltage. Mass transport of reactant to the interface of electrode and electrolyte is a diffusion process, where the flux is proportional to the concentration gradient and the diffusion coefficient, governed by Fick's law of diffusion. If the diffusion of reactant can be approximated as semi-infinite linear diffusion, Warburg element, Z_W can be used to describe the change in reaction with voltage signal which has the following forms

$$Z_W = \frac{A_W}{\sqrt{\omega}}(1 - j) \quad (6)$$

where A_W is the Warburg coefficient. The Warburg impedance show a 45° angle in the Nyquist plot as it is proportional to $(1 - j)$. The electrolyte impedance is usually approximated as a resistor element, R_{el} which connects in series with other process.

The resulting equivalent circuit, with $R_{el}(C_{dl}(R_{ct}Z_W))$ is known as the Randles circuit and it is often used to fit the measurement data from the EIS. There are several variations to the Randles circuit depending on the setup and cell condition. For example, Warburg element could be substituted with finite length diffusion element when the diffusion length is finite. When the applied bias is in the range that no electrochemical reaction could occurs, the charge transfer reaction part can be

omitted. The grain boundary region in solid electrolyte has different time-constant compared to the grain region, and hence could be separated into two parts corresponding to the grain ionic resistance and grain boundary ionic resistance with different RC element.

Figure 3-2: Example of equivalent circuit used to model the impedance response from thin film electrolyte.

Figure 3-2 shows one of an example that can be used to model the impedance response from thin film electrolyte system. $R_{ct,a}C_{dl,a}$ and $R_{ct,c}C_{dl,c}$ are the contribution of reaction from anode side and cathode side respectively. To model the response of small local electrode probe in contact with thin film electrolyte and large counter electrode embedded beneath the electrolyte, such model with appropriate modification can be used. The electrolyte resistance can comprise from grain and grain boundary resistance, similar to the brick-layer model discussed in Chapter 2. Since the area of WE or the probe in contact with the electrolyte is much smaller than the area which CE contact with the electrolyte, the contribution of CE could be insignificant compared to the WE, therefore can be omitted for simplicity of the model. The spreading resistance from the small contacting electrode probe should be used instead. Let $h = b/a$, where b is the thickness of the film and a is the contact radius, the spreading resistance can be approximate as follow⁸¹:

a) For $h \rightarrow 0$: $R_s = \rho \frac{b}{\pi a^2}$

b) For $h \rightarrow \infty$: $R_s = \frac{\rho}{4a}$

c) For $0 < h < 2.6$:

$$R_s \frac{a}{\rho} = 0.31338h - 0.25134h^2 + 0.12512h^3 + 0.03436h^4 + 0.003908h^5$$

where ρ is the resistivity.

For the data presentation of impedance for the measured frequency range, there are at least three variables to present for each data point, which are the frequency of the data and the real and imaginary part of impedance. Nyquist plot expresses the negative of imaginary part versus the real parts of the impedance for every frequency measured. On the other hand, Bode plot usually expresses the magnitude of the impedance, and phase with different frequency, in logarithmic scale.

3.3 High Temperature Conductive AFM for Electrochemical Measurement

AFM is a powerful technique to resolve the topography of the sample. Grain boundary feature can be resolved by topography imaging of flat surface. Due to grain boundary grooving at elevated temperature, atoms diffuse away from the triple junction of grain boundary and resulting in a dent at the junction while pilling up nearby bump.⁸² Therefore, by measuring the topography of the smooth sample after high temperature annealing, we could identify the grain and grain boundary region from the topography image. In the following section, the working principle and approach for conductive AFM (CAFM) on solid oxide electrolyte system is explained.

3.3.1 Principle of AFM Measurement

The construction of AFM probe consists of a sharp tip attached on a cantilever. The sharp tip is used to scan the surface of the sample. Due to the repulsion between

atoms at close range, the repulsion force is exerted to the tip when the tip is pressed toward the sample surface. The repulsion force deflects the cantilever which holds the sharp tip. The amount of deflection on the cantilever of the AFM probe can be measured by optical lever method.

The typical build of an AFM system includes a scanner which uses piezoelectric drive to control the x, y and z direction of the tip. The nose cone of the scanner holds the AFM probe used for the scanning the sample surface. Strong light or laser diode is equipped in the AFM scanner to direct the light to the reflective surface of the cantilever to detect the deflection of the cantilever. The reflection of the light is detected through photodetector which calculates the deflection on the cantilever. **Figure 3-3** shows the illustration for optical level detection system in typical AFM instrument.

Figure 3-3: Illustration of optical level detection in AFM system

There are mainly two mode of AFM measurement, which are contact mode and AC mode. Contact mode AFM works on the principle that the sharp tip is in contact with the sample surface. For a constant deflection mode, the feedback system

controls the amount of deflection on the cantilever by adjusting the vertical displacement of the probe. For AC mode measurement, the probe is driven with an oscillating amplitude near its resonance frequency. When the probe tip is near the sample surface, the amplitude of the oscillation changes due to the interaction with the sample surface. The oscillation amplitude is feedback controlled by changing the z-displacement of the scanner.

For a practical AFM topography measurement, the following steps are followed:

- 1) The sample to be imaged is placed and fixed on the sample plate of the AFM. Fixing of the sample reduces the movement of the sample during AFM scanning which may result in artefact in the scan image.
- 2) AFM probe is attached onto AFM scanner and laser diode position is adjusted to focus on the AFM probe cantilever.
- 3) The photodiode is aligned and adjusted to capture the reflection of laser light from the AFM cantilever. The deflection reading from the photodiode is set to zero.
- 4) The deflection set point is set for the AFM controller. The AFM probe is then approached towards sample surface until the set deflection is reached.

The set deflection is actively feedback controlled using PI controller by the AFM controller through changing the vertical position of the probe. The P (proportional) gain and I (integral) gain can be tuned to obtain fast response of the feedback to the set deflection. For the AFM scan image, the scan size is limited to around $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$, depending on the specification of the instrument. The scan size can be adjusted according to the grain size of the sample. The scanning time of

the AFM image depends on the resolution of scan image and the scan time per line of the image.

There are three basic types of data obtained from the AFM contact mode scanning. The topography data is the z-position of the scanner during the scanning of the sample surface. The topography data describes the height or elevation of the surface. Lateral deflection data is the data recorded from the deflection in the horizontal axis. The lateral deflection data describes the friction experienced by the tip during the scanning of the sample surface. Deflection data is the data obtained from the deflection in the vertical axis. The deflection shows location which has large rate of change of height on the sample surface.

3.3.2 High Temperature Conductive AFM

Conductive AFM is a variant of AFM which allows electrical properties of the material to be measured along with the topography information. This can be achieved by using conductive AFM probe. By coating a thin layer of conductive material such as gold and Pt, the AFM probe can be made conductive. Transimpedance amplifier is used to measure the small current signal from the sample surface. The AFM probe functioned as working electrode while the counter electrode is positioned on the sample.

There are two modes of electrical measurement of conductive AFM, which are imaging mode and spectroscopy mode. In imaging mode, the electrical properties are measured concurrently during the topography scanning of the sample surface. 2D image of the electrical properties, such as the conductance of the surface can be obtained. In spectroscopy mode, the electrical properties are measured on the certain location on the sample surface. In this mode, the tip is stationary, while electrical

measurement such as I-V, cyclic voltammetry or impedance spectroscopy is carried out. Due to long electrical measurement, a selection of points is usually taken for electrical characterization.

For high temperature AFM, a substrate heater is used to heat up the sample to high temperature before performing AFM measurement. The substrate heater is connected to a temperature controller unit for temperature control. The temperature limitation of the substrate heater for AFM is around 250 °C under atmospheric pressure environment. This is due to high heat transfer from the substrate heater to the AFM could cause damage to the AFM instrument.

3.4 Atomistic Simulation of Diffusion of Oxygen Ion in YSZ Electrolyte

To further understand the effect of grain boundary structure to the ionic conductivity of the cell, an understanding from the atomistic view of ionic transport from simulation is important. Ionic transport of the electrolyte is related to the self-diffusion of oxygen ions. In atomistic view, the transport of oxygen ions in self-diffusion is due to the random atomic hopping event, where the oxygen ion has a certain probability of jumping to the next available oxygen vacancies site. By measuring the MSD of every oxygen ion after certain time, the diffusivity of the oxygen ion can be calculated. The oxygen ion movement can be simulated using MD simulation, where the movement of every ion in the simulation cell is calculated by calculating the force acting on each of every ions and the trajectory of each ion. In the next section, the principle of MD simulation will be explained and method of performing MD simulation, analysis and calculation of diffusion property of solid oxide electrolyte will be presented.

3.4.1 Principle of Molecular Dynamic Simulation

MD simulation is based on Newtonian mechanics where the system of atoms interacts and evolved with time. The trajectory of the particles is calculated based on the force exerting on the particle by other particles, together with the current velocity of the particle. The subsequent position is then calculated by integrating the acceleration and velocity with a short time interval. This process is repeated to obtain the trajectory of the particle for a certain time interval. Therefore, to obtain accurate trajectory of the particle, an accurate potential model should be used to describe the interaction between particles. Each time step should be small enough for small displacement of the particle.

In MD simulation, a simulation cell or simulation box contains the particles to be simulated. Periodic boundary condition applies to the boundary of the simulation box to include the effect of surrounding to the particles in the simulation box. A statistical ensemble is chosen for the simulation cell, where certain parameters of the simulation cell is controlled, such as the temperature, pressure and the size or volume of the simulation cell.

For the diffusivity of oxygen ions, the MSD of the ions can be calculated from the expression,

$$MSD(t) = \frac{1}{N} \sum_{n=1}^N [r_n(t + t_0) - r_n(t_0)]^2 \quad (7)$$

where r_n is the position of n^{th} particle and t_0 is the starting time. MSD is related to diffusion coefficient by the expression,

$$D = \frac{MSD}{6t} \quad (8)$$

for a 3 dimensional system. The diffusion coefficient can be converted into ionic conductivity of the material described in the previous chapter.

MD simulator is used for MD simulation. The typical work flow for performing MD simulation for solid oxide material diffusion study is as followed

- 1) The initial position of the ions in the crystal is constructed and bounded by the simulation cell.
- 2) The potential model used for the particle is selected and the coefficient for the potential is set for the types of particle.
- 3) Initial setting for the simulation including the type of ensemble, time-step, total simulation time, initial velocity and types of output data is determined. Initial velocities of the particle are randomly assigned at this moment.
- 4) Energy minimization of the simulation cell is performed to relax the energy of the system for the simulation cell. This is followed by a short equilibration MD run where the initial velocity is used as starting point of the MD simulation.
- 5) Actual MD simulation run is performed where the properties of the particle and the system is output for analysis.
- 6) Output data from the MD simulation are analyzed, for example converting the MSD value over the time of simulation to diffusivity of the sample.

For simulation of grain boundary structure, a bicrystal separated by a pair of grain boundary can be constructed. A simple structure of grain boundary can be constructed from the concept of coincident site lattice, where the two misoriented lattice coincide with each other at the boundary. In coincident site lattice, the degree of fit, Σ is the ratio of total number of sites to the coincidence site. To construct a $\Sigma 5(3\ 1\ 0)$ symmetrical tilt grain boundary, the lattice is cut at the plane of $(3\ 1\ 0)$, followed by joining to another lattice which is cut at $(-3\ 1\ 0)$, while removing the overlapping particles.

For constructing YSZ lattice with grain boundary structure, the ZrO_2 lattice is first created with Zr^{4+} ion and oxygen ion in cubic fluorite structure, with the lattice parameter of 5.21 Å. The grain boundary structure is then created as described in the paragraph above. Y^{3+} ion doping is carried out by substituting Zr^{4+} ion with Y^{3+} ions at the set concentration, which is 8 mol% of Y_2O_3 . Oxygen vacancies is created by selectively removing oxygen ion in the lattice. The constructed simulation lattice should be charge neutral.

For the potential model of MD simulation of YSZ simulation cell, a Buckingham potential with coulombic interaction between ions are used to describe the potential due to the interaction between different ions. The expression for the potential is written in this form,

$$E_{ij} = A \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} + \frac{Dq_iq_j}{\epsilon r} \quad (9)$$

where A , ρ and C are the coefficient for fitting the potential model for ion i and ion j , r is the distance between the i and j ion and ϵ is the electrical permittivity.

Statistical ensemble is the possible copies of a system for a given state of the system. Certain parameters in the system are varied over the time of simulation, such as the position and velocity of each particle, but the macroscopic observable variables remain in statistical equilibrium. Example of statistical ensemble are the microcanonical ensemble or NVE ensemble where the number of particles, volume and energy in the system is set to particular value. Canonical ensemble or NVT ensemble on the other hand has number of particles, volume and temperature of the system fixed. NPT ensemble fixes the value on number of particles, pressure on the simulation box and temperature is suitable for the simulation of solid material while relaxing the volume of the cell.

For this research work, LAMMPS⁸³ software is used as the MD simulator. Documentation and source code for LAMMPS can be accessed from the official website of LAMMPS, lammps.sandia.gov/. For LAMMPS software, an input script file is needed to run the MD simulation, where the simulation cell geometry, particle type and position, potential model and coefficient, output data and etc. are specified. Parallel computation can be used to reduce the MD simulation process time.

Chapter 4

High Temperature Conductive Atomic Force Microscopy in-situ Electrochemical Characterization

To achieve high temperature conductive AFM electrochemical studies, micro-thermal stage (MTS) was designed as a heating solution for sample heating up to 600 °C by in-chip heating element. Simulation work was performed to understand the heating characteristic of the MTS in terms of its power requirement and temperature distribution. The fabrication of MTS was done using microfabrication techniques. Temperature characterization of MTS was performed for accurate temperature sensing of the heating element. Conventional Pt-coat AFM tip is prone to thermal degradation when in contact with high temperature surface. To address this issue, Pt-metal AFM tips were fabricated from Pt wire using electrochemical etching technique. The Pt-metal tip was modified to be compatible with the existing conventional AFM setup. The fabricated Pt-tip were characterized using SEM imaging and tested in conventional AFM measurement. Preliminary electrochemical measurements were performed using MTS as heating solution and Pt-tip as AFM probe. Issues with the current MTS design and Pt-tip as AFM probe were discussed.

4.1 Introduction

The bulk property of material is a combination of all its local properties over the area or the volume of the sample. Local properties of a sample can be quite different from one location to the other. Microstructural engineering is a way to exploit the local properties to enhance the bulk properties of the material. Therefore, it is important to understand properties of material in localized manner. For example, details on ORR kinetics and ionic transport of oxygen in nano-thin polycrystalline YSZ has been puzzled researcher for a long time.⁸⁴ Most of the studies performed relies on bulk-type or area-average measurement.^{84,85} Direct local observation of ORR kinetics and ionic transport will allow us to clarify some of the question such as the effective width of triple phase boundary (TPB) and the effect of grain boundary to ionic transport. It is found that grain boundary has substantial difference in the conductivity compared to the grain region. Localized characterization will assist in observing the difference and lead to a greater understanding of the nature of grain boundary ionic transport.

AFM probe can be used as nano-scale electrode in which the electrochemical characterization can be performed when it is in contact with the electrolyte. Typical AFM measurement is able to resolve the topography of the sample and identify grain boundary region. In conventional AFM setup, high temperature measurement is achieved by using substrate heater, where the temperature of the heater is limited to around 250 °C. This is due to the high heat transfer from the heater to the AFM scanner which poses several issue to the AFM measurement, such as thermally induced vibration or deflection, and damaging the parts of the AFM scanner. However, in order to have a good signal to noise ratio for characterizing the electrochemical response, the YSZ sample needs to be heated up to higher temperature, such as ~500 °C in atmospheric environment. This is because of the

small contact area of the AFM tip used as the working electrode, which significantly increases the ionic resistance and reduces the available reaction site for the electrode. For quick estimation, for a radius of contact of 100 nm and thickness of 100 nm, the spreading ionic resistance of the electrolyte would be around 15 M Ω at 500 °C.⁹ Due to asperity of the tip and contact surface, the actual resistance will be larger than the estimated value. In comparison, the ionic resistance is about 3 order magnitude larger at 250 °C compared to 500 °C, which 10 – 100 G Ω of impedance would be expected. The accuracy of measuring such magnitude of impedance is limited by the instrument limitation, which has only 1 T Ω of electrometer impedance. Besides that, thermal degradation of conductive AFM probe which is made by metal coating is another challenge to solve for higher temperature AFM operation. The commercially available conductive tip made by coating ~15 nm thick metal on Si-based probe could evaporate or peel-off when in contact at high temperature.

For overcoming these issue, we have designed a MTS or micro-heating stage⁸⁶ which is much smaller than the conventional AFM substrate heater to minimize the thermal heat transport issue. A variety of thin film heating devices has been realized on Si platform, such as sensors^{87,88}, micro-fluidic devices⁸⁹ and phase change memory devices⁹⁰. These thin film heaters utilize Joule heating to heat up the sample by passing electrical current through resistive element such as metals, oxides, or polysilicon. Lee *et al.* used thin film Pt-heater patterned on top of a phase-change memory element which would heat up as fast as 700 °C in 50 ns.⁹⁰ Broekmaat *et al.* used Pt heating filament embedded in 2 × 2 mm² ceramic to reduce total heating power transported to AFM device.⁷⁰ We adopted some of the design principles in design and fabrication of our own MTS which suits our application for electrochemical characterization of thin film solid oxide electrolyte sample. Narrow metal pattern act as the heating element, and a metal-oxide layers are deposited on top of the embedded heater as the half-cell of solid oxide system. AFM conductive

probe is used as a mobile and nanoscale electrode. We also fabricated full Pt-metal AFM to eliminate peel-off issue during high temperature operation. Pt-metal probes are actually commercially available. However, close working distance of the probe to the AFM scanner also lead to high thermal transport to the scanner from the heater. In custom made Pt-metal probe, the working distance of the tip of the probe to the scanner can be increased to reduce the heat transfer from the heater to the scanner.

4.2 Experimental Details on Device and Tip Fabrication

For this section, the design and fabrication of MTS will be presented. Simulation on the heat transfer properties of the MTS is done and thermal characterization of MTS is carried out. The Pt-metal tip fabrication process is outlined in the subsequent sectioned, followed by the testing and characterization of the Pt-metal AFM tip. Sample plate of the AFM is modified to accommodate the MTS connection and counter electrode connection. Finally, the measurement of impedance of YSZ electrolyte sample is performed. Issues and room for improvement regarding the new approach are discussed.

4.2.1 Micro-Thermal Stage Design and Fabrication

There are a variety of heating element possible to be used in the MTS. Nichrome and Pt are the popular and viable choice of heating element for high temperature heating. Pt element is used for the heating element, as it is stable against oxidation up to 600 °C and has linear and stable thermal coefficient of resistance (TCR), which could be used to measure the temperature of the heating element. Temperature above 600 °C lead to instability of the Pt element and further heating would degrade the element and results in burned and damaged thin film.⁸⁸ On the other hand, Nichrome (80 Ni/20 Cr) is usually used for resistance wire heating, and

could operate reliably up to 1200 °C without much oxidation problem. However, Nichrome has one of the lowest TCR compared to other material, therefore results in lower temperature sensing sensitivity when used as temperature sensor.⁹¹ Therefore, we choose Pt as our thin film heating element in the MTS, as counter electrode is also made from Pt, which has the same temperature range for stability. The temperature of the heater can be obtained by measuring the resistance of the heating element. This is due to the resistance of the Pt heating element is a function of temperature.⁹² Once the resistance-temperature relation of the Pt heating element is characterized and known, the temperature of the Pt heater element can be measured in real time by measuring the electrical resistance of Pt heating element. For an accurate measurement of Pt-heater resistance, four-probe measurement were incorporated into the chip design. The measured Pt-heating element is assumed to be at uniform temperature during heating. A finite element model (FEM) simulation was carried out to verify the uniformity and measure the deviation of temperature and resistance during heating.

Figure 4-1: Schematic drawing of MTS chip design, with enlarged figure showing details on the heating element's geometry and dimension.

A schematic drawing of the samples with MTS is shown in **Figure 4-1**. P3 and P4 shown in **Figure 4-1** are the two Pt contact pads for providing input electrical power to the heating element, while P1 and P2 are the two Pt contact pads which measure the voltage difference along the heating element. The heating element is made into long strip to ensure uniform temperature distribution at the center of the heating element.

Figure 4-2: Schematics of fabrication process of MTS by microfabrication technique

Figure 4-2 shows the fabrication process of MTS. A 400 nm thick SiO₂ was deposited on top of the Si wafer (Latech Scientific Supply Pte. Ltd., Singapore) as a heat/electrical insulation layer by plasma-enhance chemical vapor deposition (PECVD). The ~7 μm AZ9260 photoresist (PR) was spin-coated on the surface of the SiO₂ deposited Si wafer. The PR was soft baked at 110°C for 4 minutes. The PR was exposed under shadow mask to pattern the Pt heating element, and developed through AZ 400K developer with 1:4 water dilution. Pt heating element with thickness of 200 nm was deposited on top of SiO₂ with PR pattern by radio frequency (RF) sputtering apparatus. Commercial Pt target (99.99% Pt, Latech Scientific

Supply Pte. Ltd., Singapore) was used for depositing Pt thin film. The deposition rate of 17 nm/min was obtained at 3 mTorr of argon pressure and 200 W of RF power at room temperature. Lift-off process was carried out to remove PR layer by rinsing with acetone, followed by isopropyl alcohol (IPA), followed by deionized water to form the patterned Pt heating element. A 200 nm thick Si_3N_4 was deposited on top of the patterned Pt heating element as electrical insulation layer by PECVD. Reactive ion etching with CF_4 and O_2 was used to etch and pattern the Si_3N_4 layer with an etching rate of 30 nm/min to expose the four contact pads for the heating element. Pt counter electrode (200 nm) was deposited and patterned on Si_3N_4 by RF-sputtering and lift-off process. Finally, 200 nm YSZ layer was deposited on top of Pt counter electrode by either two different deposited techniques, which are ALD and RF-sputtering. For sputtered YSZ, 8YSZ substrate is used as target, and deposition rate of 1 nm/min was obtained at 1 mTorr of argon pressure and 200 W of RF power. For ALD YSZ deposition, the deposition condition was 250 °C and at 150 mTorr pressure. Tetrakis(dimethylamido)zirconium ($\text{Zr}(\text{NMe}_2)_4$) and tris(methylcyclopentadienyl)-yttrium ($\text{Y}(\text{MeCp})_3$) were used as precursors with distilled water as oxidant. Zr and Y precursors were heated to 70 °C and 170 °C respectively for source evaporation while water was kept at room temperature. A 200 nm YSZ was obtained with 400 cycle, with 4 zirconia ALD cycles and 1 Y_2O_3 cycle in each cycle. **Figure 4-3** shows AFM topology image of ALD deposited YSZ thin film under contact mode measurement. Grain size of the thin film is estimated to be around 20-30 nm.

Figure 4-3: AFM topography image of ALD YSZ under contact mode measurement

The fabricated MTS was placed on AFM sample plate (Keysight Technologies 5500 AFM), with modification for spring assisted electrical connection to the chip heater, voltage probe and Pt counter electrode contact pad. The heater can be heated in an open-loop condition where fixed voltage is applied while the current is monitored to calculate the resistance and temperature of the heating element, or in closed-loop condition where feedback voltage is applied to heat the heater to the set temperature.

4.2.2 Simulation of Heat Transfer of Micro-Thermal Stage

There are three main objectives for the MTS heat transfer simulation, which are:

- 1) To estimate the power and voltage needed for operating the MTS
- 2) To understand the heating and cooling characteristic of the MTS
- 3) To obtain the thermal distribution of the surface of the heating element

Finite element method (FEM) simulation was performed to understand the heat transfer characteristic of the MTS. The commercial software COMSOL was used as the FEM tool. Transient heat conduction equation and Joule heating were used for the simulation. A 3D model was built with Si substrate, SiO₂ insulating layer and a 2D Pt heating element layer. Electrical potential was applied to the opposite end of the contact pad, which generates heat through Joule heating effect. The heat transfer occurs in the solid through heat conduction mechanism, and heat loss through the surrounding is taken as heat convection loss and heat radiation loss. Transient heat transfer simulation is used to understand the evolution of the distribution of temperature in the heating element. 25 V was applied to the heating element for 1 second, while the voltage drop was measured from the voltage probe. The resistance of the material is set to be a function of temperature.

4.2.3 Fabrication of Pt-Ir AFM Tip

All-metal AFM probe was fabricated using a commercial Pt-Ir scanning tunneling microscopy tip wire (Nanoscience Instrument; 90 Pt/10 Ir). The fabrication of Pt-Ir AFM tip can be divided into two different processes which are the electrochemical etching of the Pt-Ir tip and modification of metal wire for compatible with AFM measurement setup. The fabrication of Pt-Ir tip starts with cutting around 6 mm long Pt-Ir wire. Around half of the wire was pressed between pair of flat steel surfaces to create cantilever part of an AFM tip. For ideal reflection of laser beam in the AFM scanner the flat cantilever was further polished by fine polishing cloth (Final P, Allied Hightech Products) with a 3 μ m alumina suspension in a mechanical polisher (MetPrep, Allied Hightech Products). The polished tip was extracted from its mold and attached to the bulky chip of a standard AFM probe using epoxy adhesive. The standard AFM probe was used as a carrier for the wire tip, hence it is compatible with the AFM setup. The probe cantilever was then tested for laser

reflection in the AFM system before the wire was electrochemically etched. The overall process of tip fabrication is shown in **Figure 4-4**.

Figure 4-4: Schematic of fabrication process of Pt metal AFM tip from Pt-Ir wire

After the Pt-tip was electrochemically etched, the Pt-tip was immersed in hot water for cleaning and removing the sealant that protect the reflective surface of the cantilever. The tip was then bend to an angle around 80° with the flat cantilever using pairs of tweezers. This creates a longer working distance from the end of the tip to the scanner compared to conventional AFM probe, while the tip end is visible under optical microscope of AFM, which is crucial for easy location of position of the tip during AFM measurement.

For the etching of Pt-Ir tips, a two-steps electrochemical etching process was adopted.⁹³ The reflective part of probe was first covered with sealant to prevent contamination from the etching solution, and was removed after the etching process was completed. The first step of electrochemical etching, termed as rough etching, aimed to remove bulk of the Pt-wire until a thin neck is formed. This was done by dipping the Pt wire around 1.2 mm into 1.5 M CaCl_2 solution and applying high

alternative voltage (28 V – 35 V), shown in **Figure 4-5a**. AC voltage was varied using an autotransformer. The Pt-wire was then moved to fine-etching setup where lower etching rate was used to fine tune the etching of the Pt-wire. This is important as over-etching would lead to blunt tip apex. The Pt-wire was inserted into a circular CaCl_2 solution suspended by a round tungsten loop, as shown in **Figure 4-5b**, which was connected to the AC power supply. A lower AC voltage (5 V to 8 V) was applied to etch the neck region of the Pt wire. A micromanipulator was used to position and control the position of the region of etching on the Pt wire. When the thin neck was broken during the fine etching, the applied power was immediately interrupted to prevent over-etching.

Figure 4-5. Electrochemical tip etching process. a) Rough etching by high AC voltage. Note that lower tip is the reflected image on the aqueous solution. b) Fine etching with low AC voltage (< 10 V). For fine etching, wire of internal diameter of ~ 3 mm was used to hold the electrolyte solution in the form of membrane.

4.3 Results and Discussion

4.3.1 Simulation Result of Heat Transfer in Micro-Thermal Stage

The thin film on top of the heating element has negligible difference with the temperature of the heating element due to small thickness of the film which is in range of 100 nm. Therefore, we could use the temperature of the heater as the sample temperature. From the simulation, the temperature of the heating element with heating and cooling is shown in **Figure 4-6**, where the black line shows the temperature of heating element at the center of the heating element and red line shows the average temperature calculated from the resistance of the Pt heating element. The rise of the heater temperature is almost instantaneous after applying the voltage to the heater. The temperature does not reach steady state in the transient simulation time, but rise steady with time. This is due to the substrate being gradually heated up to higher temperature. The difference between substrate temperature and heating element is around 200 °C from the simulation.

The average temperature calculated from the resistance of Pt heating element is slightly lower than the center temperature during heating stage for around 20 °C. This is due to the side and edge of the heating element has slightly lower temperature due to higher heat transfer rate. While cooling, the temperature of the center of the heating element is equal to the average temperature calculated from the resistance drop of the heating element, as the temperature is uniformly distributed.

Figure 4-6: Temperature of the heating element when 25 V voltage is applied through the contact pad for 1 second followed by cooling in FEM simulation. (black) temperature of center of heating element. (red) average temperature of heating element calculated through the measured resistance of the heating element.

The surface temperature on heating element is shown in **Figure 4-7**. Generally, the temperature is higher at the center compared to the edge, which is reasonable as more heat transfer occurs at the edge. From the simulation, the maximum temperature occurs at the edge of the voltage probe, which could lead to initial burnt location when high current is applied to the heater. Temperature near the voltage probe is slightly depressed due to additional heat transport pathway to the voltage probe. From **Figure 4-8**, we can verify that the temperature at the center at the heating element is quite uniform, with around 7 °C difference when the area is around $200\ \mu\text{m} \times 30\ \mu\text{m}$ center at the center of the heating element.

Figure 4-7: 2D surface temperature of MTS at 25 V applied voltage after 0.8 second. The maximum temperature occurs at the edge of the voltage probe with the heating element.

Figure 4-8: Surface temperature variation of the heating element along the x-direction (horizontal) and along the y-direction (vertical).

For the power requirement, at 0.8 s, the temperature of the heating element reaches 546 °C with power output of 10.6 W. A total power output of 18.8 W is supplied to the MTS which includes the heating and ohmic losses in electrical connection to the heater.

4.3.2 Micro-Thermal Stage Characterization

The resistance change with temperature properties of Pt heater element was used to measure and control the temperature of the MTS. In order to characterize the relation of the resistance and temperature, the MTS was placed into a temperature-controlled chamber and its resistance was measured at different temperatures. The resistance of the Pt heater was quantified by calculating the ratio of potential difference between the voltage probe to a constant applied current of 1 mA. The resistance and temperature relation of the heating element is fitted with a second order polynomial equation in the following form⁹⁴

$$R(T) = R_0(1 + AT + BT^2) \quad (10)$$

where T is in unit °C and the coefficient of the equation, R_0 , A and B were extracted. Therefore, by measuring the resistance of the heating element, the temperature of the heating element can be calculated. **Figure 4-9** shows the resistance measurement of the Pt-heating element under temperature controlled environment. The chamber temperature was measured using a K-type thermocouple inserted into the furnace chamber, while the furnace was programmed to have heating rate of 2 °C/min and hold for 1 hour at each set temperature. The slow change in voltage measured was attributed to slow temperature equilibration time of the enclosed chip in heat insulating fixture for the electrical contact. **Figure 4-9b** shows the resistance with temperature taken form average over 100 second at the end of 1 hour holding time

at each set temperature. The fitted curve and coefficient were used to for calculating temperature during operation of the MTS.

Figure 4-9: Resistance measurement of Pt heating element at different temperatures in a temperature controlled environment. a) temperature of furnace measured with thermocouple (black) and the potential difference across Pt heating element under constant applied current of 1 mA (red). b) measured resistance as a function of temperature. Data point was fitted with 2nd order polynomial equation.

The power versus temperature of the MTS was characterized by applying variable DC voltage while the potential different of heating element and current passing through the heating element is measured. The resulting power is then plotted against the temperature calculated from the resistance as shown in **Figure 4-10**. Approximately 6 W of power was needed to bring the heating element up to 600 °C. It is noted that the required heating power to reach a set temperature decreases with time due to the heating of substrate temperature with time. Around half of the power input is lost to the ohmic loss for the contact to the heating element.

Figure 4-10: a) Potential difference of Pt-heating element and current measured by application of voltage from a variable DC power supply. b) Temperature of heating element as function of output power.

In a separate study, high voltage was applied to the MTS until the heating element was burned, as shown in **Figure 4-11**. From the figure, the burnt area is at the end of the Pt-heating element. This coincides with the FEM simulation results for maximum temperature of the heating element during heating. This implies that the actual maximum temperature where the MTS can be safely operated is actually limited by the maximum temperature within the heating element, while the average temperature at the center is slightly lower than the maximum temperature. Defects along heater element could also lead to higher heating temperature due to higher local resistance value.

Figure 4-11: Optical microscope image of a burnt Pt heating element after applying high voltage to the heating element.

4.3.3 Characterization of Pt-Ir Atomic Force Microscopy Tip

The etched Pt-Ir tips were characterized using scanning electron microscopy (SEM) imaging to observe the tip shape and apex radii, and were used to scan substrate in contact mode to test the compatibility with conventional AFM setup. **Figure 4-12** shows the SEM images of typical tips prepared by electrochemical etching described in the fabrication section above. The successfully etched Pt-Ir tips show apex radii in the range of 100 nm and above, while over-etched tip usually shown tip apex radii in the range of μm . A typical AFM contact mode topography image using etched Pt-Ir tip, as shown in **Figure 4-13** allows us to determine the location of the scan area. The custom made Pt tips were found to function properly as an AFM probe and have good radius to be used as nanoscale electrode. Custom fabrication also provide flexibility in controlling cantilever geometry, such as the tip height and tip apex radius. A longer tip height increases the working distance between heated sample and the scanner, therefore reduces the heat transfer to the instrument. By positioning the tip at the center of the heating element, the

electrochemical properties of the sample can be obtained by electrochemical measurement.

Figure 4-12: SEM images of Pt-Ir tips fabricated using electrochemical etching

Figure 4-13: AFM topography image obtained using a custom-made Pt-Ir tip in contact mode.

4.3.4 High Temperature Electrochemical Impedance Measurement in AFM

A MTS chip and Pt-Ir tip were integrated together in an AFM setup, with an impedance measurement instrument (Biologic, SP-200) connected between the Pt-Ir tip and the Pt counter electrode in the two-electrode setup. The Pt tip was first approached to the sample surface and the surface of the sample was scanned to locate the approximate location of the sample. This process was continued until the Pt-tip was positioned near the center of heating element. The Pt tip was then retracted while the sample was heated in an open-loop condition. The Pt-tip was then approached to the sample surface and impedance measurement were carried out.

Figure 4-14: Nyquist plot of impedance measurement of MTS chip with 200 nm thick Pt/YSZ from 490 °C to 520 °C, after correction with the open circuit condition.

Figure 4-14 shows the Nyquist plot of impedance measurement of MTS chip with 200 nm thick YSZ layer on Pt counter electrode from 490 °C to 520 °C after correction with the open circuit condition. Open circuit impedance measurement showed positive phase element (or negative capacitance) which may be resulted from

the interference from the heating current of the MTS, or other type of stray capacitance which is not taken into account. After correcting the measured impedance by subtracting the open circuit impedance, the resulting impedance shows negative phase at low frequency region, from 500 Hz to 20 Hz in **Figure 4-14**, which is likely due to the low reaction kinetics rate from the ORR. In-depth analysis and experimental works need to be carried out to identify the meaning of the impedance data.

4.4 Other Discussions and Conclusion

The stiffness of commercially available AFM probes ranges from 0.05 N/m to 50 N/m. Softer cantilever much more sensitive to the interaction force between the sample surface and the tip, while experience less damage to the sample surface or sharp tip radius during AFM contact mode measurement. Higher stiffness AFM probes were utilized in tapping mode AFM measurement as the resonance frequency of the cantilever is higher. In our custom-made Pt-Ir AFM tip, the stiffness is estimated to be in the range of 3 kN/m to 30 kN/m based on the cantilever geometry and the Young's modulus of the material. Due to limited sensitivity of deflection sensing, it is difficult to control the pressing force of a few nN to a few μ N with these stiff probes. This could be a problem during high temperature scanning as the sample material such as Pt metal soften at high temperature and the tip could damage the sample surface under such condition. This is illustrated in **Figure 4-15** where tracks of the scanning of the tip is visible under optical microscope. This damage could cause electrical short-circuiting between the counter electrode and the tip, which destroy the MTS to be used for electrochemical measurement device. This issues can be resolved by significantly reduction of cantilever stiffness by adjusting the cantilever dimensions. A thinner, narrower and longer cantilever will reduce the stiffness of the cantilever.

Figure 4-15: Optical microscope image of Pt-heating element damaged during AFM scanning at high temperature using Pt-tip due to high stiffness of the cantilever and softening of the material at high temperature.

Reported MTS from the literature usually only range from a few Watt of power. However, the power requirement of the current MTS is a bit higher for high temperature operation. This is due to high heat transfer to the substrate material. This can pose some issue to the AFM measurement system as the temperature of the surrounding will gradually increase with heating time. Higher thickness of insulation layer may be deposited to decrease the heat loss to the substrate. Alternatively, flat insulating wafer substrate such as borosilicate glass can be used as substrate material to reduce the heat transfer to the substrate to reduce the total amount of power to heat out the sample. Back-etching of the substrate to form membrane structure is another way to reduce the power required for the MTS.

The presence of interference from the surrounding causes some problem in the EIS measurement. An addition of electric shielding layer might be necessary to prevent the cross-talk between the heating current and the electrochemical

measurement. This can be implemented through an additional layer in between the Pt heating layer and the Pt counter electrode layer with Si_3N_4 layer in between as insulating layer. The electrical shielding layer is then grounded to the instrument to minimize interference signal to the measurement.

For current MTS, the maximum allowable heating temperature is around 600 °C due to instability of Pt element at this temperature. Higher operation temperature is possible by selecting different material for the heating element and counter electrode material. Nichrome is a potential candidate as heating element for higher operational temperature, while ceramic based counter electrode such as lanthanum strontium cobalt ferrite (LSCF) can be used.

As conclusion, we have presented a viable solution for high temperature conductive AFM measurements by the use of MTS and custom made Pt-Ir tips. This MTS minimizes the total amount of heat transfer to the AFM scanner, therefore allowed for higher operation temperature. Pt-tips are free of thermal peel-off problem, which is an issue for Pt-coated AFM probe at high temperature. We demonstrated the functionality of MTS in heating and reading of the temperature from the resistance value. Pt-tip were successfully fabricated and used in normal operation of AFM measurement. We have shown the promise of this approach for nanoscale study by impedance spectroscopy at high temperature in atmospheric environment. Further detail study on the electrochemical properties of the electrolyte will be carried out to understand the effect of microstructure to the impedance of the cell.

Chapter 5

Molecular Dynamic Simulation of Ionic Transport in YSZ Bicrystals

MD simulation studies are used to investigate the ionic properties of YSZ bicrystal structure. Two different approaches on calculating oxygen ionic transport were used to identify the mechanism and regional conductivity of YSZ electrolyte. YSZ simulation cell with a pair of $\Sigma 5(310)$ grain boundary was constructed for MD simulation. An analysis of the oxygen ion jump rate and vacancies location provide insight on the structure of the grain boundary region, which shown excess of oxygen vacancies at grain boundary core while depletion of oxygen vacancies in nearby grain boundary region. The rate of oxygen ion jump is also lower at the grain boundary region compared to the bulk region. For the second simulation, electric field was applied parallel to the grain boundary of YSZ to drive oxygen ion migration in the direction of electric field. The ionic conductivity calculated from the oxygen ion migration shows that grain boundary region has significantly lower ionic conductivity compared to bulk region. In conclusion, there is no evidence of fast ionic conduction by having high density of grain boundary along the oxygen ion transport direction.

5.1 Introduction

YSZ is one of the commonly used solid electrolyte for SOFC due to its high ionic conductivity at high temperature, excellent chemical stability in reducing or oxidizing environment and good mechanical stability at high temperature. Much of the recent research effort are put into designing SOFC which could operate at lower temperature to enable greater selection of lower cost building materials and reduce the thermal related damage caused by high temperature operation. One of the approach is to use thinner electrolyte layer to reduce the ionic loss of the device. Thin film in the range of nm can be deposited using advanced deposition technique such as sputtering, pulse laser deposition and ALD. These thin films often demonstrated nanocrystalline grain structure and the grains are found to be in columnar structure. Therefore, there is a high density of grain boundary parallel to the oxygen ion transport pathway in these type of thin film. However, there are contradict evidences on how the oxygen ion transport along or parallel to the grain boundary. It is very challenging in separating the contribution of grain boundary to grain for the ionic transport in experiment as the multitude of grain size and orientation of the grain structure in the sample. Therefore, in this study, we aim to resolve the oxygen ion transport in grain structure of YSZ.

The ionic transport for a solid oxide electrolyte can be described in terms of its ionic conductivity. The ionic conductivity of solid oxide electrolyte depends mainly on two parameters, which are 1) the concentration of ‘free’ charge carrier and 2) mobility of the ‘free’ charge carrier. In the microscopic and atomistic view, ionic transport in YSZ solid oxide electrolyte involves oxygen ions hopping through oxygen vacancies under influence of the electrochemical forces. In the case of no external electrochemical force acting on the oxygen ion, the oxygen ion will

randomly diffuse to the neighboring site, which is also known as self-diffusion. The frequency of oxygen hopping event determines the ionic conductivity of the material.

Grain boundaries in YSZ plays an important role in oxygen ions transport and ORR kinetics, as these properties are different with region in the bulk of the grain. Excess of oxygen vacancies are found to be located at the grain boundaries core.⁶⁴ However, this causes depletion of regional oxygen vacancies around the grain boundary region. The oxygen ions hopping is found to be dependent on its local environment, where the jump environment with lowest of dopants are preferred.⁵⁷ When Y^{3+} ion segregated to the grain boundary core, the ion transport in grain boundary region could be impeded. Oxygen diffusion property is characterized by measuring the MSD of the oxygen ion in MD simulation. Gonzalez-Romero *et al.*⁹⁵ reported lower grain boundary region diffusion, in either in-plane or out-of-plane diffusion compared to the bulk region from MD simulation work. Change *et al.*¹¹ also reported better diffusion properties of oxygen ion in structure which is lack of grain boundary compared with structure that has grain boundary. In recent work by Huang *et al.*⁵⁶, found that oxygen ion in grain boundary region has higher activation energy of diffusion and lower diffusion compared with the oxygen ion in grain region in all diffusion direction.

While the use of MSD to calculate diffusion of oxygen ion in electrolyte is simple and straight forward, the application of MSD to measure the properties in different region in the simulation cell is not as straight forward. This is due to nature of atom diffusing out or into the region which the MSD is calculated during MD simulation. In MD simulation software, the atoms in the region of interest is first specified, properties of the group or set of atom is calculated over simulation time. The group is not updated when it diffused out of the region or new atom diffused into the region, unless the group is specified to be updated during the simulation.

The effect of diffusion into/out of the region is usually small and can be omitted by shorter simulation running time or updating the group of atoms in interest at certain interval of simulation. However, for a very small region of interest, the effect of atoms diffusion into/out of the interest is significant. For this, we proposed a slightly different approach to locally study the grain boundary oxygen diffusion. In short, the rate of oxygen ion jump in the individual lattice point in the YSZ structure is quantified to calculate the diffusion rate of oxygen ion. The rate of oxygen ions jump, assuming there is a valid jump, can be expressed in the following equation

$$\Gamma = A \exp\left(-\frac{E_a}{kT}\right) \quad (11)$$

where A is the attempt frequency or pre-exponential factor, E_a is the activation energy for the jump. The attempt frequency is a slowly varying function of temperature. We suggest that there is a spectrum of activation energies when grain boundary structure is present, which depends on the location and local environment of the lattice.

Additionally, we also want to study the effect of grain boundary on ionic conduction. Most of the reported MD studies used the self-diffusion properties of oxygen ion to study the diffusivity and ionic conductivity of the electrolyte. However, in a real functioning of electrolyte in SOFC, the oxygen ions are mainly driven by the electric field to the opposite electrode interface. Therefore, it is reasonable to calculate the ionic transport of the material through the oxygen ion transport after an application of electric field. The ionic conductivity or ionic transport along grain boundary structure can be verified through application of electric field parallel to the grain boundary. Therefore, in this work, we will be extending the MD simulation by

application of electric field to the simulation cell to investigate the ionic transport along grain boundary structure in YSZ.

5.2 Simulation of Grain Boundary Model of YSZ

5.2.1 Construction of YSZ Bicrystal

For MD simulation of YSZ, each of the ions with its initial lattice position are created. ZrO_2 cubic fluorite structure is first created with 4 Zr^{4+} ions occupying the face-centered cubic (fcc) lattice sites and 8 O^{2-} ions occupying the 8 tetrahedral sites of the fcc lattice unit, forming a simple cubic anion sublattice in a unit lattice of ZrO_2 . Larger lattice can be formed by stacking and repeating the unit lattice.

Two types of grain boundary were constructed and investigated in MD simulation, which are the $\Sigma 5(3\ 1\ 0)$ and $\Sigma 13(5\ 1\ 0)$ symmetric tilted grain boundary. For the $\Sigma 5(3\ 1\ 0)$ grain boundary, two ZrO_2 crystals are tilted toward each other with an angle of 36.9° ($2 \tan^{-1}(1/3)$), with an axis of rotation parallel to the z axis. In other words, the two ZrO_2 crystal were cut at $(3\ 1\ 0)$ and $(-3\ 1\ 0)$ plane, and joined together to create the grain boundary structure. The overlapping ions were replaced by a single ion. Pair of closely separated cations or anions at the grain boundary are replaces by a single cation or anion at the center location of the pairs. This is to ensure no pairs of similar ions are created too closely to each other as it would increase the total energy of the system. Each repeating unit lattice is now $\sqrt{10}a_0 \times \sqrt{10}a_0 \times a_0$ in size, where a_0 is the lattice constant of YSZ which is around $5.18\ \text{\AA}$ at 1000 K. For the simulation, each grain is $3\sqrt{10}a_0 \times 2\sqrt{10}a_0 \times 6a_0$ in size, and a pair of grain are joined together forming the simulation cell with overall dimension of $6\sqrt{10}a_0 \times 2\sqrt{10}a_0 \times 6a_0$. Periodic boundary condition is applied to the simulation cell. The simulation cell is shifted a quarter length in x-direction so that

the two grain boundary are shown at the $\frac{1}{4}$ and $\frac{3}{4}$ length of the simulation cell in x-axis. 8% mol of Y_2O_3 is added to ZrO_2 simulation cell by substituting certain Zr^{4+} with Y^{3+} , and oxygen vacancies is created by deletion of oxygen ion to maintain the overall electro-neutrality of the simulation cell. For the $\Sigma 5(3\ 1\ 0)$ YSZ simulation cell, a total of 2412 Zr^{4+} ions, 420 Y^{3+} ions and 5454 O^{2-} ions were created. Similar steps were used to create $\Sigma 13(5\ 1\ 0)$ simulation cell, with $4\sqrt{26}a_0 \times 2\sqrt{26}a_0 \times 6a_0$ in dimension and total of 2106 Zr^{4+} ions, 366 Y^{3+} ions and 4761 O^{2-} ions for the simulation cell. **Figure 5-1** shows the x-y view of YSZ simulation cell where the location of grain boundary is pointed out.

Figure 5-1: a) $\Sigma 5(3\ 1\ 0)$ and b) $\Sigma 13(5\ 1\ 0)$ YSZ simulation cell used in MD simulation

5.2.2 YSZ MD Simulation Setting and Parameters

The potential model used in the simulation consists of Born-Mayer-Buckingham potential (BMB) which describes the short range interaction between

ions and Coulomb potential which describes the long range electrostatic interaction between ions. The BMB potential is a function of distance between pairs of ions in the form shown below,⁹⁶

$$E = Ae^{-\frac{r}{\rho}} - \frac{C}{r^6} \quad (12)$$

The A , ρ and C parameters are listed in **Table 1**. LAMMPS⁸³ software was used for the MD simulation. The input script of MD simulation for LAMMPS is attached in Appendix A. NPT ensemble or isothermal-isobaric ensemble with Nosé-Hoover thermostat is adopted. Time step of 1 fs was chosen for all the following simulation.

Table 1: Parameters for Born-Mayer-Buckingham potential in MD simulation^{64,97-99}

Ion pair	$A(\text{eV})$	$\rho(\text{\AA})$	$C(\text{eV}\text{\AA}^6)$
Zr-O	985.86	0.376	0.0
Y-O	1345.1	0.3491	0.0
O-O	22764.0	0.149	27.879

Energy minimization was first applied on the simulation cell using conjugate gradient method. This step aims to find stable arrangement or geometry of collection of atoms in the simulation cell from the potential field. When the net inter-atomic force on the atom are close to zero, or potential is at the minimum, the energy minimization step is completed. After energy minimization step, an equilibration step is performed for the simulation cell at the desired operation condition, such as at 1000 K temperature. This step is necessary as the system takes time (a number of time steps) to reach steady state. When the system is in steady state, the state and properties of the atom, such as displacement can be obtained over the simulation time-step.

5.2.3 Procedure and Analysis Method for MD Simulation

There are two types of simulation performed in this work, namely 1) the study of oxygen transport through atomic jump frequency and 2) the study of oxygen transport through migration of oxygen ion under electric field.

For study of oxygen transport through atomic jump frequency, the oxygen lattice sites during initial construction of ZrO_2 simulation cell were used as the reference oxygen lattice site. Energy minimization was performed and equilibration run was carried out for 1.5 ns in NPT ensemble conduction. This is followed by MD simulation run for another 0.5 ns where the positions of all the oxygen ions were record for every 50 fs, or 50 time-steps.

The analysis of the oxygen position data is described as followed. During MD simulation run, oxygen ions occasionally jump from its oxygen lattice site to the adjacent vacant oxygen lattice site. The goal of the analysis of the oxygen ions position data for every interval of time is to find out and identify the event of oxygen jump. When a lattice site recorded change of oxygen ion to oxygen vacancies, or oxygen vacancies to an oxygen ion, an oxygen jump event has occurred. The challenge of the analysis is to assign individual oxygen ions to the oxygen lattice point available. Most of the time, the oxygen ions vibrate at center location of its lattice site, following a Gaussian type of probability distribution. **Figure 5-2** shows the superimposed image or snap shot of an extracted single layer of oxygen ions and cations of YSZ simulation cell. Every point in the figure shows the location of the ions travel during the simulation time. The cations were observed to vibrate at its own lattice point during the simulation, while the oxygen ion has greater travel distance during the simulation.

Figure 5-2: Superimpose of multiple snap shot of a single layer oxygen ions and cations from YSZ simulation cell showing the location of oxygen ions and cation travelled during simulation.

Figure 5-3: Oxygen ions distribution obtained by multiple instances of simulation snap shot in YSZ. The distribution can be approximated as a Gaussian distribution centering the lattice point of the oxygen ion.

Figure 5-3 shows the distribution of oxygen ion on its lattice point by obtaining multiple instance of the ions during the MD simulation. The oxygen ions distribution can be approximated by a Gaussian distribution centering the oxygen lattice point with a standard deviation value. To simplify the analysis and assignment of oxygen ions to oxygen lattice points, we adopted an algorithm which assigned every oxygen ion into each lattice points when the distance of the position of the oxygen ion to the lattice point is less than $0.8 \text{ \AA}$. In other words, spherical region of $0.8 \text{ \AA}$ centering at the lattice point is the region where the oxygen ion is assigned to the lattice point. This value is chosen as it is more than three times of the standard deviation value obtained from the Gaussian distribution fitting, therefore more than 99.7% of the time, the oxygen ions will fall in this region. There is possibility of oxygen ions falling out of the range from the lattice point. This could occur during transition of oxygen ion into the adjacent oxygen vacancy site. When this occurs, the oxygen ion is treated as remaining at the previous lattice site, until it successfully enters into the range of lattice point without oxygen ions previously. There is also possibility for unsuccessful jump when the oxygen ion travel into the transition region and back to its own lattice point. By tracking the number of changes of oxygen ions in the lattice point, for example, from oxygen vacancy site to oxygen site, the number of jumps occurred in the lattice point can be calculated.

For the second type of simulation which study the oxygen ions transport parallel or along the YSZ grain boundary by application of electric field, the simulation details and analysis is presented as followed. Each ion in the simulation cell experience additional force due to the applied electric field, $F = qE$. Since the grain boundary is parallel to z-axis in the simulation cell, the applied electric field is set to the z-direction to simulation ionic transport along grain boundary. Electric field of $-0.02 \text{ V/\AA}$ is applied to the simulation cell which drives the oxygen ions to migrate

in the positive z-direction as the oxygen ion carrier negative charges. Equilibration time was set to 100ps while each MD run was set to 500ps.

For calculating the ionic transport properties in this simulation, the displacement of the oxygen ion with simulation time were recorded and used to calculate the ionic conductivity of the region. The current density from the applied electric field can be calculated from the rate of charge displacement per unit volume of the region

$$j = \frac{d\delta}{dt} \frac{1}{V_{\text{cell}}} \quad (13)$$

The charge displacement is defined as the product of displacement and the charge carried by the atom. From the current density, the ionic conductivity can be calculated from the ratio of the current density to the applied electric field.

The simulation cell is divided into grain boundary region and bulk region based on the location of the grain boundary core. **Figure 5-4** shows the schematic of YSZ simulation cell with location of grain boundary region and bulk region. The grain boundary region is set with a width of 20 Å centering the grain boundary core. The sum of displacement of all the oxygen ion in the bulk region was obtained during the MD simulation for certain interval of time in the simulation. The current density and ionic conductivity of the region can then be calculated from the equation described above. Similarly, the current density and ionic conductivity of the grain boundary region was calculated using the similar method, where the sum of displacement of all oxygen ion in the grain boundary region is calculated in MD simulation.

Figure 5-4: Schematic of YSZ simulation cell and classification of grain boundary region and bulk region in the simulation cell. The oxygen ions migrate in the positive z-direction as the applied electric field is in negative z-direction.

5.3 Results and Discussion

For the first YSZ simulation study, the oxygen vacancies concentration at each location was calculated over the simulation time. **Figure 5-5** shows the average oxygen vacancies concentration at different location along the x-direction. It is found that excess of oxygen vacancies accumulated at the grain boundary core, while depleting the number of oxygen vacancies in the nearby grain boundary region. This results agree well with the other studies which also found that grain boundary depletion of oxygen vacancies due to excess accumulation of vacancies at the core region. An *et al.*⁶³ experimentally showed depletion of oxygen ions at the grain boundary core, while grain boundary region showed around 25% increase in oxygen ion concentration. The depletion of oxygen vacancies could lead to decrease in oxygen ion transport as there is less site available for the oxygen ion to diffuse. On the other hand, exceptionally high concentration of oxygen vacancies may not be ideal for oxygen ionic transport, as there is less oxygen ion to transport in the region.

Figure 5-5: Time-average oxygen vacancies distribution per lattice site for $\Sigma 5(3\ 1\ 0)$ simulation cell.

Figure 5-6: Average oxygen ion jumps count per lattice point for $\Sigma 5(3\ 1\ 0)$ simulation cell

The rate of oxygen ion jump was calculated for the simulation cell at every individual lattice site. **Figure 5-6** shows the frequency or average oxygen ion jumps count per lattice point for the $\Sigma 5(3\ 1\ 0)$ simulation cell during MD simulation run. The average number of oxygen jump at the bulk region, or far away from the grain

boundary core region is around 20 per lattice site. At grain boundary region, the average number of oxygen ion jumps is significantly lesser (around 4 times lower) than then the bulk region, despite showing some high count of oxygen jump at certain lattice spot. Similar experimental procedure was conducted for $\Sigma 13(5\ 1\ 0)$ simulation cell, and similar results were obtained. From this simulation result, it is clear that grain boundary region does not show any enhance in oxygen ion diffusion, even if all the oxygen ion travels along the grain boundary.

For the simulation with applied electric field, the total displacement of the oxygen ion in the bulk region and oxygen ion in the grain boundary region was extracted from the simulation. **Figure 5-7** shows the total displacement of the oxygen ions in the bulk region and in the grain boundary region with simulation time at temperature of 1000 °C. The oxygen ions in the bulk region has net positive displacement under applied electric field in negative direction. The oxygen ions in the grain boundary region experiences much smaller magnitude of displacement under applied electric field. The calculated ionic conductivity for bulk region is 0.384 S/cm while the calculated grain boundary ionic conductivity is estimated to be 0.00717 S/cm, which is around 2 order of magnitude lower than the bulk region. However, the signal to noise properties of grain boundary is very poor, due to low ionic conductivity at the grain boundary region for the observed simulation time. In conclusion, we do not find any enhance ionic conduction pathway in region boundary region, despite having electric field applied parallel to the grain boundary structure.

Figure 5-7: Total displacement of oxygen ion in bulk region (black) and in grain boundary region (red) with simulation time at temperature of 1000 °C.

Figure 5-8: Arrhenius plot of conductivity of the bulk region in YSZ simulation cell with temperature.

We have performed MD simulation study under electric field for a set of temperature range from 400 °C to 1000 °C. **Figure 5-8** shows the Arrhenius plot for the calculated conductivity in the bulk region of the simulation cell, where the ionic conductivity is a function of temperature. The displacement signal in the grain boundary region is too low to be extracted from the noise level. This is due to short simulation time for the ions in grain boundary region to have significant movement in the region.

However, there are several shortcomings in the above mention simulation method and results. For the first method which assign each of every ion into individual oxygen lattice point, the analysis step is complicated and requires huge amount of computational time and resources compared to the calculation of MSD. The lattice point is slightly shifted from the initial lattice point during MD simulation due to the defects in simulation cell such as the oxygen vacancies and dopants. These errors were not corrected for during the analysis step. Another possible source of errors would be coming from the potential field or interaction potential used for the YSZ simulation cell.

As conclusion from the MD simulation, there is no evidence of improvement of oxygen ionic transport for having high density grain boundary structure in YSZ electrolyte. The oxygen ion jump approach in measuring the ionic transport come to the same conclusion as other simulation studies where no enhance of grain boundary in ionic transport is observed, in all direction compared to bulk region. In fact, the presence of grain boundary causes excess of oxygen vacancies in grain boundary core, while depleting oxygen vacancies at grain boundary region, which decrease the ionic conductivity of the grain boundary region. For the YSZ MD simulation with applied electric field parallel to the grain boundary, no enhancement in ionic conductivity of the grain boundary region is measured. The ionic conductivity of the

grain boundary region is almost 2 order magnitude lower than the ionic conductivity in the bulk region at the temperature of 1000 °C. Therefore, from the simulation, in order to improve the ionic transport of oxygen in YSZ solid electrolyte, it is preferred to have highly crystalline thin film with low density of grain boundary.

Further work on oxygen ion assignment to oxygen lattice can be improved by using segmentation of region of lattice using Voronoi tessellation. This will improve the oxygen ion assignment to a particular oxygen ion lattice point.

Chapter 6

Conclusion and Future Work

Based on the results from YSZ MD simulation, we concluded that YSZ grain boundary has poorer ionic conductivity with ionic transport along the grain boundary compared to bulk ionic conductivity. This information can be used to design an electrolyte microstructure with better device performance. The electrochemical measurement of solid oxide electrolyte has been demonstrated in high temperature AFM setup which could be used to verify the simulation results in the future. Other future works include improvement on micro-thermal stage design, Pt-tip quality and accurate simulation parameter studies.

6.1 Conclusions

The MD simulation works in this studies suggested that grain boundary structure has impeding ionic transport properties for YSZ solid oxide electrolyte. The results from two different approaches for quantifying the oxygen ionic transport in the simulation agrees with the results from other simulation work. There are a few behaviors which may explain the lower transport of oxygen in the grain boundary region. Grain boundary has usually higher diffusivity properties compared with bulk, as it contains more defects which provide easier path for atomic diffusion. In the case of YSZ, the particles in the electrolyte are made from charge particles, or ions. The interface or grain boundary core has a net positive charge compared to the bulk region. Space charge effect lead to different distribution of oxygen vacancies and dopant across the grain boundary region. The excess of oxygen vacancies at the grain boundary core depletes the surrounding grain boundary region oxygen vacancies. Since oxygen vacancies are responsible for ionic transport, the reduction in oxygen vacancies in such region lead to significant reduction in ionic conductivity. Fast ionic path may be present at location of the grain boundary core for transport parallel to the grain boundary, but it does not compensate the reduction in ionic conductivity caused by the nearby region.

Based on the simulation results, lower density of grain boundary should be a target for better performance of ionic transport in the thin film solid oxide electrolyte. This can be achieved by performing heat treatment to the thin film sample at high temperature for grain growth for a long time. If better electrode kinetics is related to high density of grain boundary, a higher density grain boundary functional layer can be deposited on top of the large grain YSZ to improve overall performance of the SOFC.

High temperature AFM electrochemical measurement for thin film YSZ sample is challenging, as conventional AFM system does not support such high temperature measurement. In this study, we demonstrated possibility of using MTS as heating solution and custom fabricated Pt-metal tip to perform electrochemical measurement under high temperature. Further detail electrochemical measurement needs to be performed in the future to spatially resolve the electrochemical properties of the thin film solid oxide electrolyte. Though from simulation results, we have already shown impeding ion transport behavior along the grain boundary, we hope that we could confirm our finding from experimental results by characterizing the grain boundary region using scanning probe investigation. In addition, the localize ORR kinetics on YSZ sample can be investigated using scanning probe method.

6.2 Future Work

For simulation work, additional MD simulation can be done to investigate the effect of different type of grain boundary to the ionic transport in YSZ. Besides that, an accurate interaction potential for YSZ should be considered for accurately determining the activation energy of ionic transport at lower temperature. Longer MD simulation time can be performed to extract useful information on the grain boundary ionic conductivity properties with temperature.

For experimental investigation of solid oxide thin film at high temperature, the MTS can be further improved for its temperature range by using different heating element which is stable at higher temperature such as Nichrome. Additional conductive layer can be added in between the heating element and counter electrode to minimize electric signal interference during electrochemical measurement. Higher insulating substrate can be used in MTS to reduce heat loss from the MTS to the surrounding.

For the custom made Pt-metal AFM probe, fine tuning of the stiffness of Pt-wire cantilever can be performed to improve the quality of the signal and prevent damage of the sample from the AFM probe. Last but not least, different types of solid oxide material can be investigated in a similar manner to identify ideal electrolyte and condition for low temperature SOFC.

APPENDIX A

MD LAMMPS Input Script for Oxygen Ionic Transport under Electric Field

The following attachment shows the input script for the MD simulation under applied electric field at 1000 °C using LAMMPS MD simulation software. The YSZ simulation cell data was imported into the software using a separate data file containing the initial position of the YSZ simulation cell structure.

```
# YSZ Diffusivity Simulation

# ----- Initialize Simulation -----
-----
clear
units metal
dimension 3
boundary p p p
atom_style charge

# ----- Create Atoms -----
-----
read_data LAMMPS_MinimizeYSZ.data

# ----- Define Interatomic Potential -----
-----
pair_style buck/coul/long 10.0
# Zr-Zr
pair_coeff 1 1 0.0 1.0 0.0
# Zr-Y
pair_coeff 1 2 0.0 1.0 0.0
# Y-Y
pair_coeff 2 2 0.0 1.0 0.0
# Zr-O
pair_coeff 1 3 985.86 0.37600 0.00000
# Y-O
pair_coeff 2 3 1345.1 0.34910 0.00000
# O-O
pair_coeff 3 3 22764.0 0.14900 27.87900

#----- Define Settings -----
-----
```

```
kpace_style ewald 1.0e-4
timestep 0.001
variable t equal 1273
variable d string dump_dir_1273K_E
variable b string 1273K_E

group zr type 1
group y type 2
group o type 3

compute eng all pe/atom
compute eatoms all reduce sum c_eng

#-----Run Minimization-----
-----
print "-----"
print "Run Minimization"
print "-----"
print ""

reset_timestep 0
fix 1 all box/relax iso 0.0 vmax 0.001

thermo 100
thermo_style custom step temp pe lx ly lz c_eatoms

dump mini all atom 1000 $d/dump_mini_*.xyz
dump_modify mini pad 6

min_style cg
minimize 1e-25 1e-25 5000 10000

unfix 1
undump mini

#-----Run NPT Equilibrium-----
-----
print "-----"
print "Run NPT Equilibrium"
print "-----"
print ""

reset_timestep 0
fix 2 all npt temp $t $t 0.1 iso 1.0 1.0 0.1
fix 3 all efield 0.0 0.0 -0.01
thermo 1000
run 100000
unfix 2
```

```

unfix 3

#----- Run NPT Production-----
-----
print "-----"
print "Run NPT Production"
print "-----"
print ""

reset_timestep 0

region bulk1 block -10 14.7132 -10 50 -10 50 units
box
region gb1 block 14.7132 34.7132 -10 50 -10 50 units
box
region bulk2 block 34.7132 64.1396 -10 50 -10 50
units box
region gb2 block 64.1396 84.1396 -10 50 -10 50 units
box
region bulk3 block 84.1396 100 -10 50 -10 50 units
box

group bulk1all region bulk1
group gb1all region gb1
group bulk2all region bulk2
group gb2all region gb2
group bulk3all region bulk3

group bulkall union bulk1all bulk2all bulk3all
group gball union gb1all gb2all

group bulko intersect bulkall o
group gbo intersect gball o

fix 4 all npt temp $t $t 0.1 iso 1.0 1.0 0.1
fix 5 all efield 0.0 0.0 -0.02

# compute mean square displacement
compute msdo o msd
compute msdbulko bulko msd
compute msdgbo gbo msd

# compute displacement of oxygen atom

compute dis_bulk_O bulko displace/atom
compute dis_sum_bulk_O bulko reduce sum
c_dis_bulk_O[1] c_dis_bulk_O[2] c_dis_bulk_O[3]

```

```
fix out_dis_bulk_O bulko ave/time 1 1 100
c_dis_sum_bulk_O[1] c_dis_sum_bulk_O[2]
c_dis_sum_bulk_O[3] file $d/$b_dis_bulk_O.txt

compute dis_gb_O gbo displace/atom
compute dis_sum_gb_O gbo reduce sum c_dis_gb_O[1]
c_dis_gb_O[2] c_dis_gb_O[3]
fix out_dis_gb_O gbo ave/time 1 1 100
c_dis_sum_gb_O[1] c_dis_sum_gb_O[2]
c_dis_sum_gb_O[3] file $d/$b_dis_gb_O.txt

thermo 1000

fix allmsd all ave/time 1 1 100 c_msdo[1] c_msdo[2]
c_msdo[3] c_msdo[4] file $d/$b_msd.txt
fix allmsdbulko all ave/time 1 1 100 c_msdbulko[1]
c_msdbulko[2] c_msdbulko[3] c_msdbulko[4] file
$d/$b_bulk_msd.txt
fix allmsdgbo all ave/time 1 1 100 c_msdgbo[1]
c_msdgbo[2] c_msdgbo[3] c_msdgbo[4] file
$d/$b_gb_msd.txt

dump dumpbulko bulko atom 10000
$d/dump_oxygen_bulk_*.xyz
dump dumpgbo gbo atom 10000 $d/dump_oxygen_gb_*.xyz
dump_modify dumpbulko pad 6
dump_modify dumpgbo pad 6

run 500000

unfix 4
unfix 5
unfix out_dis_bulk_O
unfix out_dis_gb_O
unfix allmsd
unfix allmsdbulko
unfix allmsdgbo

print "All done!"
```

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