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Fabrication and Analysis of Compositionally Graded Functional Layers for Solid Oxide Fuel Cells

Jared Ray McCoppin
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FABRICATION AND ANALYSIS OF COMPOSITIONALLY GRADED
FUNCTIONAL LAYERS FOR SOLID OXIDE FUEL CELLS

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Engineering

By

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B.S.M.S.E, Wright State University, 2008

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Solid Oxide Fuel Cell (SOFC) structures must be optimized for high performance, increased life, and low cost. Fabrication methods are an area of research interest in bringing down the total cost of SOFCs, and can also impact cell life and performance. Graded functional layers have been shown to enhance cell performance, but current fabrication methods require multiple fabrication steps. This thesis describes a novel fabrication method capable of compositional gradation of functional layers for SOFCs. Using colloidal spray deposition technology, a controlled co-deposition strategy was utilized to fabricate SOFC’s with compositionally graded cathode and anode functional layers (CGCFL/CGAFL). In this research, compositionally graded CGCFL/CGAFL SOFCs were tested and analyzed using current-voltage measurements and energy impedance spectroscopy methods. Scanning electron microscopy and elemental mapping were utilized for structural characterization. The fabrication technique presented in this thesis allows for the rapid and precise, single-step deposition of a compositionally graded SOFC interlayer, and should facilitate the optimization of SOFC stack designs.
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1 Introduction

Solid oxide fuel cells (SOFC’s) are effective electrochemical devices that convert chemical energy into useful electrical energy. Many efforts have been made to bring down the cost through materials research, fabrication processes, and stack design. In the last few years it has been discovered that the use of a functional layer in the stack design benefits the SOFC by decreasing the polarization resistance (Tsai and Barnett). It was further investigated by Hart et.al that by dividing the functional layer into multiple layers with graded composition that the polarization resistance could be reduced even further (Hart, Brandon and Day). The process of implementing multiple layers with graded composition effectively introduces additional fabrication steps whereby making it less desirable as an optimization process. This thesis entails a fabrication process that eliminates the need for a multiple stepped process to obtain a compositionally graded electrode functional layer.

1.1 Objective

The objective of this thesis is threefold. The primary objective of this thesis is to develop a fabrication method that allows for compositional controlled deposition of two ceramic inks. Having compositional control will allow for a single step composition gradation of the functional layer between the electrode and electrolyte of a SOFC. The second task of this thesis is to build button cells and implement both an anode and cathode compositionally graded functional layer using the fabrication method developed during the first objective. The last objective of this thesis is to identify, test, and compare
any relative benefits of the compositionally graded cathode/anode functional layers (CGCFL/CGAFL) deposited by this method. The electrochemical performance of the compositionally graded functional layer will be compared to that of a standard cathode functional layer (SCFL) and a solid oxide fuel cell (SOFC) with no cathode functional layer (NCFL) as a control. Microstructure analysis will also be used to identify any relative benefits of the CGCFL/CGAFL when compared to the SCFL and NCFL cells.
2 Background of Fuel Cells

It’s well known that combustion engines are a conventional means of performing a transformation of fuel energy into heat and mechanical energy by reacting fuel with air. This mechanical work can further be transformed into electrical energy with the caveat that with each transformation, the total efficiency will decrease. Fuel cells on the other hand provide an efficient controlled means to perform this transformation. Fuel cells avoid combustion and directly converting chemical energy into electrical energy. Fuel cells are any electrochemical devices that when feed a continuous stream of fuel will release stored chemical energy into useful electrical energy by direct conversion. The history of fuel cells dates back to 1839 when Sir William Grove, knowing about electrolysis, tried to reverse the process (Grove). It wasn’t until 50 years later that the first hydrogen-oxygen fuel cell using a quasi-solid electrolyte saturated with dilute sulfuric acid was fabricated (Mond and Langer).

2.1 Basic Fuel Cell Operation

The basic operation of a fuel cell is divided into four parts. They are reactant delivery, electrochemical reaction, ionic and electronic conduction, and finally product removal. To initiate the operation of the fuel cell, the anode side of the cell is provisioned with fuel while the cathode side is provisioned with an oxidant. The two individual half reactions that occur at each electrode are separated by an electrolyte. The current produced originates when the reactant, the electrode and the electrolyte meet. This location is referred to as a triple point. (Laramie and Dicks) Once the
electrochemical reaction occurs, the ions and electrons that are generated travel through their respective pathways to the electrode where they will be consumed. As the ions and electrons are consumed at the electrode a byproduct will form and requires removal to avoid performance degradation.

2.2 Types of Fuel Cells

There are five major types of fuel cells that are categorized based on the type of electrolyte they employ. By convention, the type of electrolyte used is incorporated into the name of the fuel cell. The five major types are the polymer electrolyte membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC), and the solid-oxide fuel cell (SOFC). All five fuel cell types operate on the same underlying electrochemical principals but each fuel cell has its individual material makeup, fuel sensitivity, and reaction/operating temperatures shown in Table 1.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>PEMFC</th>
<th>PAFC</th>
<th>AFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge Carrier</td>
<td>H⁺, H₃PO₄</td>
<td>H⁺, KOH</td>
<td>OH, CO₃²⁻</td>
<td>CO₃²⁻, O₂⁻</td>
<td></td>
</tr>
<tr>
<td>Operation temperature</td>
<td>80°C</td>
<td>200°C</td>
<td>60-250°C</td>
<td>650°C, 600-1000°C</td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel, Perovskites</td>
<td></td>
</tr>
<tr>
<td>Cell components</td>
<td>Carbon</td>
<td>Carbon</td>
<td>Carbon</td>
<td>Stainless, Ceramic</td>
<td></td>
</tr>
<tr>
<td>Fuel</td>
<td>H₂, methanol</td>
<td>H₂</td>
<td>H₂</td>
<td>H₂, CH₄, H₂, CH₄, CO</td>
<td></td>
</tr>
</tbody>
</table>
Table 1: Description of Fuel Cell Types

Of the five major types of fuel cells the SOFC and the PEMFC stand out as having potential to be used as long term energy solutions (M. Cifrain). Both have good potential for high power and energy density while each one uses solid components rather than liquid electrolytes.

2.2.1 Polymer Electrolyte Membrane Fuel Cell

Polymer electrolyte fuel cells (PEMFC) use a thin polymer membrane as an electrolyte and have great potential to be an affordable low cost fuel cell. PEMFC operate from 50-90°C allowing for low cost materials to house the reaction. The basic operation of the PEMFC requires the reaction of hydrogen fuel with air as an oxidant. A Pt/carbon supported anode oxidizes hydrogen and the proton is then conducted through a water solvated perfluorinated sulfonic acid polymer membrane (e.g. Nafion) to the cathode where it combines with oxygen ions to form water. (Laramie and Dicks) (O’Hayre, Cha and Colella) Due to the proton conduction nature of the electrolyte the electrochemical half-cell and overall cell reactions for the PEMFC are as shown in the following Equation 1-3.

Equation 1  \[ 2H_2 \rightarrow 4H^+ + 4e^- \text{ (anode)} \]

Equation 2  \[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (cathode)} \]

Equation 3  \[ 2H_2 + O_2 \rightarrow 2H_2O \text{ (overall)} \]
The complete assembly of the PEMFC is referred to as the membrane electrode assembly (MEA) and is on the order of 1mm thick. Water management is the main problem with the PEMFC due to the conductivity of the electrolyte being highly dependent on humidity. The required presence of liquid water in the electrolyte limits the operating temperature to 90°C or lower due to the increased fuel cross over that will occur as the electrolyte dries out. Since water is the byproduct of the electrochemical reaction care must be taken to avoid an access of water in the electrolyte. If the electrolyte is flooded, the reaction surface area is diminished and cell performance drops off rapidly. Despite the need for critical water management, the PEMFC has the highest power density of all the fuel cell classes, it has good start – stop capabilities, and the low operation temperature makes it suitable for portable application.

2.2.2 Phosphoric Acid Fuel Cell

The basic construction of the Phosphoric acid fuel cell (PAFC) consist of liquid $\text{H}_3\text{PO}_4$ electrolyte contained by a SiC matrix that is located between two porous graphite electrodes coated with a platinum catalyst. (S. Basu) The electrochemical reaction utilized by the PAFC is the same as the PEMFC. One of the major issues with the operation of the PAFC is controlling the temperature. The $\text{H}_3\text{PO}_4$ electrolyte of the PAFC has to be maintained above an operating temperature of 42°C to avoid the solidification of the electrolyte which could result in destructive stresses being placed on the SiC matrix. While operating at elevated temperatures the electrolyte evaporates releasing acidic gasses and requiring continuous replacement of the depleted electrolyte. Also, the temperature of the $\text{H}_3\text{PO}_4$ electrolyte cannot exceed 210°C due to an
unfavorable phase transformation. Despite the disadvantages of PAFC, it is a relatively low cost mature technology with excellent reliability/long-term performance.

2.2.3 Alkaline Fuel Cell

The Alkaline fuel cell (AFC) operates by employing an aqueous potassium hydroxide electrolyte, allowing for an OH⁻ ion to be conducted from the cathode to the anode. The presence of CO₂ in an AFC degrades the KOH electrolyte by the following two reactions.

Equation 4 \[ 2OH^- + CO_2 \rightarrow CO_3^{2-} + H_2O \]

Over time the concentration of OH⁻ declines in the electrolyte and the KOH is reacted.

Equation 5 \[ KOH + CO_2 \rightarrow K_2CO_3 + H_2O \]

Mitigation of these reactions is achieved by refreshing the KOH electrolyte, using CO₂ scrubbers and by using pure fuels. Pure hydrogen fuel is fed to the anode while Air oxidant is supplied to the cathode. The anode and cathode reactions are therefore as follows.

Equation 6 \[ 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^- \text{ (anode)} \]

Equation 7 \[ O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \text{ (cathode)} \]

Equation 8 \[ 2H_2 + O_2 \rightarrow 2H_2O \text{ (overall)} \]

From this equation it can be seen that water is produced twice as fast at the anode than it is consumed at the cathode. Excess water can decrease the performance of the AFC so
care must be taken to avoid allowing the excessive water to dilute the KOH electrolyte. AFC’s have high power density and efficiency but due to their limitations they are not practical for long term energy production. Alkaline fuel cells were used during the Apollo Space Program. While in space the AFC’s had no problems with CO₂ contamination but on earth the AFC’s cannot tolerate atmospheric levels.

### 2.2.4 Molten Carbonate Fuel Cell

The Molten carbonate fuel cell relies on a mixture of molten Li₂CO₃ and K₂CO₃ bound in a LiALO₂ ceramic matrix as the electrolyte. The charge carrier in the MCFC is a carbonate ion, CO₃²⁻ that travels from the cathode to the anode resulting in the following reactions.

\begin{align*}
\text{Equation 9} & \quad 2H₂ + CO₃^{2⁻} & \rightarrow 2H₂O + 2CO₂ + 4e⁻ \quad \text{(anode)} \\
\text{Equation 10} & \quad O₂ + 2CO₂ + 4e⁻ & \rightarrow 2CO₃^{2⁻} \quad \text{(cathode)} \\
\text{Equation 11} & \quad 2H₂ + O₂ & \rightarrow 2H₂O \quad \text{(overall)}
\end{align*}

Both electrodes in the MCFC are nickel based. The cathode consists of a lithiated nickel oxide that allows for the reduction of carbon dioxide and oxygen to form the charge carrying carbonate ion. The anode of the MCFC is a nickel/chromium alloy that oxidizes the hydrogen fuel, allowing for the completion of the reaction. The MCFC has the advantages of fuel flexibility and high efficiencies but suffers from corrosion and life time issues. (O’Hayre, Cha and Colella)

### 2.3 Solid Oxide Fuel Cell
Solid oxide fuel cells (SOFCs) are electrochemical solid-state devices that convert the chemical energy of a reaction directly into electrical energy with no moving parts. The electrical efficiency of a SOFC can be easily achieved in the range of 40-50%. Conversely, a conventional heat engine has a typical electrical efficiency of 20-30%, particularly for less than 1MW class, due to the limitation of the Carnot cycle. (Gasik) The increased efficiency of the SOFC translates to lower CO$_2$ emissions and thus is considered a greener technology. Although the SOFC has great potential to provide higher fuel efficiencies with the added benefits of reduced pollution, development of SOFC technology is proving to be a challenge. Currently, SOFC materials, operating conditions, and cell fabrication need to be optimized if the hope of commercial production is to be realized.

SOFCs operate at high temperatures ranging from 650-1000°C. The high operating temperatures of the SOFC have both minor disadvantages and some unique advantages. The disadvantage of high operating temperature is that SOFC have to meet certain criteria and thus are constructed from relatively expensive metallic and ceramic materials. (Gasik) The unique advantage of the SOFC is that it has more fuel flexibility than the other classes of fuel cells. SOFCs can operate on hydrocarbons (e.g. propane, butane, heptane, decane, dodecane...etc.) (Steele), logistic fuels (e.g. JP-3, JP-8) (Zhou, Gallo and Pague), commercial fuels (e.g. octane, diesel, biodiesel) (Costa-Nunes, Vohs and Gorte) and syngas, (carbon monoxide and hydrogen mixture) as well as pure hydrogen. (Park, Vohs and Gorte) Unfortunately, there are fouling and degradation issues with some of the fuels. The deposition of carbonaceous material and sulfur poisoning at the anode tend to decrease performance due to decreased reaction sites as well as
catalytic degradation. (Aguilar, Zha and Li) The degradation occurs due to the high temperature reactions between Ni-based oxidation catalysts and corrosive impurities present in the fuel. Currently research is being conducted to develop novel anode materials that don’t suffer from performance degradation as well as to understand the mechanism of catalyst degradation and its long-term effects on performance. (Cheng and Zha)

2.3.1 Operation

The overall driving force for a SOFC is the gradient of chemical potential of oxygen existing between a cathode of high partial pressures of oxygen and an anode of low partial pressures of oxygen. (Gasik) The functionality of the cathode is the reduction and thus ionization of diatomic oxygen, \( \text{O}_2 \) into \( \text{O}^{2-} \). The oxygen ions are subsequently absorbed into the lattice of the electrolyte via oxygen vacancies. A concentration gradient of oxygen chemical potentials develops resulting in ion migration across the electrolyte via vacancy transport from the cathode to the anode. (O'Hayre, Cha and Colella) At the anode the hydrogen molecules are oxidized releasing electrons that, via an external load, travel to the cathode assisting in the oxygen reduction process. Upon arriving at the anode, the oxygen ions combine with protons of oxidized hydrogen to form water. (Skinner and Kilner) Depending on the fuel, \( \text{CO}_2 \) may also be a byproduct. The produced water is of a vapor state and is easily removed from the cell allowing for the process to continue. The maximum cell voltage depends on the temperature, load and fuel composition. Typically a single cell will produce 1.2 volts and is stacked with other
cells to produce a reasonable source of power. A basic schematic of the SOFC is presented below in Figure 1

![Solid Oxide Fuel Cell Schematic](image)

**Figure 1: Schematic of Solid Oxide Fuel Cell**

### 2.3.2 Components

There are three active elemental components in a SOFC. They are the electrolyte, cathode, and anode. Table 2 below is based on a table from (Fergus, Hui and Wilkinson) and shows the microstructure, and property requirements of SOFC component layers. Currently, 8-mole % yittria-stabilized zirconia, $8\text{Y}_2\text{O}_3-\text{92ZrO}_2$ (YSZ) is the most common SOFC electrolyte due to its low cost and sufficient conductivity, however other doped-zirconia and ceria compounds (e.g. $\text{Sc}_2\text{O}_3-\text{ZrO}_2$, $\text{Gd}_2\text{O}_3-\text{CeO}_2$, $\text{Sm}_2\text{O}_3-\text{CeO}_2$) have been studied (Fergus, Hui and Wilkinson). Cathode materials currently used with YSZ are strontium doped lanthanum based perovskites, where the B-site cation is either
manganese or cobalt (e.g. La$_{0.85}$Sr$_{0.15}$MnO$_3$, La$_{0.6}$Sr$_{0.4}$CoO$_3$, and La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_3$). The anode is a composite electrode made up of the electrolyte material (YSZ) and a catalytically active metal such as nickel. The combination of a metal and ceramic, as in the case of the anode, is termed a ‘cermet’ (Fergus, Hui and Wilkinson).

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous, many triple-phase boundaries, stable to sintering.</td>
<td>Dense, thin, free of cracks and pinholes</td>
<td>Porous, many triple-phase boundaries, stable to sintering.</td>
<td></td>
</tr>
<tr>
<td>Electrical</td>
<td>Electronically and preferably ionically conductive.</td>
<td>Ionically but not electronically conductive.</td>
<td>Electronically and preferably ionically conductive.</td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>Compatible with other layers, especially electrolyte</td>
<td>Compatible with other layers especially structural support layers.</td>
<td>Compatible with other layers, especially electrolyte</td>
</tr>
<tr>
<td>Chemical Compatibility</td>
<td>Minimal reactivity with electrolyte and interconnect</td>
<td>Minimal reactivity with anode and cathode</td>
<td>Minimal reactivity with electrolyte and interconnect</td>
</tr>
</tbody>
</table>

Table 2: Microstructure and Property Requirements of SOFC Component Layers

2.3.2.1 Anode

The anode of the SOFC is an engineered structure designed to facilitate operational requirements. These requirements for the SOFC anodes are; stability in reducing atmospheres, catalytic activity to hydrogen oxidation, high electronic and ionic conductivity, gas diffusion and chemical and physical compatibility with surrounding components. (Park, Vohs and Gorte) Since there are no adequate mixed-conducting
materials available to perform both functions, ceramic-metallic or ‘cermet’ composites of electronic and ionic conducting materials are used. The electronic conducting material is a catalytically active metal and the ionic conducting material is the same material as the electrolyte. Typical anodes are made using a Ni and YSZ cermet to satisfy these requirements. There are five major advantages of this composite when used as an anode. First, it mitigates the large thermal expansion mismatch that exists between Ni and YSZ, which increases the resilience to thermal cycling. Second, it provides a large number of triple point boundaries (TPB) sites for fuel-oxidation reaction facilitating the anode kinetics. Third, the porous structure ensures the gaseous reactants diffuse into the TPB sites and the gaseous products diffuse out to the bulk fuel stream with minimal resistance. Fourth, the affinity provided by the ZrO$_2$ based materials in both anode and electrolyte enhances the adherence and avoids interfacial cationic interdiffusion. Fifth, the presence of ZrO2 prevents Ni particles from sintering, which would lead to a loss of catalyzing surface area. (O’Hayre, Cha and Colella)

The performance of the anode is highly dependent of the characteristic of the volumetric ratio of the phases, porosity, thickness, relative and absolute particle size distributions of ZrO2 and Ni particles and sintering temperature. (Park, Vohs and Gorte) Anode performances can vary from one batch to the next if care is not taken to ensure that fabrication practices are not consistent. The general consensus in the SOFC community to producing an optimal anode is to use a volume ration of YSZ/NiO in the rage of 50/50 to 40/60. Other conventions are to use finer YSZ particles with $d_{50}$~0.5um and coarser NiO particles with a bimodal distribution at $d_{50}$~0.5um and $d_{50}$~10um and a volume ratio 6:1 for each mode respectively (Fergus, Hui and Wilkinson). Typically the
anode and electrolyte are co-sintered in the range of 1300\(^0\)C and 1400\(^0\)C to achieve a dense electrolyte while maintaining an anode with 30vol% porosity. (Dura, Lopez de la Torre and Vazquez)

2.3.2.2 Cathode

Like the anode of the SOCF, the cathode is constrained by specific requirements that are currently known to only a few materials. The cathode material must be stable in an oxidizing environment while having an electronic conductivity of at least 50\(\Omega^{-1}\)cm\(^{-1}\). (O’Hayre, Cha and Colella) Ionic conductivity, as well as the thickness of the cathode electrode, plays a role in improving the activation over potential. (Saunders, Preece and Kendall) Just as the Anode requires porosity for gas diffusion, the cathode also requires a 30% porosity level. Cathode materials also need to exhibit good activity for oxygen reduction under operating conditions while having a thermal expansion coefficient that matches with the other cell components. The Cathode composition should to be compatible with both the interconnect material and the electrolyte, not allowing for high temperature reaction phases to develop.

The most common cathode materials for oxygen reduction are perovskites-based doped transition metal oxides (e.g. La\(_x\)Sr\(_{1-x}\)MnO\(_{3+\delta}\), La\(_x\)Sr\(_{1-x}\)CoO\(_{3+\delta}\), LaFeO\(_3\), LaCO\(_3\)). LaMnO\(_3\) perovskites-based oxides have shown to have the best balance of all the major criteria concerning electrical conductivity, chemical reactivity, electro-catalytic activity, and thermal expansion. LaCoO\(_3\) is superior to LaMnO\(_3\) in both electrical conductance and electro-catalytic activity and would be a better choice when the higher CTE disparity is not a concern; as in non-cathode supported SOFCs. (Dura, Lopez de la Torre and
Vazquez) It should be noted that LaCoO$_3$ is more reactive with ZrO$_2$ than is LaMnO$_3$. LaMnO$_3$ is not considered a good electrical conductor nor is it a good catalyst for oxygen reduction but it can be doped sufficiently with alkaline-earth elements (e.g. Ca, Sr) to alter these deficiencies. The thermal expansion coefficients (CTE) of doped LaMnO$_3$ are directly affected by the type of dopant, level of dopant and the change of the percent of oxygen in an isothermal condition. (Park, Vohs and Gorte)

The cathodes polarization behavior is very important in determining the performance of the SOFC. The polarization process originates from two sources: molecular diffusion and oxide-ion transfer. Molecular diffusion gives rise to what is termed concentration polarization while oxide-ion transfer is the cause of activation polarization. Reducing the thickness of the cathode electrode alleviates concentration polarization resulting in activation polarization as the dominant cathode polarization. The activation polarization is determined by a rate limiting step in the multiple steps of reducing O$_2$. In the LaMnO$_3$-based cathode it is thought to be the last step when the absorbed oxygen is ionized. (Dura, Lopez de la Torre and Vazquez) A simplified Butler–Volmer equation expresses the activation polarization $\eta_{act}$ with current density $j$ by Equation 12 where $j_{ex}^{eff}$ is the effective exchange current density dependent on percent oxygen.

$$\eta_{act} = \frac{RT}{0.5F} \arcsin h \left( \frac{j}{2j_{ex}^{eff}} \right)$$

Lastly, one of the most significant parameters in determining the activation polarization is the concentration of triple phase boundaries (TPB). The activation
polarization is greatly reduced by increasing the density of the TPB. (Park, Vohs and Gorte) The most common technique is to use a cathode functional layer composed of the electrolyte and cathode materials with a relative volume ratio of 50:50. (Dura, Lopez de la Torre and Vazquez) In this thesis research a different approach was taken to determine if the 50:50 interlayer’s can be improved upon by grading the interlayer from 50:50 to 0:100 starting with the electrolyte and grading to the cathode.

2.3.2.3 Electrolyte

The electrolyte of a fuel cell separates the anode from the cathode while allowing only a specific ion to conduct through its structure. In the SOFC the electrolyte is made from a solid ceramic that generally conducts oxygen ions. Ion conduction is orders of magnitude slower than electron conduction and thus the rate of ion conduction limits the overall current of the cell. The oxygen ion conducts through the crystal lattice of the electrolyte via a hoping mechanism that is thermally activated. To achieve a successful hop from one lattice position to another an oxygen vacancy is required. As the ion hops to the new lattice site it leaves behind a vacancy and so on. (Saunders, Preece and Kendall)

The most studied electrolyte material thus far is Yttria Stabilized Zirconia (YSZ). Pure zirconia exists in three different structures: monoclinic, tetragonal, and cubic phase. (Skinner and Kilner) The monoclinic phase is stable at room temperature while the desired cubic phase is only stable at elevated temperatures. Dopants, such as yittria, are added to stabilize the high temperature cubic structure down to low temperature. The $Y^{3+}$ cations substitute the $Zr^{4+}$ on the lattice, stabilizing the cubic phase but also increasing
the oxygen vacancies. This increase in oxygen vacancies can be seen in Kroger-Vink notation in Equation 13.

\[ Y_2O_3 \rightarrow ^{ZrO_2}Zr_2O_3 + V_0 + 3O_0^X \]

Equation 13

Increasing the concentration of the dopant increases oxygen vacancies. This is beneficial to oxygen ion conduction but, doping concentration is limited to 8mol% Yittria. It has been observed that addition of dopant past 8mol% shows no noticeable increase in ion conductivity. (Steele) Two other areas of study on YSZ are the effects of ageing at elevated temperatures and the grain boundary effect on conductivity. (Zhou, Gallo and Pague).

2.4 Fabrication

SOFC anode support substrates can be fabricated by bulk ceramic processes. The most common are uniaxial pressing (powder compaction) and tape casting. For this research uniaxial pressing was chosen. Additional structures i.e. anode functional layers (AFL), electrolyte, cathode functional layers (CFL), and cathode are fabricated by either direct deposition techniques or wet ceramic processing methods. Powder compaction and tape casting can also be used to apply the additional structures.

2.4.1 Uniaxial Pressing

Uniaxial pressing is commonly the choice for fabricating the anode support structure of the SOFC used in laboratory scale research. It is quite labor intensive and is not typically used for large scale fabrication. Form experience gained in this research,
the main factors that affected the green strength of the compact were moisture content, and pressing force. Excessive force during compaction cracked the edges while insufficient force resulted in cracks through the body of the disk. It was also observed that on humid days the compact would stick to the die and upon retrieval it would crumble. The green strength is not the only attribute affected during fabrication, the SOFC performance can be affected as well by adjusting the compaction pressure as seen in the research by Lee et al. In their studies, they found a tradeoff between conductivity and permeability occurs at approximately 4Mpa.

2.4.2 Tape Casting

Tape casting is the most common processing method used to fabricate the support layers of a planar cell. As the name implies, a thin film of slurry material is spread out over a clean flat surface (usually a sheet of glass) in the form of a long tape. The material is spread out and flattened using a doctor blade. The height of the doctor blade and the viscosity of the slurry are adjusted to control the thickness of the tape cast. The viscosity of the slurry is adjusted by the use of organic additives that act as binders, plasticizers, and dispersants. (Fergus, Hui and Wilkinson). After the slurry is laid out, the solvent evaporates leaving behind a thin flexible tape film. Tape casting allows for excellent control of particle size grading as well as composition and porosity grading. (Hart, Brandon and Lapen-a-Rey)
2.4.3 Direct Deposition Technique

There are several common direct deposition techniques that have been employed in the fabrication of SOFCs: electro-deposition, electro-chemical vapor deposition, chemical vapor deposition, plasma spraying, spray pyrolysis, laser ablation and sputtering. (Barthel and Rambert) Direct deposition is used in fabrication of SOFC components when high temperature sintering is to be avoided. High temperature sintering introduces the possibilities of oxidizing metal supports, unwanted inter-reactions, and excessive microstructure coarsening. (Fergus, Hui and Wilkinson) Direct deposition also allows for faster manufacturing by eliminating the long high temperature sintering step common to most other fabrication routes.

2.4.4 Wet Ceramic Processing Methods

Wet ceramic processing methods typically employ a ceramic powder suspended in a liquid carrier combined with other organic constituents that control the properties of the suspension. The most commonly used wet ceramic processes are Screen printing, painting, spin coating, slurry coating and colloidal spray deposition. When fabricating SOFCs via the wet ceramic process, a high temperature sintering step is usually required.

2.4.5 Sintering

Sintering is required to densify the green layers, consolidating them to achieve good contact and bonding between the particles. The electrolyte and cathode are usually sintered in two separate firing steps to allow optimization control over porosity, connectivity and electrochemical performance (Fergus, Hui and Wilkinson). For the first
step, the electrolyte is co-sintered with the anode support. A high firing temperature needed to fully densify the electrolyte – typically 1400°C for most electrolytes. The second firing step is carried out at a lower temperature to consolidate the cathode.

In this research the sintering followed two steps. For the first step, substrates consisting of support anode and electrolyte layer were co-sintered in a tube furnace. A heating profile of 15°C/min ramp up to 600°C then 10°C/min up to 900°C, then 5°C up to 1300°C and finally 1°C up to 1400°C was used. The samples were held for three hours at 1400°C to allow the electrolytes to fully densify. The cooling of the cells started with a 2°C/min down to 1200°C followed by a 5°C/min down to 1000°C and then allowed to cool naturally to room temperature. The sintering of the substrates resulted in a 20% reduction of volume. After further processing of the SOFCs i.e. deposition of a CFL and cathode, the cells were ready for the second sintering step. For the second sintering step, the cells were ramped at 10°C/min up to 900°C changing to 2°C/min up to 1200°C. The cells were then sintered for 2 hours followed by a slow cool of 5°C down to 900°C and then allowed to naturally cool to room temperature.

Sintering the cathode requires exacting control to avoid connectivity issues and excessive coarsening at low and high temperatures respectively (Gasik). It is also shown in work by Song et.al that starting particle size and sintering temperature is critical to the TPB concentration and resultant electrochemical performance (Song, Kim and Hyun). Song et.al points out that depending upon the starting particle size; the optimum sintering temperature differs, finding that smaller particles could be sintered at lower temperatures than larger particles achieving the same electrochemical performance. There have also been concerns of the possibility of forming a second phase at high temperatures based on
the compatibility of the LSM with YSZ. Sahu et.al has identified that this is not the case in their research showing no secondary phases forming in an YSZ/LSM composite that was sintered up to 1400°C and held for six hours (Sahu, Ghosh and Sun).
3 Literature Review

Solid oxide fuel cells (SOFC) are a branch of fuel cells characterized by the use of a solid ceramic material as an electrolyte. Yittria stabilized zirconia (YSZ) is a common electrolyte choice and starts to conduct oxygen ions at high temperatures ranging from 600°C to 1000°C (Singhal and Kendall). It is well known that SOFC’s are highly efficient at converting chemical energy into usable electrical energy but high operating temperatures limit the applications of SOFC and increase the cost to operate. To make the SOFC more feasible, lowering the operating temperature and increasing the power density are main areas of interest (Mogenson, S. and M.J.). The processing techniques and the micro structure of the SOFC are factors in bringing down the cost and operational temperature (Fergus, Hui and Wilkinson). Furthermore, Huss et.al state that based on the spatially varying requirements of the cathode, a layered cathode structure with varying catalytic activity as a function of distance from the electrolyte surface might enhance performance (Huss, Doshi and Guan).

3.1 SOFC Processing Factors

Each component of the SOFC requires specific processing steps to achieve optimal function. In the case of the anode, proper integration of the electrolyte material and pore former into the microstructure are used to mitigate CTE mismatch and allow for fuel delivery/ removal. (Basu, Blass and Buchkremer). The adjustment of the parameters used in the anode fabrication i.e. compaction pressure can be used to fine tune the resistivity and fuel permeability (Lee, Lee and Kim). The sintering temperature and
dwell time of the electrolyte are crucial in achieving a fully dense layer (Kuznecov, Otschik and Trofimenko). The cathode layer thickness, composition, application methodology, and firing temperature are also processing factors impacting electrochemical performance (Liu, Han and Miao). Processing temperatures of the cathode has shown to have a major impact on the performance of the SOFC. According to Fergus et.al, high sintering temperatures result in an overly densified microstructure and increased polarization resistance while low sintering temperature result in a cathode-electrolyte interface with poor contact and increased series resistance (Fergus, Hui and Wilkinson). Jorgensen et al. also showed that lowering the sintering temperature of the cathode decreased the polarization resistance but would be counteracted by an increase in series resistance (Jorgensen, Primdahl and Bagger). The polarization resistance on the cathode side of the SOFC has been shown to improve by the addition of a CFL composed of the cathode and electrolyte material (Tsai and Barnett). Kuznecov et.al showed that different perovskites can also affect the polarization resistance in the CFL (Kuznecov, Otschik and Trofimenko). Hart et.al, also showed in their research that using a composite cathode consisting of LSM and gadolinia-doped ceria gave improved performance over cathodes using YSZ (Hart, Brandon and Lapen-a-Rey).

3.2 Compositional Grading

Reduction in polarization resistance has been show by compositionally grading the CFL with multiple discreet layers (Hart, Brandon and Day). Specifically, the promotion of triple phase boundaries is critical to ensure effective oxygen reduction kinetics and high electronic conductivity (Herbstritt, Weber and Ivers-Tiffee). Computer modeling has shown that grading the CFL should increase the oxygen reduction rate.
The CFL also helps in the matching of the coefficients of thermal expansion (CTE), it provides an increase in reaction sites or triple phase boundaries (TPB) and lastly, the CFL prolongs the life of the fuel cell by decreasing the polarization resistance (Wang, Jiang and Zhang).

3.3 Fabrication Techniques

The composite layer can be applied using the methods of tape casting, screen printing, ink jet printing etc. In research by Rotureau et al., they show how both the cathode and anode can be fabricated via screen printing (Rotureau, Pijolat and Caillol). A novel technique using ink jet was demonstrated by Young et al. to deposited electrolyte with a high level of control over pattern and thickness (Young, Sukeshini and Cummins). Other techniques that are uncommon, such as sol-gel coating, have also been demonstrated to be effective (Zha, Zhang and Liu). Typically, grading of the compositional CFL has been accomplished by the screen printing of different concentration CFLs onto the electrolyte. This type of grading results in an increased number of interfaces (Kong, Sun and Zhou). Plasma spraying has been shown to be cost effective and efficient at depositing a graded composite layer using dual sources of feed stock while avoiding additional interfaces (Hui, Wang and Kesler) (Barthell and Rambert). One drawback of plasma spraying is achieving a thin fully dense electrolyte layer (Xia, Zhang and Wang). Combustive CVD processes have achieved gradation in both composition and microstructure but this approach is difficult to scale up to levels required for low-cost manufacturing (Liu, Compson and Liu). Pressure atomized spray is
one approach for low-cost production and should allow the potential for greater control of cell composition (Yan, Ding and Lin).
4 Efforts to Develop a Compositional Graded Functional Layer

The purpose of this work was to address SOFC functional layer fabrication problems concerning deposition control, consistency, and cost. It was determined that an effort to perform a single deposition process with the capability to change composition in situ would facilitate the proposed requirements. The proposed solution to meet these requirements was based on modifying the colloidal spray fabrication method.

The colloidal spray fabrication method is a fast and effective technique for applying a thin layer of ceramic material onto a substrate. Typical fabrication of an anode supported SOFC by this method starts with the deposition of a thin electrolyte. Fabrication of a thin electrolyte by colloidal spray deposition was shown to be effective by Yan et.al (Yan, Ding and Lin). The second step in the fabrication process may involve the deposition of a functional layer typically consisting of 50%/50% electrolyte/cathode material respectively. If the functional layer is to be graded, traditional techniques will require additional steps effectively increasing the complexity of fabrication. The final step in the fabrication process is the application of the cathode which can also be deposited via colloidal spray deposition.

Traditional colloidal spray systems lack control over grading the micro structure and can be as time consuming as screen printing when multiple layers are desired. This can be seen as every layer requires a change of ink and a drying period. Some of the biggest engineering challenges with multi-layer fabrication techniques are; decreasing connectivity issues due to increasing discrete interfaces, decreasing the number of layers that are required to match coefficient of thermal expansion, increasing the TPB density.
via a graded cathode functional layer and decreasing processing steps. Every step that can be eliminated in the fabrication process helps in making the technique more viable to scale up. It was shown by Hart et.al in their research that it was beneficial to grade the cathode functional layer via multiple steps of screen printing; however, this is unrealistic and only suitable for laboratory experiments. Another issue that may arise with discreet multiple layers is functional connectivity between layers (Hart, Brandon and Day). Hart et.al noted that each interface introduced has the potential to add resistance to the functional processes required for proper SOFC operation. In this research we designed and developed a computer controlled device that can change the composition of the colloidal spray in situ whereby eliminating the multi-step process of tape-casting, screen printing, and traditional colloidal spray deposition required to grade a functional layer.

In this work, the benefit of compositionally grading a cathode functional layer for solid oxide fuel cells was explored. Cells were prepared wherein either a standard cathode functional layer or a linearly compositionally graded cathode functional layer was placed between the cell electrolyte and cathode current collecting regions. The electrochemical performances of these cells were compared with a SOFC cell containing no CFL. All cells were fabricated using a pressurized dual-suspension spraying system. Electrolytes, cathode functional layer, and cathode current collecting materials were deposited on a powder compacted anode support. SEM and EDAX area maps were taken to study the resulting microstructures and to verify that the desired CFL profiles were produced. The EDAX area map verified that a compositionally graded CFL and a SCFL were obtained. The cells were analyzed using impedance spectroscopy to evaluate the electrochemical performances of each cell. The open circuit voltage (OCV) and peak
power densities of all three cells were 1.04V/80mWcm$^{-2}$, 1.12V/108mWcm$^{-2}$, and 1.08V/193mWcm$^{-2}$ at 850°C for the SCFL cell, the cell without a CFL, and the compositionally graded CFL cell respectively. The results showed that this approach is a viable means for producing SOFC functional layers with unique composition and interfacial properties.
5 Experimental

The work in this thesis was novel and required additional development of equipment and techniques outside of what was on hand at Wright State and what could be obtained from the literature review. Each component of the SOFC was researched to identify typical parameters, fabrication techniques, and processing requirements. Where equipment was unavailable, suitable devices were engineered and built using resources provided by Wright State and Wright Patterson Research Laboratories.

5.1 Support Substrate Fabrication

SOFC can be supported by the cathode, electrolyte, or the anode. Each method has advantages and disadvantages which can be seen in Table 3

<table>
<thead>
<tr>
<th>Support Substrate</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Electrolyte supported| Relatively strong structural support from dense electrolyte  
Less susceptible to failure due to anode re-oxidation | Higher resistance due to low electrolyte conductivity  
Higher operating temperature required to minimize electrolyte ohmic losses |
| Anode supported      | Highly conductive anode  
Lower operating temperature via use of thin electrolytes | Potential anode re-oxidation  
Mass transport limitation due to thick anodes |
| Cathode supported    | No oxidation issues  
Mass transport limitation due to thick cathodes | Lower conductivity  
Mass transport limitation due to thick cathodes |

Table 3: Support substrate advantages and disadvantages
In this research the anode supported solid oxide fuel cell design was chosen for its high conductivity and ability to operate at relatively low temperatures. Typically the anode is composed of Nickel and YSZ. The Nickel starts out as Nickel Oxide (NiO) and is reduced during the testing phase of the research. This proves to be beneficial; as the Nickel Oxide is reduced the microstructure undergoes further increases in porosity allowing for increased gas permeability (Fergus, Hui and Wilkinson). The resulting increased porosity due to the reduction of the NiO is normally not sufficient to maximize mass transport and can be supplemented with carbon powder that is decomposed during the bisque firing step. Other benefits of a NiO/YSZ anode supported SOFC come from the intrinsic catalytic ability of nickel and its low resistivity to charge transport.

Structural anodes substrates were fabricated using uniaxial powder pressing techniques. The capability to press button cells had to be developed. To accommodate the high forces involved in uniaxial pressing, a five part die was machined out of titanium and steel. The die was used in conjunction with a lab press (Carver Model C) seen in Figure 2, to press and form the button cells.
Based on the research of (Lee, Lee and Kim), it was determined that due to the inverse nature of gas permeability with conductivity, 4MPa would be an appropriate pressure.

A base powder was made for the fabrication of the anode substrates with a combination of 55% by weight Nickel Oxide (Aldrich) and 45% by weight (Tosoh-Zirconia) TZ-8Y (YSZ). The base powder was well mixed and stored. For the first few experiments in this work, a pore former wasn’t used but was added later on when it became apparent that the cells may benefit from its use. Initially, carbon fiber was experimented with and used as a pore former until finally deciding to use carbon powder to be in accordance with the literature. Once established as the pore former, 5% by weight carbon powder was added to the base powders. The combined powder was ball milled in a glass bottle for 24 hours in ethanol with 3mm diameter zirconia balls. The resulting cermet was strained to remove the milling balls and placed into an oven at 70ºC for 2 hours. The dried cermet was broken up into clumps and sifted with a 50 mesh sieve.
until all the cermet had passed through the mesh forming a powder. The powder was used “as is” and no binders or plasticizers were added. The powder was measured out in 2g amounts and dry pressed in a 1.25in diameter die at 4metric tons. The green substrates were subsequently bisque fired in air at 900 ºC for 1 hour. During the bisque firing stage the pour former burned out leaving behind a porous structure. The bisque firing increased the green strength and allowed for easier handling of the substrates during colloidal spray deposition.

5.1.1 Carbon Fiber Pore Former

As mentioned above, during the development phase of the anode fabrication, carbon fiber was used a potential pore former. The hypothesis was believed that the addition of long channels left behind by the decomposed carbon fiber would allow for gas convection deep within the anode where the less effective “diffusion mechanism” dominates. Although no complete cells were ever fabricated and tested to determine the effects of the carbon fiber on the mass transport, it was observed that 10% by volume was sufficient to achieve interconnected channels in an unreduced nickel oxide substrate. Figure 3 below shows the microstructure left behind after the carbon fiber was burned out. Further increases in porosity would result once the sample was reduced.
It was decided that these results would be better analyzed under a different study and that using carbon powder would be sufficient and consistent with the literature.

### 5.2 Compositionally Graded Colloidal Spray Deposition

Colloidal spray deposition is a well-known thin film coating technique used in ceramic coating applications. In its simplest form, colloidal spray deposition is done free handed and lacks consistency from one sample to the next. Some efforts of timing and nozzle stabilization are employed to acquire control over consistent deposition thickness with good results. A normal setup requires the spray nozzle to be placed over a substrate situated on a thermal device. Air is often used to atomize slurry and deliver the generated mist to the substrate. In more rudimentary setups the slurry is typically gravity feed but in the research done by (Nomura, Parekh and Selman) a syringe pump was employed to meter out the slurry. Building on the research by (Nomura, Parekh and Selman), this
study employs the control methods previously mentioned and the use of two syringe pumps to compositionally grade a colloidal spray deposition process.

5.2.1 Preparation of Colloidal Inks

Inks that were formulated for use in ink jet applications were modified to suit the deposition apparatus in this research. The initial ink recipe utilized Terpineol as the solvent but was replaced with ethanol for reasons discussed further on in this work. The inks used in this experiment were tailored to have low viscosity, high volatility, and moderate particle loading. These characteristics were chosen to achieve sufficient atomization and room temperature drying of the ceramic inks.

The cathode, anode, and electrolyte of the SOFC had a respective ink developed for its deposition. The functional layer came about by the combination of the electrode and electrolyte inks. Each component ink was fabricated by mixing the respective powder with a solvent, binder and plasticizer in 50ml of ethanol. The ink was subsequently ball milled for 24hours prior to its being sprayed. The ceramic ink recipes are shown in Table 4.
<table>
<thead>
<tr>
<th>Constituent</th>
<th>LSM Ink (g)</th>
<th>YSZ Ink (g)</th>
<th>NiO Ink (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttria stabilized Zirconia powder</td>
<td>11.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lanthanum Strontium Magnate powder</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>Nickel Oxide powder</td>
<td>0</td>
<td>0</td>
<td>13.34</td>
</tr>
<tr>
<td>Solvent: Terpineol, Ethanol</td>
<td>50ml</td>
<td>50ml</td>
<td>50ml</td>
</tr>
<tr>
<td>Dispersant Polyalkylene glycol (PAG)</td>
<td>0.393</td>
<td>0.393</td>
<td>0.393</td>
</tr>
<tr>
<td>Plasticizer Benzyl butyl phthalate (BBP)</td>
<td>0.393</td>
<td>0.393</td>
<td>0.393</td>
</tr>
<tr>
<td>Binder: Polyvinyl butyral (PVB)</td>
<td>0.393</td>
<td>0.393</td>
<td>0.393</td>
</tr>
</tbody>
</table>

Table 4: Ceramic Ink Recipes

In order to spry down the layers at room temperature the inks were formulated with ethanol to replace terpineol as the solvent due to its low vapor pressure. Settling of the constituents in the inks was noticeable once mixing ceased. The settling rate was considered negligible in comparison to the time required to fabricate the required layers. The actual rates of the settling varied between the inks, with YSZ and the Nickel Oxide being very stable for > 24 hours while the LSM was slightly stable for one hour before further mixing was required.

5.2.2 Spraying System

Deposition of the cathode, electrolyte, and compositionally graded CFL was accomplished by spraying a pressure-assisted atomized mist onto a rotating anode substrate. The composition of materials in the atomized mist was controlled to allow each material to be deposited either separately or as a mixture. The composition of the deposition mist was controlled using a Harvard33 dual syringe pump having two
independently computer controlled syringe pumps. The pumps provided the ink to a pneumatic spray deposition nozzle (Central Pneumatic). The atomizing nozzle on the gun was of an externally mixed design and the spray gun body was slightly modified to allow for remote control of the incoming fluid. Two 20ml plastic syringes were used to accommodate the individual inks. The syringes were connected to the system via micro bore tubing having an inner diameter of .5mm. The two tubes were united using a compression locking tee junction. The third port of the tee junction was connected to the spray gun with the shortest possible distance from the nozzle to limit the lag in the tube from the point of mixing to the point of atomizing. Lab-View was utilized to control the composition of the atomized mist in order to deposit the electrolyte, compositionally graded CFL and cathode. The completed system can be seen in Figure 4.

Figure 4: Physical deposition apparatus
The deposition apparatus in Figure 4 allowed for control over five deposition variables that are shown in Table 5.

<table>
<thead>
<tr>
<th>Deposition Control</th>
<th>High setting</th>
<th>Low setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air flow rate</td>
<td>Increased drying rate</td>
<td>Low drying rate</td>
</tr>
<tr>
<td></td>
<td>Optimal atomization</td>
<td>Poor atomization</td>
</tr>
<tr>
<td>Ink flow rate</td>
<td>Limits gradation capabilities</td>
<td>Time consuming</td>
</tr>
<tr>
<td>Rotational velocity</td>
<td>No effect</td>
<td>Wets out the substrate</td>
</tr>
<tr>
<td>Nozzle distance</td>
<td>Insufficient solvent at impact</td>
<td>Wets out the substrate</td>
</tr>
<tr>
<td>Overspray</td>
<td>Thick center</td>
<td>Donut shape deposition</td>
</tr>
</tbody>
</table>

Table 5: Deposition parameters and effects.

5.2.3 Deposition of the Electrolyte

Proper operation of the SOFC requires the electrolyte to be dense, thin, free of cracks, and pinholes (Fergus, Hui and Wilkinson). The electrolyte has two primary functions: The electrolyte needs to be gas tight to avoid fuel cross over and it needs to be fully dense to avoid increased resistance to ion conduction. Employing colloidal spray deposition to fabricate the electrolyte is a complex task. Upon impact of the substrate, the slurry needs to have enough solvent to allow for the material to flow and settle into a close pack structure. If too much solvent is present the carrier air will force the material off of the substrate while if too little solvent is available the slurry will dry out in the spray cone and be blown away upon impact. In research by (Nomura, Parekh and Selman) a thermal control device was used to control the drying rate of the slurry after impacting the substrate. Based on (Nomura, Parekh and Selman) process, the first electrolyte deposition trials of this research used a small Kapton® heating element to obtain control over the drying rate. Depending on the solvent i.e. Terpineol, methanol, ethanol, etc. the drying rate varied drastically from 200°C down to room temperature. In
our research, it was observed that the use of the heating element cause small protruding structures to grow on the surface of the electrolyte as seen in the optical images in Figure 5.

**Figure 5:** Protruding structures on the surface of the electrolyte decreasing as a function of temperature.

The growth of these protruding structures was avoided by removing the heating element and using a combination of carrier air, nozzle distance, and rotation velocity to control drying rates. As mentioned earlier in the section on ink preparation, the solvent in the ceramic ink recipe was replaced with ethanol to help control drying rates as well, by allowing for evaporation at room temperature. Figure 6, shows an SEM image of the typical surface topography obtained using the fore mentioned methods. The substrates consisting of the anode and electrolyte were co-sintered in a tube furnace using a heating
profile of 15°C/min ramp up to 600°C then 10°C/min up to 900°C, then 5°C up to 1300°C and then 1°C up to 1400°C. The samples were held for three hours at 1400°C to allow the electrolytes to densify. The cooling of the cells followed a 2°C/min down to 1200 followed by a 5°C/min down to 1000°C and then allowed to cool naturally to room temperature. The sintering of the substrates resulted in a 20% reduction of volume.

Figure 6: SEM of the surface of the electrolyte

Despite the appearance of the pin holes seen on the surface of the electrolyte in Figure 6, effective densification was achieved. A cross sectional view of the electrolyte can be seen in Figure 7 where the pin holes appear to be isolated and therefore would not allow for fuel cross-over. It’s possible the pinhole density may attributes to an overall increase in ionic conductivity resistance but it is typically unavoidable when using
colloidal slurry deposition. Increasing the electrolyte density can be implemented in the sintering phase but long dwell times are not practical if the process is to be scaled up.

![Electrolyte](image)

**Figure 7: SEM cross sectional view of the electrolyte layer**

The electrolyte layer thickness was a function of the five variables listed in Table 5. Effective settings for each variable were determined through experiment allowing for only time to adjust the layer thickness. Figure 8 shows how time and thickness were correlated by using optical images of cells with varying deposition times.
Figure 8: Optical images showing increasing thickness as a function of time.

Applying a colloidal ink on top of a substrate that was fabricated via a powder compaction method allows for differential shrinkage based on a few factors to include compaction pressure, sintering temperature, particle size, and anode composition (Ewsuk). It can be seen in Figure 8 that cracks begin to form as the thickness of the electrolyte layer is increased. This physical phenomenon is a result of differential shrinkage during the sintering process. Differential shrinkage rates of the respective components give rise to in-plane tensile and compressive stresses that help in the densification of the electrolyte but also may result in warping of the substrate and cracking of the electrolyte layer. It was determined by this experiment that this deposition method was capable of crack free, 10um layers.
5.2.4 Deposition of the Functional Layer

A program was written in lab view to control the composition of the atomized mist from the spray gun in order to deposit a functional layer. The algorithm that controlled the compositionally graded functional layer follows Equation 14 given by (Deseure, Dessemond and Bultel).

\[
\varepsilon_a = \frac{x}{L} \Delta \varepsilon_a + \frac{2 \varepsilon_a - \Delta \varepsilon_a}{2}
\]

Equation 14 gives the volume fraction of YSZ at thickness x while L is the total layer thickness determined by deposition time. The lab view program used the input factors of total deposition time and combined maximum flow rates to determine the percentage of flow to each syringe over the course of the deposition. The full derivation of the algorithm is given in appendix C. Figure 9 shows the actual portion of the Lab View program that contains the algorithm for controlling the linear gradation.

Figure 9: Algorithm for controlling gradation from Lab View Program
Figure 10 shows an SEM image of an interface that formed as a result of the continuous gradation of the nickel oxide ceramic ink with the YSZ ceramic ink. The compositional grading started with 50% of the total flow rate applied to each syringe and then by iterating every second, the flow rate decreased for one syringe and increased for the other syringe until one syringe was at 100% of the flow rate and the other was at 0%. By applying this algorithm based on Equation 14, the distribution of the volume fraction of YSZ appears to follow a linear deposition seen in Figure 10.

![SEM image](image)

**Figure 10: SEM of anode / electrolyte interface highlighting the physical gradation**

Figure 11 is an EDAX area map of four half cells with their anode/electrode interface graded to verify proof of concept and determine the correlation between deposition time and layer thickness as was done before with the electrolyte. The EDAX
area maps show how the gradation layer increases with time and how the gradation appears to stay linear with thickness.

![Area Maps]

**Figure 11:** Graph and EDAX area maps of 4 cells showing the effect of increasing the gradation deposition time.

### 5.2.4.1 Percolation Threshold

A typical functional layer is a binary mixture of ionic and electronic conduction particles in a predetermined volume fraction. Depending on the volume fraction, a percolation probability is assumed (Chen, Lin and Zhu). Three different types of clusters can form depending on the percolation probability. The first type is a long percolated cluster that extends through the entire layer from the cathode to the electrolyte. The second is a short percolated cluster that is connected to the electrolyte and only travels a short distance into the functional layer. The last type is an isolated cluster that is ineffective at conduction. Chen et al. proposes a model that identifies parameters that predict a composite electrode composition that allows for percolation. When compositionally grading a functional layer it is advisable to avoid volume fractions that are below the percolation threshold. Chen et al. provides a non-dimensional graph that shows the effective TPB per unit volume as a function of the electrode/electrolyte particle
diameter ratio and the volume fraction of electrode material. Using these graphs, it is evident that a linearly gradation that includes compositions below 20wt% of the electrode material, regardless of the particle diameter ratio, should be avoided. The 20wt% ratio was also pointed out by Hart et.al. In their research a multi-layer functional layer was fabricated that included a 20wt%LSM/wt80%YSZ layer. Of the cells they tested, the cell that contained this ratio had the highest series resistance. In their conclusion, Hart et.al attributes the high resistance of the cell to the 20wt%LSM/80wt%YSZ layer being below the percolation threshold and effectively adding electrolyte thickness. In this research the anode gradation started with a 50ink%NiO/50ink%YSZ deposition and graded to 0wt%NiO/100wt%YSZ while the cathode started with a 0%inkLSM/100ink%YSZ deposition and graded to 100%LSM/0%YSZ. Due to the anode and cathode functional layers being graded to a composition of 0ink% /100ink% a portion of the electrode functional layer was below the percolation threshold. It should also be noted that when using a linear grading function, any zone that may be less effective is scaled in proportion to those that may be more effective, i.e. the composition below the percolation threshold seen in Figure 12. Due to the scaling effect of linear depositions, other algorithms were constructed that could perform error function and exponential gradation for future experiments in an effort to minimize ineffective zones.
Figure 12 Three E.D.S. area maps converted into elemental composition as a function of layer thickness.

5.2.4.2 Percolation Model

A model was developed to compare the data obtained by EDS mapping with the deposition parameters. The derivation for the model is shown in appendix C. Based on the work by Chen et. al, electrode functional layers having LSM and YSZ with approximately the same particle diameter will have a function capability between 30 to 70 volume percent (Chen, Lin and Zhu). The continuously graded cathode functional layer in this research was graded from 0 volume fraction up to 100 volume fraction and follows a distribution analogous with the analytical model in appendix C. Based on the model and using Chen et.al as a reference, approximately 75% of the continuously graded CFL in this research was outside of the percolation zone. This can be seen in Figure 13.
5.2.5 Deposition of the Cathode

The electrolyte side of the sintered substrates was masked allowing only a 1cm$^2$ circle of area exposed. The CFL was deposited over the mask and allowed to dry at room temperature prior to the deposition of the cathode layer. The mask were removed, placed into a high temperature tube furnace and sintered in air at 10°C/min up to 900°C changing to 2 °C/min up to 1200°C. The cells were then sintered for 2 hours followed by a slow cool of 5°C down to 900°C and then allowed to naturally cool to room temperature. Figure 14 shows the successive steps required to fabricate a finished button SOFC.
Figure 14: Stages of cell fabrication

5.3 Cell Preparation for Testing

A 6” silver wire was formed into a W shaped collector and attached to the cell using silver paint (Ted Pella Inc. Leitsilber 200). The two leads coming off the W shaped silver wire were secured to the cell surface with ceramic glue (Aremco ultra temp 516). The process was repeated for both sides of the cell. Figure 15 shows the anode and cathode sides of both a pretest button cell and a post-test button cell. The pretest cell has a dark green color indicative of unreduced nickel oxide where the posttest cell has a light metallic grey color. The current collector for the button cells is the combination of the silver wire and the silver paint. There were concerns that the silver may affect the
concentration polarization but according to research by (Coles), permeability of oxygen above 630°C through silver is as follows:

\[
\log Q_0 = -2.108 - \frac{2841}{T} \quad \text{if } T > 630°C
\]

Equation 15  \(T \text{ in } K, Q_0 \text{ in } l \text{ torr sec}^{-1} \text{ cm}^2 \text{ mm atm}^{-1}\)

This shows the permeability of silver from 650 to 850°C is between .0056 to .01 L torr sec\(^{-1}\) cm\(^2\) mm atm\(^{-1}\). With regards to Equation 15, the silver current collector has no effect on concentration polarization allowing for relatively unrestricted gas flow.

**Figure 15: Left: SOFC button cell posttest. Right: SOFC button cell pretest**

Once the ceramic paste cured, the cell leads were twisted onto 20” silver wires and the twisted connections were coated with silver paint for increased strength and conductivity. The cell was attached to an alumna tube of 1” diameter using the ceramic glue and allowed to cure at room temperature for four hours. The cell was placed in the test station at room temperature. The two leads from the SOFC button cell were connected to an EG&G model 274 potentiostat. The potentiostat was connected to a control computer running Electrochemistry Power Suite. The design of the test station was developed based off the proposed design found in Fuel Cell Fundamentals (O’Hayre, Cha and Colella). The test station seen in Figure 16 was built based on the size and operational requirements of a SOFC button cell. The design of the cell placement portion
of the test station was modeled after a tube within a tube design found in previous experiments (Souza, Visco and De Jonghe). The tube within a tube design allows for two independent gas chambers when the cell is securely attached to the inner tube. The apparatus was placed into a tube furnace. The test station heating elements were set at a ramp rate of 1°C/min and ramped/dwell to 650 °C all the while reducing in 5% Hydrogen 95% argon at 5cc/m for a total of 24 hours prior to testing. This slow thermal ramp allowed the ceramic glue to set properly and the nickel oxide to fully reduce.

Figure 16: SOFC test station
6 Testing Results

Once the development of the deposition apparatus, along with the identification of variable settings was complete, small 1” button SOFC’s were fabricated. Initial test were designed to identify any benefits of a compositionally graded anode functional layer along with the effect of increasing the layer thickness. Further test were performed to identify relative benefits of a compositionally graded cathode functional layer. This was done by fabricating a SOFC’s without a CFL, one cell with a standard CFL having no gradation and one cell with a CGCFL.

6.1 Testing procedures

The cells were individually tested by placing them in the test station at room temperature. Each cells reduction was accomplished in 5%Hydrogen/95% argon at 650°C for 24 hours prior to testing (1°C/min ramp, 5cc/m flow). On the day of its test, the cell was allowed to equilibrate for 2 hours at 650 °C in pure hydrogen with a flow rate of 20cc/m. After allowing the cell to equilibrate, electrochemical impedance spectroscopy (EIS) was performed using an EG&G model 274 potentiostat. The EIS was taken at intervals starting from 650°C and iterating by 50°C up to 850°C. Each cell was tested over these five temperatures of: 650, 700, 750, 800, and 850°C.

The impedance and polarization was collected using the two point probe method and in retrospect it should have been taken using the four probe method. The two point probe method is adequate for general purpose resistance measurements and I-V curve generation. However, when the resistance being measured is relatively low, or the
resistance of the contacts is relatively high, a four point probe will yield more accurate results. In the two point method a known current is sourced and flows through the cell. The voltage that develops is measured and can be divided by the applied current to determine the resistance using Ohm’s law. The problem with this method is that the resistance is a combination of the cell, the leads, and the contacts. On the other hand, when using the four point method, the second set of leads are used for sensing the voltage drop while the primary leads are used to deliver the current. This allows for a more accurate I-V curve generation. Because the two point method was used for this research, the I-V graphs may be in question as to their accuracy.

The polarization curves were collected from 0.0V to 1.0V at 0.1V per minute in order to allow for cell equilibrium between current collections. Typically the current is adjusted and the voltage is collected but the power suit software provided only voltage control. After each polarization curve was collected a Nyquist plot was collected from 0.1 ohms to 100k ohms at open circuit voltage. Once each cell was tested they were examined in cross-section by SEM (JEOL 7401-FE-SEM) and subsequently EDAX area-mapped.

6.2 Compositional Graded Anode Functional Layer

The first cells that were fabricated in this work consisted of compositionally graded anode functional layers. Two cells were fabricated, each cell having a different CGAFL thickness via a 1 minute and a 2 minute deposition. The cross-section of each cell can be seen in Figure 17.
The two cells were sent out for testing and returned for analysis. The results of the test are plotted in the polarization graphs below in Figure 18. Polarization graphs are a useful tool in identifying specific problem areas of the overall fuel cell performance. The activation polarization results from a deficiency of TPB and the thermal energy required to initiate fuel reduction. It is suggested that a rough interface should provide an increase in TPB and is a supporting factor for the incorporation of electrode functional layers (O'Hayre, Cha and Colella). The ohmic resistance is a function of layer thickness and ionic conductivity. Typically, the incorporation of an electrode functional layer increases the thickness whereby increasing the ohmic resistance, but when optimized; the benefit of increased TPB may outweigh the incurred resistance. Also, to avoid ohmic resistance it is common to make the YSZ electrolyte layer as thin as possible, sometimes ranging on 5 to 10µm (Fergus, Hui and Wilkinson). The mass transfer or concentration losses are usually not an issue in SOFC’s. The high operating temperature ensures that all fuel and products remain in the gaseous phase resulting in easy transport throughout the cell.
Figure 18: IV of SOFC with CGAFL, a. 1 minute deposition, b. 2 minute deposition

It is apparent from the polarization curves that the cell having only one minute of deposition time performed better than the cell having a 2 minute deposition time. The polarization graph of the one minute gradation shows the latter portion of the curve extending out further than that of the two minute deposition graph. This portion of the polarization curve represents the ohmic polarization where an increase in the cell resistance increases the slope of the graph. This increased slope is seen in the two minute deposition. It can be attributed to the scaling effect of the longer linear deposition which results in an increased composition below the percolation threshold. The increased ineffective percolation zone essentially translates into increased electrolyte thickness. When comparing the polarization curves with their respective SEM cross-section, it’s difficult to correlate between the images and their performance. This is where the EDS area mapping is effective. Figure 19 shows the ineffective composition below the percolation threshold from a 1 minute to a 2 minute deposition being extended by approximately 20um. This added thickness correlates to the observed increased ohmic polarization seen in the polarization graphs in Figure 18.
Figure 19 EDS area maps of the SOFC’s with 1 minute and 2 minute compositionally graded anode functional layers

6.3 Compositionally Graded Anode and Cathode Functional Layer

The second round of experiments consisted of both the cathode and anode functional layers being subjected to compositional grading. A single cell was fabricated with both its anode and cathode functional layers graded. SEM images of the cells cross section are shown in Figure 20.

Figure 20: SEM of SOFC having both a CGAFL/CGCFL
The SEM image shows well defined regions where the gradation is located. It is difficult to identify the cathode gradation from the SEM image but the gradation profile is confirmed using EDAX area maps shown in Figure 21.

Figure 21: EDAX area map of SOFC having both anode and cathode functional layers compositional graded.

Polarization data was collected for this cell to compare any benefit of adding the cathode functional layer in conjunction with the anode functional layer. The results are shown in Figure 22. The polarization curve for this cell indicates the performance was comparable to the cells from the previous experiments having only the CGAFL. Due to the difficulties of identifying any additional benefits, it was decided that each functional layer should be examined independently to determine its contribution.

Figure 22: Polarization curves of the SOFC having both CGAFL and CGCFL
6.4 Compositionally Graded Cathode Functional Layer

In the last set of experiments, a SOFC with a compositionally graded CFL was compared to a SOFC with a SCFL and one with NCFL to quantify the relative benefit of a compositionally graded cathode functional layer deposited via the pressurized duel suspension spraying technique.

The polarization curves for the compositionally graded CFL are shown in Figure 23. The polarization curve taken at 650°C initially has a steep slope that gradually decreases. This indicates that the CGCFL has minimal effect on the performance at low temperatures possibly due to a lack of activation. It can also be observed from the plot that as the temperature increases the slope of each successive polarization curve decreases. This decrease in slope indicates that the CFL and the electrolyte are becoming less resistive. The compositionally graded CFL had the maximum power density of all three cells tested. The maximum power densities of the CGCFL cell were 175, 136 and 83 mWcm⁻² at the current density of 351, 279 and 159 mAcm⁻² for 850, 800, 750°C respectively. The Nyquist plots for the CGCFL in Figure 24 shows the resistive element portion of the curve (0 to the first data point on the x axis) decrease from 1.6 Ωcm⁻² at 650°C to .78 Ωcm⁻² at 850°C giving to a drop in resistance of 0.82 Ωcm⁻². This also indicates that the CGCFL and the electrolyte become less resistive as the temperature increases. This decrease in resistance is a direct effect of the increase in ion conduction of YSZ as a function of temperature given through the Nernst equation.
Figure 23: Polarization curves of the CGCFL from 650 to 850 C

Figure 24: Impedance plots of the GDCL from 650 to 850 C
The diameter of the semicircular portion of the Nyquist plot along the x axis represents the total interfacial polarization resistance of the anode $R_a$ and cathode $R_c$. The total interfacial polarization resistance of the functionally graded interlayer cell decreases from approximately 5.5 $\Omega\text{cm}^2$ at 750°C to 3$\Omega\text{cm}^2$ at 850°C giving to an approximated drop in resistance of 2.5$\Omega\text{cm}^2$. This decrease in resistance as the temperature increases typically indicates that the TPB’s are increasing in activity.

6.4.1 Assessment of the SCFL

The polarization curves for the standard CFL is shown in Figure 25. When the slopes of the lower temperature curves of the SCFL are compared to the similar curves of the CGCFL it becomes apparent that the continuous gradation of the CFL has a significant effect on the low temperature operation. It appears that by grading the CFL the lower temperature operation is improved. It should be noted that this assumption is not conclusive as the composition of the SCFL was just tested at 50/50 and its possible this is not the most optimal ratio of LSM to YSZ. The SCFL didn’t perform well at higher temperatures having the lowest power density of all three cells tested. The maximum power densities of the SCFL-cell were 80, 44 and 29mWcm$^2$ at the current density of 131, 134 and 96mAc$^{-1}$m$^2$ for 850, 800, 750°C respectively. The Nyquist plot for the SCFL cell shows the resistive element portion of the curve decrease from 1.3$\Omega\text{cm}^2$ at 650°C to .57 $\Omega\text{cm}^2$ at 850°C giving to a drop in resistance of .73 $\Omega\text{cm}^2$. 

59
Figure 25: IV curves of the SCFL from 650 to 850°C

Figure 26: Nyquist Plots of the SCFL from 650 to 850°C
The total interfacial polarization resistance of the SCFL cell decreases from approximately 14Ωcm$^2$ at 750°C to 3.5Ωcm$^2$ at 850°C giving to a drop in resistance of 10.5 Ωcm$^2$. The fracture surface shows the SCFL cell as having 21um thick electrolyte with an approximated 16um interlayer and 9.5um cathode. The combined thickness of the inner layer and cathode is 26um and the total thickness of the electrolyte, interlayer and cathode is approximately 48um.

6.4.2 Assessment of the NCFL

The polarization curves for the SOFC that didn’t have a CFL (NCFL) are shown in Figure 27. When comparing the NCFL curves with that of the other two cells it is important to note the shape of the curves. Below 850°C the activation losses for the NCFL are much higher than for the other two cells. This is indicated by the left side of the curve having an almost vertical slope and the cause is most likely due to the lack of a CFL. The lack of a CFL does however improve the ohmic resistance which can be seen as the curve recovers at the lower voltages. The NCFL has approximately the same power density as the SCFL but performs just slightly better. The maximum power densities of the cell were 89, 46 and 35mWcm$^2$ at the current density of 155, 151 and 133mAcm$^{-2}$ for 850, 800, 750°C respectively. The Nyquist plot for NCFL shows the pure resistive portion of the curve doesn’t vary as the temperature is increased. This is due to the lack of the interlayer which requires higher temperatures to decrease resistance. The total interfacial polarization resistance of the no interlayer cell decreases from approximately 40Ωcm$^2$ at 750°C to 7.5Ωcm$^2$ at 850°C giving to a drop in resistance of 32.5 Ωcm$^2$. 
Figure 27: IV curves of the NCFL cell from 650 to 850 C

Figure 28: Nyquist plots of the NCFL cell from 650 to 850 C
7 Discussion of Testing Results

It is well known that exchange current density or kinetic performance can be improved by increasing the number of possible reaction sites (i.e., increase the reaction interface roughness) per unit area. Increasing the functional surface area is typically done by the addition of a CFL between the electrolyte and cathode. In this research it is believed that the addition of a compositionally graded CFL increases the functional surface area. To show this, a SOFC with a compositionally graded CFL was compared to a cell with a SCFL and one with NCFL to quantify the relative benefit of a compositionally graded cathode functional layer deposited via the pressurized duel suspension spraying technique.

7.1 Comparative Electrochemical Analysis of Polarization and EIS

Electrochemical analysis was performed on each SOFC design to identify the relative cell performances. The EIS Nyquist plots in Figure 29 show an example of the EIS results for each of the three different profiles at 850°C and illustrate the origins of the proposed activation and ohmic loses.
Figure 29: EIS Impedance spectra of SOFC unit cells at 850°C with different CFL schemes (CGCFL: □; SCFL: ○; NCFL: ▼)

The Nyquist plot is subdivided into two regions that correlate to the ohmic, and electrode losses. On the left side of the graph is the point where the semicircle crosses the x axis. This represents the inherent ohmic losses of the system, and is referred to as the area-specific ohmic resistance (ASOR). The ASOR includes the losses due to the 2 point vs. 4point connectivity, the test lead resistance, and cell connectivity resistances. The electrode losses are represented by the semicircles (O’Hayre, Cha and Colella). The difference between the point at which the larger projected semicircle crosses the x axis on the right side of the graph and the ASOR is referred to as charge transfer resistance (CTR). The charge transfer resistance results from complex phenomena within the electrode and functional layer. The rates of catalectic reactions, diffusion of absorbed oxygen, and incorporation of absorbed oxygen in triple phase boundary all contribute to the CTR (Singhal and Kendall). The three prominent semicircles in Figure 29 represent the combined anode, cathode, and CFL contribution to the decrease of the activation
losses. The NCFL cell has the largest CTR, indicating a lower concentration of TPBs. The compositionally graded CFL has a lower CTR than the SCFL, suggesting that it may have the highest concentration of TPBs of all three cells.

Figure 30 gives the ASOR as a function of temperature for all three cells. The ASOR of the cells decreased from 650°C to 850°C. At 650°C the SCFL and CGCFL had larger ASOR than the NCFL but all three cells had comparable ASOR at 850°C. The reduction in the ASOR of the cells is associated with an increase in conductivity of YSZ as the temperature increases. The EIS data suggests that the addition of a cathode functional layer adds to the ASOR during low temperature operation. Despite the increase in the ASOR (due to the addition of a CFL) the overall interfacial resistance appears to decrease even at low temperatures.

![Figure 30 ASOR of the three SOFC's as a function of temperature](image_url)
Figure 31 Arrhenius plot of ASOR for the NGCFL, SCFL, and CGCFL

Figure 31 uses an Arrhenius plot to show the activation energy of each cell profile. From the plot it can be seen that higher activation energy is required for the two cells that have functional layers indicating that the ASOR measurement is effected by the addition of a functional layer.

Figure 32 shows polarization and power density curves of the SOFC cells with different CFL schemes at 850°C. The SOFC with the compositionally graded CFL had the highest power density of 193mWcm$^{-2}$ while the SOFC with the SCFL had the lowest of 80mWcm$^{-2}$. The SCFL polarization curve in Figure 32 exhibits the lowest performance. This is associated with the thickness and poor ionic/electronic conduction of the SCFL. From the graph it appears that the activation losses of the SCFL are comparable to the CGCFL. The polarization curve of the NCFL shows increased activation losses, possibly due to the lack of a CFL, which drive down the performance of
the cell until approximately 300mA. The slope of the NCFL polarization curve after 300mA decreases less than that of the CGCFL, suggesting that the lack of the CFL helps in decreasing ohmic losses. Finally, it should be noted that the sprayed layers in this work were not optimized for overall cell performance, which is evident in the relatively high overall activation losses and ohmic losses in comparison to state-of-the-art SOFC data.

Figure 32: Polarization curves and current-power density curves of SOFC unit cells with different CFL schemes at 850°C (CGCFL: □; NCFL: ▼; and SCFL :○)

7.2 Analysis of SEM Images

Figure 33 shows the SCFL and compositionally graded CFL respectively, capturing the cross-sectional microstructure of the cathodes, CFL’s, and electrolytes, as deposited by the pressurized dual-spraying system onto the anode substrates.
Figure 33 SEM photograph of a. SCFL showing a discrete CFL and cathode, b. CGCFL showing compositional gradation of the CFL and cathode

It can be seen in Figure 33 that the SCFL has two discrete interfaces (electrolyte-CFL and CFL-cathode) while the compositionally graded CFL only has one discreet interface located at the electrolyte. The compositionally graded CFLs lack of a discernable interface between the cathode and the CFL implies that continuous gradation has occurred. As both samples were physically cleaved to expose the micro structure for SEM analysis, only the SCFL appears to have delaminated at the cathode and CFL interface. This was the case for multiple SCFL cells, and locating an intact cell displaying a cathode layer during microscopy was challenging. This was not the case for the compositionally graded CFL. The compositionally graded CFL’s increased physical resilience to delamination may be a result of having a better interconnected micro structure at the graded interface.

The SOFC with the compositionally graded CFL appears to have an increasing porosity gradient from the cathode to the electrolyte respectively. This is due to a coarsening effect as the concentration of the cathode material increased. Typically,
graded porosity is accomplished by grading the particle size (Muller, Herbstritt and Ivers-Tiffee). However, in this instance the porosity gradation was unanticipated and most likely due to the compositional gradation process. This is not seen in the SOFC with the SCFL having an average porosity. The graded porous microstructure of the compositionally graded CFL with thickness δ has the potential to increase the overall limiting current density \( j_L \) by increasing the effective diffusivity \( D_{ij}^{\text{eff}} \) as seen in Equation 16.

\[
\text{Equation 16} \quad j_L = nF D_{ij}^{\text{eff}} \frac{c_{n}}{\delta}
\]

The compositionally graded CFL decreases the amount the nominal diffusivity \( D_{ij} \) is modified. This is accomplished by having an effective contrasting porosity \( \varepsilon \) and tortuosity gradient \( \tau \). The modification is illustrated in equation 3.

\[
\text{Equation 17} \quad D_{ij}^{\text{eff}} = \varepsilon^{\tau} D_{ij}
\]

A fuel cell cannot produce a higher current density than that determined by its limiting current density.

### 7.3 Analysis of EDAX Image Plots

In order to attempt a limit quantification of the compositionally graded profile, energy dispersion analysis (EDAX) area maps were made. The EDAX area maps were taken over a resolution of 256 (pixel width) by 200 (pixel depth) where one pixel
represented a surface area of 0.014 μm². The elemental intensity of each pixel was recorded as a numerical value and summed along its respective row. Figure 34 shown below compares the EDAX area map juxtaposed with its respective intensity plot.

Figure 34 EDAX area maps converted to single intensity values per 2D row

The average intensity was plotted as a function of depth into the SOFC. Figure 35 and Figure 36 show EDAX plots of the elemental intensities of the SCFL and compositionally graded CFL, respectively, as a function of distance from the cathode to the electrolyte. Each point is summed and normalized from an EDAX 256 X 200 (38 X 30μm) area map. The cathode is located at ~20-30μm, and the CFL is located at ~10-20μm on the x axis. The electrolyte is located before 10μm on the x axis.
Figure 35 X-ray count intensities profile plot showing Zirconium: ○ and Manganese: ▼ of SOFC cell having a SCFL.

Figure 36 X-ray count intensities profile plot showing Zirconium: ○ and Manganese: ▼ of SOFC cell having a CGCFL.

The SCFL cell seen in Figure 35 shows a rapid drop in Mn intensity occurs at approximately 20μm. This correlates to the cathode/SCFL interface. Prior to 20μm the
intensity is relatively stable until the SCFL/electrolyte interface located at approximately 10 μm, where it further decreases to noise levels.

The plot of the compositionally graded CFL cell seen in Figure 36 shows a trend of increasing Mn intensity while the intensity of Zn linearly decreased from 15μm, at the CGCFL/electrolyte, to 20μm, the cathode/CGCFL interface. The volume fraction distribution of the YSZ in the compositionally graded CFL matches the linear assumptions made by Deseure et al. in their model. The EDAX area mapping looks to be useful tool in future work to correlate cell performance with deposition concentration profiles as a function of CFL thickness. It should be noted that EDS quantitative results are readily obtained without standards. The accuracy of the standard-less quantitative analysis is highly dependent on the samples structure and composition.

7.4 Discussion

In this research, a compositionally graded CFL was fabricated based on the model proposed by Deseure et al. In this model, Deseure et al. sought to determine the effects of the volume fraction distribution of YSZ through compositionally graded CFL linearly with respect to thickness. The model predicted that charge transfer resistance is reduced due to enlarging the LSM-YSZ intimate contact cross-sectional area. In this research, Figure 35 and Figure 36 show that a comparable linear distribution of YSZ occurred. The results of the impedance analysis verify that the compositionally graded CFL showed improvement over the other two cells, supporting the conclusions drawn by Deseure et al.

Hart et al fabricated SOFCs with varying levels of graded cathode functional layers using screen printing. Three of the four cells that were fabricated by screen
printing in Harts’ research are comparable to the three cells fabricated in this study. Hart et al. concluded that overall polarization resistance decreased as the level of grading increased. In regard to polarization resistance, the results of this research were consistent with Hart’s findings. It was also concluded that the 20%/80%, LSM/YSZ respectively, layer should be avoided due to poor electronic conductivity as it’s below the percolation limit of LSM and effectively adds thickness to the electrode. As the number of layers of screen printing increases so does the cost and complexity of fabrication making it difficult to scale up. By implementing the novel pressurized duel suspension spraying system, complex fabrication of graded cathode functional layers can be reduced to a single deposition step while avoiding multiple interfaces.

8 Conclusion

Solid oxide fuel cells with a compositionally graded AFL, a compositionally graded CFL, both compositionally graded AFL and CFL’s, a NCFL and a SCFL between the cathode and electrolyte were built using a pressurized duel colloidal spraying system. The EIS data showed that the addition of the compositionally graded CFL or the SCFL increased the ASOR, but was overall effective at reducing the charge transfer resistance when compared to the NCFL cell. The IV data indicates that the SCFL may have suffered from poor conductivity, possibly due to a lack of optimization i.e. ratio of YSZ to LSM. The compositionally graded CFL outperformed both of the other cells in power density. The SEM images of the compositionally graded CFL clearly showed the lack of a discreet interface between the cathode and CFL, possibly contributing to improved interfacial contact with the cathode. It is known that porosity grading is beneficial to decreasing concentration losses and it is favorable that compositionally graded CFLs
have intrinsic porosity grading. The data in this work supports previously reported evidence that compositionally graded CFLs can improve SOFC performance.

It’s this researcher’s belief that an optimized SOFC implementing the deposition technique described in this thesis to facilitate a functional layer with an optimal profile containing effective constituent distribution would effectively impact the performance at high current densities. An SOFC having the proper constituent distribution would allow the catalytic, the conductive and electrochemical aspects of the SOFC at high current demands to improve. The optimized profile would allow for high rates of catalysis near the electrode where atomic oxygen is in the highest demand. The graded structure of the conduction pathways would allow for reduced polarization due to increasing cross sectional area along the conduction pathways. Furthermore the grading of the interface effectively increases the triple phase boundaries by increasing the contact surface area between the electrode and electrolyte material allowing for an increased number of reactions to take place.

The performances of the cells in this research are considered to be below the state of the art due to the components of the cells not being optimized. The anode substrate was fabricated in a ratio of 55/45wt% NiO/YSZ where it has been shown that 45/55wt% NiO/YSZ performs better (Fergus, Hui and Wilkinson). The cathode was sintered at 1200°C and research by Jorgensen et.al showed that this may be too high resulting in over densification and unwanted second phases (Jorgensen, Primdahl and Bagger). The main reason that the CGCFL and the SCFL had low performance was due to miscalculating the deposition rate of the cathode ink to match the desired wt% distribution in the functional layer. It is also believed that a linearly gradation is not the most optimal gradation profile
due to the scaling effect of the ineffective percolation zone. The use of a parabolic or exponential profile may be beneficial in decreasing the zone below the percolation threshold. Despite these optimization issues, this thesis demonstrates that an inexpensive and easily scalable deposition system can be used to produce a viable SOFC with a compositionally graded electrode functional layer.
Appendix A: Algorithm used for deposition

Total deposition rate = \( R_T \)

Deposition rate of syringe A at loop count \( i = R_A \)

Deposition rate of syringe B at loop count \( i = R_B \)

Loop counter value = \( i \)

Total loop count = \( N_i \)

- **Anode Functional Layer**

\[
R_A = \left[ \frac{R_T}{2} + \left( \frac{R_T}{N_i \cdot 2} \right) \cdot i \right] \\
R_A = R_T \left[ \frac{1}{2} + \left( \frac{i}{N_i \cdot 2} \right) \right]
\]

\[
R_B = \left[ \frac{R_T}{2} - \left( \frac{R_T}{N_i \cdot 2} \right) \cdot i \right] \\
R_B = R_T \left[ \frac{1}{2} - \left( \frac{i}{N_i \cdot 2} \right) \right]
\]

- **Cathode Functional Layer**

\[
R_A = \left[ \frac{R_T}{N_i} \right] \cdot i \\
R_A = R_T \left[ 1 - \left( \frac{i}{N_i} \right) \right]
\]

\[
R_B = R_T \left[ 1 - \left( \frac{i}{N_i} \right) \right]
\]
Appendix B: Analytical model to predict percolation feasibility.

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Flow of LSM:

$$LSM = \left( \frac{F_{total}}{t_{total}} \right)_{ml/sec} \left( \frac{1}{sec} \right) f_{LSM}$$

Flow of YSZ:

$$YSZ = \left( \frac{F_{total}}{t_{total}} \right)_{ml/sec} \left( 1 - \frac{C_{sec}}{1} \right) f_{YSZ}$$

Total ceramic flow:

$$TCF = \left( \frac{F_{total}}{t_{total}} \right)_{ml/sec} \left( 1 - \frac{t}{t_{total}} \right) + f_{LSM} \left( \frac{t}{t_{total}} \right)$$

$$= 0.00833_{ml/sec} \left[ 0.035 \left( 1 - \frac{t}{120} \right) + 0.0074 \left( \frac{t}{120} \right) \right]$$

$$= \int 0.00833_{ml/sec} \left[ 0.035 \left( 1 - \frac{t}{120} \right) + 0.0074 \left( \frac{t}{120} \right) \right]$$

$$TCF = 2.9155 \cdot t - 4 \cdot t + 9.5795 \cdot t^2 + C \quad 0 < t < 120$$

$$TCF = 0.00029155$$

$$2.9155 \cdot t - 4 \cdot 9.5795 \cdot t^2 + C = 0.00029155$$

$$C = 2.9155 \cdot t - 4$$
Volume Fraction of LSM: 
\[
V_{LSM} = \frac{\left( \frac{F_{\text{total}} \text{ ml}}{\text{sec sec}} \right) t_{\text{sec}} f_{LSM}}{t_{\text{total sec}}}
\]

Volume Fraction of YSZ: 
\[
V_{YSZ} = \frac{\left( \frac{F_{\text{total}} \text{ ml}}{\text{sec sec}} \right) \left( 1 - \frac{t_{\text{sec}}}{t_{\text{total sec}}} \right) f_{LSM}}{t_{\text{total sec}}}
\]

Geometric deposition adjustment factor:
\[
F_{\text{geo}} = \frac{V_{\text{CFL}}}{TCF} = \frac{\pi \cdot r^2 \cdot H_{\text{final}}}{TCF}
\]

\[
H = \frac{F_{\text{geo}} \cdot TCF}{\pi \cdot r^2}
\]

Parametric equation:

LSM
\[
x = H \cdot \int F_{\text{total}} \frac{\text{ml}}{\text{sec}} \left( f_{YSZ} \left( 1 - \frac{t}{t_{\text{total}}} \right) + f_{LSM} \left( \frac{t}{t_{\text{total}}} \right) \right)
\]

\[
y = V_{LSM} = \frac{\left( \frac{F_{\text{total}} \text{ ml}}{\text{sec sec}} \right) t_{\text{sec}} f_{LSM}}{t_{\text{total sec}}}
\]

YZS was calculated the same way.
Analytical accumulated

Height

Volume Fraction

Vol. Fraction vs. Thickness
Works Cited


