# A COMBINATORIAL STUDY OF YTTRIA STABILIZED ZIRCONIA AS AN ELECTROLYTE CANDIDATE FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

A Thesis

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by Natalie Becerra January 2012 © 2012 Natalie Becerra ALL RIGHTS RESERVED

#### ABSTRACT

Combinatorial research can have two main uses. The first is to perform cursory measurements of many materials to find a composition whose properties are ideal for some known application. The second function of combinatorial research is to test many materials for ideal values of a particular property in order to learn more about that property and variables that can alter it.

This study focused on adequately measuring, modeling and calculating the parameters that affect the ionic conductivity of a particular binary spread of yttria stabilized zirconia. At three separate temperatures, the resulting ionic conductivity vs. composition graphs showed trends similar to those found in the literature for bulk materials, which validate the methods that were developed and optimized in this thesis. Further studies of activation energy and phase structure were performed and produced results that also match data found in the literature.

Future work can expand on the methods detailed here and examine other combinations of materials such as zirconia co-doped with yttria and scandia or gadolinium-doped ceria.

#### **BIOGRAPHICAL SKETCH**

Natalie Becerra was born and raised in a suburban town called Corona. There, she learned reading, writing and most importantly: arithmetic. She had several inspirational teachers as a young child: Mr. Allen, Mrs. Martin, Mrs. Yamano-Gray, and Linda Linville.

Natalie worked hard in school and attended a rigorous and prestigious academic institution where she learned the basics of many advanced scientific topics. Caltech prepared Natalie well for her master's degree at Cornell.

There was a great transition from her quiet, small and focused school in LA county, only a short drive from her family, to a large university in small town Ithaca which is a 1/2 day's plane ride from so many familiar faces. However, perseverance (and cycling) helped her through and she learned how to research and study materials.

Cornell offered many lessons, some of the more memorable being about xray diffraction, diffusion, Arrhenius plots, band-gaps, impedance spectroscopy, ice cream, waterfalls, cycling, winter coats, and seasons. One important thing Natalie learned about materials science is that it is as diverse and challenging as it is rewarding. So is life. For all the ups and downs she experienced at Cornell, she wouldn't trade these lessons for anything in this world. This thesis is dedicated to my lovely family. You're always just a phone call away.

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## CHAPTER 1 INTRODUCTION TO FUEL CELLS

Fuel cells play an increasingly vital role in energy storage. Therefore, it is valuable to understand how fuel cells function, what their limitations are and how their applications can be broadened with technological improvements.

#### 1.1 Necessity of Alternative Energy and Energy Storage

There are two main reasons to concern oneself with the search for alternative energy sources to fossil fuels. In the short-term, it is believed that the  $CO_2$  that results from burning fossil fuels is the main source of anthropogenic global-warming [1]. It is hoped that by utilizing renewable energy sources over burning fossil fuels, global warming can be decreased or stopped.

The second reason to find alternatives to fossil fuels for energy is the more longterm outlook that fossil fuels are limited since they are known to be only renewable on a large geographic time-scale (hundreds of millions of years [2]). Some even argue that running out of fossil fuel is a short-term concern. As David Goodstein describes in 'Out of Gas': "The world will soon start to run out of conventionally produced, cheap oil. If we manage somehow to overcome that shock by shifting the burden to coal and natural gas, the two other primary fossil fuels, life may go on more or less as it has been–until we start to run out of all fossil fuels by the end of this century. And by the time we have burned up all that fuel, we may well have rendered the planet unfit for human life. Even if human life does go on, civilization as we know it will not survive, unless we can find a way to live without fossil fuels." [3] One way to live without fossil fuels is to take advantage of the many available renewable energy sources. However, most renewable energy sources, such as solar, hydro, and wind energy have inherent drawbacks associated with their inconsistent availability. For example, the sunshine can be reduced by cloud-cover and is only available for a limited amount of hours each day. Similarly, wind blows at different speeds depending on the location, climate and time of day. These varying operating conditions make it difficult to design systems that can distribute energy at all times. Therefore, these energy sources must be supplemented with efficient storage and conversion devices to allow uninterrupted energy access. The most common form of energy storage and chemical to electrical energy conversion is a battery, but once electricity is transformed into chemical energy, fuel cells can effectively convert the chemical energy back to electrical energy.

#### **1.2** Electrochemical Cells for Energy Storage

A fuel cell is very similar to a battery: they are both electrochemical cells that convert chemical energy into electrical energy via reduction/oxidation reactions. In both systems ions from the anode and cathode cross through an electrolyte while electrons are forced through an external load.

However, batteries have limitations that fuel cells avoid. Rechargeable batteries store their reactants internally and recharge by reversing the discharge reaction. By comparison, most fuel cells utilize abundant oxygen in the surrounding environment for the cathode reaction while the fuel is supplied by a methane or hydrogen reservoir [4]. Additionally, recharging batteries can cause physical damage to the internal microstructure of the materials in the system as they undergo chemical change. For example, in Li-metal batteries (or Li-ion batteries) dendrites may form and penetrate the polymer that separates cathode and anode, reducing the cell's cycle life or even causing catastrophic failure.

Another large advantage fuel cells have over batteries is the greater energy density in the reactants. For example, methanol and air fuel cells have an energy content of 6,200 W·hr/kg and pure hydrogen and air fuel cells have 33,000 W·hr/kg of stored chemical energy. The reactants for rechargeable batteries such as lithium and carbon-cobalt-oxide batteries have only 130 W·hr/kg stored electrochemical energy and nickel metal hydride batteries have only 60 W·hr/kg stored energy [4].

The relatively large energy density of lithium ion batteries makes them ideal for portable applications such as laptops, however fuel cells or even a combination of a small battery and a fuel cell would produce many more kilowatt hours per kg. In fact, replacing a 660 gram Li-ion battery pack (including 340 gram charger and wires) with a 320 gram fuel cell (including 180 grams of fuel) will produce 530 W·hr/kg over the 44 W·hr/kg in the Li-battery set-up, as calculated by Dyer in [5].

#### 1.3 Types of Fuel Cells

Fuel cells are broadly categorized by their fuel type, operating temperature, and by the type of electrolyte they use, since the latter varies greatly by phase and type of conducting ion [6]. For example, Proton Exchange Membranes (PEM) fuel cells conduct protons across the electrolyte. Molten Carbonate Fuel Cells (MCFCs) are so-called because the electrolyte is a molten mixture of alkali metal carbonates. The electrolyte of Solid Oxide Fuel Cells (SOFCs) is a solid ceramic that conducts oxygen ions. This thesis is concerned with the behavior of SOFC electrolytes so the following section will describe SOFC operation in detail.

## CHAPTER 2 BACKGROUND INFORMATION

## 2.1 How SOFCs work

SOFCs are simpler than other systems because they only require two phases: gas and solid. A gaseous fuel containing hydrogen (such as H<sub>2</sub>, methane, ethanol, or biofuel, etc.) is supplied to the anode where the hydrogen is oxidized. This produces protons as well as electrons, which are free to conduct across an external circuit (see Figure 2.1). At the cathode, air enters and oxygen is reduced to  $O^{2-}$  ions using the electrons from the external circuit. The electrolyte is an ionconducting and gas-tight membrane that allows oxygen anions to cross from the cathode to the anode [7]. Resulting products at the anode are mostly water vapor and, when hydrocarbons are used as fuel, gaseous  $CO_2$  is produced.

The overall reaction of a pure-hydrogen solid oxide fuel cell is:

$$H_2 + (1/2)O_2 = H_2O \tag{2.1}$$

The ideal electrolyte is, under operating conditions, an electrical insulator so the electrons from the anode avoid the electrolyte and are forced to the cathode through the external circuit load[8]. Thus, the three main components of a SOFC are the anode, electrolyte and cathode, which will be described in greater detail in the following sections.



Figure 2.1: Schematic of a solid oxide fuel cell.

#### 2.1.1 Anode

SOFC anodes must have a high porosity (20-40%) to allow reactant and product gases to be transported through them [9]. The essential reaction that occurs at the anode is as follows:

$$H_2 + O^{2-} = H_2 O + 2e^- \tag{2.2}$$

This reaction occurs at the "triple-phase boundary" where the ionic-conducting electrolyte meets both the fuel-supplying atmosphere and the electron-conducting metal that carries the current to the load. The electron-conducting material often doubles as a catalyst in fuel cells that operate at high-temperature.

Most SOFC anodes are cermets comprised of metallic nickel and an oxide skeletal structure. This structure inhibits sintering and matches the thermal expansion coefficient with that of the electrolyte. Both cathode and anode materials are more effective if they are oxygen ion and electron conductors. This is because such mixed conductors extend the triple-phase boundary of the electrode. For the anode, developers are studying Gd-doped ceria combined with zirconia and yttria and other TiO<sub>2</sub>-based materials as candidate replacements [9].

### 2.1.2 Electrolyte

SOFC electrolytes allow oxygen ion transport to occur and must be electrically insulating to keep electrical current limited to the external circuit. The most commonly employed electrolyte material is yttria-stabilized zirconia (YSZ). In fact, many zirconia based electrolytes are good ionic conductors, and thus efficient electrolytes. Investigations of other candidate electrolyte materials include  $Bi_2O_3$ ,  $CeO_2$ , and  $Ta_2O_5$ . Some materials have higher ionic conductivities than YSZ but many are unstable at the anodes [9].

#### 2.1.3 Cathode

Like the anode, the cathode must have a porous structure for the rapid transport of reactant and product. The cathode also has a triple-phase boundary for the reduction reaction to occur:

$$(1/2)O_2 + 2e^- = O^{2-} \tag{2.3}$$

A common cathode material is strontium-doped lanthanum manganite  $(La_{0.84}, Sr_{0.16})MnO_3$ , which is a p-type semiconductor. Mixed electron/ion conductors are advantageous, especially at lower operating temperatures. Such conductors include lanthanum strontium ferrite, lanthanum strontium cobaltite and even n-type semiconductors [9].

#### 2.2 Defining an Ideal SOFC Electrolyte

When looking for candidates for ideal SOFC electrolytes, there are many criteria to consider. Chemical, mechanical, and thermodynamic stability, cost, as well as operation life are important but the most stringent requirements are on the electric and ionic conductivity.

## 2.2.1 Ionic Conductivity

High ionic conductivity is a priority for selecting electrolytes since current is conserved throughout the fuel cell and thus requires all the electrons flowing into the external circuit to have an equal flow of ions through the electrolyte. The resistance associated with this ionic motion is  $\frac{L}{\sigma_o A}$  where L is the width of the electrolyte, A is the surface area of the electrode, and  $\sigma_o$  is the ionic conductivity. These components and the resistances of both the anode  $(R_A)$  and the cathode  $(R_C)$  make up the total resistance of the system:

$$R_{system} = \frac{L}{\sigma_o A} + R_A + R_C \tag{2.4}$$

The power lost due to the system resistance is

$$P_{lost} = I^2 R_{system} \tag{2.5}$$

so it is critical to keep  $R_{system}$  to a minimum. Electrolytes with high conductivity  $(10^{-3} \text{ S/cm})$  are generally required.

A particularly good ionic conductor,  $PbF_2$ , which forms in the fluorite structure as in Figure 2.2. This was discovered by Faraday in 1839 and showed that materials formed in the fluorite structure can be good at conducting ions [8]. This is because the lead atoms occupy the corners and face centers of the FCC lattice structure while the fluorine atoms occupy the tetrahedral interstitial sites. When there are vacancies at these sites, the fluorine can easily migrate through the open interstitial sites. Since oxygen atoms are similar in size to fluorine, they can replace them easily and the high ionic conductivity property can be extended to some oxides with the fluorite structure. This idea was validated by many oxide electrolytes that are good ionic conductors such as stabilized zirconia, ceria, and delta-bismuth oxide, since these are all fluorite structures.



Figure 2.2: Example of fluorite structure [10], where the light/gray-colored atoms in the FCC structure represent lead or zirconia atoms and the dark/yellow-colored atoms represent fluorine or oxygen atoms.

#### 2.2.2 Electrical Conductivity

Another consideration for an ideal SOFC electrolyte is the electrical conductivity. The free electrons that pass through the electrolyte from the anode to the cathode, obviously do not go through the external circuit to provide useful energy. So it is important to minimize  $\sigma_e$ . The ratio  $t_o$  is defined as:

$$t_o \equiv \frac{\sigma_o}{\sigma_o + \sigma_e} \tag{2.6}$$

and represents the transport efficiency; ideally a SOFC electrolyte would have a transport efficiency of 1, but an acceptable ionic conductor should have  $t_o \gtrsim 0.95$ .

Zirconia  $(ZrO_2)$  has a relatively high electrical conductivity so it is a poor candidate for solid oxide fuel cell electrolytes. However, it takes the cubic fluorite structure at temperatures above 2400°C. This structure can be stabilized at room temperature by employing aliovalent doping with atoms of lower valency than zirconium. To maintain charge balance, oxygen vacancies are created; these vacancies strongly increase the oxygen diffusivity. The amount and type of dopant affects the structure and the resulting properties of the material. So various dopants and phase diagrams have been studied.

#### 2.2.3 Dopants

Yttria was chosen as an appropriate dopant to research because YSZ is particularly well-studied and is therefore an excellent standard oxygen electrolyte system. The phase structure and electrical properties of YSZ are affected by both dopant concentration and temperature. At room temperature, the equilibrium bulk temperature of YSZ changes structure from monoclinic to tetragonal to cubic as the dopant concentration increases. An entire phase diagram is presented in Figure 2.3(a) and a narrower range of compositions is shown in Figure 2.3(b).



Figure 2.3: (a) Overall phase diagram of YSZ showing the transition of phase structures for a given temperature from monoclinic to tetragonal then to face centered cubic. (b) Expanded view (0-20 mole%  $YO_{1.5}$ ) of a phase diagram of YSZ by Scott [11].

Figures 2.3(a) and 2.3(b) are commonly accepted versions of the YSZ phase diagram and Figure 2.4 shows a more recent phase diagram (1997) [12]. In Figure 2.3(a) it can be seen that amounts of YO<sub>1.5</sub> greater than about 16 mole% YO<sub>1.5</sub> yield simple phase cubic zirconia at room temperature. For this amount of YO<sub>1.5</sub>, the phase structure remains cubic up to +2500 °C.

At low amounts of yttria, grain size plays an important role in phase structure. As shown by Lange et al. compositions with 2-3 mol%  $Y_2O_3$  will retain the tetragonal phase over monoclinic at lower temperatures if the grain size is below a critical value. The critical grain size increases from 0.2 to 1  $\mu m$  with increasing yttrium composition (2 to 3 mol%  $Y_2O_3$ ) [13].



Figure 2.4: Updated phase diagram shows a close up of 0-20 mole%  $YO_{1.5}$  and 400-1600°C [12].

#### 2.3 Thin Films

Thin films can exhibit properties substantially different from bulk electrolytes of the same phase, due to the non-equilibrium condition of the films, which are essentially quenched from the vapor. Since thin films are not necessarily in thermal equilibrium they do not exhibit the bulk phase diagram. As shown by Joo and Choi, bulk materials can show multiple clear peaks that indicate a particular phase but for the same materials as thin films a diffraction peak can entirely disappear from the  $\theta - 2\theta$  powder pattern [14].

Hartmanova showed that by depositing thin films onto substrates heated to  $T_{substrate} \gtrsim 830^{\circ}$ C improved the ionic conductivity measured at low operating temperatures (see Figure 2.5) [15]. By increasing the temperature, the phase became predominately face-centered cubic which is more ionically conductive. Since we cannot deposit films above 500°C in our sputter system, we decided to deposit

our films at room temperature and anneal them at  $T_{substrate} = 850^{\circ}$ C. In another study, Yuan et al. showed that films deposited in our system at 500 °C exhibited much-lower conductivity.



Figure 2.5: Ionic conductivity at different deposition temperatures. Materials represented by the square( $\blacksquare$ ) were deposited at room temperature, the triangle( $\blacktriangle$ ) represents materials deposited at 700°C, and the circle ( $\bullet$ ) represents materials deposited at 830°C [15].

Another consideration for a commercially viable electrolyte is the method of production. Usually, electrolytes are deposited onto the cathode or anode of an SOFC using tape-casting or spin-coating which creates large amorphous grains. To allow us to study the effect of structure and to allow high-throughput sample production, sputtering onto thin films was employed. The ultimate goal associated with this project is to identify new high ionic conductivity thin films. If thin films with outstanding low-temperature conductivity were found, we expect that the corresponding bulk material would comprise larger grains and an even higher conductivity. An additional benefit of studying SOFC electrolytes as thin films is they can be directly used in small or mobile devices in the form of thin-filmmembrane SOFCs.

## 2.4 The High-Throughput Approach

In the high-throughput approach to studying specific materials properties, many compositions are made on a single test wafer to explore the property as a function of composition. When two materials are co-sputtered onto a substrate, the sample is called a binary spread and when three materials are used the sample is a ternary spread. To make oxides, the targets are reactively sputtered in an oxygen/argon ambient, giving the samples an extra component and making them pseudo-binary and pseudo-ternary surfaces of the phase diagram. A key advantage of the high-throughput method is that many compositions are produced from a single deposition, reducing sample-to-sample error and random variation.

High-throughput research is different from many other scientific projects in which the researcher tests the functionality of one specific material at a time and uses the result to motivate synthesis and testing of a new material. In this approach it is important to obtain accurate results to correctly move forward. The purpose of combinatorial research, however, is to perform a broad search for a desired new material to optimize a specific property. This de-emphasizes the requirements on accuracy and instead focuses on producing studies of trends within a large range of compositions.

However, any discovery or claims about a new material must be based on previously verified methods. So the first step in any combinatorial study is to prove the validity of one's synthesis and measurement methods. In this thesis, the methods for measuring electrical impedance in electrolytes materials were verified by testing an established material (YSZ) so the results could be compared to previously published and accepted data in the literature. The goal of this thesis is to demonstrate the validity of our methods.

Yttria-stabilized zirconia was chosen for this purpose since it is a well-studied material. Examples of other appropriate dopants for  $ZrO_2$  include calcium and scandium and were considered candidates for a combinatorial study of their ionic conductivity. Concurrent studies include psuedo-ternary spreads of YSZ + scandia while future studies may involve doped-ceria materials.

#### 2.5 Impedance Spectroscopy Theory

Once a binary or ternary spread was made, the ionic conductivity was measured as a function of composition. Since ionic conductivity is difficult to measure directly in a method compatible with high-throughput, it was inferred by measuring frequency-dependent electrical impedance. The composition and the structure of a material determine its impedance.

The term impedance describes the linear relationship between voltage and current. At frequencies  $\omega = 2\pi f > 0$  the voltage and current need not be in phase. Ohm's law can be written as

$$V = I|Z|e^{i\theta} \tag{2.7}$$

where |Z| is the magnitude of the impedance and  $\theta$  is the phase shift (also known as the phase angle) between the voltage and current. Physically, one applies a voltage, at a frequency  $\omega$ :

$$V(t) = V_o[sin(\omega t)] \tag{2.8}$$

and measures the resulting steady state current:

$$I(t) = I_o[\sin(\omega t + \theta)]$$
(2.9)

Here  $\theta$  is the phase difference between voltage (V) and current (I) and is zero if the behavior is purely resistive. For  $\theta = 0$  the relationship is simply  $V = IZ_R$ where  $Z_R = R$ .

However, if a capacitance or inductive reactance are present in a system, the phase will be nonzero. This is because the relation between the voltage and current involves a time derivative,  $V_L = L \frac{dI}{dt}$ , for an inductor and  $I_C = C \frac{dV}{dt}$  for a capacitor. The results of the phasor analysis are:

$$Z_R = R \tag{2.10}$$

$$Z_C = i/\omega C \tag{2.11}$$

$$Z_I = i\omega L \tag{2.12}$$

where  $Z_R$  is the impedance associated with a resistive reactance,  $Z_C$  is the impedance associated with a capacitative reactance, and  $Z_I$  is the impedance associated with an inductive reactance [16]. In general the impedance is a complex value.

When more than one impedance is present in a circuit, the overall impedance is defined using Kirchoff's Laws, and the result is a generally neither purely real nor purely imaginary, but a complex number represented as  $Z = |Z|e^{i\theta} = Re(Z) + iIm(Z)$ . The impedance of such a circuit will vary with frequency so Re(Z) can be graphed along the x-axis and Im(Z) can be graphed along the y-axis. A plot



Figure 2.6: Example of real vs. imaginary impedance, also known as a Cole-Cole Plot. Original YSZ data of composition  $Zr_{1-x}Y_xO_{2-x/2}$  where x=77.2 from private communication with Chao-Chen Yuan[17].

of the real part vs. the imaginary part of the impedance is shown in Figure 2.6, for a typical YSZ film.

The impedance associated with different aspects of the behavior of a material could be represented as a combination of real and imaginary impedances. For example, the resistance of a material is related to its bulk conductivity, and the measured capacitance and inductance could define a space charge polarization region or other processes at the electrode. A constant phase element (CPE) could describe non-localized processes such as diffusion or inhomogeneities such as surface roughness [18]. The impedance elements and calculations that apply to the YSZ system (like CPE networks) are discussed in detail in Chapter 5.

### 2.5.1 Impedance Spectroscopy Model for YSZ

This thesis is focused on the study of yttria-stabilized zirconia (YSZ). Bulk YSZ has been shown to exhibit a simple microstructure that can be modeled, for the purpose of impedance spectroscopy, as a set of grain interiors (called grains) and grain boundaries. When an ac voltage is applied, the resulting current must pass through a blocking electrode (platinum) before it is carried by ions through a network of grains and grain boundaries. Each of these can be combined as their own set of similar components.

The repeating components that define the grains and grain boundaries can be represented by two series-connected Voigt elements, which is a closed-loop within a circuit. A series capacitor and resistor are used to model the blocking electrode and lead resistance, respectively. This model (Figure 2.7) provides a good description of the frequency-dependent impedance, and is based on the well-established Bauerle "brickwork" model in Figure 2.8, which was used to interpret the properties of bulk cubic zirconia [19].



Figure 2.7: Circuit Equivalent Model which is calculated in Equation 5.1.



Figure 2.8: Circuit Equivalent According to Bauerle.

Parameter	Value
$C_{gi}$	4.8 pF
$\mathrm{R}_{gi}$	$2.1M\Omega$
$C_{gb}$	1.7nF
$R_{gb}$	$1.5M\Omega$
$C_e$	$2.0\mu F$
$\mathbf{R}_{e}$	$5.0M\Omega$

Table 2.1: Typical values of the parameters associated with the model in Figure 2.8 for the impedance spectrum of Figure 2.9.

In some cases, each circuit component corresponds to a distinct arc in the Re(Z) vs. Im(Z) plot. An example of relevant data from Macdonald et al. is shown as experimental data in Figure 2.9(a) and the model simulation is shown in Figure 2.9(b), which used the circuit parameters listed in Table 2.1 and the model from Figure 2.8 [18].



Figure 2.9: Cole-cole plots representing impedance spectroscopy data plotted from (a) experimental results and (b) simulated parameters [18].

#### CHAPTER 3

## CREATING A SAMPLE COMPOSITION SPREAD OF YTTRIA STABILIZED ZIRCONIA

The overall process of creating an oxide sample with a composition gradient involves four steps: (1)substrate preparation, (2)thin film deposition, (3)high temperature anneal, and (4)lithography and deposition of the electrodes.

This process was significantly modified when the electrode configuration was changed from top and bottom capacitor contacts to interdigitated electrodes. In addition to reducing the space-charge effect (see Section 3.1.5), the change in contacts allowed the sample to be annealed after deposition. The interdigitatedelectrode configuration has proven essential for achieving a conductivity in the thin films that is comparable to that observed in bulk.

#### 3.1 Substrate Selection and Heating

The interdigitated configuration required that the sample had to be deposited on a substrate that would not act as a capacitive short. The substrate be insulating and also yield highly adherent YSZ films. Initially, 500 micron-thick fused quartz substrates were used but these cracked or broke when they were heated to the highest operating temperature (500°C).

Many techniques were tried to keep the substrate from cracking during heating, such as achieving better thermal contact with thermal paste, holding the substrate down with small weights (allowing the substrate to move and not holding it in place), using alumina or copper intermediate plates between the substrate and the heater (to achieve better temperature uniformity), heating the substrate very slowly for 8 hours, and even breaking the substrate into smaller pieces to lower the accumulated stress. All attempts to avoid cracking were performed on practice quartz wafers which did not have YSZ deposited on them. Unfortunately, none of the attempts at heating the substrate to 500°C without breaking were successful.

The surface of the lab-made heater (described in greater detail in Section 4.2) was measured with a K-type thermocouple in various positions at a constant setpoint temperature, however the measured temperature often varied by 10-30°C. Sometimes the temperature difference was even greater and it appeared that the temperature of the heater was lower on the side that was nearest the work-bench edge (rather than the side nearest the wall). It was concluded that the low thermal uniformity of the heater combined with the low thermal conductivity of amorphous  $SiO_2$  (1.7 W/mK compared to 76.2 W/mK for Si [20]) caused the substrate to crack or break at temperatures below 500°C.

Therefore, an alternative substrate was sought. A relatively thick (1 mm) wafer of sapphire was used as the substrate for impedance spectroscopy measurements. This substrate withstood temperatures of 300, 400, and 500°C for many hours before showing initial indications of cracking. Both quartz and sapphire wafers withstood the annealing process, accomplished with a closed Thermolyne type 48000 furnace at 850°C for 8 hours.

### 3.2 Vacuum Sputtering

Sputtering is a thin film deposition technique that uses low-pressure ion bombardment to knock target materials onto a substrate. To do this, a vacuum chamber will contain sputter guns mounted through the walls of the chamber. Many vacuum chambers have several guns to allow many different types of targets to be deposited simultaneously or to allow many depositions to occur in sequence with out breaking vacuum. The configuration of the guns is also significant in that placing a target close and parallel to a substrate will make a film of only that target. This is called on-axis sputtering. However, if the target is placed perpendicular to and above the substrate, multiple guns can be pointed at the substrate and the resulting sample would have composition gradients involving materials from all the targets. Figure 3.1 shows the overall configuration.



Figure 3.1: Schematic of the sputter process.

In order to keep the deposition rates constant, RF-sputtering was employed [21]. This means the targets were excited with a radio frequency power. During the positive portion of the voltage cycle, the positively charged target molecules oxidized on the substrate, in the oxygen gas, and at the target. This built an oxide layer at the substrate and target surfaces, which would reduce the deposition rate for the targets. However, during the negative portion of the voltage cycle, the targets were negatively charged which drew argon-ion bombardment, thus knocking off more target molecules.

In our system, the chamber was pumped down to about  $3-4 \times 10^{-6}$  Torr prior to sputtering. Argon and oxygen gasses were introduced into the chamber at rates of 15 standard cubic centimeters per minute (sccm) and 10 sccm, respectively, and were ionized with secondary electrons from the targets. The argon ions are then accelerated to the negatively-charged targets, and sputter atoms that move through the chamber until they condense on the substrate. For YSZ samples, 103 watts forward power was applied to the zirconium target and 50 watts was applied to the yttrium target. The ions bombarded the targets, knocking individual molecules off into the chamber causing some target molecules to fall onto the substrate. To increase film density, the substrate was also electrically charged with -50 volts dc bias [22]. After sputtering for 100 minutes, a film of about 189 nm thickness, measured at its center, was produced. The thickness measurement was acquired by Leo Small [22] and applied here since the deposition parameters were identical and the reproducibility of the deposition rate is better than 3% [23].

#### 3.3 Anneal

The substrate wafer is often heated during deposition to increase the ionic conductivity of the deposited oxide electrolyte. As shown in Figure 2.5 Hartmanova, et al. [15] found that increasing the deposition temperature from 700°C to 830°C increased the ionic conductivity more than an order of magnitude. This is a large improvement for a relatively small increase in annealing temperature. Since our vacuum-chamber heating system was limited to 600°C, we sputtered our YSZ at room temperature and then annealed the film at 850°C in an enclosed Thermolyne 48000 furnace. To avoid fracturing the substrate, the temperature of the furnace was ramped at a rate of 20.7°C/hour before dwelling at 850°C for 8 hours. The sample was then ramped back down to room temperature at the same rate.

### 3.4 Interdigitated Contacts

#### 3.4.1 Calculating the Optimal Design

For the original sandwich configuration, a shadow mask was used to deposit platinum electrode dots onto the sample as top contacts. The sample, about 200 nm thick, had been deposited on a layer of platinum that served as the base electrode. We have found that the sample was so thin that at low frequencies the charge carriers could traverse the thickness of the film during a single half-cycle. Thus, the charge built up at the electrodes at low applied frequencies, altering the impedance measurements in a way that is inadequately modeled. This created unacceptable ambiguity to the interpretation of impedance spectroscopy graphs. The phenomenon of building up charge due to inadequate distance between the electrodes is a form of space charge effect and can be significantly reduced with a different contact configuration.

New electrodes were designed that improve low-frequency performance as described below. Since they had finer detail than the planar contacts, a new method of fabricating the electrodes was developed. The new configuration involves interdigitated contacts deposited on the surface of the sample and patterned using
photolithography. The mask was designed to maximize the distance between the platinum contacts but also ensuring an impedance in the range of our LCR meter  $|Z| < \sim 10 \text{ M}\Omega$ . The distance between adjacent contacts was 5  $\mu m$  thick. These readings were achieved using contacts in long parallel rows that alternated perpendicular connection to two buss-bars on opposite sides of the device (see Figure 3.2).



Figure 3.2: Schematic of interdigitated electrode fingers as a pair of contacts in one square. Not drawn to scale. Each square is  $1 \text{ mm} \times 1 \text{ mm}$ .

This design was developed by taking into account the limitations of the maskwriting equipment, resolution of the photolithography process, and the requirements for the sample. For example, each device was  $950 \times 950$  microns and was spaced 50 microns from the adjacent square, to yield devices spaced on 1 mm centers. This is a good match to the compositions spread, which has a gradient of 1%/1 mm, so measurements can be made with 1% composition resolution.

The electrodes were designed with many interdigitated fingers in parallel in order to decrease the impedance to values compatible with the LCR meter. A conductivity of 10<sup>-6</sup> S/cm in a 200 nm-thick YSZ film would give an impedance of 260 M $\Omega$  for a single electrode pair 950  $\mu m$  long with a 5  $\mu m$  separation. Putting n fingers in parallel would decrease the resistance to 260/n M $\Omega$ . So the number of fingers was maximized with the limitation that a reliable minimum feature-size achievable with the Hiedleburg mask writer is 5 microns. This meant we were able to fit 47.5 pairs of fingers in the 1 mm × 1 mm footprint.

Another important consideration for the design ensuring that the resistance associated with the YSZ film was at least 100 times larger than the resistance of a single platinum finger so the YSZ would dominate the impedance readings. To minimize the resistance of the platinum, the area (width of fingers × thickness of fingers) was maximized. The width was already set to be 5 microns to maximize the number of pairs so the thickness was chosen to be as large as possible to reduce the resistance, but as small as possible–to conserve platinum. Thus the finger dimensions were chosen to be 5 microns wide, 100 nm thick and 650 or 750 nm long to accommodate two 100-micron wide strips of platinum on either side of the device. Each strip was connected to a contact pad at opposite corners of the square for the palladium needles to touch and connect to the impedance analyzer. The pad was  $200 \times 200 \ \mu m$ . See Figure 3.2 for a schematic of a single pair of contacts.

To understand the resistance measurements of the sample, notice that the

charge carriers move between the contact-fingers whose surface area is  $A_{sample}$ (depth of the sample × the longest dimension of the fingers). The space between the fingers is the  $L_{sample}$  of the material being measured because it is the distance the charge-carriers must cross to reach the other electrode. The resistance reading,  $R_{total}$  includes measurements for all the fingers  $R_i$ , so to calculate the resistivity, all the  $A_{sample}$  of YSZ must be combined:

$$\frac{1}{R_{total}} = \Sigma \frac{1}{R_i} = \frac{\Sigma A_i}{\rho L_i} \tag{3.1}$$

 $L_i$  is the same for all fingers = 5  $\mu m$ 

$$\rho = \frac{R_{total} \Sigma A_i}{L} = \frac{R_{total}}{L} (10 pairs \times A_{ShortFingers} + 27.5 pairs \times A_{LongFingers}) \quad (3.2)$$

 $A_{ShortFingers}$  is the cross-sectional area of the short fingers and is 650  $\mu m \times$  thickness.  $A_{LongFingers}$  is the cross-sectional area of the longer fingers and is 750  $\mu m \times$  thickness. The conductivity is therefore:

$$\sigma = \frac{1}{\rho} = \frac{L}{R_{total} \times \Sigma A_i} \tag{3.3}$$

Each set of fingers is a pair, so the area is doubled. Also, it is assumed that thickness is uniform and  $\approx 200nm = 2 \times 10^{-5}cm$ 

$$\sigma = \frac{5\mu m}{R_{total} \cdot 2 \cdot (20 \cdot 650\mu m + 27.5 \cdot 750\mu m) \times 2 \times 10^{-5} cm}$$
(3.4)

$$\sigma = \frac{5\mu m}{R_{total}(26,000\mu m + 41,250\mu m) \times 2 \times 10^{-5} cm}$$
(3.5)

$$\sigma = \frac{3.717S/cm}{R_{total}} \tag{3.6}$$

Therefore, to calculate the conductivity from the resistance parameters, one must divide  $\approx 3.7$  by the measured  $R_{total}$ .

### **3.4.2** IDE Production Process

Depositing the interdigitated electrodes added numerous steps to the process of producing measurable devices. Before the electrodes could be deposited, the new mask had to be produced. This was done with the Heidelberg Mask Writer DWL2000. This piece of equipment accepts GDSII files and writes the appropriate pattern onto a blank chrome mask, which can be purchased in the CNF. The image on this mask was a negatively-drawn resist, so the contact-deposition process required the lift-off image reversal process. In the future it would be easier to have the image be a positive resist. This would use a different type of photoresist that becomes soluble upon exposure to uv-light and would reduce the process since it does not involve the use of LoR.

After the composition spread was deposited and annealed, it was brought to the Cornell Nanofabrication Lab where the IDE deposition process was executed. This process, as listed in Figure 3.3, requires photoresist (PR) to be deposited, exposed through the mask, and developed. This left a reverse pattern on the sample appropriate for lift off. The layer of platinum subsequently deposited is removed when the PR is fully washed away, leaving only the platinum in contact with the YSZ film.

To ensure that the metal layer on the PR area and the metal layer on the exposed sample did not remain connected, the photoresist was supplemented by lift-off resist (LoR). This material is not affected by exposure to UV light, but is uniformly removed by the development process. The necessary amount of LoR and photoresist were determined by considering the smallest feature-size of the electrodes (5  $\mu$ m) and calculating how much would be removed by the develop/exposure process, comparing this to the thickness of the metal deposited.



Figure 3.3: Metal lift-off resist using image-reversal.

Considering 0.1  $\mu m$  of metal would be deposited on the PR and the rate the developer can remove the LoR, the LoR should be 10× thicker than the metal (about 1  $\mu m$  thick) and the PR should be twice that (about 2  $\mu m$ ).

The first step of the lift-off process is to deposit lift-off resist. This was done by placing the substrate on spinner #2, applying a dropper of LOR3A, then spinning the sample at 3,600 rpm for 30 seconds (with an acceleration of 10,000 rpm/second). Next, the volatile solvents were driven off by putting the substrate on a hotplate set to 180°C for 3 minutes. Then the substrate was placed on Spinner #1, a dropper of PR1805 was applied, the sample was spun at 3,000 rpm for 30 seconds (with an acceleration of 10,000 rpm/second), and finally placed on a hotplate set to  $115^{\circ}$ C for 1 minute and 30 seconds.

The next step of the process required trial and error optimization. To determine the ideal PR exposure, multiple exposure tests were executed. The ABM Contact Aligner was used to expose the PR/LoR-coated substrate to ultra-violet (UV) light through the mask. The default settings were used and a hexagonal-shaped plastic mask with a hole allowed 8 exposure tests. At first, these tests ranged between 10 and 20 seconds and were used with a thicker photoresist (PR1813). About 15 seconds of exposure-time appeared to work well as judged visually after development, but once the contacts were deposited and lifted off, superfluous lines of platinum were noticed between adjacent fingers. This was probably caused by an overexposure of UV light that allowed the PR to wash away where it should have remained. To avoid this, a second sample allowed for the use of a thinner PR, which needed another set of exposure tests. These were preformed on bare Si substrates for 2.2 - 4.0 seconds and appeared to be neither over-exposed nor had residual PR after development for 2.2 seconds.

The sample was developed by placing it in AZ 300T photoresist stripper (1methyl-2-pyrrolidone and 1,2-propanediol) for about one minute, then rinsed with water and air. After exposing and developing the photoresist, the pattern was examined using an optical microscope in the photolithography room. Next, the sample was cleaned in the Oxford 81 using the descum process (oxygen clean) for 30 seconds. This was done to clean the surface of the lowest layer, the YSZ material, of any excess photoresist or lift-off resist before depositing the platinum.

100 nm of platinum was deposited using the SC4500 Odd-Hour Evaporator at

a rate of about 0.7 to 1.3 Å/min. It took about 30 minutes to pump-down the system to the  $10^{-6}$  Torr range. Ideally, the base-pressure would be about  $2.0 \times 10^{-6}$  Torr but the lowest pressure in these experiments was  $3.5 \times 10^{-6}$  Torr. The power to the e-beam source was slowly increased to 16.8%. At about 10%, some spitting at the platinum target occurred but stopped when the power was increased more slowly. The biggest difficulty in depositing the platinum involved positioning the electron beam appropriately on the platinum. One must also remember that when loading the platinum, it does not not have a crucible, rather it goes straight into the bottom hearth. The results after platinum deposition can be seen in Figure 3.4.



Figure 3.4: Platinum-layered substrate before washing away the PR. The visible pattern is made of the PR, LoR and platinum deposited on top of each other making it looked slightly raised. The un-raised portions are the actual platinum contacts deposited on the YSZ.

The final step for producing the electrodes was to lift off the excess platinum, photoresist, and lift-off resist since the patterned platinum adhered to the oxidesample. Removing the PR, LoR and platinum layers was performed by soaking the sample in acetone for a minute, then rinsing the sample with fresh acetone, isopropyl alcohol (IPA) and water, finally drying the sample with compressed air. Unfortunately, some of the electrodes on the rightmost third and near the middle of the sample washed away. It is possible that by soaking the sample in acetone for a shorter time or using a thicker layer of photoresist this could have been prevented. The end-result was a sample that had intact devices over the composition range of 0.08 < x < 0.32 in  $Zr_{1-x}Y_xO_{2-x/2}$ .

Overall, the YSZ deposition process was based on previous recipes developed in the group, but the annealing and contact design-deposition were novel contributions. The general process of depositing platinum contacts used known techniques, but the details involving the resist thickness and exposure times were determined during the course of this research.

#### CHAPTER 4

## METHODS: MEASURING THE IONIC CONDUCTIVITY OF THE SAMPLE

To characterize the ionic conductivity of the sample, the impedance was measured and the resulting graph was modeled to determine appropriate parameters like resistance, and conductivity. The impedance measurements are described in Section 4.3, but measuring the impedance required an extra step because the samples had to be heated to work. The heater is described in Section 4.2.

Ideally, electrolytes would function at room temperature but common materials such as YSZ require over 800 °C to achieve adequate conductivity. Our ultimate goal is to identify materials with comparable conductivity at much lower temperatures: 300 °C to 500 °C.

### 4.1 Variables and Constants

To take impedance spectroscopy measurements at a particular composition, a small current is sent through platinum contacts on the wafer, through the sample, and back through a set of contacts. Alternating current (ac) was used rather than direct current because otherwise the charge would build up at the blocking electrodes and current would vanish. Alternating current was applied at 42 different voltage frequencies ranging logarithmically from 100 Hz to  $10^{6}$  Hz. The frequency and electrolyte composition were the independent variables for the experiment. The resulting dependent variables were the real and imaginary parts of the complex impedance. It is standard to plot the data from a particular composition as a graph with Re(Z) plotted on the x-axis and -Im(Z) plotted on the y-axis with the

frequency as a parameter. This graph is called a Cole-Cole plot; an example is seen in Figure 4.1. It is important to remember that high frequencies generally have low impedance values and low frequencies often have high impedance values.



Figure 4.1: Example of a Cole-Cole Plot made of real data from private communication with Chao-Chen Yuan (YSZ at x=11.9 in  $Zr_{1-x}Y_xO_{2-x/2}[17]$ ).

As described in Section 3.5.1, the space charge effect causes charge to build up at the electrodes at low frequencies so impedance values increase. This lowfrequency effect obscures any intrinsic property associated with grain boundaries or intragrain ionic conductivity. Figure 4.1 illustrates data that lacks clear characteristic arcs (as are seen for bulk YSZ in Figure 2.9(a)) associated with either grains or grain boundaries. Similar data are obtained for almost all devices in the planar capacitor configuration, making it difficult to confidently infer  $\sigma_{grain}$  and  $\sigma_{grainboundary}$ .

Two approaches were taken to increase the confidence of inferred conductivities.

The first approach involved a change in the analytical method. We developed a method for judging the reliability of the fit, one able to differentiate incorrect models from accurate ones. A python program [24] was written to accomplish this automatically. The program separates the models into subnetworks based on the physical components they represent, such as the impedance due to grains or that due to the grain boundaries, and is described in detail in the next chapter.

The second approach to resolving the ambiguity caused by the space charge effect involved the design and deposition of interdigitated electrode contacts and is described in the previous chapter. The success of this approach is presented in the next chapter.

### 4.2 Heating Apparatus and Program

Samples were measured using a probe station capable of heating substrates to 500°C in air and allowing access to two palladium-needle probes for electrical connection to the impedance analyzer. The probe station was constructed by Leo Small and is shown in Figure 4.2. It consists of a 3" diameter US Heater surrounded by a water-cooled copper pipe on the sides and two copper plates on top and bottom to shield the electrical probes and human fingers. An additional iron plate was attached on top to allow the magnetic bases of the xyz probe-positioners to be located securely yet moved easily.

A Labview program was used to heat the substrate displays the "temperature setpoint" and "last read temperature" in an indicator. The program calculates the difference between the "temperature setpoint" and the "last read temp" i. e., the error. Using a feedback loop, the error was constantly minimized by calcu-



Figure 4.2: Station used to heat sample with probe needles and mounts.

lating heater power adjustments using a PI-controller. This controller multiplies the error by the "P-constant" (which can be adjusted), then adds the result of the error integrated over time multiplied by an "I-constant" (also adjustable). Using this, the temperature error can be reduced in such a way that the temperature approaches the setpoint gradually with minimal overshoot. Other control mechanisms (such as PID control) might give slightly improved performance but were deemed unnecessary for these experiments.

Ideally, the temperature measured by a k-type thermocouple mounted inside the heater would be the same as the temperature of the sample. However, a large amount of heat is lost through conduction and air convection so the temperature of the sample must be calibrated and carefully monitored during heating. By monitoring the sample's temperature with a thermocouple it was noted that the quartz wafers could not reach 500 °C without breaking, and that heating the samples on sapphire drove the heater's power supply to it's maximum. To make the surface of the sample reach about 500 °C, the "Temperature Setpoint" of the program must be set to 610 to 620°C. The temperature of the sample was verified using a separate K-type thermocouple with a small tip. This type of tip is important because thermocouples consist of two wires of different materials positioned next to each other and the thermocouple monitor measures the difference in potential between them due to the temperature with respect to a standard junction. In future work, it would be ideal to have a thermocouple connected to the probe holder so the temperature could be accurately measured at each composition immediately before or after the impedance measurements.

### 4.3 Testing the Composition as a Function of Position

A Labview program was used to take at least 10 measurements at each of the 42 chosen frequencies to produce a single representative (median) datum for that frequency. Taking 10 measurements allows us to remove noisy measurements attributed to unreliable contact by the probes. Values for the real part of the impedance greater than  $10^{36} \Omega$  or less than  $0 \Omega$  were deleted, along with values of the imaginary part of the impedance smaller than  $-10^{36} \Omega$  or greater than  $0 \Omega$ . The results were passed on to a routine that grouped the 10 measurements into clusters looking for groups of similar data so as to remove outliers. For example, if a set of 10 measurements yielded the values 3, 3, 3, 4, 4, 4, 5, 5, 5 and 9 then the program would recognize the groups of 3's, 4's and 5's and remove the 9 as an outlier. Similarly, if 9 measurements of 3  $\Omega$  and 1 measurement of 4  $\Omega$  were taken, then the program would toss out the 4  $\Omega$  measurement as an outlier. The program would then request that the system take one more data point and if the result was within the set error range (generally chosen to be 2% error), the average of the group would be returned as the final output value. If the data point did not

fall within the error-range of the group, the program would continue to request measurements until a valid datum was found or the number of loops exceeded a set value. This algorithm was applied at every frequency. Once filtered, the average and standard deviation of the final 10 data points were saved in a file.

To make contact with the electrodes, palladium needles were mounted on an L-shaped piece of metal that could be raised or lowered by a Rucker & Kolls, Model 221 xyz mount. It is important to be careful with the needles since they are damaged fairly easily by ramming them into the sample.

# CHAPTER 5 DATA ANALYSIS

The ultimate goal of this thesis was to study conductivity vs. composition. To do this, both variables had to be carefully measured and calculated. In this chapter, the particulars of calculating both the conductivity and composition are discussed.

The real vs. imaginary impedance graphs had to be accurately interpreted, which was difficult given the problems with the space charge effect and ambitious data. So stringent analytical methods to identify good and bad models fits were developed and are detailed here. To calculate the exact compositions at the tested sample-positions, deposition-rate calculations were performed. The percentage of yttria-content was characterized in methods described in Section 5.2.

### 5.1 Residuals Plots

Given a full set of frequency-dependent complex impedances and an appropriate model (Figure 2.7) was created, one can use a nonlinear least squares fitting algorithm to determine the best values for the parameters of the model. For our purposes a simple fitting program, EIS [25], was utilized to find regression curves that converged on fitting parameters. For some samples and measurement conditions the impedance data permit a well-conditioned and reliable fit by the model, but other samples and conditions give rise to data that is not straightforward to interpret. This is the motivation for developing the protocol described below for estimating the confidence of the fit.

An example of a dataset which provides an acceptable regression (given ap-

propriate initial values for the parameters) is shown in Figure 2.6. This data was obtained from measurements on a thin film of YSZ with approximate composition  $\operatorname{Zr}_{1-x}\operatorname{Y}_x\operatorname{O}_{x-x/2}$  where x=77.2, measured at 500°C in air, with platinum electrodes in the parallel plate configuration. This plot shows a clear arc associated with high frequencies, and is therefore attributed to conduction across grains. But the low-frequency data does not clearly reveal a second arc followed by a diagonal line at the lowest frequencies. This is because the impedance at low frequencies (<1 kHz) has 2 overlapping contributions of comparable magnitude. One component is the impedance associated with grain boundary conductivity and the second is the impedance caused by the blocking electrode. Additional measurements at even lower frequency or under other conditions (temperature, electrode configuration, electrode composition, etc.) might help discriminate these contributions to the impedance.

In less felicitous cases, the impedance due to the blocking electrode may substantially overlap the grain conductivity arc due to small grain resistivity. An example of such data is shown in Figure 4.1 for a YSZ thin film with approximately x=11.9 in  $Zr_{1-x}Y_xO_{2-x/2}$ , measured at 500°C in air with platinum electrodes.



Figure 5.1: Regression function (green line) and raw data (black dots).



Figure 5.2: EIS regression function.

Parameter	Value	Percent Error
$R_S$	$1.963 \times 10^{3}$	240%
$C_S$	$3.5 \times 10^{-9}$	84%
R <sub>Grain</sub>	$1.5 \times 10^{5}$	8%
P <sub>Grain</sub>	$9.5 \times 10^{-10}$	13%
n <sub>Grain</sub>	$6.2 \times 10^{1}$	1%
$R_{GrainBoundary}$	$1 \times 10^{7}$	150%
$P_{GrainBoundary}$	$1.2 \times 10^{-8}$	5%
$n_{GrainBoundary}$	$5.6504 \times 10^{1}$	1%

Table 5.1: EIS parameters used to make the regression function in Figures 5.1 and 5.2. Each parameter has a % error calculated by EIS. These errors do not discriminate appropriate regression functions from poor fits since the % error is often large for all parameters.

To examine the validity of the EIS regression analyses, residual graphs were produced by a program written in Python. The program isolates the impedance equations that define the separate sections of the model-circuit and compares them with the model as well as the actual data. Figures 5.1 and 5.2 show the regression function of the data in Figure 4.1 calculated in EIS as a green line. The same function is broken down by components as three blue lines in Figure 5.2.

The model function (green line) was obtained by fitting using the EIS program and is defined by the parameters in Table 5.1. These parameters were used in the total impedance equation:

$$Z = \left(\frac{1}{R_{Grain}} + \frac{1}{-(i\omega P_{Grain})^{n_{Grain}}}\right)^{-1} + \left(\frac{1}{R_{GrainBoundary}} + \frac{1}{-(i\omega P_{GrainBoundary})^{n_{GrainBoundary}}}\right)^{-1} + (R_S + i\omega C_S)^{-1}$$
(5.1)

Each component can be isolated by calculating its defining impedance equation. For the grain interiors and grain boundaries, this equation is a resistor (R) and a constant phase element (CPE) network in parallel. The equation that represents this circuit component is:

$$Z^{-1} = \frac{1}{R} + \frac{1}{-(i\omega P)^n}$$
(5.2)

where  $\omega$  is the angular frequency, which is  $2\pi f$ . These frequencies, f, ranged between 100 Hz and 1 MHz. P represents ion diffusion through barriers with a broad distribution of barrier heights in the grain and R represents the dissipation in the grain (i.e., reflecting the ionic conductivity). The appropriate cole-cole plot for the grain is Figure 5.3(a) and for the grain boundaries and equipment, the appropriate plot is shown in Figure 5.3(b).

As seen in Figure 5.3(a), residual plots for the grain interiors were made using the measured frequencies and appropriate fit parameters ( $R_{Grain}$ ,  $C_{Grain}$ ,  $p_{Grain}$ , and  $n_{Grain}$ ).

Similarly, the fit-parameters for the other 2 components were used to calculate their impedance plots as shown in Figure 5.3(b). These components were then subtracted from the observed data. The result of these calculation was the combination of the impedance for the first component and the residual errors, as shown in red in Figure 5.4.



(a) Data (black dots) and grain regression (b) Data (black dots) and regression function (blue line).

functions for grain boundaries (blue line:) and equipment (rightmost blue line).

Figure 5.3: The equation that describes the grain interior and grain boundary impedance values is:  $Z^{-1} = \frac{1}{R} + \frac{1}{-(i\omega P)^n}$  The equation that describes the impedance of the equipment is: Z = R + iwC.



Figure 5.4: Data (black dots) and observed data minus grain boundary and equipment regression functions (Red Line).

So the blue line in 5.3(a) is the regression function for the grains component and the red line is the observed data minus the other two fit components resulting in the residual graph, Figure 5.4. Therefore, the extent to which the red and blue lines lie on top of each other allow one to visually evaluate how well the regression function fits for a particular component. This can be seen in Figures 5.5(a) and

5.5(b).



(a) Circles are the model fit and the grains (b) Closer look at the grains component component of the model fit. The triangles are residual graph and model fit. the residual graphs of the grains component.

Figure 5.5: Regression function vs. residuals graph.

The residuals plot (red triangles) in Figures 5.5(a) and 5.5(b) are scattered far from the regression function (blue circles) especially as the frequency decreases. However, the fit produced by EIS in Figure 5.1 looked initially reasonable so only the residuals plots imply the regression function should be recalculated or the data reconsidered. In such cases, multiple regression function and residual graph comparisons were created without satisfactory overlap. Since other attempts at creating regression functions that closely fit the appropriate residuals graphs were similarly unsuccessful, the reliability of this data point was discounted.

A new regression function was created from different data in EIS (Figure 5.6(a)) but with a clear alignment between the regression function and the residuals graph (see Figure 5.6(b)). The new regression function more accurately represents the grains data as shown by Figure 5.6(b). In this diagram, the grains' regression function lies almost directly on top of the residuals graph.

Since the blue and red lines lay on top of each other well (more than they did in Figure 5.3(b)) one can conclude that the parameters used in this model accurately



Figure 5.6: YSZ data taken with the composition  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=23.4[17].

represent the grain interiors contribution to the impedance. This is important because the grain boundaries contribution to the total impedance is difficult to accurately fit. Similar calculations were applied to understand the grain boundary impedance. In this case, the grain boundaries also fit well (see Figure 5.7).



Figure 5.7: New regression function vs. residuals graph for grain boundaries.

For other compositions, some regression functions appeared to correctly describe part of the spectrum, usually the curve that represents the grain interiors, but the rest of the regression function would not match the data. Overall, this method allows one to gather information about regression function parameters from data that is unclear or whose grain/grain boundary impedances are not sufficiently separated from each other. Additionally, the program can be used to verify the accuracy of groups of ionic characterization parameters.

### 5.2 Measuring Composition

Once the sample was sputtered and measured, the compositions had to be accurately calculated. This was done by calculating the deposition rates of the individual zirconia and yttria targets. If these rates are known, the deposition rate of yttria can then be divided by the rate of yttria and zirconia combined to get the composition of yttria at a particular position. The same can be done for zirconia.

Calibration samples were made by sputtering individual samples of zirconia then yttria for 40 minutes each. The resulting thickness of various positions on the samples were measured using ellipsometry. From these measurements, an overall thickness map was created and equations defining deposition rates were produced. Previous thickness measurements made from the same sputtering chamber showed that the thickness maps of sputtered materials make concentric ellipses of similar thicknesses with the center located in the middle of the targets. Once the thickness at a particular position is known, the deposition rate was found by multiplying by the density of the material and a small square area defining the position and then dividing by the atomic weight and deposition time (40 minutes).

$$Rate of Material Deposition = \frac{Thickness \times \rho \times SquareArea}{AtomicWeight \times DepositionTime}$$
(5.3)

## CHAPTER 6 RESULTS

The major results of this thesis include studies of the phase structure based on x-ray diffraction graphs shown in Section 6.1, impedance spectroscopy examples and residuals plots are in Section 6.2, conductivity vs. compositions graphs are examined in Section 6.3, and activation energy calculations taken from conductivity measurements at three temperatures in Section 6.4.

### 6.1 X-Ray Diffraction

A Rigaku Smartlab X-ray diffractometer was used to gather phase data for select points on the composition-spread. The six points that were examined had the composition  $\operatorname{Zr}_{1-x}\operatorname{Y}_x\operatorname{O}_{2-x/2}$ , where x=8.7, 11.7, 15.6, 23.2, 26.4, and 29.8. These points were chosen because the first two represent zirconia-rich compositions and the last three represent yttria-rich compositions. Such measurements were made to study the types of phase structures that were produced by the range of compositions.

A Cu-K $\alpha$  x-ray of wavelength 1.541867 Angstroms, 40 kV, and 44 mA was directed at the sample. A continuous scan of 3 degrees/minute was made at each position and an x-y stage was used to measure the diffraction at planned positions. The scan step was 0.010 degrees for a scan range of 20.0-70.0 degrees. The resulting diffraction peaks can be seen in Figure 6.1 and in greater detail in Figures 6.2 and 6.3.

Given the x-ray wavelength, a shaping factor (K) of 0.9, an estimated full width range at  $1/2 \max (\beta)$  between 0.0021 and 0.0092 radians and an estimated  $\theta_B$  of



Figure 6.1: X-ray diffraction graphs of intensity diffractions had the composition  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=8.7, 11.7, 15.6, 23.2, 26.4, and 29.8. The graphs are stacked by increasing composition as indicated. The strong peaks representing the platinum electrodes and aluminum oxide substrate are labelled.

about 0.264 radians for the measured composition range, the grain sizes could be calculated by the Scherrer Equation. The resulting grain sizes were about 15-30 nm. This is consistent with previous calculations made by Leo Small [22].

Jade version 9.3.1 searched the International Center for Diffraction Data (ICDD) Database, which contains about 250,000 patterns, to find and match diffraction peaks at given  $2\theta$  values to previously measured peaks.

Figure 6.1 shows two major peaks. The peaks at  $39.76^{\circ}$  and  $46.2^{\circ}$  are indicative of platinum which, according to pdf #01-071-3756, has (111) and (200) peaks at

 $39.758^{\circ}$  and  $46.237^{\circ}$ , respectively. The peak at  $37.75^{\circ}$  indicates the presence of aluminum oxide as the substrate, according to pdf #01-070-7050 which has a peak at  $37.766^{\circ}$ . The peak at  $33.9^{\circ}$  was unidentified and could not be detected on the general area detector diffraction system (GADDS).



Figure 6.2: X-ray diffraction graphs of intensity diffractions had the composition  $\operatorname{Zr}_{1-x}\operatorname{Y}_x\operatorname{O}_{2-x/2}$ , where x=8.7, 11.7, 15.6, 23.2, 26.4, and 29.8 with a  $2\theta$  range of 27-31°. The graphs are stacked by increasing composition as indicated. This shows the transition from the monoclinic and tetragonal  $\operatorname{ZrO}_2$  phases for  $8.7 \le x \le 11.7$  compositions to the cubic and tetragonal YSZ phases at compositions with greater amounts of yttria.

As shown in Figure 6.2 the zirconia-rich compositions have two peaks around  $28.1^{\circ}$  and  $30.2^{\circ}$  which come from monoclinic and tetragonal  $ZrO_2$  as these have strong (-111) and (101) peaks at  $28.050^{\circ}$  (pdf #01-074-0815) and  $30.233^{\circ}$  (pdf #01-070-6627), respectively. The yttria-rich compositions have two merging peaks

around 30.1° from cubic and tetragonal YSZ, which have strong (111) and (101) peaks at 30.102° (pdf #01-070-4426) and 30.169° (pdf #01-070-4436), respectively. By studying the diffraction graphs at 30.2° and 30.1°, one can see the transition of the (101) diffraction plane change from the  $\text{ZrO}_2$  tetragonal phase in zirconiarich compositions to the YSZ tetragonal phase in yttria-rich compositions. Close-inspection of increasing yttria-rich compositions graphs show the broadening of the peaks to include the (111) plane of cubic YSZ. Figure 6.2 shows the overall transition from monoclinic and tetragonal  $\text{ZrO}_2$  to tetragonal and cubic YSZ.



Figure 6.3: X-ray diffraction graph of intensity diffractions had the composition  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=8.7, 11.7, 15.6, 23.2, 26.4, and 29.8 with a  $2\theta$  range of 27-31° with a  $2\theta$  range of 58-64°. The graphs are stacked by increasing composition as indicated. This shows the transition from the monoclinic  $ZrO_2$  at (-213) phase to the cubic YSZ phase at (311).

Additionally, Figure 6.3 shows a peak for the zirconia-rich compositions at  $61.8^{\circ}$ , which is the (-213) peak at  $61.637^{\circ}$  for monoclinic  $\text{ZrO}_2$ . The picture also shows the yttria-rich compositions have a peak around  $59.7^{\circ}$ . This coincides with the strong (311) cubic YSZ peak at  $59.636^{\circ}$ . Figure 6.3 supports the hypothesis of monoclinic  $\text{ZrO}_2$  in the zirconia-rich compositions as well as cubic YSZ in yttria-rich compositions. The transition between monoclinic  $\text{ZrO}_2$  and cubic YSZ is obvious around x=15.6 since the monoclinic peak disappears. Also the peaks at  $59.3^{\circ}$  and  $59.9^{\circ}$  are hypothesized to represent tetragonal YSZ which has a (103) peak at  $59.419^{\circ}$  and a (211) peak at  $59.850^{\circ}$  according to PDF #01-082-1241.

The sample was annealed at 850°C and the measurements were made at the compositions  $Zr_{1-x}Y_xO_{2-x/2}$ , where 8.7 $\leq$ x $\leq$ 32.0. Phase diagrams by Stubican [26] and Scott [11] suggest the zirconia-rich side of x=8 should have tetragonal structures and at x=32 the composition should contain face-centered cubic structures.

Interestingly, monoclinic  $\operatorname{ZrO}_2$  structures were observed in positions with  $8.7 \le x \le 11.7$  along with tetragonal  $\operatorname{ZrO}_2$ . This implies that the majority of the grains are  $\operatorname{ZrO}_2$ , which would explain the low conductivity levels for these compositions. Also, the  $8.7 \le x \le 11.7$  range of compositions and those that immediately follow represent a phase transition in which the conductivity fluctuates. This is seen clearly in the left-half of Figure 6.4. The higher conductivities grow out of the compositions with higher amounts of yttria. Cubic YSZ at compositions with  $x \ge 23$  coincide with the phase diagrams.



Figure 6.4: Composition vs. conductivity of grains tested at 500°C on a linear scale. Notice the low conductivity for  $Zr_{1-x}Y_xO_{2-x/2}$ , for  $8 \le x \le 14$  where the phase structures are monoclinic and tetragonal  $ZrO_2$ . For  $15 \le x \le 32$ , the measured conductivity is  $2 \times 10^{-4}$  S/cm or greater, and the phase structures are tetragonal and cubic YSZ.

### 6.2 Impedance Spectroscopy Data

Impedance spectroscopy data support this phase change hypothesis as well as overall composition vs. conductivity trends. For example, at 400°C, when samples with  $x \le 13$  were measured, the resulting impedance spectroscopy graphs that were easy to interpret and model (similar to the  $\blacksquare$  data in Figure 6.5). For compositions with  $Zr_{1-x}Y_xO_{2-x/2}$ , where  $13\le x\le 16$ , the impedance spectroscopy was measured and the resulting graphs were difficult to discern (like the • data in Figure 6.5). For compositions with  $x\ge 16$ , measuring the impedance spectroscopy resulted in graphs that were easier to read again (like the  $\blacksquare$  data in Figure 6.5). This trend of differently shaped impedance spectroscopy graphs implies there is some change in the material due to composition, like a phase change.



Figure 6.5: Two impedance spectra taken at the same temperature  $(400^{\circ}C)$  and composition (x=13.5). The • symbols represents data that was taken first, but was difficult to interpret. So the data was retaken and is represented as  $\blacksquare$  symbols.

Data that was similar to the initial  $\bullet$  data was generally not used in data analysis. This explains the lack of data for the composition range  $13 \le x \le 16$  in the composition vs. conductivity graph.

The relationship between impedance and resistivity for YSZ was calculated in Equation 5.1 and examples of impedance spectroscopy data are shown in Figures 6.6 and 6.7. Both data sets (which were measured at 500°C and 300°C, respectively) show that as the yttria content increases, up to about x=23, impedance values decrease because the resistivity of the material decreases. For compositions with  $x\geq 23$ , the resistivity is greater, making the impedance measurements larger.

Examples of the residuals plots for measurements are shown in Figures 6.8(a)



Figure 6.6: Examples of impedance spectroscopy data at 500°C. Compositions represented by squares ( $\blacksquare$ ) had x=11.2, red circles ( $\bullet$ ) represent compositions of x=14.5, green triangles ( $\blacktriangle$ ) represent compositions containing x=22.1, and the blue triangle ( $\checkmark$ ) represents compositions of x=29.4.

and 6.8(b). Additional examples are shown in Figures A.1, A.2, and A.3 taken at 500°C and Figures A.4, and A.5 for 300°C.

These residuals graphs of the grains show much stronger agreement with the models than the graphs produced from samples with parallel plate contacts, as in Figures 5.5(a) and 5.5(b). Not only do these graphs show very little error for the grains, grain boundaries models that fit the data are easily discernible from models with a lot of error. For an example of this, see Figures A.4 and A.5 as residuals graphs representing well- and poorly-modeled grain boundaries (respectively).



Figure 6.7: Examples of impedance spectroscopy data at 300 °C. Compositions represented by squares ( $\blacksquare$ ) had x=10.8, red circles ( $\bullet$ ) represent compositions of x=14.9, green triangles ( $\blacktriangle$ ) represent compositions of x=23.6, and the blue triangle ( $\checkmark$ ) represents compositions of x=29.4.



(b) Residuals plot at x=14.9 for  $300^{\circ}$ C.

Figure 6.8: Residuals graphs taken at similar composition at different temperatures using interdigitated electrodes.

### 6.3 Ionic Conductivity Analysis

Figure 6.9 shows that for this study (×) there is an overall increase in conductivity as the x in  $Zr_{1-x}Y_xO_{2-x/2}$  increases to a critical value, x=26.8, after which the conductivity decreases. This is similar to the literature although the composition of peak conductivity for thin films made by Jung et al. has a peak at x=13[27]. Despite the difference in peak conductivity amounts of yttria, the experimental results have similar curvature and relatively large ionic conductivities when compared to literature values, like the bulk single crystals studied by Filal et al.[28]. Additionally, the experimental results achieved with interdigitated electrodes have higher ionic conductivities than previous results found with planar electrodes. This shows that the methods have been improved and are relevant to the field.



Figure 6.9: Composition vs. conductivity of grains (including literature values).

### 6.3.1 Experimental Results & Literature Values

The overall shape of the conductivity vs. composition graphs is affected by the amount of yttria in the YSZ samples. As the material is doped with more yttria, the measured conductivity increases because there is a higher concentration of oxygen ion vacancies. However, the conductivity reaches a maximum value, around x=27, at which point increasing the amount of yttria causes the conductivity to decrease. This is caused by an overabundance of oxygen vacancies stuck in clusters of associate pairs, which is when a yttria ion and oxygen ion form a bond [29]. If a material has too many associate pairs, the associated oxygen ions are immobilized. This also inhibits the movement of other ions. Doping zirconia with more than x=27, decreases the measured conductivity and the energy to break the associate pair bonds (disassociation energy) increases.

### 6.3.2 Measured Conductivity

Conductivity was calculated as the inverse of resistivity from impedance spectroscopy models. However, this conductivity includes all charge carriers in the sample. Since the charge carriers could be electrons and holes in addition to oxygen ions, the measured conductivity cannot be called oxygen ionic conductivity. Literature experiments and this thesis assume that the measured conductivity is mostly ionic conductivity with only a negligible effect from electrons, holes, or non-oxygen ions. However, it is important to acknowledge the possible existence of other charge carriers in the system.

### 6.3.3 Sources of Error and Variance

The residuals plots allow one to visually discern models which accurately represent grain-parameters from models that do not. This was the limit of error analysis for the models because any variance from this would still produce values well within an order of magnitude of the true result and choosing appropriate models is the best way to improve the accuracy of this part of the system. The goal of this combinatorial study was to measure ionic conductivity, within an order of magnitude, for a wide range of YSZ compositions. So, for our purposes, the accuracy produced by checking the models against residuals plots was sufficient.

However, there are other sources of error and variability that must be considered; mainly the equipment used for data acquisition. The effects of the resistance and capacitance of the palladium needles, wire and set-up are accounted for and removed by the circuit model. One way to quantify the variance is to take ten impedance measurements at 10 different positions corresponding to the same composition. By taking multiple measurements in the same place, the grain conductivity can be calculated for each and compared. The range of results would show how much variance a measurement has. By performing the same experiment at different positions with the same composition, one can quantify the effect of position.

The position is sure to increase the measurement variance. The range of results of different positions will probably be greater than the range at the same position due to temperature variation. This hypothesis comes from the 10-30°C change in temperature that was measured across the sample with a k-type thermocouple. It is possible that the ionic conductivity isnt linearly affected by temperature as assumed in this hypothesis. To more precisely examine how temperature affects ionic conductivity, it would be ideal to take multiple impedance spectroscopy measurements at the same position at a few different temperatures with the sample on an enclosed heater. By isolating the temperature variable one can calculate how a variation of 30° C would affect the ionic conductivity and error bars could be applied accordingly.

An enclosed heater was not available so such experiments were not performed for this study. The variance was found by calculating a trend line through seven points in the composition vs. conductivity graph. The actual ionic conductivity values were subtracted from the trend line conductivity values, squared, and added together. This root mean square was divided by the average of the original data and multiplied by 100 to achieve a variance of about 15.4%.

### 6.3.4 Error Bars

Most conductivity vs. composition graphs in the literature do not include error bars. A notable exception is the study by Jung et. al for which error bars were calculated based on the data fitting procedure [27]. The data fitting procedure for this research has been discussed through the residuals graphs, so error bars were calculated by temperature variation. Each composition experiment was performed at three different temperatures which varied by about 100°C, so the appropriate change in conductivity for each temperature was calculated. Then the conductivity corresponding to 30°C change was applied as error bars. The result is shown in 6.10. Some error bars are disconnected from the graph because the error exceeds the measured value. This generally occurs for compositions of  $x \leq 17$ , but the overall trends remain. In the future these composition samples especially need temperature control.


Figure 6.10: Logarithmic graph of composition vs. conductivity measurements of samples at 500°C ( $\times$ ), 400°C ( $\blacksquare$ ), 300°C (+). Error bars were calculated from the temperature variability of the sample.

### 6.4 Activation Energy Calculation

Figure 6.11 compares the conductivity vs. composition of YSZ for the three temperatures:  $300^{\circ}C$  ( $\blacktriangle$ ),  $400^{\circ}C$  ( $\bullet$ ), and  $500^{\circ}C$  ( $\blacksquare$ ). Lines were calculated to fit each temperature to calculate activation energies for each temperature. All three datasets show that conductivity increases with increasing composition up to a plateau before hitting a critical value and decreasing. As described in the previous section, this trend is also seen in the literature. An important difference between experimental results and the literature is the activation energy. The activation energy of a system can be calculated using an Arrhenius plot. This is because the

equation for activation energy is

$$\sigma_o T = A + exp(-E_a/kT) \tag{6.1}$$

$$ln(\sigma_o T) = ln(A) - (E_a/kT) \tag{6.2}$$

 $\sigma_o$  is the conductivity of the composition at a given temperature, T. A is related to diffusion, and k is Boltzmann's constant. Thus, taking the natural log of both sides drops the  $\ln(A)$  term as a constant and graphing against  $\frac{1}{kT}$  leaves the activation energy as the slope of the line.

By performing these calculations using the conductivities from the model lines in Figure 6.11 the activation energies were approximated. At  $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$  where x=11.5, the activation energy was estimated around 0.644 eV and at x=12.3, the activation energy was estimated to be about 1.08 eV. This is comparable to Wanzenberg's x=11 sputtered samples which had activation energies around 1.16 eV [30].

The reason the conductivity is tested at lower temperatures is to find the lowest temperature and overall resistance for a potential electrolyte.  $R \ (= \frac{thickness}{\sigma A})$  at 300°C or 400°C is larger than ideal (10<sup>-3</sup> S/cm or lower) but the material could be made an order of magnitude thicker or in be produced in bulk (which would lower the ionic conductivity) to make it suitable for mobile products.

Activation energy is significant because it is a combination of the enthalpy of migration and the enthalpy of disassociation. The enthalpy of migration is the amount of energy required to move an oxygen ion from one interstitial site to another interstitial site. The enthalpy of disassociation is the energy required to break oxygen ion and yttrium ion associate pairs that form as a result excess yttrium. This should be considered in further  $E_A$  analysis.



Figure 6.11: Log graph of composition vs. conductivity at three different temperatures:  $300^{\circ}C(\blacktriangle)$ ,  $400^{\circ}C(\bullet)$ , and  $500^{\circ}C(\blacksquare)$ . Includes fitting lines for each temperature.

# CHAPTER 7 DISCUSSION

The major achievement of this project was proving the ionic conductivity data from a binary YSZ composition spread to be better than the bulk material for some compositions. This is seen for compositions of  $Zr_{1-x}Y_xO_{2-x/2}$ , where x;20 compared to Filal et al. in Figure 6.9 [28]. These promising results encourage further testing of other materials combinations and signify improvements in the process of making the sample. Designing and fabricating interdigitated electrodes allowed for a more appropriate range of resistance measurements and will allow for high ionic conductivity measurements to be taken of future materials.

The purpose of this study was to verify combinatorial methods and learn about how changes in composition affect ionic conductivity. It was shown that increasing the amount of an appropriate dopant in zirconia increased the oxygen conductivity, until about x=26, after which the oxygen conductivity decreased. Another interesting observation is that the ionic conductivity has a peak at about x=26 while literature values show a peak around  $9 \le x \le 15$ . By these measurements, it would seem advantageous to study compositions of  $x_i^2 20$  since studies in the literature generally do not explore this area but our experiments found a peak conductivity around x=26.

The YSZ results should be taken further by testing YSZ doped with scandia and analyzed with a ternary spread. Scandia is an appropriate candidate because, like yttrium, scandium is a group 3 element with an ionic radius that is smaller than zirconium. The positive charge of the dopant ion draws the oxygen ions, but having a smaller radius is advantageous because it leaves more space for the oxygen ions to pass. Also, scandia-doped zirconia is known to have a higher ionic conductivity than YSZ [31], so a combinatorial study of both dopants should result in high ionic conductivity measurements at relatively low temperatures.

The scandia-doped YSZ should also be studied at 300, 400, and 500°C, although the heating-mechanism could be adjusted for improved accuracy of the impedance measurements. The accuracy of the heater is less important, but the temperature uniformity could be improved. In previous experiments, measurements on a wafer could vary from 10-30°C which make it difficult to attribute a change in conductivity to a variation in composition rather than temperature.

Another possible combination that could be explored is gadolinium or samariumdoped cerium-oxide since cerium ions are +4 charged and can be replaced by similarly-sized lanthanide-ions to conduct oxygen ions.

## APPENDIX A

#### ADDITIONAL RESIDUALS GRAPHS

Residuals plots of compositions at 500°C and 300°.



Figure A.1: Residuals plot of data taken at 500°C with  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=11.2 using interdigitated contacts.



Figure A.2: Residuals plot of data taken at 500°C with  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=22.1 using interdigitated contacts.



Figure A.3: Residuals plot of data taken at 500°C with  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=29.4 using interdigitated contacts.



Figure A.4: Residuals plot of data taken at 300°C with  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=10.8 using interdigitated contacts. The grain boundaries are relatively well-represented by the model.



Figure A.5: Residuals plot of data taken at  $300^{\circ}$ C with  $Zr_{1-x}Y_xO_{2-x/2}$ , where x=23.6 using interdigitated contacts. The grain boundaries are not well-represented by this model. To use this grain boundary data, it would have to be fit to new model parameters.

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