A MULTI-LENGTH SCALE APPROACH TO CORRELATING SOLID OXIDE FUEL CELL POROUS CATHODE MICROSTRUCTURE TO ELECTROCHEMICAL PERFORMANCE

By

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To my parents Marijana and Dragan Gostović (Mama i Tata)
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Solid oxide fuel cells (SOFCs) are a fuel and application flexible technology which may help the United States on its path to energy independence. The commercialization of intermediate-temperature SOFCs (IT-SOFCs) is limited by cathode and electrolyte polarization resistance. In an effort to understand the effect that sintering and doping processing conditions have on cathodic polarization, a multiple length scale characterization approach has been developed to study SOFCs. The technique utilizes a focused ion beam / scanning electron microscope (FIB/SEM), transmission electron microscope (TEM) and a local electron atom probe (LEAP).

The electrochemically active region of a strontium iron doped lanthanum cobaltite (LSCF) cathode was for the first time reconstructed in three dimensions using a FIB/SEM. Various microstructural properties were measured including overall porosity, closed porosity, graded porosity, surface area, tortuosity, and pore size. Electrochemical Impedance Spectroscopy (EIS) data was correlated to microstructure.

Microstructure and chemical segregation of composite cathodes were also analyzed using the FIB/SEM technique. The cathode/electrolyte interface was characterized with TEM-Energy Dispersive Spectroscopy (TEM-EDS) where calcium doping was found to have a significant
effect on cathode microstructure. Higher calcium concentration samples had a coarser composite cathode microstructure. The cathode/electrolyte composite cathode interface was characterized via TEM-EDS line and point scans. The most significant difference seen was the coarser sample having a higher calcium content in both electrolyte and cathode phases by 1 and 1.4% respectively. The active regions of composite cathodes were further analyzed and for the first time the complex 3-D network topological connectivity has been measured. Such novel connectivity quantification allows for an advanced understanding of the transport processes in composite materials.

An atomic resolution, LEAP microscope has been used for the first time to characterize SOFC materials. Two separately processed Siemens Energy Incorporated composite cathodes were analyzed. The scandium doped zirconia (SSZ) / calcium doped lanthanum manganate (LCM) buried interface was micro-machined into an atom probe tips and analyzed with the LEAP. Magnesium was found to segregate beyond the 10 nm wide interface another 10+ nanometers. Interfacial voids were found to be hydrogen enriched. Two-dimensional concentration profiles offer a glimpse at atomic segregation near electrochemically active triple phase boundaries (TPBs).
CHAPTER 1
GENERAL INTRODUCTION

Solid oxide fuel cells, often referred to as SOFCs are efficient, environmentally friendly, and fuel flexible electrochemical devices which generate electrical power, heat and water. They consist of three basic layers: cathode, electrolyte, and anode. The functional requirement for the cathode is that it is a porous catalyst for the reduction of O$_2$. The anode layer is a porous catalyst for the oxidation of fuel (H$_2$). Sandwiched in between the cathode and anode is the electrolyte which needs to be sufficiently dense to prevent mixing of the H$_2$ and O$_2$, an ion conductor and an insulator to electrical current. A representative schematic of an Oxygen ion conducting SOFC can be seen in Figure 1-11.

The deregulation of power companies in recent decades, combined with growth in consumer electronics has brought intermediate-temperature SOFCs (IT-SOFCs) to the forefront of portable power. Everything from laptops, to cell phones, to military radios, to automobile and aviation air conditioning systems require a durable, high-power density mobile power source to run for long periods of time (5,000 hours). Fuel cells have a power density and size advantage over the current state of the art Li-ion batteries. They can potentially provide ten times the power density (3000Watt-hours per liter versus 300 Wh/l, (Figure 1-22), of such batteries. IT-SOFCs are feasible for mobile applications due to their sub-800 °C operating temperatures which accommodate consumer electronics thermal cycling requirements better than traditional high temperature SOFCs. Intermediate temperature operation allows the material requirements on the interconnect and balance of plant materials to be less stringent, and less expensive. This cost reduction associated with the IT-SOFC’s balance of plant materials makes them more commercially viable than traditional high temperature SOFC systems. A disadvantage of reduced operating temperatures is increased cathodic polarization. This
polarization loss may be reduced with material selection of fast kinetics materials such as La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-δ}$ (LSCF), and optimization of microstructure for low temperature operation. But the effect on long term durability must also be better understood when using such fast kinetics materials often with nano-sized microstructures. Stability of IT-SOFCs is a key requirement for successful commercialization.

In accordance with these issues and requirements, the proposed study’s focus is the correlation of microstructure and electrochemical performance of various SOFC cathodes. The study will be three pronged: (a) processing of various microstructure single phase, and composite cathodes, (b) performance testing of these materials using electrochemical impedance spectroscopy (EIS) and (c) characterization of electrochemically active cathode regions using a dual-beam focused ion beam/scanning electron microscope (FIB/SEM), a transmission electron microscope (TEM), and a local electron atom probe (LEAP).
Figure 1-1. Schematic Diagram of Solid Oxide Fuel Cell

CHAPTER 2
BACKGROUND

2.1 Cathode Background

The basic function of an SOFC cathode is to reduce oxygen species using the electrons coming from the external load connection. The basic chemical formula of this process is shown in Equation 2-1.

\[ \frac{1}{2}O_2 + V_o^{**} + 2e^- = O_o^x \]  

(2-1)

Due to the high operation temperatures of SOFCs (600-1000 °C) only noble metals and electronic conducting oxides are feasible as cathode. Initially the most widely studied noble metals were platinum and silver. The problem with noble metals was their high cost and lack of long term stability due to coarsening, cracking and evaporation.\(^6\)

The first SOFC cathode suitable perovskite metal oxide was La\(_{1-x}\)Sr\(_x\)CoO\(_3\)-\(\delta\) (LSC) which was first published in 1966.\(^7\) In 1973 the favored perovskite SOFC cathode became La\(_{1-x}\)Sr\(_x\)MnO\(_3\)-\(\delta\) (LSM)\(^8\) thanks to its high electronic conductivity. Its crystal structure is based on the ABO\(_3\) perovskite structure\(^9\) and it conducts electrons via a small polaron conducting mechanism which results in electronic conductivities in excess of 100 S cm\(^{-1}\) at 950 °C.\(^10\) LSM is limited for IT-SOFC application by its low ionic conductivity of 10\(^{-7}\) S/cm (measured at 900 °C).\(^11\)

A SOFC with a purely electronic conduction cathode relies on the two-dimensional (2D) triple phase boundary (TPB) to reduce oxygen. The triple phase boundary (TPB) is the site between cathode, air and electrolyte where O\(_2\) can be directly reduced and incorporated into the oxygen vacancy, V\(_o\)^\(\cdot\) rich electrolyte. The regime in which this triple phase boundary exists is referred to as the active region. For cathodes such as LSM the typical TPB length for a cathode fired at 1100 °C is on the order of ~1 \(\mu\)m\(^{-1}\).\(^12\) This is a result of TPB distance divided by active area.
2.2 Mixed Conductor SOFC Cathode

The reduced operating temperature of IT-SOFCs makes highly electrocatalytic cathodes desirable. Use of a perovskite (Figure 2-1) mixed ion and electron conducting cathode (MIEC) boosts performance by extending the active layer depth thus improving the kinetics at intermediate temperatures (< 800 °C) regime\(^9,13\). MIEC cathodes such as La\(_{1-x}\)Sr\(_x\)Co\(_{1-y}\)Fe\(_y\)O\(_{3-\delta}\) (LSCF) are effective in extending this active region because the reduction of oxygen can occur anywhere on the surface of the cathode, and is not limited to a TPB\(^14\). A schematic comparison of the purely electronic cathode (LSM) and the MIEC cathode (LSCF) active regions can be seen in Figure 2-2. LSCF of typical composition La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.2}\)Fe\(_{0.8}\)O\(_{3-\delta}\) has an ionic conduction is 0.2 S cm\(^{-1}\)\(^{15}\), which is orders of magnitude higher than LSM\(^9\), despite LSM’s high electronic conduction. The \(\delta\) indicates oxygen non-stoichiometry, caused by crystallographic point defects. The use of such a MIEC with an extended active region and high ionic conduction is that the activation polarization of the cathode is decreased thus effectively increasing the potential power output of the IT-SOFC\(^{14}\).

2.3 Electrolyte Background

The modern electrolyte owes its origins to physicist Walther Nernst who initially proposed stabilized zirconia as a light bulb filament for incandescent light in the 1890s. But the considerable start up time required by zirconia to reach the 600°C operational threshold made it inferior to tungsten for this application\(^{16,17}\). These original startup time problems still plague SOFCs over a hundred years later.

The electrolyte must be stable in both oxidizing and reducing environments and have sufficiently high ion conductivity paired with low electronic conductivity in the SOFC operational temperature window. The first such feasible electrolyte was yttrium stabilized zirconia (YSZ). The initial 15 wt% Y\(_2\)O\(_3\) doping of ZrO\(_2\) was accomplished by Nernst in the
1890s, it was first used as a SOFC electrolyte by Baur and Preis in 1937. Throughout the years fluorite-structured and perovskite type materials have been applied as SOFC electrolytes. The main issues with the perovskite type electrolytes have been reaction with electrodes and higher cost than fluorite type electrolytes. Bismuth oxide, the highest oxygen ion conductor to date has been omitted from the study due to intermediate temperature degradation issues arising from a reduction around 600 °C. One of YSZ’s disadvantages is its reaction with LSCF above 1100 °C to form insulating phases. This study accordingly utilized a La	extsubscript{0.8}Sr	extsubscript{0.2}Co	extsubscript{0.2}Fe	extsubscript{0.8}O	extsubscript{3-δ} composition to further reduce the reaction with YSZ than the standard La	extsubscript{0.6}Sr	extsubscript{0.4}Co	extsubscript{0.2}Fe	extsubscript{0.8}O	extsubscript{3-δ} composition.

Zirconia possesses a fluorite structure at SOFC operating temperatures. Mobile oxygen vacancies are created by substituting Zr	extsuperscript{4+} with lower valence rare earth ions such as yttrium as shown in Equation 2-2.

\[
Y_2O_3 \xrightarrow{ZrO_2} 2Y_{Zr} + V_{O}^{\ast\ast} + 3O_X
\]  

(2-2)

From the electroneutrality condition we can surmise the oxygen vacancy concentration from the doping level, \([Y_{Zr}]=2[V_{O}^{\ast\ast}]\). This implies that the vacancy concentration is linearly related to doping with the trivalent cation. The ionic conductivity can thus be expressed as Equation 2-3.

\[
\sigma = zen\mu
\]  

(2-3)

Here \(z\) is the charge number, \(e\), the unit charge, \(n\) the number of charge carriers, \([e^+]\), and \(\mu\) the mobility of the vacancies. In the case of ion conductors like YSZ, analyzing their conduction using Arrhenius plots at various temperatures allows for the extraction of an activation energy. As seen in Equation 2-4 where \([V_{O}^{\ast\ast}]\) is the site fraction of mobile oxygen vacancies and 1-
the site fraction of unoccupied oxygen vacancies. To conduct ions the electrolyte has to have sufficient unoccupied oxygen vacancies in close coordination to the occupied ones so that

$$\sigma = \frac{A}{T} [ \text{Vo}^\cdot ] (1 - [\text{Vo}^\cdot]) \exp(-E/RT) \quad (2-4)$$

where A is the pre-exponential constant (which includes the number of equivalent sites per unit volume, temperature, particle charge, the Boltzmann constant, lattice constant, and vibrational frequency), E is the activation energy, R, the gas constant and T, the temperature. The total conductivity of zirconia depends on the dopant selection and doping concentration. The conductivity is maximized at specific concentrations which have been experimentally observed to occur at lower dopant concentrations than those predicted by Equation 2-4. Possible explanations for this are associated defect pairs formed between the dopant cation and the oxygen vacancy which effectively reduce vacancy mobility.

2.4 Research Method

The field of materials science and engineering exploits the relationship between a material’s microstructure, processing, properties, and performance. In this work we have studied the interfacial chemical segregation and microstructure of SOFC cathodes, and how they change with sintering temperature, doping and composition.

Much IT-SOFC work has been done on improving power density and reducing operating temperature, but not much has been done to correlate performance to actual 3-D microstructural or chemical properties. To achieve this, both composite and single phase cathodes were characterized in 3-D.

Two different cathode groups have been characterized: single phase cathodes comprised of sub-micron powders and micron sized composite cathodes. The single phase cathode has been deposited on micron grain sized, 100 micron thick YSZ substrates using a screen printing method which has been proven as a high power density IT-SOFC electrolyte deposition
technique \textsuperscript{23}. To eliminate variations in the cathode a commercially available LSCF powder (Praxair), a texanol-based vehicle (Electro Science Products) and a Thinky planetary centrifugal mixer, were used with thorough, uniform mixing of the screen printing ink \textsuperscript{24}. The symmetric cell cathodes were then sintered at an appropriate temperature (800-1200 °C) to yield a uniform film. Composite cathodes were processed by Siemens Energy, Inc. Similar composite cathodes have been previously studied by various groups \textsuperscript{19-23}.

\subsection*{2.5 Electrochemical Impedance Spectroscopy}

The single phase cathodes were analyzed in a symmetric cell setup using electrochemical impedance spectroscopy (EIS). EIS is commonly used to gauge the various polarizations occurring in an SOFC. A polarization is a loss of voltage theoretically available at a particular current density. This term is also known as an overvoltage and is commonly represented by the symbol $\eta$. There are three types of polarizations found in SOFCs: (a) ohmic; (b) concentration; and (c) activation.

Ohmic polarization stems from the fact that most materials exert a resistance to the flow of charged particles, which can often be described Ohm’s law. In an SOFC each of the electrodes and the electrolyte exhibit resistance to the flow of the respective charged particles, be they vacancies, electrons or holes. When all of the contributions are combined the ohmic overpotential, $\eta_{\text{Ohm}}$ is represented by Equation 2-5.

$$\eta_{\text{Ohm}} = \left( \rho_{\text{electrolyte}} l_{\text{electrolyte}} + \rho_{\text{cathode}} l_{\text{cathode}} + \rho_{\text{anode}} l_{\text{anode}} + R_{\text{contact}} \right)$$  \hspace{1cm} (2-5)

Here $\rho$ represents the specific layer’s porosity corrected resistivity, and $l$ represents the layer thickness. Any contact resistance in the system is represented by $R_{\text{contact}}$ \textsuperscript{17}. This polarization contribution can be modeled by a resistor since the response time is very fast.
Ohmic polarization would thus be affected by microstructural parameters such as film thickness, and by the composition of the electrode which is a materials selection issue.

Concentration polarization stems from the flow of gaseous reactants through the electrodes to the electrochemically active areas and the resultant outflow of reacted gases. On the cathode side it is linked to the binary diffusion of \( \text{O}_2 \) and \( \text{N}_2 \), \( \text{D}_{\text{O}_2-\text{N}_2} \), the cathode microstructure, partial oxygen pressures, and the specific current density. On the anode side it is linked to the binary diffusion (in the simple case) of \( \text{H}_2-\text{H}_2\text{O} \), the anode microstructure, partial hydrogen and water pressures and the specific current density. The cathode concentration overpotential is represented as Equation 2-6 \(^{17}\).

\[
\eta_{\text{conc}}^{\text{cath}} = \frac{RT}{4F} \ln \left( 1 - \frac{i}{i_{cs}} \right) \tag{2-6}
\]

Here \( R \) is the gas constant, \( T \), temperature, \( F \), Faraday’s constant, \( i \), specific current density, and \( i_{cs} \) the cathode limiting current density \(^{25}\), beyond which mass flow starts to limit electrochemical performance. The limiting current density term includes the partial pressure, effective diffusivity, temperature, and microstructural parameters \(^{17}\):

\[
i_{cs} = \frac{4Fp_{\text{O}_2}^{\text{cath}}D_{\text{cath}(\text{eff})}}{\left( p - p_{\text{O}_2}^{\text{cath}} \right) RTl_{\text{cath}}} \tag{2-7a}
\]

Where \( F \) is Faraday’s constant, \( p_{\text{O}_2}^{\text{cath}} \) the partial oxygen pressure on the cathode side, \( R \), the gas constant, \( T \), temperature, and \( l_{\text{cath}} \), cathode thickness, and \( D_{\text{cath}(\text{eff})} \), the effective cathode diffusivity is defined as seen in Equation 2-7b \(^{26}\).

\[
D_{\text{cath}(\text{eff})} = \frac{V_{\tau} \left( \text{D}_{\text{O}_2-\text{N}_2} \right)}{\tau} \tag{2-7b}
\]
where $D_{O_2-N_2}$ is binary diffusivity of O$_2$-N$_2$, $V_r$ is volume porosity fraction, and $\tau$ is tortuosity$^{26}$. Thus from Equations 7a-7b we can see the direct connection between cathodic concentration polarization and specific microstructural parameters.

From Equation 7 we also see that concentration overpotential increases non-linearly with current density. This polarization is commonly modeled by an equivalent circuit known as a Warburg element which is represented by a variety of resistors and capacitors$^{27}$. Here the non-zero capacitance capacitors ensure a non-zero response time, unlike the ohmic model circuit.

The time dependence can not be described by simple first order kinetics, but a characteristic time is defined based on the cathode thickness, $l_{\text{cathode}}$ and cathodic effective diffusivity, $D_{\text{cathode(eff)}}$ (Equation 2-8). Typically the characteristic time for a cathode is in the millisecond range$^{17}$.

$$t_{\text{characteristic}} \sim \frac{l_{\text{cath}}^2}{D_{\text{cath(eff)}}} \tag{2-8}$$

SOFC electrode concentration polarization is dominated by the cathodic contribution for two main reasons: (a) binary diffusion of H$_2$-H$_2$O (common SOFC fuel) on the anode side is upwards of five times faster than that of O$_2$-N$_2$ on the cathode side mainly due to the low molecular weight of hydrogen; and (b) partial pressure of hydrogen on the fuel side is greater than the partial pressure of oxygen on the air side. In short, we want to optimize and study the cathode, because it has a bigger effect on cell performance than the anode.

Activation polarization comes from the transfer of charge within the cathode, anode, or electrolyte phase which converts neutral species to charged ones and vice versa. For the reduction of oxygen there is a multiplicity of pathways for the reactions to occur and this is especially the case in an MIEC cathode which can conduct both electronic and ionic charges$^{28}$. This thermally activated process is in the simplest view limited by the slowest reaction step. It is directly related to the cathodic current flow, which has an associated loss in voltage known as the
activation overpotential. This overpotential is a function of material properties, microstructure, temperature, atmosphere and current density. The Butler-Volmer equation gives the current density as a non-linear function of activation polarization which for the cathode side is shown in Equation 2-9 17.

\[ i = i_0^{\text{cath}} \left\{ \exp \left[ \frac{\beta z F \eta_{\text{act}}^{\text{cath}}}{RT} \right] - \exp \left[ - \left( 1 - \beta \right) z F \eta_{\text{act}}^{\text{cath}} \right] \right\} \]  

(2-9)

where \( i_0^{\text{cath}} \) is the cathodic exchange current density, \( \beta \) is the transfer coefficient, \( z \) is electric charge, \( F \) is Faraday’s constant, \( \eta_{\text{act}}^{\text{cath}} \) is the cathode activation polarization. Note that this relationship is an implicit, nonlinear relationship between the activation polarization and the current density. Thus we can not explicitly solve for \( \eta_{\text{act}}^{\text{cath}} \) as a function of \( i \) unless we evaluate it at the limits; namely at the exchange current density (low \( i \), \( \left[ \frac{\beta z F \eta_{\text{act}}^{\text{cath}}}{RT} \right] << 1 \)) and the limiting current density (high \( i \), \( \left[ \frac{\beta z F \eta_{\text{act}}^{\text{cath}}}{RT} \right] >> 1 \)). For the low \( i \) case the relationship simplifies to 17:

\[ |\eta_{\text{act}}^{\text{cath}}| \approx \frac{RT}{z F i_0^{\text{cath}}} i \]  

(2-10)

For the high \( i \) case the relationship can be approximated as the Tafel equation 17, Equation 2-11.

\[ |\eta_{\text{act}}^{\text{cath}}| \approx \frac{RT}{\beta z F} \ln i_0^{\text{cath}} - \frac{RT}{\beta z F} \ln i \approx a + b \ln i \]  

(2-11)

Note here that the \( \frac{RT}{z F i_0^{\text{cath}}} \) term is in units of \( \Omega \text{cm}^2 \) and is known as the charge transfer resistance. Activation polarization’s thermal dependence tends to dominate IT-SOFC polarization at reduced operational temperature 17, 4 but to date a definitive relationship has not
been developed between the charge transfer resistance and microstructural parameters for MIECs. Hence, this research has an excellent opportunity to develop this relationship.

All three overpotentials sum to yield total cathodic polarization. The cathodes with the lowest symmetric cell total polarization under accelerated testing conditions will be promoted as candidates for durability testing. The IT-SOFC polarization may then be correlated to 3D microstructural and chemical changes.

2.6 Microstructural Analysis

Since cathode microstructure and morphology have a strong effect on cathode polarization, dual beam FIB/SEM will utilized to reconstruct actual 3-D models of the single phase and composite cathodes, and their electrolyte interfaces. This high resolution, 3-D technique allows for the quantification of critical microstructural properties such as surface area, tortuosity, interfacial porosity, and connectivity and correlation to electrochemical polarization.

The semiconductor industry has used the FIB since the 1980s to deposit, etch, micromachine, and image specimens during different stages of circuit processing. This technology was brought forward to reconstruct 3-D, geometrically complex sub-micrometer structures. With the advent of 3-D modeling software nano-tomography utilizing the dual beam FIB/SEM technique was used to quantify nano-ceramic suspended powders. This technique was recently applied to SOFC cermet anodes to quantify microstructural properties such as porosity, TPB length, and degree of anisotropy via tortuosity. Subsequently we have developed a similar technique to reconstruct a cathode and the cathode/electrolyte interface, and correlated EIS measured polarization to selected microstructural properties.

The automated sectioning and imaging will be conducted with a FEI Strata DB 235 FIB/SEM dual beam system. A schematic of the dual beam orientation is shown in Figure 2-3. The ion and electron pole pieces are oriented at 52°. The system has an in-situ liquid metal-
organic ion source (LMIS), for the deposition of protective platinum layers. Rastering the FIB across the region of interest physically sputters away material, which is redeposited locally. The field emission gun (FEG) SEM is utilized to image the freshly milled surface with a Through-Lens-Detector (TLD) down to a maximum resolution of 3 nm. The TLD deep hole contrast was used to distinguish between the electrolyte and cathode phases (Figure 2-4). To distinguish between the different detectors on the FIB/SEM please see Figure 2-5.

This process of slicing and imaging was automated with the use of Auto Slice and View software package (FEI Company). After the images are acquired Amira™-ResolveRT™ version 4.0 (Mercury Computer Systems Inc.) was utilized to align, segment, and concatenate the serial images into a 3-D triangular mesh (movie: http://hitec.mse.ufl.edu/, (Figure 2-6.6). Amira was used to quantify the surface area, volume porosity, graded porosity, and connectivity of the various phases.

Various groups have studied such phenomena as SOFC “break-in” during which IT-SOFC performance stabilizes, which last from 100-300 hours, but the microstructure analysis has been limited to 2-D. The combination of the EIS and the FIB/SEM technique allows us to reconstruct cathode microstructure so see what microstructural changes are occurring as a result of processing differences. This imaging was done at room temperature, under a $1 \times 10^{-7}$ torr pressure.

2.7 Chemical Analysis

Cathodes have been studied with transmission-electron-microscope/ energy-dispersive-spectroscopy (TEM/EDS) analysis to track chemical composition changes across the interface. When the FIB/SEM images are collected a TEM foil may be created using common liftout techniques. This chemical analysis will elucidate the presence of interfacial cross-diffusion during various stages of long term testing. The local electron atom probe (LEAP) technique has
allowed us to quantify the atomic segregation across cathode/electrolyte interfaces. A more in depth discussion of this is presented in Chapter 5.
Figure 2-1. Perovskite crystal structure. LSCF constituents are color labeled.

Figure 2-2. Common strategies for SOFC cathodes. (a) porous single-phase electronically conductive oxide such as (La,Sr)MnO3 (LSM); (b) porous single-phase mixed conductor; (c) porous two-phase composite. Reproduced in part with permission from Adler S.B. "Factors governing oxygen reduction in solid oxide fuel cell cathodes. Chem. Rev. 2004;104:4791 Copyright 2004, American Chemical Society.
Figure 2-3. FIB/SEM. (a) FEI Strata DB 235 Focused Ion Beam / Scanning Electron Microscope (FIB/SEM) (b) Beam orientation incident upon sample.

Figure 2-4. FIB/SEM phase contrast. Using the dual beam FIB/SEM it is possible to distinguish between electronic and ionic conducting phases as seen in this SEM image of a polished cross section of ruthenium doped bismuth oxide and bismuth oxide composite cathode.
Figure 2-5. Various TLD detector settings. (a) scanning, (b) backscatter -150V, (c) charging, (d) deep hole and (e) back scatter -250V
Figure 2-6. Schematic depicting transformation of 2-D images into a 3-D reconstruction and graded porosity.
COMPREHENSIVE QUANTIFICATION OF POROUS LSCF CATHODE MICROSTRUCTURE AND ELECTROCHEMICAL IMPEDANCE

3.1 Introduction

Current SOFC performance is limited by cathode polarization, which increases with decreasing operational temperature \(^{29,8}\). The SOFC cathode is a porous, conductive catalyst for the reduction of oxygen:

\[
\frac{1}{2}O_2 + V^{**}_o = O^{Y}_o + 2h^*
\]  

(3-1)

Cathode microstructure and morphology have a strong effect on this polarization \(^{29,8,30}\).

In an MIEC such as LSCF there are three primary polarizations in addition to the ohmic and concentration contributions. They are: charge transfer (which occurs when an oxygen ion is incorporated into the electrolyte), adsorption (where diatomic oxygen is dissociated into oxygen species on the cathode surface) and ionic conduction (where an oxygen ion is conducted through the cathode bulk). Possible pathways for the three additional processes are shown in Figure 3-31. We see that one pathway is oxygen diffusion to the TPB boundary via open pores. Another possible pathway is adsorption of oxygen onto the cathode surface where it dissociates and either is incorporated into the LSCF phase to be conducted by vacancy mechanism or is conducted along the LSCF surface en route to the electrolyte/cathode interface. Another possible route is grain boundary conduction of reduced oxygen which is reduced at the cathode/air surface. It is important to note that there is a multitude of possible pathways \(^{28}\), and we are not limited to just the three modes shown in Figure 3-31.

In this study a dual beam focused ion beam/scanning electron microscope (FIB/SEM) was utilized to reconstruct actual three-dimensional (3-D) models of La\(_{0.8}\)Sr\(_{0.2}\)Co\(_{0.2}\)Fe\(_{0.8}\)O\(_{3-\delta}\) (LSCF) cathodes, and their interface with a dense yttrium-stabilized-zirconia (YSZ) electrolyte. This high resolution, three-dimensional technique advances the understanding of the cathode
microstructure’s effect on performance. The identification of critical microstructural properties such as surface area, tortuosity, interfacial porosity, and topological connectivity were correlated to the ionic, electronic, and catalytic processes for a better fundamental understanding of electrochemical performance.

3.2 Experimental

Square LSCF symmetric cell cathodes (8 X 8 mm) were screen printed using premixed LSCF ink (NexTech Materials, Inc) on both sides of a 100 μm thick polycrystalline yttrium-stabilized-zirconia (YSZ) electrolyte (Marketech International, Inc.) using common screen printing techniques. After low temperature drying to eliminate the organic vehicle, the samples were sintered at various temperatures for one hour with a 5 degree per minute ramp up and down. The study incorporated sintering temperatures every 50 degrees between 850 and 1100 °C for a total of six sintering conditions. The resulting porous cathode films were approximately 20 μm thick.

Potentiostatic impedance measurements were collected at various atmospheres (300 ppm to 20.9% oxygen) and at various temperatures ranging from 550 to 700 °C at every 50 °C interval using a Solartron 1260 frequency-response analyzer under a potentiostatic modulation of 50mV. The frequency range was 10 MHz to 10 mHz with ten points per decade. Electrode contacts were made using a platinum mesh pressure contact and leads.

The automated sectioning and imaging was conducted with a FEI Strata DB 235 FIB/SEM dual beam system. The field emission gun (FEG) SEM was utilized to image the freshly milled surface with a Through-lens-detector (TLD) down to a maximum lateral resolution of 3 nm. The TLD’s charging contrast was used to distinguish between the electrolyte, cathode and open pore phases. The use of epoxy impregnation increased the open pore phase contrast and allowed for a 2-D image free of 3-D artifacts in the slice and viewing process (Figure 3-42). After
impregnation, the sample stub was polished down to a 1 μm roughness to planarize the surface and for assurance of the top surface being orthogonal to the interface. Epoxy mounting also allowed for mounting of all samples on one specimen holder, and four repeats were collected for each sintering condition, on both sides of the symmetric cathode (Figure 3-53). This FIB method was used to create a trench around the region of interest (ROI). The slicing (z-axis) resolution was 50 nm, which is optimal z-axis resolution for the >250 nm particle diameters. This process of slicing and imaging was expedited with the Auto Slice and View software package (FEI Company). Ion images were captured at regular intervals during the automated slicing, so as to corroborate the z-direction slice thickness. 20,000X was the imaging magnification during the slice and view for optimal microstructure resolution and quantification.

Amira™-ResolveRT™ version 4.0 (Mercury Computer Systems Inc.) was utilized to align, segment, and concatenate the serial images into a 3-D triangular mesh. The reconstruction volumes were cropped to 125 μm³ for each sample, with four (total 500 μm³) samples per sintering condition.

3.3 Results and Discussion

3.3.1 Microstructural Quantification

Six typical reconstructions of the blue/dark electrolyte phase and orange/light cathode phase (Figure 3-64) allow for qualitative observation of microstructure coarsening, as sintering temperature is increased. The microstructural properties of porosity, surface area, TPB length, particle diameter, tortuosity, were quantified for all six samples. Subsequent 3-D skeleton networks were quantified for connectivity, average topological length and orientation in the form of the measured average z-orientation (MAZO) angle.

The Amira™ tissue-statistics module was used to calculate the volume pore fraction. This module is able to count up all of the voxels of a phase in order to determine the volume pore
fraction. The porosity volume fractions ($V_v$) were tabulated in Table 3-1 and plotted in Figure 3-75. The volume porosity decreases with increasing sintering temperature. The 850 °C sample had a volume fraction of 0.56 which deviated slightly from the trend, but was identical to the 950 °C sample. The volume porosity versus sintering temperature trend agrees with coarsening theory whereupon as sintering temperature is increased, volume porosity decreases due to particle sintering.

Tortuosity ($\tau$) was measured using Amira™’s center of mass calculations. Tortuosity was quantified by tracking the center of mass of each pore as it goes from the surface of the cathode to the YSZ interface. The total length of this path was divided by the Euclidian distance between the air/cathode interface and cathode/electrolyte interface. Error bars were calculated from the standard deviation of the data for each sintering condition. There were four repeats for each sintering condition. Figure 3-75 (Table 3-1) displays the tortuosity versus sintering temperature. Maximum tortuosity is observed at the 950 °C processing condition. This occurs in the transition region between fine, loosely connected low sintering temperature and coarser high sintering temperature cathode particles. The intermediate well interconnected cathode may exhibit the highest tortuosity, as a result of the high surface area, high TPB length and connectivity.

The concentration polarization is related to the effective diffusivity of air through the porous cathode. The volume fraction of porosity divided by the tortuosity is related to the effective diffusion coefficient, $D_{(eff)}$ as shown in Equation 3-2.

$$D_{(eff)} = \frac{D \cdot V_v}{\tau} \quad (3-2)$$

$D$ is the diffusivity of $O_2$ through an unconstrained volume of air. A reduction in $V_v / \tau$ decreases the effective $O_2$ diffusion through the cathode resulting in an increase in any cathodic
polarization attributable to gas diffusion. It is evident that as the cathode is sintered the $V_v/\tau$ term decreases (Figure 3-5) due to coarsening of the microstructure at higher sintering temperature. Thus we would expect the concentration polarization to increase at higher sintering temperatures. The relationship between these (and other) microstructural features and measured impedance are shown in a subsequent section.

Amira™ tissue statistics module allowed for measurement of the surface area between the cathode, and open pores. The measured surface area (Table 3-1, Figure 3-86) is within the standard deviation of the previous studies and shows a maximum value near the 950 °C sintering condition. The volume normalized surface area (SA/Volume) results indicate that as the cathode sinters, the separated particles start to form necks, increasing surface area then with sufficient thermal energy the necks thicken and the cathode coarsens.

Another indication of microstructural coarsening is the triple phase boundary (TPB) length per unit area. The cross-sectional area normalized TPB length trend (Table 3-1, Figure 3-86) is similar to the surface area trend and shows a maximum value at the 950 °C processing condition. Just as neck formation increases surface area, it also increases the TPB length at the cathode/electrolyte interface. The initial dispersed particle TPB length is low and it increases with neck formation attributable to the coarsening process, which is common in covalently bonded solids such as this perovskite cathode. Such solids prefer to coarsen over sintering due to relatively high vapor pressures, which are caused by high vapor/cathode interfacial energy.

A common technique for particle/pore size calculations is the use of the BET formula $d=6V/S^{36,50}$. Measurement of both open pore and cathode particle diameters were conducted. The average cathode particle diameters (Table 3-1, Figure 3-97) exhibit the expected parabolic dependence on sintering temperature. It increases from 350 nm at the 850 °C processing
condition to ~500 nm for the 1100 °C condition. The lowest sintering condition appears to be an outlier (in diameter terms), perhaps because it is below the synthesis temperature for the precursor powders. This high diameter is also affected by the relatively low porosity for this sample. We see that the 850 °C sample appears to be an outlier in multiple microstructural properties, but we can not be sure without an even lower sintering condition, such as 800 °C, which was not studied due to poor adhesion to YSZ substrate.

The average open pore diameters (Table 3-1, Figure 3-97) decrease as sintering temperature increases through the necking regime, but then increases at high temperatures as sintering starts to occur. The latter affect being due to the formation of fewer but larger pore structures.

3.3.2 Connectivity Quantification

The connectivity was quantified using a newly developed skeletonization technique with the aid of the Amira software. Skeletonization takes the cathode or pore 3-D reconstruction, and through a number of iterations, thins the microstructure until only the structural center of mass is left (Figure 3-108). This center of mass network displays the interconnected nature of each phase, and allows us for the first time, to quantify topological connectivity. For a more in depth background of topological connectivity please refer to Gostovic et al. The pertinent connectivity values that were quantified were N, the number of vertices or nodes; E, the number of edges; \( <k> \), the mean degree or “connectivity”; L, the average topological network edge length; and \( k_{\text{max}} \) the maximum degree of a network (Table 3-2).

The open pore phase number of vertices for each sintering condition is shown in Table 3-2. The number of open pore vertices tends to decrease (within a fixed volume) as sintering temperature is increased. This indicates that the number of pores is decreasing. The cathode phase number of vertices for each sintering condition is also shown in Table 3-2. The number of
cathode vertices tends to decrease (within a fixed volume) as sintering temperature is increased. This indicates that the number of cathode particles is also decreasing.

The open pore phase number of edges for each sintering condition, shown in Table 3-2, indicates that there pore channels are formed as the cathode is sintered. The cathode phase number of edges for each sintering condition (Table 3-2) indicates that there are less inter-particle connections (or number of grain boundaries) as the cathode is sintered. The only exception is the 850 °C processing condition, which has less nodes and edges than the 900 °C condition. This is possibly caused by insufficient thermal energy relative to the LSCF powder synthesis (because at 850 °C, all that has happened is that the screen printing vehicle has been burned off) and what remains is a loosely connected and well dispersed volume of particles. The number of vertices and edges also indicates that we have sufficient numbers of particles and pores for proper counting statistics.

The mean degree or topological connectivity of both open pore and cathode phases are shown in Figure 3-119 and tabulated in Table 3-2. We can see that the connectivity is maximum at the 950 °C processing condition, for both the cathode and pore phases. This may indicate that the highest surface area, and highest TPB length is synonymous with highest connectivity microstructure. The fact that both phases exhibit similar connectivity magnitudes confirms that this is in fact a volume and size independent property. The difference in the profiles for the cathode and open pore phases may be attributable to the fact that the cathode phase starts to dominate the volume fraction at higher sintering temperatures, due to the occurrence of partial sintering in the cathode’s contraction.

The open pore and cathode phase average topological lengths (L) are plotted in Figure 3-1210 (Table 3-2) and both trend up with increasing sintering temperature. The trends agree with
the observation that the microstructure is coarsening (with the exception of 850 °C sample). Furthermore this corroborates particle diameter trends. It also shows that utilizing the BET formula for the pore particle size has its limitations because it uses global porosity and surface area measurements which do not distinguish between agglomerates and well dispersed particles. The network topology method separates the cathode and pore phases into individual particles which allows for a more precise measurement of particle size (topological length between adjacent particle/pore centers of mass). The network topological length is roughly half the magnitude of the cathode and open pore diameters due to the fact that two large particles are rarely going to be nearest neighbors in a hard shell, close packed system with a normal particle size distribution. The topological length distribution is skewed toward the short distance end which results in more short than long edge lengths. Furthermore, the cathode average topological length trend in Figure 3-1210 is greater than the pore phase because the pore network is more difficult to alter because is it not dependant on the transfer of mass which occurs during coarsening. Thus the pore phase network is more robust during the increased sintering conditions.

A way of quantifying the maximum mean degree within each network is to list the $k_{\text{max}}$ (Table 3-2). This property also helps to identify volumes where particle agglomerates may be present. This indicates that the 900 °C sintering condition had a massive vertex where 43 different pores were connected. Table 3-2 also indicates that the 1050 °C sintering condition had a massive vertex where 31 different cathode particles were connected. It is important to note that the $k_{\text{max}}$ was observed in just one volume, but there were three other volumes which may not have had such a high $k_{\text{max}}$. This means that although the $k_{\text{max}}$ was measured for all four repeats,
the $k_{\text{max}}$ was highest in one repeat. The lack of a trend in $k_{\text{max}}$ across sintering conditions indicates that agglomerates are randomly distributed.

A method for quantifying particle or pore orientation has also been developed. The measured average z-orientation (MAZO) of the skeleton network, is calculated with respect to the z-axis which is orthogonal to the cathode/electrolyte interface (Figure 3-1311). As the angle increases from 0° to 90° the path becomes longer and deviates from the z axis which is normal to the electrolyte/cathode interface. Thus, $\tau$ should increase with increasing MAZO and one would expect a MAZO angle of 45° for a completely random cathode network.

Figure 3-1412a-d shows the trends in orientation quantification which consists of: (a) the skeleton network orientation quantification MAZO angle (the average angle between all of the connecting edges in the skeleton); (b) MAZO SD (the standard deviation of all MAZO angles in the range 0 to 90°); (c) Not In Plane (NIP) angle, (which is identical to MAZO angle except that it omits edges which are in the Z-plane thus runs parallel to the cathode/electrolyte interface); and (d) percent In Z-Plane (% IZP) (quantification of the percentage of total edges which are in the Z-plane {parallel to the cathode/electrolyte interface}).

Figure 3-1412a (Table 3-2) plots the MAZO angles for both cathode and open pore phases. The open pore phase MAZO angles trend indicates that the open skeleton orientation is stable at the lower temperatures and starts to increase under high sintering conditions. The cathode phase MAZO angle trend indicates that the cathode skeleton orientation trends up with sintering temperature. For an in depth discussion of the definition of MAZO please refer to $^{51,52}$. In Figure 3-1412a we see that the MAZO angle tends to increase with coarsening starting close to the 54.7° angle that exists between adjacent, close packed atoms in the (110) plane and the $<100>$ direction in a BCC close packed hard sphere model. The increasing MAZO angle is in
agreement with the changes that occur during sintering attributable to cathode shrinkage. We see that both pore and cathode phase exhibit the same trend caused by cathode coarsening and partial sintering.

Figure 3-1412b plots the MAZO standard deviation (SD) and is an estimate of how wide the MAZO angle Gaussian profile is when incorporating the whole volume. Additionally the MAZO SD may have a slight decline due to the declining number of nodes as sintering temperature is increased.

Figure 3-1412c is a plot of NIP angle, which is the MAZO angle minus the edges in the plane parallel to the cathode/electrolyte (Z-plane). A rising trend in NIP angle is observed (similar to MAZO angle), but the low end starts around 45° which is expected when you have a 50% volume porous microstructure. This is proof that the rising trend in the MAZO angle is not limited by the slice thickness of the reconstruction. If the NIP angle trend was different from that of the MAZO angle then there would be concern that the cathode network is limited by the z-axis slicing thickness. Thus this NIP angle just considers edges which are not perpendicular to the z-axis. These lateral network connections in the z-axis effectively increase the MAZO angle of the sample as a whole even though they are not responsible for vertical flow of charge carriers from the air/cathode surface down to the cathode/electrolyte interface.

Figure 3-1412d is the percent of edges in-z-plane (%IZP). The %IZP plot indicates that roughly 20% of the total edges in a typical cathode (or pore) network volume are in the Z-plane. The lack of a trend in the %IZP may be indicative of a relatively isotropic network. The %IZP indicates how many of the total network connections allow for lateral flow of air and charge carriers. This property may be important for studying the critical dimensions of current
collectors on top of cathodes. Thus if 20% of the total surface of a cathode is laterally connected
this would aid researchers selecting current collectors of appropriate mesh size.

3.3.3 Electrochemical Impedance Spectroscopy

Prior to serial sectioning, electrochemical impedance spectrometry (EIS) was performed on
all six symmetric cathode samples at various temperatures and oxygen partial pressures. The
study utilized EIS to characterize the cathode performance across the various sintering
conditions. A typical Nyquist plot of the impedance scans collected at 700 °C in air is shown in
(Figure 3-15). The x-axis intercept is used to calculate the cathode ohmic resistance, once the
electrolyte contribution is subtracted out. We notice that with high sintering temperatures the
polarization resistance increases dramatically. All of the samples imaginary and real
polarizations increase with sintering temperature, except for at the lowest end, where the 850 °C
sample appears to have higher real impedance than the 900 °C processed sample, thus bucking
the trend. This may be a result of the poorly connected microstructure, once again isolating that
sample relative to the rest. If we look at the Bode plot of the same data (Figure 3-16) we
notice that the low sintering temperature samples have very low imaginary resistance but that all
of the processes become more convoluted due to less frequency separation.

J.R. Smith’s dissertation and recent publication discusses the process of deconvoluting
the different contributions to the polarization resistance in LSM, a predominantly electronic
conductor. As in the case of LSM, the highest and lowest frequency impedance is caused by
ohmic and concentration polarization, respectively. In the LSM we measured two additional
impedances caused by charge transfer polarization and adsorption polarization. However, here
we show the results of impedance deconvolution and relationship to microstructure for LSCF,
which is an MIEC, and thus has potential additional polarization contributions due to ionic
transport.
In order to deconvolute the gas diffusion process, low partial pressures of oxygen were used to resolve the different processes which contribute to concentration polarization. A plot of the 950 °C sintered sample measured at 700 °C with varying oxygen concentrations is shown in Figure 3-1715. Above 1% oxygen concentration two significant processes are readily discernable, one high frequency and one intermediate frequency. However, below 1% additional intermediate and low frequency processes appear. If we reduce the oxygen partial pressure further (Figure 3-1816) we enter a regime (below 0.32%) where bulk gas diffusion polarization resistance becomes larger than both intermediate frequency processes. Process 1 (whose polarization resistance is R1) is the highest frequency component and is commonly understood to be the charge transfer process contribution. The intermediate processes 2 and 3 (whose polarizations are referred to as R2 and R3, respectively) may be due to adsorption and ionic conduction (since this is an MIEC). Process 4 is dependant on pO\textsubscript{2} and is commonly regarded as gas diffusion polarization.

The process of deconvolution utilized herein is the series Voigt element approach where each process is modeled by a single resistance variable constant phase element, (R-CPE) in series as shown in Figure 3-1917. This process is described by J.R. Smith et al. 46,47. However, it is important to note (as pointed out in our previous work 46,47) that the process is somewhat subjective, may introduce some deconvolution error, and, moreover, a nested circuit model may be more appropriate. Unfortunately, the nested approach is more complex and we were not able to do it with the current data set. However, the overall results remain quite useful in understanding what effect microstructure has on the different polarization contributions.

The result of the deconvolution is shown in a plot of individual process polarization resistance versus sintering temperature (Figure 3-2018). In air (Figure 3-2018a) we see that the
ohmic contribution has a slight negative dependence on the sintering temperature perhaps caused by the previously observed decrease in porosity. Process 1 and 2 both increase significantly with sintering temperature, and the concentration process increases slightly with sintering temperature. Process 1 and 2 appear to have minima around the sintering condition near the sample with the highest TPB length (Figure 3-86).

At pO$_2$ ≤ 900ppm (Figure 3-18b), we are able to deconvolute an additional component, process 3 (R3) (Figure 3-1816). In Figure 3-2018b we see that this additional process (R3) has a slight negative dependence on the sintering temperature. This may be caused by an improvement in the path length of the cathode phase network. The bulk gas diffusion (concentration) process has a higher overall impedance than in air but seems to be independent of sintering condition, which is most likely due to the high porosities observed in these cathodes (~50 vol. %). With the reduced oxygen concentration, there is less dependence on the microstructure because the pores have excess pathway volume.

The O$_2$ partial pressure dependence is shown in Figure 3-2119. This confirms the assignment of the lowest frequency component to concentration polarization with a strong negative dependence on partial pressure. The ohmic and process 3 contributions have slight positive dependence on partial pressure, which can be attributed to the p-type conductivity of this material. Processes 1 and 2 have unclear dependencies throughout this range.

The measurement temperature dependence is shown in Figure 3-2220. In air (Figure 3-2220a) the ohmic, R1 and R2 activation energies are -0.5, -1.7, -1.4 eV, respectively. The ohmic polarization activation energy for this 50% porous cathode is twice as larger as previously measured ohmic activation energy (-0.08-0.29 eV) of dense cathodes$^{53}$. When the partial pressure is reduced to 900 ppm (Figure 3-2220b) the ohmic, R1, R2, R3 and concentration
activation energies are -0.4,-1.6,-1.6,-1.5, 0.4 eV, respectively. We see that the ohmic activation energy is decreased slightly, along with the R1 activation energy. The R2 activation energy increases at the reduced partial pressure. R3 has an activation energy in between that of R1 and R2. Concentration polarization activation energy is positive, and opposite the trend of all other processes confirming its not a thermally dependant process.

3.3.4 Microstructure-polarization Relationships

Increases in sintering temperature cause the concentration polarization resistance to increase due to the coarsening and eventual sintering of the microstructure (Figure 3-2018). This polarization resistance is affected by the effective diffusion coefficient of the cathode. When the negative of $1 - \frac{V_v}{\tau}$ is plotted versus concentration polarization (Figure 3-2321) a logarithmic relationship is seen with concentration polarization as Virkar shows for other SOFC concentration polarizations $^{14}$. This $-(1 - \frac{\tau}{V_v})$ effective diffusion term increases with the concentration polarization which means that it is more difficult for oxygen molecules to arrive at the electrochemically active region of the cathode as tortuosity increases and/or porosity decreases. Thus as the cathode is coarsened and then sintered the gas transport starts to become limited. The effect of this inverse $V_v / \tau$ term on concentration polarization is not significantly affected by the measurement temperature.

Similarly there is a relationship between the open pore phase MAZO angle and concentration polarization (Figure 3-2422). Concentration polarization increases with the pore phase MAZO angle. Thus as the MAZO angle increases the oxygen channel path becomes longer due to the increased average angle, thus increasing bulk transport resistance. We see that as the temperature is reduced this effect is magnified, thus the MAZO angle has great implications for IT-SOFC cathode concentration polarization.
If we compare the ohmic polarization measured in air at 600 and 700 °C to the cathode phase MAZO angle we also see a direct relationship (Figure 3-2523) which indicates that as the cathode phase’s MAZO angle increases so does the cathode’s ohmic resistance. This means that as the path deviates from being parallel to the z-axis, the ohmic polarization increases as would be expected for the increased path length.

The process 3 (R3) polarization resistance decreases with increasing cathode particle diameter and cathode connectivity (Figure 3-2624). This indicates that process 3 may be related to ionic resistance. This ionic resistance/conduction is dependant on the both the cross sectional area (cathode diameter) and the number of possible paths available (connectivity). Thus a porous cathode with a higher connectivity and a larger particle cross sectional area will have lower resistance to ionic conduction.

If we plot the R1 and R2 polarizations versus surface area and L\textsubscript{TPB} in air and at 900 ppm we see that both processes (higher R values) trend better with L\textsubscript{TPB} than with surface area (Figure 3-2725). This seems to agree with previous LSM studies\textsuperscript{46} where both charge transfer and adsorption processes had a strong dependence on L\textsubscript{TPB}. In that study by Smith et al. the slope of the series equivalent circuit fit of R\textsubscript{CT} as a function of L\textsubscript{TPB} was -3.5 and for the fit of R\textsubscript{ads} as a function of L\textsubscript{TPB} was -2.8. Additionally Smith showed that the slope of the series equivalent circuit fit of R\textsubscript{ads} as a function of surface area was -1.8. In our study the slope of the series equivalent circuit fit for R1 as a function of L\textsubscript{TPB} was -13.9 in air and -10.3 at 900 ppm O\textsubscript{2}. The slope of the series equivalent circuit fit for R2 as a function of L\textsubscript{TPB} was -10.7 in air and -11 at 900 ppm O\textsubscript{2}. As a function of surface area the R1 slopes were -30 and -21 for the air and 900 ppm conditions, respectively. The R2 slopes, as a function of surface area, were -23.5 and -20.1 for the air and 900 ppm conditions, respectively. Although the power slopes are very high
compared to LSM this is most likely due to the limitation of using a series Voigt model as opposed to a nested model. The general trend in the polarization versus surface area plot is similar to previous LSM studies of adsorption versus surface area\textsuperscript{46}, but the power fit slopes in the LSCF system are much higher than that of the LSM, indicative of increased LSCF sensitivity to changes in surface area and \( L_{TPB} \). In the LSCF system’s \( L_{TPB} \) dependence trend, R1 has a larger polarization resistance magnitude in air, but when the partial pressure is reduced to 900 ppm, R2’s polarization resistance magnitude becomes larger than R1’s. When comparing R1 and R2 polarization resistances with surface area, R1’s resistance is larger in air, but R2 is larger at the reduced partial pressure (900 ppm). This may be a sign that R2 is more dependant on partial pressure of oxygen which may indicate that R2 is the adsorption polarization related process. R2 is a lower frequency process than R1 (Figure 3-16) which indicates that it may be attributable to adsorption which is typically a slower process than activation polarization.. R2 has a lower residual for all plots (Figure 3-2725a-d) which makes it difficult to conclude that R2 is only attributable to the adsorption (surface area dependant) process. Likewise it is difficult to conclude that R1 is only related to the charge transfer process. With LSCF being an MIEC cathode the reduction reaction is not limited to the TPB site but it can occur anywhere on the LSCF surface. Thus the LSCF charge transfer process may exhibit a dependence on both the \( L_{TPB} \) and the surface area. The surface area and TPB length relationships with R1 and R2 are not conclusive, and further work needs to be done to separate out these two processes, which appear to be heavily intermingled in the LSCF porous cathode. One method to improve on this understanding may be to utilize a nested circuit model instead of a series circuit model when deconvoluting the EIS spectra.
3.4 Conclusion

In this study we successfully reconstructed in 3-D twenty four actual LSCF cathodes. We quantified the porous cathode microstructures at the sub-micron level. This technique has allowed us to quantify microstructural properties as a function of sintering temperature. Further, this technique has allowed us to develop the direct links between the microstructure and performance relationship of five different polarization contributions (including Ohmic) in the LSCF/YSZ system. The concentration polarization process was related to the effective diffusivity which is a function of volume porosity and tortuosity. An intermediate frequency process attributable to the mixed ionic electronic conduction in LSCF correlates well with cathode diameter and cathode topological connectivity. Two higher frequency processes attributable to activation and adsorption polarization had similar correlation to triple phase boundary length and volume normalized surface area. Although the power fits indicate that future nested circuit modeling is required for the MIEC LSCF system to fully understand the relationship between these two high frequency processes and microstructure. The triple phase boundary dependence should have diminished significance in an MIEC because the reduction process is not limited to the cathode/electrolyte interface. This reduction reaction may occur across the whole surface of the MIEC cathode. Despite this need for future study of the high frequency processes, we have developed direct links to microstructure using the series Voigt model for the ohmic, concentration and intermediate processes of the LSCF cathode.
Table 3-1. Microstructure quantification

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Porosity (fraction)</th>
<th>SA/Volume (1/μm)</th>
<th>Cathode diam. (μm)</th>
<th>Pore diam. (μm)</th>
<th>Tortuosity</th>
<th>tβ L (1/μm)</th>
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<tr>
<td></td>
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<td>avg SD</td>
<td>avg SD</td>
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<td>0.35 0.03</td>
<td>0.55 0.09</td>
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<tr>
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<td>1.44 0.02</td>
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<td>0.53 0.14</td>
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Table 3-2. Connectivity quantification

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<th>E</th>
<th>&lt;k&gt;</th>
<th>L (μm)</th>
<th>kmax</th>
<th>MAZO (°)</th>
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<table>
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<td>0.20 ± 0.01</td>
<td>18</td>
<td>55 ± 24</td>
</tr>
<tr>
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<td>5765</td>
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<td>2.97</td>
<td>0.22 ± 0.00</td>
<td>17</td>
<td>54 ± 24</td>
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<td>0.22 ± 0.00</td>
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<td>2.81</td>
<td>0.28 ± 0.03</td>
<td>31</td>
<td>56 ± 23</td>
</tr>
<tr>
<td>1100</td>
<td>4112</td>
<td>11545</td>
<td>2.78</td>
<td>0.27 ± 0.01</td>
<td>10</td>
<td>58 ± 24</td>
</tr>
</tbody>
</table>

N=number of vertices; E=number of edges; <k>=mean degree; L=average topological length
kmax=max degree; MAZO=Measured Average Z-Orientation angle *equal volumes compared 62.5 μm^3
Figure 3-3. Multiple oxygen reduction/conduction pathways in MIEC cathode.

Figure 3-4. Epoxy impregnated samples increased the analysis speed. Platinum cap was deposited over active cathode (a), trench was made around ROI (b), and phase contrast between the electrolyte, pore and cathode were excellent (c).
Figure 3-5. Six symmetric cathode samples mounted in cross section.

Figure 3-6. Six reconstructions of various sintered cathode/electrolyte interfaces.
Figure 3-7. Tortuosity, porosity and the porosity to tortuosity ratio plotted as a function of sintering temperature.
Figure 3-8. Cathode volume normalized surface area per unit volume and triple phase boundary length per unit area plotted versus sintering temperature.
Figure 3-9. Open pore and cathode particle diameters plotted versus sintering temperature.
Figure 3-10. Skeletonization in 2-D. Depiction of skeleton generation of single 2-D slice of pores in black and cathode in white (a), through multiple thinning iterations (b-d), and the final skeleton (e) with a higher magnification view of one vertex, (f).
Figure 3-11. Topological connectivity of cathode (open square) and open pore (solid circle) phases plotted versus sintering temperature.
Figure 3-12. Topological length of open pore (solid circle) and cathode (open square) phases as a function of sintering temperature.
Figure 3-13. MAZO angle schematic
Figure 3-14. Skeleton network orientation versus sinter temperature. Cathode phase (filled squares), open pore phase (open squares). (a) MAZO angle, (b) MAZO standard deviation, (c) NIP angle and (d) %IZP.
Figure 3-15. Nyquist plot of LSCF polarization measured at 700 degrees C. Ohmic resistance is at x-axis intercept.
Figure 3-16. Bode plot of imaginary impedance versus frequency, collected in air at 700 degrees C.

Figure 3-17. The partial pressure dependence on polarization resistance (Bode plot).
Figure 3-18. Bode plot of the 950°C sintered sample, collected at 700°C with varying low pO2.

Figure 3-19. Bode plot which displays the deconvolution process using Voigt elements in series.
Figure 3-20. Polarization resistance sintering temperature dependence (a) in air and (b) at 900 ppm oxygen measured at 700 C.
Figure 3-21. Partial oxygen pressure dependence of various processes for 950 C sintered sample measured at 700 C.
Figure 3-22. Measurement temperature dependence and activation energies (a) in air and (b) 900ppm of 950°C sintered sample.
Figure 3-23. Concentration polarization dependence on inverse of effective diffusion term at measurement temperatures.
Figure 3-24. Concentration polarization dependence on MAZO angle of open pore phase at various measurement temperatures in air.
Figure 3-25. Ohmic polarization dependence on MAZO angle at measurement temperatures.
Figure 3-26. Process 3 polarization is related to both cathode diameter and cathode connectivity. Measured at 700 C and 900 ppm oxygen.
Figure 3-27. Relationship between R1, R2 polarization resistance and TPB length at 900ppm (a) and in air (b), and surface area at 900ppm (c) and in air (d). Fits are power.
CHAPTER 4
THREE-DIMENSIONAL RECONSTRUCTION OF COMPOSITE CATHODES

4.1 FIB/SEM Microstructure Quantification of Composite Cathode

4.1.1 Experimental

An initial LCM/YSZ cathode supported sample was provided by Siemens Energy Inc., for a initial study to show the FIB/SEM 3-D analysis capabilities. We will call this Sample 1. This sample was analyzed utilizing SEM-EDS and FIB/SEM techniques, in order to gauge segregation at the LCM/YSZ interface. After the results on this sample were finished, two additional, different cathode supported SOFC samples were provided by Siemens Power, Inc. Sample 3 is the standard Siemens doped lanthanum manganate composition (WPC3) and Sample 4 is their new cathode material, similar to Sample 3 but with higher levels of calcium.

All three samples consisted of a composite cathode phase approximately 20 μm thick sandwiched between a coarse cathode support and dense electrolyte phase. A sample 1 cross section may be seen in Figure 4-281. A Struers EpoVac system was used to both impregnate the open pores of the samples and to mount them in cross section (Figure 4-292). Impregnation of open pores was conducted on samples 3 and 4 in order to allow for identification of closed pores. This resulted in better contrast over sample 1. Grinding/polishing was conducted down to 1 μm roughness to expose the cathode-electrolyte interface and to planarize the surface.

An FEI Co. Strata dual beam FIB/SEM was used to deposit a protective platinum layer over the area of interest, and then a C-trench was milled around it to reduce redeposition curtaining (Figure 4-303). The focused (Gallium) ion beam (FIB) serial milling and SEM imaging was automated using Auto Slice and View software (FEI Co.) with a slice thickness of 150 nm for sample 1 and 500 nm for sample 3 and sample 4. The sample 1 slice dimensions were found to be overkill for the 2-5 μm average cathode particle diameters. In order to increase
efficiency, and maintain a resolution of around five slices per particle the slice thickness was increased for samples 3 and 4.

Furthermore the slicing orientation for sample 1 was orthogonal to the cathode/electrolyte interface, which allowed all three phases to be imaged in each slice (Figure 4-281). In order to be able to quantify tortuosity the slicing direction was made parallel to the cathode/electrolyte interface for samples 3 and 4 (Figure 4-314).

Amira software was used to stack and segment the images yielding a three-dimensional (3-D) model and to quantify the microstructure. Surface area and porosity were measured using Amira’s Tissue statistics module. Average particle size was measured using the BET formula which stipulates that the average particle diameter is equal to six times the volume of a phase divided by the surface area of that phase \( d = \frac{6V}{S} \). Tortuosity was calculated using Amira’s Moment of Inertia module along with the 3-D formula for Euclidian distance. Amira was used to track the center of the open pore phase through the respective volume and then the 3-D Euclidean distance was calculated for all of the pores from the air-cathode free surface down toward the electrolyte-cathode interface. Tortuosity was measured as Euclidean distance sum over the thickness of the cathode.

Sample 1 was sliced over 160 times at 150 nm intervals to allow for a three-dimensional reconstruction. The voxel dimensions of the reconstruction were 118 x 153 x 150 nm. The reconstructed volume of 1250 \( \mu m^3 \) had outer dimensions of approximately 22 x 50 x 10 um. Sample 3 was auto slice and viewed as seen in Figure 4-3 with a total of 160 slices 0.5 \( \mu m \) thick. Sample 4 was sliced into 147 similar slices.

SEM imaging was conducted using a Through-Lens-Detector (TLD), which yielded excellent imaging contrast between open pore, cathode and electrolyte phases (Figure 4-314).
The TLD solid state detector is positioned within the SEM pole piece and was used on the deep-hole setting in order to get a better signal to noise ratio by attracting more stray electrons from the imaging interaction volume surface. The TLD allowed us to utilize the low kV increased Z-contrast in combination with charging contrast of the low electronic conductivity electrolyte phase to distinguish between the bright, electrolyte, mid-level, cathode, and dark, epoxy/pore phases. This was an extremely important contribution to the SOFC reconstruction field, as we were the first group to succeed distinguishing the electrolyte and cathode phases in a composite cathode. This work was submitted to Siemens Power Inc. in a 2007 preliminary report. The vertical striations observed are stray ion channels, which were “air-brushed” or cleaned in the reconstruction process.

4.1.2 Results and Discussion

Initial cross sections of Sample 1 indicated that the actual chemical interface was difficult to see using the JOEL high resolution FEG (field emission gun) SEM, due to insufficient contrast. Due to sample geometry complications backscattered detector images were not collected, which would have also been useful in identifying the true chemical interface. Thus SEM-EDS background scan was conducted to identify all of the elements present in the cross section (Figure 4-325). The main constituents observed were yttrium, zirconium, lanthanum, manganese, and calcium. A 16.7 μm long linescan was then collected with over 10,000 total counts, to allow for sufficient counting statistics (Figure 4-336). It was difficult (due to electrolyte charging) to identify the cathode/electrolyte interface without doing the EDS linescan. The linescan profiles (Figure 4-347) show that all the elemental profiles were relatively abrupt with the exception of the calcium, which seemed to be more segregated about the interface. This allowed us to identify the true cathode/electrolyte interface despite the electrolyte charging artifact. The interface seems to be lined with a collection of small pores (Figure 4-358).
The 150 nm thick stack of images was used to create 3-D reconstruction seen in Figure 4-369 with Amira software (Mercury Computer Systems, Inc.). The electrolyte is shown in orange and has some small closed pores 150-1100 nm in diameter. The blue composite cathode is 20 μm above the dense electrolyte (Figure 4-3710a-c). This composite cathode is characterized by pores larger than those found in the electrolyte but smaller than those found in the cathode support region as can be seen in the graded pore structure of Figure 4-3710d. The composite cathode pore diameter ranges between 1400-3300 nm. The cathode support pore diameter range is 2400-7500 nm.

To gauge the progression of the microstructure a phase fraction versus distance from electrolyte plot is shown in Figure 4-3811. We see that the YSZ is over 95% dense on the far left. The composite cathode thickness of 20 μm is further corroborated with this plot. The YSZ phase fraction starts to decrease at 11 μm and drops to zero at the 33 μm x axis mark. Beyond this region is the support cathode. The porosity of the composite cathode and the cathode support has an increasing trend between 10 volume % and 20 volume % moving away from the dense electrolyte. The low porosity was similar to the composite cathode porosity of 12-13 volume % seen in samples 3 and 4.

Sample 3 images were stacked, segmented and reconstructed to yield a total volume of 78246 μm³ (Figure 4-3912 and Table 4-31). The corresponding volume for sample 4 (Figure 4-4013 and Table 4-31) was 66527 μm³. The composite cathode was ~20 μm thick for both samples, similar to sample 1.

Graded porosity plot was created to visualize differences in phase volume fractions through the reconstructed volume with the X-axis representing distance from electrolyte and the Y-axis representing phase fraction (Figure 4-4114). The graded porosity plot allows for
quantification of the differences in phase fraction between Sample 3 and Sample 4. The main difference appears to be the profile of the cathode and electrolyte phases in the composite cathode. In Sample 3 the crossover is half way through the composite cathode region (denoted by gray arrow in Figure 4-4114a), where as in Sample 4 the cross over is close to the bulk electrolyte. The graded porosity plot also indicates that the average electrolyte phase fraction in the composite region of Sample 3 is 43% and the average cathode phase fraction of the composite region is 44%, indicative of a 48:52 volume ratio. The corresponding values for Sample 4 are 39% electrolyte and 48% cathode, a 41:59 volume ratio in the composite region. Additionally the Sample 4 graded porosity plot appears to have a large pore (denoted by a black arrow in Figure 4-4114) at the bulk electrolyte interface, which adversely affects the surface area within the composite region.

In order to further quantify the composite cathode and cathode support the Sample 3 reconstructed volume was split up into ten divisions as seen in Figure 4-4215. The divisions through the composite cathode and the support cathode divisions were 5 and 10 μm thick, respectively. Sample 4 was similarly divided into eleven divisions (Figure 4-4316) with an extra division made through the bulk electrolyte. The divisions were used to quantify volume, surface area, particle/pore average diameters, porosity, two phase surface area, surface area packing factor and tortuosity, Tables 4-1 to 4-4. Cathode, electrolyte and pore diameters as a function of distance from electrolyte are shown in Figure 4-4215 for Sample 3 and Figure 4-4316 for Sample 4.

The composite cathode of Sample 3 average open pore diameter, average cathode diameter, average electrolyte diameter, and average closed pore diameter were 0.95, 2.91, 2.46, and 1.81 μm, respectively, with an average volume porosity of 12.33 ± 1.22 %. The cathode
support of Sample 3 average open pore diameter, average cathode diameter, average electrolyte diameter, and average closed pore diameter were 3.11, 7.50, 4.24 and 2.53 μm, respectively, with an average volume porosity of 28.66 ± 2.36 %. The composite cathode of Sample 4 average open pore diameter, average cathode diameter, average electrolyte diameter, and average closed pore diameter were 1.09, 4.10, 2.23 and 2.03 μm, respectively, with an average volume porosity of 13.01 ± 2.69 %. The cathode support of Sample 4 average open pore diameter, average cathode diameter, average electrolyte diameter, and average closed pore diameter were 3.18, 7.84, 2.92 and 2.54 μm, respectively, with an average volume porosity of 28.11 ± 4.07 %. The Sample 4 composite cathode exhibits a coarser cathode particle size than Sample 3 (4.10 versus 2.91 μm, respectively). Sample 4 cathode support also has a slightly higher average porosity and standard deviation when compared to Sample 3 (Table 4-31), 13.01±2.69, 12.33±1.22 % by volume, respectively. This is evident in the graded porosity profiles (Figure 4-4114b) and most likely caused by the presence of the aforementioned large interfacial pore. The cathode support particle diameters for the two samples are all very similar with the exception of average electrolyte particle diameter, but this is most likely due to the small number of impurity particles seen in the cathode support, thus not allowing for good comparative statistics.

The coarser composite cathode particle size of Sample 4 causes the cathode and electrolyte surface areas of Sample 4 to be smaller than those of Sample 3. Plots of the volume normalized surface area can be seen in Figure 4-4417a for Sample 3 and Figure 4-4417b for Sample 4. The plot includes surface area measurements through each volume for all four phases. Table 4-42 has the values for the normalized surface area. The composite cathode surface area of Sample 3 has a volume normalized surface area of 10.95 μm$^{-1}$. It has an average open pore surface area, average cathode surface area, average electrolyte surface area, and average closed pore surface
area of 0.78, 0.96, 0.96, and 0.04 μm\(^{-1}\), respectively. The cathode support surface area of Sample 3 has a volume normalized surface area of 5.84 μm\(^{-1}\). It has an average open pore surface area, average cathode surface area, average electrolyte surface area, and average closed pore surface area of 0.56, 0.56, 0.04, and 0.01 μm\(^{-1}\), respectively. The composite cathode surface area of Sample 4 has a volume normalized surface area of 9.38 μm\(^{-1}\). It has an average open pore surface area, average cathode surface area, average electrolyte surface area, and average closed pore surface area of 0.72, 0.91, 0.67, and 0.04 μm\(^{-1}\), respectively. The cathode support surface area of Sample 4 has a volume normalized surface area of 5.60 μm\(^{-1}\). It has an average open pore surface area, average cathode surface area, average electrolyte surface area, and average closed pore surface area of 0.54, 0.54, 0.03, and 0.01 μm\(^{-1}\), respectively. The biggest difference between the two samples lies in the cathode and electrolyte surface areas of the composite cathode which may be due to the aforementioned volume phase fraction differences and the finer nature of Sample 3’s microstructure. The higher total volume surface area in Sample 3’s composite cathode agrees with particle size trends. The cathode supports have very similar surface areas for all phases.

Further quantification of surface area was conducted through the measurement of two phase surface area between all four phases: open pore, cathode, electrolyte, closed pore. Figure 4-4518 shows the individual values while Table 4-53 sums them for the composite cathode and cathode support regions. These values show the relative dominance of the various two phase boundaries in the microstructure. The important side note in Table 4-53 is that the balance (9% of total for Sample 3 and 14% for Sample 4) of the surface area fraction is found in the electrolyte bulk which was excluded from the calculations.
The composite cathode of Sample 3 is dominated by the cathode-open pore, electrolyte-open pore and electrolyte-cathode two phase interfaces with sums of 0.13, 0.13, and 0.19, respectively. The cathode support of Sample 3 is dominated by the cathode-open pore surface area with a fraction sum of 0.42. The composite cathode of Sample 4 is dominated by the cathode-open pore, electrolyte-open pore and electrolyte-cathode two phase interfaces with average fractions of 0.19, 0.10, and 0.17, respectively. The cathode support of Sample 4 is dominated by the cathode-open pore surface area with a fraction sum of 0.42. A comparison of Sample 3 and Sample 4 two phase surface area shows that Sample 3 has equal cathode-open pore and electrolyte-open pore surface area fractions (0.13 and 0.13) which are both less than the electrolyte-cathode fraction (0.19). But in Sample 4 we see that the dominant surface area fractions are cathode-open pore and electrolyte-cathode (0.19 and 0.17) as compared to the electrolyte-open pore surface area fraction (0.10). This difference is possibly due to the lower volume fraction of electrolyte in the composite cathode of Sample 4. Both composite cathodes have an equal fraction of total surface area (0.47). This is indicative of the high concentration of surface area present in the composite cathode when compared to the bulk electrolyte and cathode support.

For comparison of surface area between the two samples a surface area packing factor was devised, to compare the relative concentration of surface area through the reconstructions. This consists of dividing the surface area of each division by the total reconstruction surface area, and dividing that quantity by the volume of each slice divided by the total reconstruction volume. These plots are shown in Figure 4-4619. The main difference that we notice is that Sample 3 has a higher maximum surface area packing factor which abruptly drops approaching the electrolyte interface in the composite cathode. This indicates that Sample 3 has a more abrupt interface than
Sample 4 (as corroborated by Figure 4-4114) perhaps indicative of weaker interfacial adhesion between the composite cathode and the bulk electrolyte. Although Sample 4 has a large pore at the dense electrolyte interface which would give weaker adhesion.

Triple phase boundary (TPB) length was also calculated by summing all of the points in each composite cathode where the cathode, electrolyte, and open pore phases intersected in a triple point (Figure 4-4720). All of these points were turned into segments through each slice, and the total length was divided by the total composite cathode reconstructed volume to yield the TPB of 0.037 μm/μm³ for Sample 3, and 0.046 μm/μm³ for Sample 4. These values are comparable to each other and about an order of magnitude less than the LSCF/YSZ studies from Chapter 3. The reason for the increased TPB in Sample 4 is most likely due to the increased interfacial porosity as observed in the graded porosity (Figure 4-4114).

Tortuosity was also measured for the two samples (Figure 4-4821 and Table 4-64). Sample 3’s tortuosity in the composite cathode is 1.58, and 1.40 in the cathode support. These are higher than the tortuosities of Sample 4’s composite cathode and cathode support of 1.44 and 1.31, respectively. Figure 4-4821 shows a plot of tortuosity versus distance from dense electrolyte/cathode interface. The overall tortuosity is the y intercept value. The tortuosity is calculated by starting at the cathode/air interface and tracking the inertial center of the open pore phase in each reconstructed slice as we progress through the cathode support, then through the composite cathode and stop at the dense electrolyte. The Euclidian distance is divided by the cathode thickness to calculate the tortuosity. This plot shows how that value updates with every slice, starting at 70 μm and moving towards 0 μm. It is evident that it takes at least ten slices for the tortuosity value to stabilize towards the right end of the plot because it is with respect to the initial slice. This is indicative of the length scale of the pores in the cathode support, which are
typically less than five μm in diameter. It is also evident that the tortuosity profile is more torid in the cathode support’s coarser microstructure than the composite cathode’s finer microstructure. A more torid path is more difficult for gas to diffuse through than a less torid path. This difference in roughness between the support cathode and composite cathode exists because each support cathode pore has a larger effect on the overall tortuosity than a smaller pore within the composite cathode. This accounts for the higher roughness in the support cathode region of the graded tortuosity plot. In addition, the slice thickness of 500 nm more effectively captures the larger cathode support pores, which also contributes to the higher apparent graded tortuosity plot roughness.

The slope of the graded tortuosity gives us insight about the uniformity of the pore channels as the oxygen molecules traverse the cathode support on through the composite cathode. In the composite cathode region, where the reduction reaction occurs in the proximity of triple phase boundaries, Figure 4-4821 shows that the graded porosity slope is 68% greater in Sample 4’s composite cathode than in Sample 3’s (slope = -0.007). This indicates that the tortuosity has a faster rate of increase through the composite cathode in Sample 4 than in Sample 3. But Sample 4 has lower overall tortuosity for an oxygen molecule traveling from the cathode/air interface towards the bulk electrolyte. Although no electrochemical data is present to fully characterize the effect that this slope difference has on electrochemical polarization, it is plausible that the gas phase diffusion resistance (concentration polarization) into and out of the composite cathode of Sample 4 is lower than for Sample 3. This increased slope combined with the lower magnitude may also be a side effect of having a low porosity bottleneck half way through the composite cathode in Sample 4. If we look in Figure 4-4114 we can see that Sample 3 has a composite cathode porosity with lower standard deviation (12.3 ± 1.2 % by volume),
where as Sample 4 has a higher composite cathode porosity, and a higher standard deviation (13.0 ± 2.7 % by volume). The increased standard deviation in Sample 4 is a result of low (sub 10 % by volume) porosity in the middle of the composite cathode being sandwiched by high porosity a the electrolyte interface (approaching 20 % by volume) and high porosity at the composite cathode, support cathode interface (>15 % by volume). Thus it is this bottleneck present in the Sample 4 composite cathode which leads to a sharp increase in the tortuosity slope while maintaining a lower tortuosity magnitude.

4.1.3 Microstructure Summary

The FIB/SEM serially sectioned Sample1 reconstruction shows the interconnected nature of the composite and support cathode pore networks. The cathode support has large, interconnected pores. The composite cathode has smaller, interconnected pores, and interconnected YSZ. The electrolyte has closed small pores in comparison to the cathode regions. In addition, the composite cathode is observed to be about 20 μm thick. This initial work helped isolate critical mill dimensions, orientation charging effects, and created a need to quantify the interconnectivity of these networks, which was done in Samples 3 and 4.

Cathode supports of both Sample 3 and Sample 4 had very similar microstructural characteristics, when compared to one another. Cathode support surface area and average particle/pore particle sizes were relatively equal. An impurity phase with similar imaging contrast to the electrolyte phase was seen but not chemically identified. Composite cathode of Sample 3 had a 48:52 percent by volume electrolyte to cathode ratio, while Sample 4 had a 41:59 percent by volume electrolyte to cathode ratio. The coarser Sample 4 composite cathode microstructure had lower volume normalized surface area. Sample 4 had lower tortuosity throughout the cathode most likely caused by coarser microstructure. Sample 4 also exhibited a more drastic tortuosity increase through the composite cathode.
4.2 TEM-EDS Characterization of LCM/YSZ Interface in Composite Cathode

4.2.1 Experimental

The electrolyte/cathode interface of both samples was located and a TEM foil was milled with the FIB. In situ lift out was conducted with a micromanipulator (Omniprobe, Inc.), (Figure 4-4922) and the foils were attached to copper alloy Omniprobe grids,(Figure 4-5023 and Figure 4-5124). SEM images of the mounted foils show that the epoxy has penetrated the smallest of open pores at the bulk electrolyte interface as pointed out with the white arrow in Figure 4-5023.

The foils were thinned down to a thickness of ~100 nm to allow electron transmission. Chemical analysis was conducted with a model 2010 JOEL high resolution TEM equipped with an Oxford Scientific Instruments EDS detector.

4.2.2 Results and Discussion

An interface between the cathode and electrolyte phases in the composite cathode was located in Sample 3 (Figure 4-5225). A sum spectrum was collected to identify all the elements present in the area (Figure 4-5326). The copper and gold peaks are artifacts from the TEM grid. An EDS line scan was collected to visualize the element profiles across the interface (Figure 4-5427). Manganese and lanthanum are the dominant EDS signal species in the cathode, and zirconium is the dominant species in the electrolyte. Calcium is present on both sides of the interface. A series of point scans were then collected across the same interface in order to quantify the weight percent elemental composition of each phase (Figure 4-5528). Both manganese and calcium seem to have appreciably diffused across the interface.

A similar interface between the cathode and electrolyte phases in the composite cathode was located in Sample 4 (Figure 4-5629). The sum spectrum was collected to identify all the elements present in the area (Figure 4-5730). The copper and gold peaks are artifacts from the TEM grid. An EDS line scan was collected to visualize the element profiles across the interface.
Manganese and lanthanum are the dominant EDS signal species in the cathode, and zirconium is the dominant species in the electrolyte. Calcium is present on both sides of the interface. A series of point scans were then collected across the same interface in order to quantify the weight percent elemental composition of each phase (Figure 4-5932). Similar to Sample 3 manganese and calcium seem to have diffused across the interface.

The Sample 3 electrolyte phase (Figure 4-6033a) has a higher average lanthanum and oxygen content, while Sample 4 has higher calcium, manganese and zirconium content. When comparing the cathode phase chemical composition (Figure 4-6033b) it is evident that Sample 3 has a higher average lanthanum and oxygen content, which correlates to the same differences in the electrolyte phase. Sample 4 has higher average composition for all other elements, which is in agreement with the electrolyte phase (Table 4-75). A closer look into the calcium content of both samples (Figure 4-6134) reveals that Sample 3 has a lower calcium concentration in both electrolyte and cathode phases by 1 and 1.4 percent, respectively.

4.2.3 TEM Summary

TEM line and point scans were used to quantify chemical composition across the cathode/electrolyte interface for both samples. The most substantial difference between the two samples was the calcium content which may explain the coarser microstructure seen in the Sample 4 composite cathode because calcium is known to act as a sintering aid.

4.3 Topological Connectivity

4.3.1 Introduction

Topological connectivity is a volume independent intrinsic property which affects transport in any composite or porous material. Understanding the connectivity of a material is essential in understanding transport in three dimensions (3-D). In this work we have quantified in 3-D the connectivity of two separately processed composite solid oxide fuel cell (SOFC)
cathodes. This microstructural property is related to all of the transport processes which occur within the fuel cell. For example, cathode connectivity affects ion/electron conductivity. The connectivity also plays a role in the transfer of mechanical stresses associated with thermal and or mechanical loads. While previous researchers have quantified connectivity in 2-D\footnote{14} this is the first work in which 3-D topological connectivity quantification may be related to quantified microstructural properties. Other researchers have quantified volume connectivity percentages\footnote{54} in cathodes, but this is a volume sensitive measurement which is sample size dependent. Some have been able to quantify 3-D characteristic length scales\footnote{55}, but none have been able to quantify the interconnected nature of the topology.

A solid oxide fuel cell (SOFC) efficiently converts fuel and air into electricity and heat\footnote{6}. In order to increase performance (by decreasing polarization resistance) the electrochemically active triple phase boundaries (TPBs) of SOFC cathodes are extended by mixing the primarily electron conducting cathode phase and the primarily ion conducting electrolyte phases in a composite cathode. Our previous studies have reconstructed SOFC electrodes\footnote{46,48} using the dual beam focused-ion-beam/scanning-electron-microscopy (FIB/SEM) approach, but were not able to gauge the topological connectivity of the complex 3-D network. In addition to characterizing microstructural properties, such as volume porosity, particle size, TPB length, surface area and tortuosity, the mean degree or connectivity of the electrochemically active composite cathode has been quantified for the first time. The quantification of topological connectivity paired with 3-D microstructural quantification has far reaching impacts on fields beyond SOFCs such as tissue scaffolds, vascular systems, particulate filters, structural ceramics, and oil field exploration just to name a few. Quantifying the connectivity allows for intelligent engineering and modeling of complex 3-D networks.
4.3.2 Results and Discussion

4.3.2.1 Connectivity quantification

Thus far, a variety of SOFC microstructural parameters have been quantified with the aid of three-dimensional FIB/SEM reconstructions, such as volume porosity, particle size, surface area, TPB length, and tortuosity \(^{39,48}\). Here, we present the microstructural parameter of topologic/structural 3-D connectivity, which has for the first time been quantified for a man-made 3-D material network. Connectivity has been quantified in two dimensions by various 2-D methods \(^{56,57}\). The advent of 3-D reconstruction software paired with confocal microscopy allowed Wagner and coworkers \(^{42}\) to quantify corrosion cast, rabbit kidney capillaries by visualizing and counting the number of edges and vertices of a single specimen in 2006. More recently Perna and coworkers utilized x-ray tomography to reconstruct termite nests in order to quantify the 3-D network’s topological efficiency \(^{58}\).

Such a topological connectivity is an intrinsic microstructural property which may be related to all of the transport processes which occur within the fuel cell. For example, cathode connectivity affects ion/electron conductivity, pore connectivity affects gas transport to and from TPB boundaries, and electrolyte connectivity affects ion conductivity. In addition, the connectivity of both the cathode and electrolyte play a role in the transfer of mechanical stresses associated with thermal expansion/contraction during thermal cycling.

The SOFC cathode connectivity was quantified with the Skeletonize module of Amira software, which examines each phase and through a number of iterations, peels the outside layer off until all that exists is the mass centroid, or skeleton of that phase in 3-D (Figure 4-6235). The same method is show in 2-D for Figure 4-6336. This 2-D skeletonization representation allows us to visualize vertices with two, three, and four edges. After the skeleton network has been created in 3-D we use the chamfer map tool to calculate the distances between the nodes where
more than one branch intersect. This 3-D network for a composite cathode may subsequently be visualized. A schematic of the progression from SEM images, to a 3-D reconstruction and the final 3-D skeleton is shown in Figure 4-6437. The Amira skeletonization by blocks for large 3-D datasets method was developed in 2004 by Fouard et al.\textsuperscript{59}. It was first utilized to study Indian ink injected human brain micro-vascularization structures imaged with a confocal microscope. Generating the skeleton block by block ensures that homotopy, thinness and medialness are all maintained. Homotopy requires that the skeleton be topologically identical to the original 3-D structure. Thinness ensures that the skeleton is one point wide at all points except at junctions where it may be thicker. This thinness is adjusted in our work because we have a finite thickness to the skeleton which is scaled to the original structure’s thickness. Medialness requires that the skeleton be centrally located (mass centroid) within the reconstructed object\textsuperscript{59}.

The skeleton of each phase consists of a series of vertices (\(v\)) or nodes, which are connected to one another via edges, \(E\), of various topological length, \(L\). Within each network, there is a node with the most edges. This is the \(k_{\text{max}}\) value for the network. It is valuable to know the highest degree of nodal connectivity present within a 3-D structure when comparing different types of systems (biological versus inorganic), because there may be a basic structural differences between nature grown biological systems and man made systems. This type of 3-D complex network quantification has previously been conducted on termite mounds\textsuperscript{58} and that method is expanded below.

The degree of a single node is defined by:

\[
k_i = E_i / N_i
\]

(4-1)

Where \(E_i\) and \(N_i\) are local quantities. When all of the nodes in the network are analyzed, the mean degree may be defined as:
\[ \langle k \rangle = \sum k_i / N \]  \hspace{1cm} (4-2)

Where N is the total number of vertices for the whole network. The average topological path length may likewise be calculated by summing the edge distances (d) for the whole volume (V):

\[ \langle L \rangle = \frac{1}{N} \sum_{v_i,v_j \in V} d_{ij} \]  \hspace{1cm} (4-3)

The 3-D reconstruction for each sample is first split into equal volumes of composite cathode, followed by a series of thinning Skeletonization iterations (Figure 4-6235, Figure 4-6336) to yield a view of the enhanced skeletons of mass centroids of all three composite cathode phases. Then each phase is evaluated for the various network topology parameters, as can be seen in Table 4-86.

Sample 3 has more nodes and edges in both the composite and support cathode regions. This is indicative of Sample 4 having coarser microstructure than Sample 3. Sample 3 has an overall lower mean degree (or connectivity) for virtually all phases, thus having lower overall connectivity than Sample 4. The \( k_{\text{max}} \) values do not follow a definite trend. However, the maximum connectivity in both samples was 11. Sample 4 has a longer average topological length, which supports the coarser microstructure as observed in the particle size, surface area and tortuosity values. The connectivity trends indicate that the sample with higher calcium doping has increased composite cathode connectivity.

4.3.2.2 Measured average z-orientation

In addition to network topology parameters such as connectivity we have implemented a python based program to calculate the Measured Average Z-Orientation (MAZO) of all of the edges in each specific skeleton. MAZO is the angle with respect to the z-axis between endpoints of edges (node to node) (Figure 4-6538). This property allows for the quantification of how well
aligned the available transport paths are with the Z-axis which is orthogonal to the porous composite cathode/dense electrolyte interface. Thus a MAZO angle of 90° would mean that the edge is parallel to the cathode/electrolyte interface, where a MAZO angle of zero degrees would indicate that the edge is orthogonal to the interface. This quantification is useful in better understanding the transport path for oxygen from the air/cathode interface down to the electrolyte. The angular orientation of the gas phase affects the path efficiency for oxygen transport. Similarly solid phase angular orientation helps us better understand the conduction path of charge carriers through the solid phases. Thus the MAZO angle will be helpful in understanding lateral current and gas flows. From Table 4-86 we can see that Sample 3 and 4 have identical composite cathode MAZO values of 55±28 degrees, indicative of similar orientation. The distribution of angular orientations are shown in Figure 4-6639 for the composite pore networks of Sample 3 (blue) and Sample 4 (yellow). The Sample 3 MAZO distribution is Gaussian, while the Sample 4 MAZO distribution has a non-Gaussian profile as shown by excess frequency of angles in the 80 degree range. As a result the Sample 4 composite pore angle is higher than that of Sample 3 (Table 4-86). This may be caused by increased sintering, and the aforementioned large interfacial porosity observed in Sample 4’s graded porosity (Figure 4-4114). The MAZO distribution (Figure 4-39) may also be an indicator of gradient uniformity, with a Gaussian MAZO angle distribution being indicative of a steady gradient. Such a steady gradient is observed in the Sample 3 graded porosity profile, as we transition from cathode to electrolyte in a smooth fashion. In the case of Sample 4 the gradient is much more abrupt, and this seems to be mimicked in the skewed MAZO angle distribution. The broad distribution of MAZO angles with the large standard deviation is typical of isotropic microstructures. As the topological network characteristic length (L) increases so does the
MAZO angle indicating that the larger particle stacking in the composite cathode is further apart in the x-y plane than that of the finer particle network.

4.4 Conclusions

Microstructures of three Siemens-Westinghouse cathode-supported solid oxide fuel cell (SOFC) samples were analyzed. The cathode/electrolyte interface was characterized with Transmission Electron Microscope-Energy Dispersive Spectroscopy (TEM-EDS). Sample 3 was the initial study which aided in identification of the electrolyte/cathode interface, and the estimation of proper slice and view dimensions. The other two samples were designated by Siemens as Sample 3 and Sample 4. Sample 4 had higher calcium content in both electrolyte and cathode phases than Sample 3. This calcium difference may be the cause of the coarser microstructure seen in Sample 4 because calcium is known to act as a sintering aid. The cathode microstructure was quantified with the aid of a Focused Ion Beam/Scanning Electron Microscope (FIB/SEM). All three samples consisted of a composite cathode on the order of 20 \( \mu \text{m} \), sandwiched between the porous cathode support and dense electrolyte. Surface area, porosity, particle size, tortuosity and, for the first time, 3-D topological connectivity were all quantified with the aid of Amira software. Sample 4 had a coarser composite cathode microstructure with 2.5 % higher composite cathode connectivity. This was the first time that true 3-D topological connectivity was quantified for an SOFC structure.

In the future, connectivity may be related to all transport processes that occur throughout the SOFC. This advancement in connectivity quantification can further the understanding of many other fields including biological systems connectivity, for example, by aiding researchers in better understanding the 3-D lattices used in synthetic tissue harvesting. Moreover, the MAZO quantification technique helps in understanding 3-D load distribution in structural
materials. The combined use of FIB/SEM and skeletonization technology allows for more intelligent design of porous micro and nano functional materials.
### Table 4-3. Particle size

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<tr>
<td>Whole volume (including bulk electrolyte)</td>
<td>76246</td>
<td>66527</td>
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<tr>
<td>Total volume (μm³)</td>
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<tr>
<td>Number of slices (each 0.5 μm thick)</td>
<td>160</td>
<td>147</td>
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#### Composite cathode

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<tr>
<td>Total volume (μm³)</td>
<td>19909</td>
<td>18221</td>
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<tr>
<td>Avg. open pore diameter (μm)</td>
<td>0.95 ± 0.07</td>
<td>1.09 ± 0.23</td>
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<tr>
<td>Avg. cathode diameter (μm)</td>
<td>2.91 ± 0.50</td>
<td>4.10 ± 1.37</td>
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<tr>
<td>Avg. electrolyte diameter (μm)</td>
<td>2.46 ± 0.27</td>
<td>2.23 ± 0.16</td>
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<tr>
<td>Avg. closed pore diameter (μm)</td>
<td>1.81 ± 0.10</td>
<td>2.03 ± 0.55</td>
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<tr>
<td>Avg. porosity (%vol)</td>
<td>12.33 ± 1.22</td>
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#### Cathode support

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<td>Total volume (μm³)</td>
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<td>36018</td>
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<tr>
<td>Avg. open pore diameter (μm)</td>
<td>3.11 ± 0.47</td>
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<td>Avg. cathode diameter (μm)</td>
<td>7.50 ± 0.95</td>
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<td>Avg. electrolyte diameter (μm)</td>
<td>4.24 ± 1.88</td>
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<td>Avg. closed pore diameter (μm)</td>
<td>2.53 ± 0.24</td>
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<tr>
<td>Avg. porosity (%vol)</td>
<td>28.66 ± 2.36</td>
<td>28.11 ± 4.07</td>
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### Table 4-4. Surface area

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<tr>
<td>Composite cathode surface area</td>
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<tr>
<td>Total volume normalized surface area (1/μm)</td>
<td>10.95</td>
<td>9.38</td>
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<tr>
<td>Avg. open pore surface area (1/μm)</td>
<td>0.78 ± 0.02</td>
<td>0.72 ± 0.04</td>
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<td>Avg. cathode surface area (1/μm)</td>
<td>0.96 ± 0.05</td>
<td>0.91 ± 0.12</td>
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<tr>
<td>Avg. electrolyte surface area (1/μm)</td>
<td>0.98 ± 0.14</td>
<td>0.67 ± 0.30</td>
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<td>Avg. closed pore surface area (1/μm)</td>
<td>0.04 ± 0.02</td>
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#### Cathode support surface area

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<td>Total volume normalized surface area (1/μm)</td>
<td>5.84</td>
<td>5.60</td>
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<tr>
<td>Avg. open pore surface area (1/μm)</td>
<td>0.56 ± 0.07</td>
<td>0.54 ± 0.07</td>
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<tr>
<td>Avg. cathode surface area (1/μm)</td>
<td>0.56 ± 0.07</td>
<td>0.54 ± 0.07</td>
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<tr>
<td>Avg. electrolyte surface area (1/μm)</td>
<td>0.04 ± 0.06</td>
<td>0.03 ± 0.01</td>
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<tr>
<td>Avg. closed pore surface area (1/μm)</td>
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Table 4-5. Two phase surface area

<table>
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<th>Composite cathode two phase surface area fraction of total surface area</th>
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<tr>
<td>Cathode-open pore</td>
<td>0.13</td>
<td>0.19</td>
<td></td>
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<tr>
<td>Electrolyte-open pore</td>
<td>0.13</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Electrolyte-cathode</td>
<td>0.19</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Closed pore-cathode</td>
<td>0.00</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Closed pore-electrolyte</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>FRACTION OF TOTAL</td>
<td>0.47</td>
<td>0.47</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Cathode support two phase surface area fraction of total surface area</th>
<th>Sample</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Cathode-open pore</td>
<td>0.42</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Electrolyte-open pore</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
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<tr>
<td>Electrolyte-cathode</td>
<td>0.01</td>
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<tr>
<td>Closed pore-cathode</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Closed pore-electrolyte</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>FRACTION OF TOTAL</td>
<td>0.44</td>
<td>0.39</td>
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</tbody>
</table>

*balance of surface area is located in bulk electrolyte

Table 4-6. Tortuosity

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<tr>
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<th>Sample</th>
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<tbody>
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<td>Composite cathode</td>
<td>1.58 ± 0.05</td>
<td>1.44 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>Cathode support</td>
<td>1.40 ± 0.10</td>
<td>1.31 ± 0.08</td>
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</tbody>
</table>
Table 4-7. TEM-EDS point scan quantification

<table>
<thead>
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<th></th>
<th>Siemens 3</th>
<th></th>
<th>Siemens 4</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La</td>
<td>Ca</td>
<td>Sr</td>
<td>Mn</td>
</tr>
<tr>
<td>Cathode average</td>
<td>61.49</td>
<td>2.79</td>
<td>0.05</td>
<td>19.96</td>
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<tr>
<td>Standard deviation</td>
<td>1.31</td>
<td>0.21</td>
<td>0.03</td>
<td>0.59</td>
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<td>Electrolyte average</td>
<td>2.96</td>
<td>1.67</td>
<td>0.02</td>
<td>4.05</td>
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<tr>
<td>Standard deviation</td>
<td>0.11</td>
<td>0.05</td>
<td>0.02</td>
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Table 4-8. Connectivity quantification

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<th>Sample 3</th>
<th>N</th>
<th>E</th>
<th>&lt;k&gt;</th>
<th>&lt;L&gt;  (μm)</th>
<th>kmax</th>
<th>MAZO (*°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite electrolyte</td>
<td>1947</td>
<td>5231</td>
<td>2.69</td>
<td>1.50</td>
<td>11</td>
<td>54 ± 27</td>
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<tr>
<td>Composite cathode</td>
<td>1581</td>
<td>4370</td>
<td>2.80</td>
<td>1.56</td>
<td>9</td>
<td>55 ± 28</td>
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<tr>
<td>Composite open pores</td>
<td>137</td>
<td>389</td>
<td>2.84</td>
<td>2.64</td>
<td>4</td>
<td>56 ± 25</td>
</tr>
<tr>
<td>Sample 4</td>
<td>N</td>
<td>E</td>
<td>&lt;k&gt;</td>
<td>&lt;L&gt;  (μm)</td>
<td>kmax</td>
<td>MAZO (*°)</td>
</tr>
<tr>
<td>-------------------------</td>
<td>--------</td>
<td>--------</td>
<td>------</td>
<td>-----------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>Composite electrolyte</td>
<td>1047</td>
<td>2847</td>
<td>2.72</td>
<td>1.63</td>
<td>7</td>
<td>57 ± 26</td>
</tr>
<tr>
<td>Composite cathode</td>
<td>1303</td>
<td>3739</td>
<td>2.87</td>
<td>1.85</td>
<td>11</td>
<td>55 ± 28</td>
</tr>
<tr>
<td>Composite open pores</td>
<td>126</td>
<td>370</td>
<td>2.94</td>
<td>2.67</td>
<td>5</td>
<td>61 ± 25</td>
</tr>
</tbody>
</table>

N=number of vertices; E=number of edges; <k>=mean degree; L=average topological length; kmax=max degree; MAZO=Measured Average Z-Orientation *equal volumes compared
Figure 4-28. FIB/SEM cross section of cathode supported SOFC sample imaged with charge contrast TLD detector.

Figure 4-29. Epoxy sample preparation. (a) EpoVac chamber used for impregnation. (b) Planarized/polished samples mounted in cross section
Figure 4-30. C-trench preparation. (a) Initial polished sample 3 cross section is (b) deposited with platinum layer. (c) C-trench is made and then the (d) cathode is automatically milled and imaged.

Figure 4-31. Phase contrast. Sample slices of sample 3 microstructure: (a) Support cathode with arrow pointing to suspected electrolyte impurity (b) composite cathode and (c) electrolyte. Redeposition curtaining is seen in the bottom portion of (b) and (c).
Figure 4-32. Background EDS scan of Siemens-Westinghouse electrolyte/cathode interface cross section.

Figure 4-33. 16.7 μm long line scan across cathode/electrolyte interface.
Figure 4-34. EDS selected element profiles of linescan displayed in Figure 4-3. The numbers next to the element name indicates the Y axis maximum value in counts. Notice the broad nature of the blue Calcium peak in contrast to all other elements. Gallium profile is flat because the element is embedded across whole profile evenly from FIB/SEM milling.
Figure 4-35. FEG SEM SE detector image of cross section region scanned for background EDS scan of Figure 4-1. There is a disparity between apparent interface as imaged by SED detector and true atomic interface revealed by EDS analysis.
Figure 4-36. Reconstructed volume of Siemens SOFC electrolyte, composite cathode, and cathode support.
Figure 4-37. (a) Reconstructed volume of YSZ electrolyte including YSZ in composite cathode; (b) reconstructed volume of YSZ and LSM cathode; (c) transparent reconstruction of electrolyte and electrode with pore network visible within the LSM cathode; (d) pore network of entire reconstructed volume.
Figure 4-38. Phase fraction (YSZ, LSM, Pore) in y axis is plotted against the distance away from the LSM/YSZ interface. A transparent image of the microstructure shows the orange dense electrolyte, 20 μm thick cathode, and cathode support.
Figure 4-39. Sample 3 3-D Reconstruction. Labeled with phases and approximate dimensions. Orange arrow points to phase with similar imaging contrast to the electrolyte phase.
Figure 4-40. Sample 4 3-D Reconstruction. Labeled with phases and approximate dimensions. Orange arrow points to phase with similar imaging contrast to the electrolyte phase.
Figure 4-41. Graded porosity plots of (a) sample 3 and (b) sample 4. Gray arrow shows crossover of cathode and electrolyte phases in sample 3. Black arrow denotes large interfacial pore in sample 4.
Figure 4-42. Sample 3 particle size. Image of sample 3 divisions used for microstructural quantification (a). Particle size versus distance from electrolyte chart for sample 3 (b).
Figure 4-43. Sample 4 particle size. Image of sample 4 divisions used for microstructural quantification (a). Particle size versus distance from electrolyte chart for sample 4 (b).
Figure 4-44. Volume normalized surface area measurements for sample 3 and sample 4.
Figure 4-45. Two phase surface area as fraction of total surface area for sample 3 (a) and sample 4 (b).
Figure 4-46. Surface area packing factor. Comparison between sample 3 (open diamonds) and sample 4 (closed squares)

Figure 4-47. Triple phase boundaries in 2-D image of the Siemens Sample 3 composite cathode
Figure 4-48. Comparative graded tortuosities of sample 3 (open square) and sample 4 (closed diamond).
Figure 4-49. TEM foil preparation. Sample 3’s cathode/electrolyte interface (a) was deposited with platinum protective layer (b). TEM cross section was milled (c) and lifted out with a micro-manipulator (d).

Figure 4-50. TEM sample 3. Back, top and front views of 100 nm thick sample 3 TEM foil mounted on copper grid. Epoxy filled pore at electrolyte interface (white arrow).
Figure 4-51. TEM sample 4. Back, top and front views of 100 nm thick sample 3 TEM foil mounted on copper grid.

Figure 4-52. Sample 3 SEM image and corresponding TEM image of composite cathode.
Figure 4-53. Sample 3 sum EDS spectrum of cathode/electrolyte interface.
Figure 4-54. TEM image and corresponding line scan profiles across the cathode/electrolyte interface of sample 3.
Figure 4-55. Sample 3 TEM EDS point scan locations (a) and elemental weight percent quantities (b).

Figure 4-56. Sample 4 SEM image and corresponding TEM image of composite cathode.
Figure 4-57. Sample 4 sum EDS spectrum of cathode/electrolyte interface.
Figure 4-58. TEM image and corresponding line scan profiles across the cathode/electrolyte interface of sample 4.
Figure 4-59. Sample 4 TEM EDS point scan locations (a) and elemental weight percent quantities (b).
Figure 4-60. TEM-EDS elemental composition. Point scan elemental comparison of electrolyte phase for sample 3 and sample 4 (a). Point scan elemental comparison of cathode phase for sample 3 and sample 4 (b).
Figure 4-61. Calcium composition comparison between electrolyte and cathode phases for sample 3, and sample 4.
Figure 4-62. 3-D Skeletonization. Depiction of skeleton generation from original volume (a), through multiple thinning iterations (b-d), and the final skeleton with a higher magnification view of one vertex, (f).

Figure 4-63. Skeletonization in 2-D. Depiction of skeleton generation of single 2-D slice of pores in black and cathode in white (a), through multiple thinning iterations (b-d), and the final skeleton (e) with a higher magnification view of one vertex, (f).
Figure 4-64. Schematic showing the transition from SEM image (top left), a stack of which is used to generate a 3-D reconstruction model (top right), which is then reduced to a mass centroid skeleton (bottom center) of each phase.

Figure 4-65. Schematic depiction of Measured Average Z-Orientation (MAZO) angle.
Figure 4-66. MAZO angle frequency distribution for sample 3 and sample 4 composite pore networks.
CHAPTER 5
LOCAL ELECTRON ATOM PROBE RECONSTRUCTION OF BURRIED CATHODE/ELECTROLYTE SOLID OXIDE FUEL CELL INTERFACES

5.1 Introduction

Solid oxide fuel cells (SOFCs) offer society a means of increasing our energy independence through increased energy conversion efficiency. The technical advantage of SOFCs is the ability to convert both liquid and gaseous fuels into electrical power and useful heat through electrochemical conversion. The main barrier to SOFC commercialization is the cost/power ratio, the reduction of which is a main concern for both commercial and institutional researchers.

As researchers seek to reduce cost and prolong stability they have made changes to the electrode/electrolyte compositions and structures. These compositional changes sometimes have deleterious effects on electrode/electrolyte interfaces. Interfacial stability evaluation is often limited to long term durability studies where sufficient amounts of tertiary phases must grow to be measured by scanning electron microscopy (SEM) energy dispersive spectroscopy (EDS) or transmission electron microscopy (TEM) EDS methods. The long term stability effect of compositional changes of the cathode/electrolyte interface may now be evaluated faster than ever before thanks to the recent breakthrough of three-dimensional atom probe (3DAP) microscopy.

3DAP allows for the 3-D visualization and analysis of chemically resolved atoms. The small radius of curvature (~25 nm) at the top of the sample tip allows for a magnified field ionization, which with the aid of a pico second pulsed laser (Figure 5-671) evaporates the tip surface monolayer in the direction of the local electrode. The laser assisted thermal-excitation evaporation mechanism works by increasing the local tip temperature which allows for low-conductivity materials to be evaporated, since field evaporation is directly proportional to temperature. It is important to note that the sample temperature should not be allowed to
exceed 200K, because this is the temperature below which surface species migration is essentially frozen\(^63\). To prevent this the chamber temperature is kept well below 100 K for routine experiments. This allows for an accurate 3-D atomic reconstruction. Once the ions pass the local/counter electrode, having attained energy equal to the tip voltage, they enter a field neutral drift region, where given enough distance (~ 1 meter) they separate according to their atomic mass and then collide with a solid state X-Y spatially sensitive detector\(^66\) which determines where on the tip the atoms originated. Due to the detector’s geometry approximately 50 percent of the atoms are detected and counted. As subsequent pulses evaporate subsequent atomic layers from the probe tip a 3-D image of the probe tip may be reconstructed with corrections applied to adjust for the tip curvature. The time-of-flight (TOF) between the pico second laser pulses allows for 10,000 nano-second wide mass-to-charge (M/C) window within each laser pulse which is able to resolve individual atoms, their isotopes and clusters or complex atoms/ions. The formula which is utilized to calculate the M/C is based on the relationship between potential energy and kinetic energy (Equation 5-1), where \(v = d/t\) (d is distance in meters, t is time in seconds), \(m\) is the mass of the ion, \(n\) is the number of charge carriers, \(e\) is the charge of one electron, and \(V\) is the applied voltage.

\[
\frac{1}{2}mv^2 = neV
\]  

(5-1)

The time it takes for the ion to travel the 90 mm from the local electrode to the detector is shown in Equation 5-2, where \(m\) is in units of kilograms, \(d\) in units of meters, and the voltage in units of volts.

\[
t = \sqrt{\frac{d^2m}{2neV}}
\]  

(5-2)
Equation 5-3 is useful when trying to deal with M/C peak drift which is caused by the increasing voltage required to evaporate an atom probe tip with a growing radius of curvature (caused by the evaporation of each successive monolayer off of the cone shaped tip). To calculate the actual M/C value or m/n value we would rearrange to yield Equation 5-3, which is in units of atomic mass units (amu) or Daltons (Da). The conversion from a kilogram based mass to the amu requires the use of Avogadro’s number, \( N_A \).

\[
\frac{m}{n} = \frac{2000eVN_A}{v^2}
\]  

(5-3)

When a single atom completes its time of flight and hits the X-Y detector, both a unique X and Y coordinate may be identified, and this event it is called a golden hit. When there are clusters of atoms that are ionized together, they may hit the detector in two adjacent spots, preventing a unique X and Y position to be detected subsequently detracting from the golden hit percentage. These composite ion evaporations are heavier than the single ions and thus will be at higher M/C values due to longer flight times.

5.2 Experimental Procedure

Two separately processed Siemens Energy, Inc. samples were cross-sectionally mounted and impregnated with epoxy using a Struers EpoVac chamber. The samples were designated as Sample 3 and Sample 4, for which 3-D FIB/SEM microstructure quantification is discussed in Chapter 4. They were subsequently ground and polished to a 1 \( \mu \)m roughness to planarize the surface. Three layers of carbon coating were sputter deposited to prevent charging. The following technique is an adapted version of the site specific atom probe preparation methods discussed by Miller \textsuperscript{67}, Thompson \textsuperscript{68}, Gorman \textsuperscript{69} and Moore \textsuperscript{70}. Using an FEI Co. Strata DB235 dual-beam focused ion beam / scanning electron microscope (FIB/SEM) equipped with a metal-organic gas injection system, platinum was deposited in a 50 X 2 X 2 \( \mu \)m pattern over the
composite cathode region, parallel to the electrolyte/composite cathode interface (Figure 5-682a). Trenches were made on either side of the platinum strip, followed by cleaning cuts to reveal a 50 μm wide by 2 μm thick foil (Figure 5-682b-d). The Through-Lens-Detector (TLD) was utilized in scanning mode to differentiate between the electrolyte, cathode and open pore (epoxy filled) phases (Figure 5-682e). Subsequent 2 μm wide fiduciary markings were made in the protective platinum cap to identify over a dozen foil regions with cathode/electrolyte interfaces (Figure 5-682f-g). The 2 μm fiduciary thickness was required for the samples to fit on the leap array posts, which is described below. The foil was then undercut at a 22° tilt, then rotated 180°, and undercut again at the same 22° tilt (Figure 5-682h). This resulted in a chamfer on the bottom of the foil, which is a common practice to ensure good contact between the sample and the leap array post, once mounted, as discussed below.

An Omniprobe, Inc. AutoProbe™ 200 micromanipulator was then made to touch the foil. A three step platinum weld was made on the top side of the sample, which allowed for the whole 50 μm long by 7.5 μm tall sample foil to be in-situ lifted up and out of the bulk sample (Figure 5-693). The first step in this micromanipulator welding process was the boring of a small ½ X ½ μm square hole into the region where the micromanipulator and foil were in contact using a 50 picoamp (pA) current aperture. The next step was to backfill that square hole with platinum using a 10 pA aperture. This reduced current allows for a more dense platinum deposition, thus increasing the adhesion between the micromanipulator and sample. This increased adhesion is necessary when dealing with such a large foil (relative to micromanipulator contact area), which is over 15 times longer than the micromanipulator contact area is thick. The sample was then cut free and the micromanipulator was used to lift it up and out of the bulk sample (Figure 5-682i).
The micromanipulator was then positioned over an Imago Scientific Instruments, Inc. manufactured, 36-specimen grid/coupon of flat top silicon microtips with a 2 μm diameter and height of 100 μm (Figure 5-704). The stage being at a zero degree tilt, and the foil liftout happening at the same stage orientation allowed for a top (end-on) electron beam view of the sample which allows it to be centered over the Si post. A side ion beam view allows for monitoring of the distance between the sample foil and the Si post, as they are brought closer together (Figure 5-715). It must be noted that the ion beam current used for imaging the sample foil from the side is much lower than the ion beam current used to shape the same foil, thus preventing drastic sample deformation while mounting. This also means that whenever the foil is imaged from the side it is being implanted with gallium ions. Thus using a lower pA aperture in viewing mode ensures that a smaller dose of gallium is implanted into the sample. Alternating between both views allows for the sample foil to be properly positioned over the Si post so that the 2 μm wide fiduciary marked region is aligned with the 2 μm diameter flat top of the Si post. The micromanipulator is moved at a speed of 100 nm/second to bring the sample in physical contact with the post. Contact is indicated by a slight deflection of the sample foil. The platinum GIS needle is then used in a similar three step welding process to attach the sample foil to the Si post. Subsequent higher current ion beam cuts are made on either side of the Si post to separate the Si mounted sample from the originating, larger sample foil (Figure 5-726). This process is repeated for all of the marked regions of the 50 μm long sample foil.

Once all of the samples are mounted atop the Si posts, similar three step welds are applied to the opposite side of the post to further ensure proper adhesion. The stage is then tilted to 52° so that the ion beam is looking straight down (end-on) onto the samples on top of the Si posts, and the electron beam now has a side view. This allows us to sharpen the samples into
atom probe tips with the FIB, while the side SEM view allows us to track the progress of the sharpening, without implanting gallium directly from the side.

The FIB annular milling is utilized at 20,000X magnification and an initial beam condition of 1000 pA at 30 kV. The FIB top view through the sharpening process may be seen in Figure 5-737. The annular mill causes the ion beam to be rastered in a circle which is expanded in size, thus allowing for the milling of a cone shaped atom probe tip\textsuperscript{67,71,72} when looked at with the electron beam side view (Figure 5-748). This 1000 pA milling is conducted until the whole sample forms a cone shape, and any micro-crowns further down on the Si post are eliminated (Figure 5-737a-b). This step takes ~6 minutes for a sample with dimensions of 2 X 2 X 2 \( \mu \text{m} \). After this step is complete the through-hole weld is visible (white arrow in Figure 5-748), indicating that we are close to our pre-marked interface of interest (Figure 5-682f). If the region of interest were not close, the current would be dropped to 300 pA and the cone would be milled further until the tip was about a micrometer from the interface of interest. The reason for the lower aperture is to prevent milling through the interface prematurely. This method is much easier on a more modern FIB/SEM system equipped with spy mode imaging where both electron and ion beam live scans may be viewed simultaneously. Once the interface of interest is within 600 nm from the tip top, the FIB is switched over to a low kV aperture (Figure 5-737c-e) in order to accomplish the final sharpening and removal of the outermost FIB damaged regions. The low kV aperture results in reduced resolution thus requiring increased contrast in order to focus on the tip of interest at sufficient magnification. The low kV cleaning in this case was conducted at 8 kV with a current of 65 pA. This cleaning is done using the FIB in live view with the fastest refresh rate possible (0.028 sec), and may last anywhere from a 2-20 minutes depending on which material is on top. The face centered cubic, zirconium rich electrolyte material typically
mills at a (2X) slower rate than the perovskite, lanthanum manganate based cathode material. This final sharpening does an excellent job of sharpening the tip to an off-center-axis angle of 15°, maximizes the electric field at the tip, and thus allows for evaporation to “turn-on” or begin at electrode voltages around 2,000 volts. Once this final low kV sharpening has been done it is extremely important not to FIB image the sharpened atom probe tip vicinity with a high potential (30 kV). A total of 51 tips were thusly made for this LEAP microscope analysis because only about half of the tips ran successfully in the LEAP microscope. Additionally, of the 51 tips, only five (~10%) yielded interfaces between cathode and electrolyte. This was a vast improvement on previous attempts where the success rate was closer to 1% with the previous 108 FIB micro-machined tips. This increased success was attributed to three changes in atom probe preparation: (1) use of three step weld, prevented premature tip weld failure, (2) use of fiduciary marks allowed for easier location of cathode/electrolyte interfaces and (3) use of low energy FIB cleaning formed tips with smaller radii of curvature, which improved evaporation turn-on rates.

Once all of the samples have been sharpened, they are ready to be analyzed on a LEAP microscope. If the time required to transport the samples is over a couple hours the whole coupon is plasma cleaned for an hour to remove any water vapor or other contaminants which may have adsorbed onto the sample coupon during transport. These samples were analyzed using a LEAP microscope located at the Central Analytical Facility at the University of Alabama in Tuscaloosa, AL. The specimens were pumped down to a pressure of 4-5 X 10^{-7} torr before being inserted into the analysis chamber where each tip was brought within a couple millimeters of the local electrode. The chamber is equipped with a cold finger which allows samples to be analyzed at sub 100 K temperatures. Both samples were analyzed at a temperature of 64.7K.
The target evaporation rates for both samples were 0.4%, with a 250 kHz laser frequency. Sample 1 had a 35 nm starting tip diameter as measured with a FEG SEM TLD-Deep hole detector. It had a golden hits ratio of 61.5% and had a total of 5.6 million detected atoms. Sample 2 had a 49 nm starting tip diameter, a golden ratio of 62.9%, with 8.4 million total detected atoms.

5.3 Results and Discussion

After reconstructing runs #3017 (called Sample 1 from here on) and #3386 (called Sample 2 from here on) using the proprietary Java based application Interactive Visualization and Analysis Software (IVAS) version 3.4.1 (Imago Scientific Instruments.), it was evident that both had cathode/electrolyte interfaces in their reconstructed volumes. Please note that the run # is indicative of order of analysis, with the larger number being analyzed in the LEAP system after the smaller number. Furthermore Sample 1 LEAP reconstruction originates from Siemens designated Sample 3 (WPC3), and all Sample 2 LEAP reconstructions originate from Siemens designated Sample 4, which had increased calcium content than WPC3. Sample 1 consists of a 81 X 81 X150 nm reconstructed volume where the first two dimensions are the x and y axes and the final dimension is the vertical z-axis (Figure 5-759). The Sample 1 reconstruction consists of a cathode region on top and an electrolyte region on the bottom. In between the two regions is the interface, with a void on one side indicated by an arrow. The void is visible in both the reconstruction and the SEM image of the tip before LEAP analysis. This void may represent an open pore, which would mean that we have reconstructed a triple phase boundary (TPB). The Sample 2 reconstruction was smaller with dimensions of 55 X 55 X 72 nm with an orientation where the electrolyte is on top and the cathode is on bottom (Figure 5-7610). The void observed in Sample 2’s reconstruction (black arrow) is not visible in the SEM image. There was no
particular reason for the two samples having opposite orientations, but this geometry made the mass spectrum analysis easier.

The mass spectrum plots of both samples are shown in Figure 5-7711. These plots have mass-to-charge (M/C) ratio in units of amu or Daltons on the x-axis while counts are on the y-axis. The first observation in comparing the two M/C plots is that the smaller cross section of Sample 2 has more noise which is believed to be caused by increased local heating from the laser due to it having a 38% smaller cross-sectional area. This reduced cross-sectional area reduces Sample 2’s ability to conduct heat away from the atom probe tip, thus increasing M/C noise. This noise is most likely not caused by differences in thermal conductivity between the cubic-electrolyte and perovskite-cathode phase, since both phases have similar thermal conductivity values. In Sample 1 the electrolyte phase on the bottom is scandium-stabilized zirconia (SSZ), similar to yttrium-stabilized zirconia (YSZ) which has a thermal conductivity of ~2.3 W/mK at room temperature. The origins of this low thermal conductivity is vacancy induced phonon scattering due to the doped zirconia’s highly defective structure which allows for oxygen ion transport at high temperatures. Perovskite, similar to the calcium doped lanthanum manganate cathode here have similar thermal conductivities of less than 2.2 W/mK, which is why both materials are viable as thermal barrier coatings, and well matched in terms of thermal expansion coefficients.

Although both samples have a number of peaks, ranging from 1 to 160 Da., we will be focusing on only seven of the major atomic constituents which (listed in rising M/C order) include hydrogen, scandium, oxygen, calcium, manganese, lanthanum and zirconium oxide. These seven peaks all occur below 60 Da. The multitude of peaks, above 60 Da, is caused by the many complex ions which are evaporated during analysis. Please note that in subsequent
discussion we are able to resolve dual peaks within each element’s M/C range, which displays the sub amu resolution of this technique.

The hydrogen peak occurs at one Da, and consists of a singly ionized hydrogen atom. It appears that hydrogen is present in high concentration at the edge of each interface as seen near the arrows of Figure 5-7812, where there appears to be a lack of other constituent atoms. Since these samples were impregnated with a hydrocarbon based epoxy it is possible that this epoxy is present at the interface in the form of hydrogen atoms.

The scandium peak located at just under 15 Da, consists of triply ionized scandium-45 (Figure 5-7913). Since scandium is utilized in the electrolyte phase we can see that it is present in high concentration in the bottom of Sample 1 and in a much smaller concentration in the top of Sample 2, because there is not much of the electrolyte phase present. This scandium distribution agrees with the phase orientations.

The oxygen-16 M/C peak shows a geometry-heating effect which we have identified in this work (Figure 5-8014). If we look at the M/C for Sample 1 we notice that there is one major peak with a considerable shoulder coming off of it. But when we look at the M/C for Sample 2 we notice that the shoulder is in the middle of two separate peaks which are less than 0.3 Da apart. We believe this is proof of heating induced M/C drift during the eight plus million run for Sample 2. If we separate this O-16 peak into three regimes (Figure 5-8115): the left most peak in blue (A), the middle shoulder in peach (B) and the right peak in purple (C), we can see how the peak drifts during Sample 2’s run. We see as we start to evaporate from the top of the sample, it is very rich in this purple O-16, and then as we progress through the run we see that the peach phase is present in higher concentration in the top electrolyte phase, but as we progress through the run the localized heating forces the ion flight time to reduce due to higher tip
temperature which shifts the oxygen peak to the left and we see that in the end the blue phase of O-16 is only present in the bottom (cathode) region of the sample. But the existence of the purple peak, and its higher content at the top shows us that the oxygen rich phase for Sample 2 is in the top, as seen with this purple O-16 peak.

For Sample 1 we notice that the highest concentration of the oxygen-16, blue peak is present in the electrolyte, as we would expect the electrolyte phase to have a higher concentration of oxygen than the cathode phase. The peach or shoulder background is present in all regions of the sample, while the purple region is present at the top of the tip and in the electrolyte with a reduction in the middle. In Sample 1 we see that background peach and purple oxygen are present basically in the whole reconstruction, but that the blue region oxygen is present in the highest concentration in the electrolyte phase. Thus to have an accurate visualization of the oxygen peaks we should visualize the purple region for Sample 2 and the blue region for Sample 1 with the peach region.

When we look at the oxygen-17 isotope we notice a similar appearance of peak spreading (Figure 5-8216). This peak exhibits the same geometry-heating effect seen for oxygen-16, except that here, for Sample 2, the three regimes exhibit three distinct peaks, with similar patterns to oxygen 16 which show that in Sample 1 the electrolyte rich phase is on the bottom and in Sample 2 the oxygen rich phase is on the top.

The doubly ionized $^{40}$Ca$^{+2}$ peak exhibits similar shifts as observed in oxygen (Figure 5-8317). In Sample 1 the red calcium peak is strong in the cathode phase which is calcium doped lanthanum manganate. As the analysis goes through the interface and into the electrolyte the calcium concentration drops off (gray peak). In Sample 2 the opposite material progression is present and the opposite trend is observed with the calcium peak, where in the beginning the red
peak is weak as the electrolyte phase is evaporated and then increases into the gray peak as we cross into the calcium rich cathode phase. Please note, as mentioned before that both red and gray peaks are in fact calcium peaks, and the M/C values are relative charge.

The same effect is observed in the doubly ionized $^{55}\text{Mn}^{+2}$ peak (Figure 5-8418), where two peaks are seen for Sample 1 because of its orientation with the manganese phase being at the top of the tip, and first to be analyzes. As we progress through the tip, the manganese peak shifts from red on the right to the yellow on the left due to localized heating. In Sample 2 there is only one dominant manganese peak (yellow), with a slight second (red) peak present on the right. Here we can also see the effect of the cross-sectional area because the peak spread is higher for Sample 2 than Sample 1 as shown by the higher background in Sample 2. This happens because Sample 2 has a smaller cross-section and conducts the thermal energy away from the evaporation surface at a slower rate.

The triply ionized $^{139}\text{La}^{+3}$ peak exhibits peak broadening with the same peak shifts observed with calcium and manganese, where there are only two regions (Figure 5-8519). The left region is labeled in pink and the right region in blue. In Sample 1 the lanthanum rich region is the cathode located on top (pink peak), and in Sample 2 the cathode is located on the bottom (pink peak). Sample 2 seems to have much more of the blue/weaker peak in the cathode than does Sample 1.

With all of these overlapping peaks, a way to confirm that the peak shift is occurring due to heating towards the end of the analysis was to take Sample 1 and separate the cathode reconstruction from the electrolyte reconstruction. The voltage history of Sample 1 (Figure 5-8620) is plotted as a voltage versus ion sequence number. As you can see the turn on voltage, or the voltage at which the tip started to emit ions was just above 2000 V. This turn on voltage is a
function of tip radius. As we progress to the right in the analysis, by removing monolayer after monolayer of atoms the tip radius of curvature increases and thus the voltage must increase in order to keep the evaporation rate, or the dose which the detector is counting, constant. The curvature in the voltage history plot is evidence of a transition from one phase (cathode on the left) to another phase (electrolyte on the right). If we split the reconstruction into a cathode (top) and electrolyte (bottom) phase with respect to the analysis direction (Figure 5-8721) we can isolate the position of the M/C peaks for each phase. Such a mass spectra is plotted in Figure 5-8822. It is shown that regardless if the peak is strong or weak in the phase (due to atomic concentration), the reason why they drift to the left is dependant on the collection sequence. The peaks on the right are collected before the peaks on the left. The cathode phase has a stronger calcium peak than the electrolyte phase, as expected because the cathode is LCM. The electrolyte phase has a stronger oxygen-16 peak than the cathode, which is also expected because the electrolyte, SSZ has higher oxygen content than the LCM. The significance of the peak drifting to the left indicates that the time of flight for the ionic species is decreasing which is most likely caused by sample heating on the order of 2-3 K.

Zirconium does not show up as a single ion, but it does show up as ZrO$_{2}^{+}$, 16 Da to the right of where the zirconium peak should appear. In fact zirconium has five prevalent isotopes of varying intensities, yielding a zirconium hand-shaped “finger” print pattern on the mass spectra plot (Figure 5-8923). The zirconium oxide peaks are represented by five peaks, four of which are unique, and one which overlaps with an iron peak at 56 Da. We can see in that this signature peak pattern is strong in Sample 1 which has a considerable volume of electrolyte phase (SSZ). Sample 2 has only a couple of the strongest peaks present because only a small portion of the electrolyte phase being present in Sample 1.
To confirm that the green peaks shown in Figure 5-8923 was a ZrO$_2$ peak and not an iron peak, a data pipe was taken through the Sample 1 reconstruction volume. A plot of atomic concentration versus distance (Figure 5-9024) confirms that the green M/C peak signal shown in pink on the concentration profile in fact mimics the zirconium oxide peak perfectly. Thus it is concluded that the green peak in Figure 5-8923 was in fact zirconium oxide and not iron.

One nanometer diameter data pipes were utilized to quantify the 1-D atomic percent concentration profiles of all seven constituent elements through both samples. The Sample 1 concentration profile may be seen in Figure 5-9125, with a magnified view of the cathode (left), electrolyte (right) interface in Figure 5-9226. We can see that in Sample 1, the manganese species has the furthest segregation into the electrolyte, zirconium profile. The manganese profile crosses the zirconium profile 4 nm further than the calcium and lanthanum profiles. The calcium and lanthanum profiles appear to segregate less across the interface boundary than the manganese.

The Sample 2 concentration profile may be seen in Figure 5-9327, with a higher magnification view of the electrolyte (left), cathode (right) interface shown in Figure 5-9428. In Sample 2 the manganese still appears to segregate further than the calcium or lanthanum into the electrolyte phase on the left. Here the sample dimensions do not allow for a measure of how far the manganese segregates into the electrolyte. We can see that the calcium segregates a nanometer further than the lanthanum in this sample. This may be due to the fact that the calcium atomic concentration is 13 at. % in Sample 2, and only 12 at. % in Sample 1. In addition the lanthanum concentration in the Sample 1 cathode is 10.5 at. % while it is only 9 at. % in Sample 2. Both the higher calcium concentration and the lower lanthanum concentration in
Sample 2’s cathode may be the cause of this segregation difference between Sample 1 and Sample 2.

In order to better characterize the Sample 2 interface, another Sample 2 atom probe tip was successfully reconstructed (Figure 5-9529). Our sample identification number for this reconstruction was 3294 (Sample 2-3294). The pre analysis tip can be seen in part (a), where there is a void present. The same void is present in part (b). If we rotate the atomic reconstruction 180 degrees in part (c) we can see the void and the presence of electrolyte at the tip marked with a letter “E”. The concentration profile of Sample 2-3294’s atomic reconstruction is seen in Figure 5-9630. This sample is the same orientation as the previous Sample 2 reconstruction with the electrolyte atop the cathode. It is apparent that the manganese profile penetrates the electrolyte further than calcium and lanthanum. The manganese concentration in the cathode bulk is 30 at. %, the calcium and lanthanum cathode bulk concentrations are 18 and 9 at. %, respectively. The void once again appears to have a higher concentration of hydrogen as previously observed in Samples 1 and 2 (Figure 5-9731). If we reconstruct just the hydrogen (H\(^{+1}\)) we observe that there is a higher concentration in the electrolyte phase near the “E” marker than the cathode. As we approach the void, the hydrogen profile jumps up four times in concentration magnitude (Figure 5-9731). This may be caused by the impregnated epoxy, or a higher concentration of hydrogen or water at the electrolyte/cathode grain boundaries.

In the previous three LEAP reconstructions, the interfaces were oriented perpendicular to the direction of analysis. A fourth tip, Sample 2-3384 was fabricated and reconstructed to yield an interface with a perpendicular orientation to the analysis direction (Figure 5-9832). This figure shows us that cathode bulk and electrolyte bulk are both present due to the flattening of
the concentration profiles. Manganese is the dominant cathode species (omitting oxygen) and segregates further than the calcium species in the “E” labeled electrolyte phase, despite calcium and manganese having equal concentrations at x-distance of 8 nm. Furthermore, the manganese concentration plateaus around 8 at. %, 15 nm away from the interface, in the electrolyte phase. This seems to solidify the observation that manganese is the species that segregates the furthest in the cathode/electrolyte interface in the LCM/SSZ system.

The presence of hydrogen at the interfacial reconstruction voids made us wonder if other elements experienced similar segregation at cathode/electrolyte interfaces. To visualize this a 2-D concentration profile was constructed for another Sample 2 reconstruction, Sample 2-3401 (Figure 5-9933). In the SEM image of Figure 5-9933 the electrolyte phase is in the front, and the cathode phase in the back. The interface between the two forms an upside down U shape, with what appears to be a void, which is shown with a black arrow. In the LEAP reconstruction the tip we see the appearance of the same void (black arrow) in the electrolyte region (denoted by the letter E). This sample is oriented with the interface parallel to the analysis direction. In Figure 5-10034 the top view atomic reconstruction is shown in part (a) where the arrow indicates the same void seen in Figure 5-9933. Electrolyte phase is denoted with the letter E, and cathode phase is denoted with the letter C. The side view is shown in part (b) where the electrolyte is on the right and cathode on the left. The side view accompanying 1-D concentration profile shows the cathode/electrolyte interface present at an x distance of 130 nm. Once again the manganese segregates the furthest into the electrolyte. If only the zirconium and manganese atoms are visualized (Figure 5-10034d) a linear interface emerges. If a 1 nm by 1 nm probe is applied to the reconstruction we are able to derive a 2-D concentration profile (as view end on with the analysis direction going into the plane of the page) for each element in the volume (Figure 5-
The void observed in the atomic reconstruction top view is seen to have a high concentration of hydrogen and oxygen. The scandium intensity is present in the top, electrolyte region, in low concentrations. The manganese concentration appears to have the furthest penetration across the length of the interface into the electrolyte region, where as the calcium’s segregation is less, and the lanthanum is even less. The scandium, oxygen manganese and calcium concentrations seem to outline this void. Although no electrochemical measurements are presented here it is possible to postulate that the hydrogen rich void is an epoxy impregnated active triple phase boundary (TPB). If this were the case, this 2-D concentration analysis may indicate that under fuel cell operation hydrogen, oxygen, scandium, calcium and manganese segregate towards the electrochemically active region. Conversely the zirconium and lanthanum species tend to segregate away from this region.

5.4 Conclusions

This work represents the first LEAP microscope 3-D atomic reconstructions of a solid oxide fuel cell. The interface between the electrolyte and cathode phases within the composite regions of two separately processed Siemens Energy Inc., SOFC cathodes were prepared into atom probe tips with tip diameters below 50 nm. The reconstructions showed what effect tip geometry has on mass-to-charge ratio graphs. The cathode phase originating manganese species appears to segregate the furthest into the scandium doped zirconium oxide, electrolyte phase. This distance appears to be over 20 nanometers. Calcium and lanthanum are found to segregate across the cathode/electrolyte boundary only around 10 nanometers, which is on the order of the interface thickness. The cathode phase calcium atomic concentration values varied by 1-2 atomic percent between Samples 1 and 2, (Sample 2 having a higher average calcium concentration of 20 atomic percent) which is comparable to previous STEM-EDS studies. This work also shows the advantage of the LEAP microscope’s atomic probe size as compared to
STEM techniques for interfacial chemical segregation studies. Many compound ions are evaporated and future work should focus on confirming their existence and position in the M/C range in order to yield more understanding to interfacial phases present at the cathode/electrolyte interface. In addition the effect of bias on interfacial segregation may now be investigated on the atomic level. The LEAP technique provides researchers with a tool for early detection of ternary phase formation at the various interfaces present in solid oxide fuel cells.
Figure 5-68. Schematic of the dual beam FIB/SEM assisted (a) deposition of platinum on the composite cathode, (b,c) trenching around the platinum, (d-e) thinning of the sample and using channeling contrast to differentiate pore, cathode and electrolyte phases, (f-g) marking the platinum with fiduciary marks for areas of interest, (h) undercutting, and (i) micromanipulator liftout of sample.
Figure 5-69. A schematic of the three-step micromanipulator welding process where (a) the micromanipulator is made to touch the sample, (b) small through hole is made at interface and backfilled with platinum, and (c) larger area platinum is deposited for reinforcement.

Figure 5-70. SEM image of an Imago Scientific flat top Si post array. The posts with white bases have been mounted with atom probe samples. The discoloration is caused by FIB damage caused during sharpening.
Figure 5-71. Depiction of (a) sample liftout and orientation of micromanipulator and GIS platinum needle with respect to sample trench, (b) top, SEM view of sample being positioned over a silicon flat top post, and (c) side, FIB view of sample being lowered down onto the silicon post.

Figure 5-72. Low current FIB micrograph of (a) sample being made to touch the silicon flat-top post, (b) platinum weld deposited at the interface between the sample and the post, and (c) use of higher current FIB to cut mounted sample free from rest of sample.
Figure 5-73. Focused ion beam top view of Si post with sample atop as high voltage (30kV) annular beam is used to form the tip (a-b), then low voltage (8kV) beam is utilized to conduct final tip shaping and cleaning (c-f).
Figure 5-74. SEM side views of the FIB annular beam tip sharpening using 30kV beam to form the cone and then an 8kV beam to remove gallium damage and form the final tip.
Figure 5-75. LEAP reconstruction of Sample 1. Axes are in units of nanometers. Top region is cathode phase and bottom region is electrolyte phase. The pre analysis SEM image of the tip is shown on the right. Arrows are pointing to the void regions on both.
Figure 5-76. LEAP reconstruction of Sample 2. Axes are in units of nanometers. Electrolyte phase is at the top. Cathode phase is on the bottom. Top region is cathode phase and bottom region is electrolyte phase. The pre analysis SEM image of the tip is shown on the right.
Figure 5-77. Mass spectrum plots of counts versus mass-to-charge ratios for Samples 1 & 2
Figure 5-78. Hydrogen atomic reconstructions along with the hydrogen mass spectrum. Arrows point to hydrogen enrichment seen near cathode/electrolyte interface of both Samples 1 and 2.
Figure 5-79. Scandium atomic reconstructions along with the mass spectra for Samples 1 and 2.
Figure 5-80. Oxygen atomic reconstructions along with the mass spectra for Samples 1 and 2.
Figure 5-81. Oxygen atomic reconstructions are divided into three distinct peaks labeled in blue, peach and purple. We can see that as the sample analysis progresses the only peak present throughout is the middle peach peak (B). The left most, blue peak is present at the end of the analysis (A). The right most, purple peak is present at the beginning of the analysis (C). This is evidence of mass-to-charge peak drift.
Figure 5-82. Oxygen isotope 17 atomic reconstruction with mass spectra for Sample 1 and 2.
Figure 5-83. Calcium atomic reconstruction with mass spectra for Samples 1 and 2.
Figure 5-84. Manganese atomic reconstruction with mass spectra for Samples 1 and 2.
Figure 5-85. Lanthanum atomic reconstruction with mass spectra for Samples 1 and 2.
Figure 5-86. Voltage history plot for the analysis of Sample 1. Y axis is voltage, X axis is ion sequence number. The analysis starts at a low voltage on the left and progresses to the right with increasing voltage. The reconstruction image is shown with cathode phase on the left and electrolyte phase on the right.
Figure 5-87. The reconstruction of Sample 1 is split up into a cathode (top) region and an electrolyte (bottom) region with respect to the analysis direction.
Figure 5-88. Sample 1's oxygen-16 and calcium mass-to-charge ratio peaks both drift to the left as the LEAP analysis progresses from the top, cathode phase to the bottom, electrolyte phase.
Figure 5-89. Zirconium oxide atomic reconstruction with mass spectra peaks for Samples 1 and 2 highlighted in purple with an possible overlap with an iron(56) peak highlighted in green.
Figure 5-90. Sample 1 atomic reconstruction is shown with analysis direction as a reference, next to a 1-D concentration profile of zirconium oxide (purple) and pink signal related to the possible iron peak. This plot confirms that the pink signal is zirconium based.
Figure 5-91. Sample 1 atomic reconstruction and 1-D atomic concentration versus distance (nm) profile. Analysis direction is from left to right.
Figure 5-92. Sample 1 high magnification atomic reconstruction and 1-D atomic concentration versus distance (nm) profile. Analysis direction is from left to right.
Figure 5-93. Sample 2 atomic reconstruction with a 1-D atomic concentration versus distance (nm) profile.
Figure 5-94. High magnification of Sample 2 atomic reconstruction with a 1-D atomic concentration versus distance (nm) profile.

Figure 5-95. Another Sample 2 atom probe tip with a void shown by arrow imaged with SEM (a), with an atomic reconstruction with the same void present (b), and a reconstruction rotated 180 degrees which shows the electrolyte region at the top marked with and E (c).
Figure 5-96. Sample 2-3294's atomic reconstruction is shown above its 1-D concentration profile.
Figure 5-97. Sample 2-3294's hydrogen atomic reconstruction and 1-D atomic concentration profile.
Figure 5-98. Sample 2-3384 atomic reconstruction top view, side view, and 1-D concentration profile. The interface is parallel to the direction of analysis.

Figure 5-99. Sample 2-3401 LEAP reconstruction is shown on the right (axes dimensions are shown in nanometers). A SEM image of the same pre-LEAP analysis tip is shown on the left. The arrows in both images point towards visible voids. E indicates electrolyte phase. C indicates cathode phase.
Figure 5-100. Sample 2-3401 is shown with (a) top view where all atoms are visible, (b) side view with all the atoms visible, (d) top view with only zirconium and manganese atoms visible and a 1-D concentration profile. Arrows point to voids seen in top views. E stands for electrolyte phase. C stands for cathode phase.
Figure 5-101. Sample 2-3401 2-D concentration profiles are shown. The concentration intensity is indicated by color, where red is the highest and blue is zero intensity. Probe size is 1 nm x 1 nm pixel.
CHAPTER 6
CONCLUSION

6.1 Conclusion

We have successfully reconstructed a 3-D model of an actual LSCF cathode. This provides the ability to quantify porous cathode microstructures at the sub-micron level. This technique allows researchers to quantify microstructural properties in between processing steps, and at specific sites. Further, this technique has allowed us to develop the direct link between the microstructure and performance relationship in SOFC cathodes \(^{78, 41}\).

Microstructures of two Siemens-Westinghouse cathode-SOFC samples were analyzed. The cathode/electrolyte interface was characterized with TEM-EDS. Sample 2 had higher calcium content in both electrolyte and cathode phases. This calcium difference may be the cause of the coarser microstructure seen in sample 2 because calcium is known to act as a sintering aid \(^{60}\). The cathode microstructure was quantified with the aid of a FIB/SEM. Both samples consisted of a composite cathode on the order of 20 \(\mu\)m, sandwiched between the porous cathode support and dense electrolyte. Surface area, porosity, particle size, tortuosity and, for the first time, 3-D topological connectivity were all quantified with the aid of Amira software. Sample 2 had a coarser composite cathode microstructure with 2.5 % higher composite cathode connectivity. This was the first time that true 3-D topological connectivity was quantified for an SOFC structure.

In the future, connectivity may be related to all transport processes that occur throughout the SOFC. This advancement in connectivity quantification can further the understanding of many other fields including biological systems connectivity, for example, by aiding researchers in better understanding the 3-D lattices used in synthetic tissue harvesting. Moreover, the
MAZO quantification technique helps in understanding 3-D load distribution in structural materials. The combined use of FIB/SEM and skeletonization technology allows for more intelligent design of porous micro and nano functional materials.

This work represents the first LEAP microscope 3-D atomic reconstructions of a solid oxide fuel cell. The interface between the electrolyte and cathode phases within the composite regions of two separately processed Siemens Energy Inc., SOFC cathodes were prepared into atom probe tips with tip diameters below 50 nm. The reconstructions showed what effect tip geometry has on mass-to-charge ratio graphs. The cathode phase originating manganese species appears to segregate the furthest into the scandium doped zirconium oxide, electrolyte phase. This distance appears to be over 20 nanometers. Calcium and lanthanum are found to segregate across the cathode/electrolyte boundary only around 10 nanometers, which is on the order of the interface thickness. The cathode phase calcium atomic concentration values varied by 1-2 atomic percent between samples 1 and 2, (sample 2 having a higher average calcium concentration of 20 atomic percent) which is comparable to previous STEM-EDS studies $^{51, 52}$. This work also shows the advantage of the LEAP microscope’s atomic probe size as compared to STEM techniques for interfacial chemical segregation studies. Many compound ions are evaporated and future work should focus on confirming their existence and position in the M/C range in order to yield more understanding to interfacial phases present at the cathode/electrolyte interface. In addition the effect of bias on interfacial segregation should, and now may be investigated on the atomic level. The LEAP technique provides researchers with a tool for early detection of ternary phase formation at the various interfaces present in SOFCs.
6.2 Future Work

6.2.1 3-D micro texture characterization of the composite cathode using FIB/SEM and EDX/EBSD

A 3-D-EBSD technique has been developed to simultaneously quantify morphology (FIB/SEM), crystallographic orientation (EBSD), and chemical composition (EDX) of a composite cathode. The system uses a joint high-resolution field emission SEM-EBSD set-up in conjunction with a focused ion beam (FIB) system in the form of a 3-D crystal orientation microscope (3-D EBSD)\textsuperscript{79}. With this technique FIB sequentially mills slices of material by sputtering with a high energy Gallium ion beam operating in gracing incidence. A CCD camera takes an EBSD pattern for each slice. Then software automatically indexes the EBSD pattern, and builds an orientation image map. Consequently, 2-D orientation image maps that consist of grain boundary of two phases highlighted in various colors represent different crystal structure orientation of each phase. The orientation image maps obtained in each serial section of the material are then used to reconstruct the composite microstructure in three dimensions including all features that can be jointly detected via EBSD and/or EDS mapping\textsuperscript{79,80}. EDS can be conducted on the flat surfaces after FIB sectioning to collect composition analysis per slice. Therefore, 3D dimensions of the composite cathode, distribution of LSM or YSZ in the composite cathode, and chemical information are all characterized by integration of EDX/EBSD and FIB/SEM.

The EBSD assisted reconstruction would allow us to image and reconstruct the grain boundaries of the composite cathode in three dimensions due to the randomly oriented nature of the electrolyte and cathode grains. With this expanded capability over the current 3-D FIB/SEM reconstructions, a more thorough understanding of the electrochemical importance of grain boundaries would be developed. This understanding could be combined with the therein
developed topological connectivity, thus allowing us to truly model the cathode performance by fully understanding how many different grains, and orientations the ions/electrons must pass in order to arrive at the electrolyte. This may also be combined with the skeletonization nodes to further understand where the skeleton nodes develop and if they have any preferred crystallographic orientation. This work should be conducted on symmetric cell composite cathodes such as LSCF/GDC so that electrochemical performance may be related to the composite cathode structure as has been done here with the single phase structure. This would allow for a more thorough understanding of the fundamental relationship between electrochemical performance of SOFCs and their microstructure.

6.2.2 LEAP standards

As we have seen in chapter five, the M/C spectrum is quite noisy for the composite oxides that make up cathodes and electrolytes, especially above 60 Da. In order to understand the multiple ion peaks, a study of various composition standards should be done. These standards should be made so as to confirm the peaks that are unique to certain compounds such as an insulating phase of strontium zirconate which appears at LSCF/YSZ interfaces at high temperatures. By making standards of known ternary phases it will facilitate the understanding of which peaks are a part of standard background LEAP analysis and which peaks may indicate actual ternary phases. One such standard should be zirconium oxide to confirm that zirconium is difficult to ionize by itself below 100 Da. A study of the compound standards would be useful to researchers in many fields, especially as the LEAP microscope starts to gain popularity across academic and industrial research labs.

6.2.3 LEAP bias study

An initial study of the effect of bias was conducted on LSCF/YSZ symmetric cells sintered at 950 °C for one hour. The purpose of the study was to investigate the effect of break-
in on these cathodes to see if we could figure out why it is that fuel cells tend to initially improve in performance before starting to degrade. This process typically happens within the first couple hundred hours of operations. In our study we biased the symmetric cathode for 12 hours with a constant current of 250 mA. We can see in Figure 6-1 the current in orange and the measured bias in blue. The interruptions in the bias were due to regularly scheduled EIS scans. We can see that as the 12 hours draws to a close that the bias required to pull the same 250 mA of current increases from -4.2 volts to -5.7 volts thus increasing by 35% (1.5V) in just 12 hours. The pre and post application of bias EIS scans confirmed that something was changing as seen in Figure 6-2. We see a 10X increase in the total polarization resistance between the initial (prebias) scan and the scan after 12 hours of direct current flowing through the symmetric cell. We theorized that something was occurring at the LSCF/YSZ interface, and sought to find proof using LEAP reconstructions. Unfortunately for us, the nano LSCF microstructure does not allow for easy micromachining of LEAP atom probe tips. Most of the tips that we made resulted in catastrophic tip failure. It may have happened due to the fine particle size, thus the same bias study should be conducted on coarser LSCF/YSZ symmetric cells to isolate what species are segregating at the electrochemically active interfaces. It may also be of interest to investigate the effect of bias on LSCF/GDC which is known to be a more stable cathode/electrolyte combination. This work could be very beneficial as part of a fast feedback loop in investigating interfacial phases or segregation which may have deleterious effects on SOFC performance. The fact that it has atomic level special and chemical resolution means that it would be applicable only on the nanometer scale interfaces of interest, not bulk properties.
Figure 6-1. Change in measured bias under constant applied current of LSCF/YSZ symmetric cell.

Figure 6-2. Effect of applied 12 hour bias on LSCF/YSZ polarization.
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BIOGRAPHICAL SKETCH

Danijel Gostović was born in Ogulin, Croatia in 1981, within the Lika province, also the birthplace of Nikola Tesla. Exposure to solar heaters and wind turbines on his grandmother’s farm sparked his interest in technology. His family immigrated to the city of White Plains, NY in February of 1990, months before the outbreak of the Yugoslavian Civil War. He went on to graduate from the White Plains Senior High School in 2000 with an Honors Regents Diploma. Danijel enrolled in Northwestern University in Evanston, Illinois in the Fall of 2000. A chance conversation resulted in Danijel enrolling in a Scanning Electron Microscopy (SEM) freshman engineering seminar class taught by Professor Vinayak P. Dravid. This class turned Danijel onto the materials science and engineering major through hands-on SEM experiments. In 2003 he accepted a co-operative education extended internship position with Functional Coating Technology, LLC. (FCT) of Evanston, IL, while still enrolled as a full time student. Danijel graduated with a Bachelor of Science., a Business Basics Certificate and a Co-operative Education Certificate in 2004. Upon graduation Danijel accepted a full time research engineer position with FCT where he learned a lot about SOFC engineering, accounting, and business management. In the Fall of 2005 he moved to Gainesville, Florida in pursuit of a Master of Science and Doctor of Philosophy degrees at the University of Florida. During his time at UF, Danijel was a founding member of the Electrochemical Society Student Chapter, and served as its treasurer for three consecutive terms. He enjoyed the interdisciplinary nature of a UF graduate education which allowed him to collaborate with researcher institutions from around the world including EMPA (Switzerland), RISØ National Laboratory (Denmark), Università di Catania (Italy), University of North Texas (Denton, TX), University of Alabama (Tuscaloosa, AL), University of Illinois (Urbana-Champaign, IL) and Siemens Energy, Inc. (Pittsburg, PA).