Title
OPTIMIZATION OF MICROSTRUCTURE AND COMPOSITION AND THE EFFECTS OF ATOMIC LAYER DEPOSITION SURFACE TREATMENT ON LSCF-BASED CATHODES FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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Publication Date
2017

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To my family. This accomplishment would not have been possible without their love and support.
ACKNOWLEDGEMENTS

I wish to acknowledge my research advisor, Min Hwan Lee, department of Mechanical Engineering at the University of California, Merced, for his supervision, guidance, and encouragement during my two years of research. I would also like to thank my colleague Alireza Karimaghaloo for his invaluable assistance in conducting experiments and interpreting experimental data. I wish to express my gratitude to Katherine Copenhagen and Duval Johnson for their helpful comments and assistance in compiling and formatting my thesis document. I would like to acknowledge Nissan Motor Co. and the NASA-funded Merced nAnomaterials Center for Energy and Sensing (MACES) for financial support of my research and for access to equipment used in collection of experimental data.
**LIST OF SYMBOLS**

- $Z$: impedance
- $Z_{\text{real}}$: real component of impedance
- $Z_{\text{imag}}$: imaginary component of impedance
- $Z_{\Omega}$ or $R_{\Omega}$: ohmic resistance
- $Z_{fA}$: anodic polarization resistance
- $Z_{f_c}$ or $R_p$: cathodic polarization resistance
- $R_{ct}$: charge transfer resistance
- $L$: inductor circuit element
- $Q$: constant phase circuit element
- $R$: resistor circuit element or resistance
- $t$: thickness
- $A$: cross sectional area
- $\sigma$: conductivity
- $\Omega$: resistance
- $V(t)$: voltage function
- $i(t)$: current function
- $\phi$: phase shift/phase angle
- $D_{50}$: median particle diameter
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<table>
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<td>LSCF</td>
<td>((La_{0.6}Sr_{0.4})<em>{0.95}Co</em>{0.2}Fe_{0.8}O_{3-\delta})</td>
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<tr>
<td>GDC</td>
<td>(Gd_{0.1}Ce_{0.9}O_{2-\delta})</td>
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<tr>
<td>SOFC</td>
<td>solid oxide fuel cell</td>
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<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
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<tr>
<td>YDC</td>
<td>yttrium-doped ceria</td>
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<td>YSZ</td>
<td>yttrium-stabilized zirconia</td>
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<tr>
<td>OCV</td>
<td>open circuit voltage</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
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<td>FEG</td>
<td>field emission gun</td>
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<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
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<tr>
<td>CCL</td>
<td>current collecting layer</td>
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<tr>
<td>FL</td>
<td>functional layer</td>
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<tr>
<td>TPB</td>
<td>triple phase boundary</td>
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<tr>
<td>MIEC</td>
<td>mixed ionic/electronic conductor</td>
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<tr>
<td>LSM</td>
<td>lanthanum strontium manganite</td>
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<tr>
<td>BSCF</td>
<td>(Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta})</td>
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<tr>
<td>ASR</td>
<td>area specific resistance</td>
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<tr>
<td>SSC</td>
<td>(Sm_{0.5}Sr_{0.5}CoO_{3\delta})</td>
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<tr>
<td>SSCC</td>
<td>(Sr_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta})</td>
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<td>PBC</td>
<td>(PrBaCo_{2}O_{5+\delta})</td>
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<tr>
<td>LSCo</td>
<td>(La_{0.8}Sr_{0.2}CoO_{3})</td>
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<td>LSF</td>
<td>(La_{0.8}Sr_{0.2}FeO_{3})</td>
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<tr>
<td>LSGM</td>
<td>(La_{0.8}Sr_{0.2}Fe_{0.83}Mg_{0.17}O_{2.815})</td>
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<tr>
<td>sccm</td>
<td>standard cubic centimeters per second</td>
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ABSTRACT

This study focuses on the development of \((La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}\) LSCF-based cathodes for solid oxide fuel cells, with the purpose of lowering operating temperature and improving cell performance for commercialization. The first part of the study investigated the effects of using \(Co_{3}O_{4}\) as a sintering aid, which was shown to enhance grain growth and interconnectivity and to dramatically lower cell impedance for both LSCF and LSCF\(-Gd_{0.1}Ce_{0.9}O_{2-\delta}\) (gadolinia-doped ceria; GDC) composite cathodes. \(Co_{3}O_{4}\) concentration was optimized for both the functional layer and the current collecting layer of the cathode. The second portion of the study explores the relationship between electrode layer thickness and cell impedance. It was shown that increasing functional layer thickness beyond a limiting value increases cell impedance, and that both ohmic resistance and polarization resistance asymptotically decrease with increasing thickness of the current collecting layer. Optimal thicknesses were found for each of the electrode layers. Finally, ultra-thin layers of yttria-doped ceria were deposited via atomic layer deposition (ALD) onto the functional layer of bilayer LSCF-GDC/LSCF cathodes as well as pure LSCF cathodes. It was shown that for both sets of cells, ohmic resistance initially increased with YDC deposition, but that subsequent increases in YDC thickness had an inverse relationship with ohmic resistance. This behavior has been observed in previous studies, and prolonged heat treatment will be needed to fully realize the benefits of the functionalization. Polarization resistance was negatively affected by YDC functionalization for both sets of cells due to a blocking of oxygen reaction sites on the surface of the LSCF electrode. In summary, \(Co_{3}O_{4}\) concentration and electrode layer thickness were optimized to maximize performance for LSCF-based cathodes, and ALD functionalization was investigated as a method for further improving cathode performance.
The fossil fuel based infrastructure that we rely on for our energy needs causes major problems such as global warming, threats of resource depletion, permanent damage to the environment human health, and economic problems. A transition away from the use of fossil fuels is inevitable, and it is acknowledged across the scientific community that the time restraint on such a transition is restrictive [4]. Fortunately, advances in hydrogen energy technologies, photovoltaic solar modules, and wind-turbine generators have created the possibility of replacing fossil fuel energy sources entirely. Although these technologies are still in development, they can be used in conjunction with one another to satisfy the energy needs of the global population. Further research and development is needed so that these resources can be commercialized on a large scale, thus diminishing the need for fossil fuel use and sparing the environment and the economy of its adverse impacts.

The current infrastructure for producing, distributing, and consuming energy is flawed in a number of ways. Perhaps the most urgent complication with fossil fuel consumption is the environmental damage caused by the combustion of coal and petroleum products. Presently, about 88% of all energy consumed is via fossil fuel combustion, and the combustion process emits billions of tons of harmful pollutants and particulates into the atmosphere every year; namely carbon-dioxide and various sulfur and nitrogen oxides [5, 6]. This pollution contaminates the air, water, and soil, and causes disease and illness, killing an estimated half a million people every year [7]. In addition, the emission of pollutants such as carbon-dioxide into the atmosphere directly contributes to increases in average global temperature, according to a report on climate change published by the United Nations in 2007 [7]. Studies have shown that the presence of carbon-dioxide in the atmosphere has increased dramatically since the Industrial Revolution, and that concentrations of this greenhouse gas are higher than they’ve been in 500,000 years [7]. The effects of continued emission of carbon-dioxide and other greenhouse gases into the atmosphere are not completely certain; however, there is a distinct possibility that these emissions could eventually (and potentially very suddenly) result in a dramatic shift in the global climate [8]. The repercussions of such a shift could be extremely far-reaching and devastating to the world population. For example, a significant global increase in temperature could cause the polar ice caps to melt, leading to a rise in sea level.
and the destruction of hundreds of millions of homes in coastal regions. In addition, continued increases in global temperature could begin to manifest itself in the form of extreme weather conditions, such as tornados, hurricanes, severe storms, etc., causing enormous amounts of damage to property and human lives [7]. Also, frequent drought could result from further increases in global temperature, which would dramatically affect food production. Besides posing serious threats to the climate and to human health, pollution is also a very expensive problem to try to control; in 1997, it was estimated that combustion of fossil fuels caused environmental damage costing $990 billion [5]. Even with all of the resources that are dumped into controlling pollution every year, it is still not under control and is still considered to be a major concern.

Reviewing the problems associated with the current energy infrastructure is a good place to start when considering the next steps in energy development, because we need to be aware of the issues to avoid in the development of the new system. The new system must provide comprehensive access to energy sources that are both reliable and affordable; thus, the energy must come from sources that are renewable and unable to be depleted. Also, consumption of the energy generated by new sources should cause very little or no damage to the environment, therefore guaranteeing a habitable climate for our generation as well as future generations. Thirdly, new technologies must be capable of producing enough energy to provide affordable options to everyone in the country, decreasing the need for foreign trade, and thus minimizing security threats posed by oil importation.

There are several technologies capable of meeting such requirements, among them is the use of hydrogen gas as both an energy carrier and as a fuel source for the transportation, corporate, and private sectors. Hydrogen can be (and has been) utilized as an energy source in a number of ways, each of which causes virtually no damage to the environment [4, 5]. As with conventional fuels, hydrogen can be combusted, and the chemical reaction that takes place during the combustion process emits only water as a byproduct, making hydrogen a zero-emission fuel. Also, the hydrogen fuel cell is a relatively new technology that efficiently recombines hydrogen and oxygen, and captures the electrical and thermal energy that is produced by this chemical reaction. As with the combustion process, this produces only water as a byproduct, and in addition, produces electrical and thermal energy to be utilized for work. Thus, methods for obtaining usable energy from hydrogen gas cause no air pollution, which covers a major requirement in the criteria for an energy resource to replace fossil fuels.

Unlike fossil-fuels, hydrogen is a completely renewable resource. As the most common element in the universe, hydrogen is found in and can be extracted from a number common materials, including water and methane gas; in fact, hydrogen production is currently a common practice, valued at $120 billion in 2010. One method for producing hydrogen gas is by the water electrolysis method, by which
an electrical current separates water molecules into respective hydrogen and oxygen atoms, the former of which is collected and stored for later use. This process is relatively efficient; electrolyzation of 3 gallons of water produces enough hydrogen to supply the daily energy needs of a large home [9]. Electrolysis requires a primary energy source to supply the electricity needed to separate the molecules. This primary source of electricity must not include the combustion of fossil fuels, otherwise the cost of the produced gas would be high, the dependence on fossil fuels would remain unchanged, and the production of hydrogen would cause just as much damage to the environment as the current infrastructure [5]. Therefore, sustainable energy sources must be used to generate the electricity needed for water electrolysis.

Fuel cell technology is developing rapidly, with fuel cell revenue exceeding $750 million in 2010 [9]. A fuel cell essentially operates in the reverse order of the water electrolysis process; inside of a fuel cell, hydrogen and oxygen spontaneously recombine to produce an electrical current, a small amount of thermal energy, and $H_2O$ as a by-product. The electrical and thermal energy produced can be directly utilized for doing work. As long as the hydrogen used in the fuel cell is produced by a sustainable energy resource, hydrogen fuel cells provide a means for producing sustainable energy in both stationary and non-stationary applications; in fact, fuel cell vehicles already exist, and Apple is considering powering future iPhones with hydrogen fuel cells [9]. Given further development of hydrogen gas storage, fuel cell systems could be put into the basements of houses and buildings, providing clean electrical energy for homes and businesses. This would eliminate the need for coal-based electricity production, thus diminishing the effects of the environmental damage caused by coal combustion. Also, fuel cells could be further integrated into the transportation sector: on-board fuel cell systems could provide power to vehicles that run on electric motors (and it is hypothesized that most vehicles in the future will) [7]. The fuel cell is technically more efficient than the internal combustion engine, and even a combination of a fuel cell with a conventional internal combustion engine would create a vehicle 2-3 more times efficient than traditional internal combustion engine vehicles [9]. The current infrastructure would need to be modified only slightly to accommodate such vehicles; gas stations would need only to be equipped with an additional pump to dispense hydrogen fuel. About 200 of such fueling stations existed worldwide as of 2010, and a 2011 Pike Research report predicted that more than 5200 of such fueling stations will be operational by 2020 [9]. Many organizations across the globe are already working to develop fuel cell technology, such as the Fuel Cell and Hydrogen Energy Association in the US, and the European Hydrogen Association and Fuel Cells and Hydrogen Joint Undertaking in Europe [9]. With further development of hydrogen fuel cells, this technology could initially supplement, and eventually replace the combustion of fossil fuels.
This paper focuses on the development of the solid oxide fuel cell, which operates at high temperature and utilizes a solid ceramic electrolyte. The fundamental components and basic SOFC operation will be described, as well as the materials and methods used to fabricate SOFCs. Methods for electrochemical characterization will be detailed, followed by an overview of atomic layer deposition fundamentals. A literature review will be given of the current state of research in the field of study covered in this paper. Research objectives will be stated, followed by a detailed description of research tasks and results, including investigation of varying sintering aid concentration on cell performance, electrode layer thickness optimization, and effect of atomic layer deposition (ALD) on SOFC cathode impedance.
Chapter 2

SOFC OVERVIEW

2.1 Operation

Solid oxide fuel cells (SOFCs) are highly efficient energy conversion devices which convert potential energy stored in chemical fuels directly into electrical power, which can subsequently be used for work. Unlike conventional combustion engines, which derive mechanical energy from heat generated in the combustion of chemical fuels, SOFCs derive electrical energy directly from chemical fuels, allowing them to be much more efficient and environmentally friendly than combustion engines.

Figure 2.1: schematic diagrams of SOFC operation [1, 2]

An SOFC consists of three major components: anode, cathode, and electrolyte (shown in Figure 2.1). These components are connected in series, with the solid ceramic electrolyte sandwiched between the two electrodes. The electrodes are connected using a wire or current collector. Air enters the porous cathode, where oxygen molecules from the air are adsorbed onto the surface of the catalytic cathode material. The $O_2$ molecules are further dissociated into oxygen atoms, and the oxygen atoms are reduced to an $O^{2-}$ state by electrons from the current collector attached to the anode. The cathode reaction is shown as Equation 2.1.

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2+}$$ (2.1)
The oxygen ions diffuse through the solid ceramic electrolyte, which becomes a conductor for oxygen ions at high temperature. Chemical fuel enters at the anode side (for this discussion, hydrogen gas will be assumed as the chemical fuel), and is catalyzed by the anode. Molecular hydrogen is adsorbed onto the surface of the catalyst, transports to the anode-electrolyte interface, where it combines with \( O^{2-} \) ions to form \( H_2O \) and heat, given by the reaction shown as Equation 2.2.

\[
H_2 + O^{2-} \rightarrow H_2O + 2e^-
\]  

(2.2)

Combining the two half reactions gives the complete reaction for an SOFC as shown in Equation 2.3.

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O
\]  

(2.3)

The difference in chemical potential between the hydrogen and oxygen ions drives the SOFC reaction, and the resulting flow of electrons from anode to cathode can be exploited to do work. The current collector connecting anode to cathode acts as an external circuit, and a load can be attached to the circuit to power an electronic device. In addition to generating free electrons and \( H_2O \), heat is a byproduct of the reaction and is also generated in the SOFC by ohmic losses and electrode over-potentials. In other words, the movement of electrons and ions generates additional heat in the SOFC [10]. Therefore, a good thermal management system is necessary to achieve maximum efficiency in an SOFC, such as using recycled heat to maintain the high operating temperature that is needed. Alternatively, the exhaust heat can be used to power a turbine, provide heat for residential or automotive applications, produce hot water, or any number of applications. A proper thermal management system can increase SOFC efficiency by up to 40%, allowing for efficiencies as high as 85-90% [2].

### 2.2 SOFC components

#### 2.2.1 Electrolyte

Solid oxide fuel cells utilize a solid ceramic oxide-ion conductor as an electrolyte, which is sandwiched between the two electrodes. The primary purpose of the electrolyte is to transport \( O^{2-} \) ions from cathode to anode as well as provide mechanical support for the cell. A material must meet several requirements to be used as an effective SOFC electrolyte. Firstly, the material must exhibit high ionic conductivity, but negligible electronic conductivity. SOFC performance is generally limited by the ohmic resistance corresponding with the flow of ions through the electrolyte [2]. Therefore, a suitable electrolyte material should be as ionically conductive as possible, and it should exhibit sufficient stability to retain its conductivity after prolonged use. Additionally, any electrons shorting through the electrolyte will
cause a voltage loss in the cell; therefore, a good SOFC electrolyte is as electronically insulative as possible. Layer thickness is also an important factor for SOFC electrolytes as the resistance, and therefore ionic flow, is sensitive to electrolyte thickness. The resistance of the electrolyte material is given by Equation 2.4.

\[ R = \frac{t}{\sigma A} \]  

(2.4)

Here, \( t \) is the electrolyte thickness, \( \sigma \) is the ionic conductivity, and \( A \) is the cross-sectional area. Equation 2.4 shows that the ohmic resistance of the electrolyte scales linearly with layer thickness; therefore, a thin electrolyte layer minimizes resistance is essential for optimal performance. However, an SOFC electrolyte that is too thin will allow electrons to short through the electrolyte. Thus, studies have shown that an optimal electrolyte thickness of around 15 \( \mu \)m will minimize ohmic resistance while preventing voltage losses due to electron shorting [11]. In addition to optimal layer thickness, an SOFC electrolyte should be as dense as possible; as a porous electrolyte results in the fuel mixing with the oxidant, which drastically decreases the voltage capacity of the cell.

Chemical and mechanical stability is another requirement for SOFC electrolyte materials. The electrolyte must be able to withstand the high-temperature reducing environment of the anode, as well as the high-temperature oxidation environment of the cathode, without experiencing any physical or chemical instability. The electrolyte should also be chemically inert, so that reactions between the electrolyte and electrodes do not occur. Reactions occurring between the electrolyte and either electrode could lead to a highly resistive phase forming, which dramatically hinders cell performance [12]. Additionally, the electrolyte will experience mechanical stress due to a mismatch in thermal expansion between electrolyte and electrodes. Therefore, electrolyte materials must have sufficient mechanical strength to withstand this stress, particularly for electrolyte-supported cells (cells which rely on a relatively thick electrolyte layer for mechanical stability). Finally, material and fabrication cost is an important barrier to mass commercialization of solid oxide fuel cell technology. Therefore, SOFC electrolytes should be relatively inexpensive to manufacture.

Yttrium-stabilized zirconia (YSZ) is the most widely used SOFC electrolyte material [10], and is the primary electrolyte used for this study. YSZ is fabricated by doping a zirconia host (\( \text{ZrO}_2 \)) with yttria molecules (\( \text{Y}_2\text{O}_3 \)), resulting in a fluorite crystal structure. During the doping process, yttrium cations (\( Y^{3+} \)) diffuse into the zirconia host material and replace zirconium cations (\( Zr^{4+} \)) in the crystal lattice. Because of the charge difference between the cations, one oxygen vacancy (\( O^{2-} \)) is created each time two yttrium cations replace two zirconium cations in the lattice, so that charge balance is maintained. This is illustrated in Figure 2.2: Figure 2.2(a) shows the undoped zirconia host, while Figure 2.2(b) shows an empty \( O^{2-} \) site
created by replacing two $Zr^{4+}$ cations with two $Y^{3+}$ cations. These oxygen vacancies are what give YSZ its ionic conductivity; as oxygen ions created at the cathode hop from one empty $O^{2-}$ site to the next, until they reach the anode. Increasing the amount of yttria doping increases the number of empty $O^{2-}$ sites in the lattice, therefore increasing the ionic conductivity. However, there exists an upper limit to doping concentration, beyond which $O^{2-}$ sites begin to interact with one another, and ionic conductivity decreases. Studies have shown that a doping concentration of 8 mol% $Y_2O_3$ is optimal for the ionic conductivity of YSZ, as shown in Figure 2.3(a) [2].

Although YSZ is the primary electrolyte material used in this study, gadolinium-doped ceria (GDC) also plays an important role, and will be briefly introduced here. At temperatures above about 800°C, YSZ reacts with $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-δ}$ or LSCF (the primary cathode material used in this study) to form SrZrO$_3$, an ionically insulating phase which dramatically impedes cell performance. A thin (5µm) layer of GDC can be placed between the YSZ electrolyte and LSCF cathode to prevent insulating phase formation from occurring during electrode sintering [13]. Like YSZ, GDC exhibits a fluorite crystal structure, and shares the same ion-hopping mechanism to facilitate ionic conductivity in the electrolyte. However, because the gadolinium dopant ions are similar in size to the host cerium ions, ceria can be doped with a higher concentration of dopant of up to 10-20% compared to the 8 mol% for YSZ. Therefore, GDC generally shows a higher ionic conductivity than YSZ, as seen in Figure 2.3(b), which shows the ionic conductivity as a function of temperature for these materials. However, GDC has several disadvantages compared to YSZ, which is why YSZ is the primary electrolyte used in this study. Firstly, GDC exhibits significant electronic conductivity in the high-temperature reducing environment of the anode, which leads to a dramatic decrease in available open circuit operating voltage (and thus a decreased overall power density). Additionally, GDC shows significant chemical expansion when exposed to a reducing environment, causing mechanical failure in the electrolyte [2]. Therefore, while YSZ is the primary electrolyte material used in this study, a thin layer of GDC is inserted to separate the YSZ electrolyte from the cathode to prevent ionically insulating phases from forming between the YSZ electrolyte and the cathode.
Figure 2.3: (a) ionic conductivity vs yttria doping concentration for YSZ; (b) ionic conductivity vs temperature for YSZ and GDC [2]

2.2.2 Cathode

The SOFC cathode has two main functions. It is responsible for reducing oxygen into $O^{2-}$ ions and transporting these ions to the electrolyte. Secondly, it transports electrons from the external circuit to the *triple phase boundary* site where the oxygen reduction reaction occurs. Therefore, a suitable SOFC cathode will exhibit excellent catalytic activity and high electronic conductivity. In addition, the cathode material should exhibit reasonable ionic conductivity, so that the electrode reactions sites, or triple phase boundary (TPB) area, is maximized. The TPB is the area at which the three important SOFC elements coincide: gas as an oxygen source, the electronic conductor, and the ionic conductor (or electrolyte). These are the sites at which essentially all electrode reactions occur; thus, maximizing this area is crucial to optimizing SOFC performance. For a standard cathode with negligible ionic conductivity, the TPB area is confined to the interface between the cathode and electrolyte, as shown in Figure 2.4(a). However, choosing a cathode material with a high ionic conductivity will extend the TPB area dramatically, allowing cathode reactions to occur at virtually any location on the cathode surface.

This is illustrated in Figure 2.4(b), where the oxygen is reduced at any point on the surface of the cathode and the oxygen ions can then travel through to cathode to the electrolyte. Furthermore, fabricating a composite cathode using a mixture of electrolytic and cathodic materials can also dramatically increase performance by further increasing ionic conductivity. In contrast to the electrolyte, the cathode should be sufficiently porous to allow oxygen gas to permeate the electrode, maximizing reaction sites. In addition, the cathode material needs to have sufficient mechanical and chemical stability to withstand the high-temperature oxidation environment of the cathode. The thermal expansion of the cathode must match relatively well with the electrolyte to prevent electrode delamination, and the material should have the mechanical stability to withstand repeated heating/cooling cycles.
The cathode should also be chemically compatible (nonreactive) with the electrolyte material and the interconnecting materials, and as with the electrolyte, should be relatively inexpensive to fabricate.

LSCF \((La_{1-x}Sr_xCo_{1-y}Fe_yO_3)\) is among the best performing and most widely used cathode materials for intermediate-temperature SOFCs, and it is the primary cathode chosen to be used in this study. LSCF exhibits excellent catalytic activity at intermediate temperatures, and has been shown to outperform conventional cathode materials such as lanthanum strontium manganite or LSM. LSCF is a mixed ionic-electronic conductor (MIEC); in other words, in addition to being electronically conductive at intermediate temperatures, it also displays reasonably high ionic conductivity of 0.2 S cm\(^{-1}\) at 900°C, whereas LSM shows ionic conductivity of 10\(^{-7}\) S cm\(^{-1}\) at 900°C [14]. Thus, LSCF has a higher TPB area (more reaction sites) compared with LSM, and additionally shows a much higher oxygen diffusion coefficient and comparable electronic conductivity (230 S cm\(^{-1}\) at 900°C, compared with an electronic conductivity of 200-300 S cm\(^{-1}\) for LSM).

Although LSCF has shown better overall performance than conventional LSM cathodes, it exhibits comparatively poor chemical compatibility with the YSZ electrolyte. Chen et. al. showed that at sintering temperatures of 850°C or higher, LSCF and YSZ react to form impurity phases \(La_2Zr_2O_7\) and \(SrZrO_3\), both of which are insulators for oxide ions. The formation of these impurity phases at the electrode-electrolyte interface caused cathode impedance to increase by approximately 750 times, from 0.129 \(\Omega\) cm\(^2\) to 97.619 \(\Omega\) cm\(^2\) at 700°C [15]. Therefore, for an LSCF cathode to be compatible with the YSZ electrolyte, a barrier layer must be placed between the electrode and electrolyte so that interfacial reactions are prevented. Mai et. al. showed that sputtering or screen printing a 5\(\mu\)m layer of \(Ce_{0.8}Gd_{0.2}O_{2-\delta}\) (GDC) on top of the YSZ electrolyte effectively inhibits the phase-forming reactions between LSCF and YSZ [13]. Therefore, in this study, a 4-8\(\mu\)m layer of GDC is always placed between the YSZ electrolyte and the LSCF electrode.

Recall that in comparison to conventional cathode materials such as LSM, LSCF exhibits high ionic conductivity in addition to high electronic conductivity.
It has become common practice to further enhance the ionic conductivity of the cathode by adding a second ionically conductive phase (usually YSZ or GDC) to form a composite cathode. Leng et al. showed that an LSCF-GDC composite cathode (40:60 wt%) showed approximately seven times smaller polarization resistance compared to a pure LSCF cathode (0.17 Ω cm² for LSCF-GDC, compared with 1.2 Ω cm² for pure LSCF at 600°C operating temperature) [16]. This dramatic decrease in polarization resistance in the composite LSCF-GDC cathode is a result of the increased density of TPB sites from the introduction of the ionically conductive GDC phase. Furthermore, Kim et. al. showed that cathode resistance can be further decreased by adopting a bi-layered cathode approach. In this study, a cathode consisting of a composite LSCF-GDC layer (hereafter referred to as the functional layer) adjacent to the electrolyte, and pure LSCF layer (hereafter referred to as the current collecting layer) adjacent to the functional layer, exhibited lower polarization resistance than a single-layer LSCF-GDC composite cathode (0.35 Ω cm² at 660°C for the bi-layered cathode, as compared with 0.66 Ω cm² for the single-layer cathode) [17]. The study showed that the charge transfer between the electrode and electrolyte, as well as the charge transfer from the external circuit to the electrode, can be significantly enhanced by adopting the bi-layer cathode approach. In addition, Jung et. al. showed that adopting the bi-layer approach also improves the mechanical integrity of the cathode [18]. For a single layer LSCF cathode, there is significant mismatch in thermal expansion coefficient between the LSCF-based electrode and the YSZ electrolyte. Because of this, heating and cooling the cell causes mechanical strain, and can lead either to cracking in the electrode, or even complete delamination from the electrolyte. A bi-layered cathode with a composite functional layer introduces a gradient of thermal expansion coefficients, which reduces the mechanical strain caused by thermal mismatch and improves the mechanical integrity of the cell. Therefore, bi-layered LSCF-GDC/LSCF cathodes are used throughout this study, with a thin GDC barrier layer sandwiched between the electrolyte and the functional layer.

2.2.3 Anode

The focus of this study is primarily cathode optimization, with some focus on electrolytic materials as well. However, the final component of SOFCs is the anode, a detailed investigation of which is outside the context of this study. Many of the requirements of the SOFC anode are similar to those of the cathode. The anode material must exhibit high catalytic activity for the hydrogen oxidation reaction, should have excellent electronic conductivity for electron transport from TPB sites to the external circuit, and should show at least marginal ionic conductivity to maximize the TPB site density. The anode material should have sufficient chemical and mechanical stability to withstand the high temperature oxidation environment of the anode and the repeated reduction/oxidation (redox) cycles required for regular
operation. The material should be chemically compatible with other SOFC components such as the electrolyte and the circuit interconnect materials, and should have a thermal expansion coefficient that matches relatively well with other SOFC components. The anode should be sufficiently porous (>30 vol%) to allow permeability of gaseous fuel, and should sufficiently stable to maintain performance after extended operation (>90,000 h) [11].

The most extensively used SOFC anode material is a Ni-YSZ composite cermet material (material that is comprised of both a ceramic and a metal component). In Ni-YSZ anodes, nickel provides the high catalytic activity and electronic conductivity, and the YSZ provides the ionic conductivity, structural support, aids in the matching of thermal expansion between the anode and electrolyte, and suppresses agglomeration of nickel particles during operation (a common problem for pure Ni anodes). Ni-YSZ anodes are extremely stable in high temperature oxidation environments, and they essentially satisfy all of the requirements for an SOFC anode. As with the cathode, a multi-layer approach is often used to improve performance and maximize thermal expansion compatibility [2].

2.3 Characterization Methods

Several methods exist for characterizing the performance of solid oxide fuel cells, including, but not limited to: electrochemical impedance spectroscopy (EIS), current-voltage (i-V) characterization, open circuit voltage (OCV) measurements, and scanning electron microscopy (SEM) for characterizing electrode microstructure. In the present study, only cathode performance is studied, and all experiments are conducted using symmetric cells (a symmetric cell has two cathode electrodes, whereas a full cell has one cathode and one anode). Current-voltage characterization and open circuit voltage measurements are generally only used for full cell characterization. Thus, electrochemical impedance spectroscopy and scanning electron microscopy are the primary characterization methods used in this study.

2.3.1 Electrochemical Impedance Spectroscopy

The electrochemical reactions in a single solid oxide fuel cell can theoretically generate up to 1.23 V of electric potential [19]. In practice, however, an SOFC suffers performance losses due to anode and cathode activation losses (caused by electrochemical reaction kinetics) and electrolyte/electrode ohmic losses (caused by electronic and ionic conduction). EIS is a popular characterization method that allows the user to accurately differentiate between the major sources of loss in the cell. Impedance is the ability of a system to impede the flow of electrical or ionic current. Impedance is an extension of resistance, in that it also deals with time-dependent phenomena. The impedance $Z$ of a system is defined as the ratio of voltage to current as is shown as Equation 2.5.

$$Z = \frac{V}{I}$$
As mentioned, the voltage and current need not be steady state values; they are time- (or alternatively, frequency-) dependent functions. To measure the impedance of a system, the system is subjected to a small sinusoidal voltage perturbation, and the resulting current is measured. In general, the current response may lag behind the voltage input, which introduces the phase shift \( \phi \). The impedance of a system can then be described in terms of magnitude \( Z_0 \) and phase angle \( \phi \), or alternatively as a real component \( Z_0 \cos \phi \) and imaginary component \( Z_0 j \sin \phi \). Purely resistive circuitry elements such as resistors have only real components of impedance, whereas time-dependent elements such as capacitors have both real and imaginary components of impedance.

\[
Z = \frac{V(t)}{i(t)} \tag{2.5}
\]

Figure 2.5: Nyquist plot showing sample SOFC electrochemical impedance spectroscopy data for illustration; \( Z_\Omega \) is the cell ohmic resistance, \( Z_{fA} \) is the anodic polarization resistance, and \( Z_{fc} \) is the cathodic polarization resistance [2]

To perform electrochemical impedance spectroscopy, the impedance of the system is measured over several orders of magnitude of AC voltage frequencies (for this present study, the range is 50 mHz-7 MHz). The resulting data is plotted in terms of the real and imaginary components of the impedance values, with the real components \( (Z_{\text{real}}) \) plotted on the x-axis and the negative imaginary components \( (-Z_{\text{imag}}) \) plotted on the y-axis. The useful imaginary components generally have negative values, and therefore it makes more sense graphically to plot these values
This graphical representation of impedance data is known as a Nyquist plot, and it summarizes the impedance behavior of a system over a wide range of frequencies. An example of a Nyquist plot for an SOFC is shown in Figure 2.5. To understand the shape of the Nyquist plot for an SOFC, some fuel cell modeling principles must be described first. An SOFC can be represented by an equivalent circuit, the elements of which describe the actual physical processes occurring during fuel cell operation. The simplest equivalent circuit representation for an SOFC is shown in Figure 2.6.

Each electrode can be represented by a parallel resistor-capacitor (RC) circuit. The resistor represents resistance to the electrochemical reactions occurring at the electrode; in other words, the resistance value is directly related to the electrode kinetics, or the speed of the electrochemical reactions. At the electrode-electrolyte interface, a buildup of ions in the electrolyte causes a buildup of electrons in the electrode to balance the charge, in much the same way that the accumulation of charge in one capacitor electrode causes a buildup of charge in the opposing electrode. Thus, SOFC electrodes exhibit electronic behavior that is similar to a parallel RC circuit, and can be modeled as such, as shown in Figure 2.6. The two electrodes are connected serially, with the electrolyte in between them, which can be modeled as a simple resistor.

Now that the basic concepts of SOFC equivalent circuitry have been explained, the shape and significance of the Nyquist plot of Figure 2.5 can be described. As mentioned, the Nyquist plot is generated by measuring the impedance of the SOFC over many orders of magnitude of input voltage frequencies. The resistive elements of the SOFC have purely real components of impedance, and the capacitive elements have purely imaginary components. At very low frequencies (data shown on the right side of the Nyquist plot), the capacitive elements act as open circuits, and all current flows through the resistive component of the electrode. Thus, the impedance values have no imaginary components and lie on the $Z_{\text{real}}$ axis, representing the effective impedance of the resistor. Conversely, at very high frequencies (furthest to the left side of the Nyquist plot), the capacitive elements act as short circuits, with all current flowing through the capacitive element of the electrode. Thus, the effective impedance of the electrode is zero [2].

As Figure 2.5 illustrates, a standard Nyquist plot for an SOFC shows two semi-circular arcs, one larger than the other. The SOFC Nyquist plot provides many pieces of useful information regarding cell performance, a few of which will
be described here. The cathodic activation resistance (resistance related to electrochemical reaction speed) is given by the difference in the two $Z_{\text{real}}$ intercepts of the large arc; in other words, the distance between the two intercepts gives a direct measurement of the electrochemical reaction speed taking place at the cathode. Similarly, the anodic activation resistance is given by the distance between the two $Z_{\text{real}}$ intercepts of the smaller arc. It should be noted that the semicircle corresponding to cathodic activation loss is much larger than the semicircle corresponding with the anodic activation loss. This is because the oxygen reduction reaction taking place at the cathode is much more sluggish than the hydrogen oxidation reaction taking place at the anode. Thus, the cathodic activation resistance is generally the limiting factor in SOFC performance, and therefore much SOFC research is dedicated to decreasing cathodic activation resistance to improve overall cell performance. One additional piece of information that can be gleaned from an SOFC Nyquist plot is the ohmic resistance, or resistance to the flow of ions and electrons, of the cell. As was mentioned, at very high frequencies, the activation impedance of the electrodes is effectively zero, and the resulting intercept on the $Z_{\text{real}}$ axis represents the ohmic resistance of the cell. In general, electronic resistance is negligible, and the ohmic resistance represents resistance to the flow of oxygen ions. Furthermore, much of the ohmic resistance in an SOFC generally comes from the electrolyte. In summary, EIS provides a method for quantifying the major sources of loss in a fuel cell. It is an extremely useful tool for experimental SOFC work, as it allows the user to quantitatively compare the effects of different SOFC fabrication processes and compositions, and it is the primary characterization technique used in this study. It should be noted that since all cells in this study were symmetric (having a cathode on either side of the electrolyte) the Nyquist plot shows only a single arc, from which cathode activation resistance and ohmic resistance can be obtained.

2.3.2 Scanning Electron Microscopy

In addition to characterizing fuel cell performance using electrochemical characterization methods, it is also important to examine the microstructure of SOFC electrodes, in order to explore the relationships between electrochemical performance and the physical structure of the electrode. Some microstructural characteristics that effect electrode performance include particle size and interconnectivity, electrode porosity and tortuosity, electrode layer thickness and uniformity, and electrode/electrolyte adhesion. High magnification (>10,000x) and excellent image resolution is required to properly observe these features. The scanning electron microscope (SEM) allows for detailed observation of features on a micrometer ($\mu$m) or even a nanometer (nm) scale. Although a detailed description of SEM operation is beyond the scope of this paper, a brief overview will be given.

In the SEM, a finely focused beam of electrons is scanned across the surface of the sample to be examined. Several types of interactions occur between
the electrons and the sample, including (but not limited to) backscattered electron interactions and secondary electron interactions, which provide information about sample composition and surface topography, respectively [20]. Backscattered electrons come directly from the focused electron beam, are deflected by the molecules or atoms making up the sample, and are collected by a backscattered electron detector. The number of backscattered electrons that are deflected depends upon the atomic number of the elements making up the sample; heavier elements deflect more electrons. Therefore, backscattered electron signals give information about the sample composition; darker spots on the formed image represent the heavier elements in the sample, and lighter spots represent lighter elements. In contrast, secondary electron interactions do not come directly from the focused electron beam. Secondary electrons are outer shell electrons belonging to the atoms making up the specimen. Electrons with sufficient energy coming from the electron beam can knock these outer electrons out of orbit, allowing them to pass through the specimen and to be collected by the secondary electron detector. Secondary electron collection is highly directional; that is, most of the electrons that are collected are ones that exit the specimen facing the detector. Because of this, secondary electron signals provide information about the surface topography of the specimen; surfaces facing the detector appear to be illuminated, while surfaces facing away from the detector appear to be shaded. Additionally, because of the relatively low energy of the outer shell electrons, only secondary electrons emitted near the surface of the specimen are collected. Because of the small sampling depth, secondary electron signals provide very detailed, high resolution images of the surface of the specimen. Using a combination of backscattered electron and secondary electron signals, the SEM can generate highly detailed images of the specimen to be studied, allowing for extensive study of microstructural characteristics of the material. In this study, SEM is used extensively in conjunction with EIS to investigate correlations between electrode microstructure and electrochemical performance.
Chapter 3

ATOMIC LAYER DEPOSITION OVERVIEW

Atomic layer deposition (ALD) is a relatively new vapor deposition technique for depositing a large variety of ultra-thin films with extreme precision. It has become an important tool in many research-oriented and industrial applications, such as semiconductor manufacturing, photovoltaics, lithium-ion batteries, heterogeneous catalysts, and solid oxide fuel cells [20]. Because of the sequential, self-limiting nature of the reaction process, ALD allows for the deposition of highly uniform layers of carefully controlled thickness, down to the angstrom level.

A typical ALD process is shown in Figure 3.1. The substrate is first placed in an evacuated chamber, generally between 200-350°C [3, 21]. The surface of the substrate may be naturally functionalized, or may have to be treated for functionalization to facilitate reactions with the precursor functional groups. The first precursor (Precursor A) fills the chamber, and the precursor functional groups attach to reaction sites on the functionalized surface of the substrate.

The ligands attached to the precursor molecules can only react with reaction sites on the substrate; they cannot react with each other. Therefore, assuming that the dwell time (amount of time that precursor molecules are allowed to remain in the chamber) is sufficiently long, all reaction sites on the substrate surface will be occupied by one single layer of precursor molecules. It is this characteristic of the atomic layer deposition process that allows for uniform, highly conformal deposition of the most complex high-aspect ratio and nanoporous structures.

After Precursor A has been given sufficient time to react with the surface of the substrate, an inert gas such as nitrogen or argon flows through the chamber to purge any remaining byproducts or precursors that did not react with the surface, as shown in Figure 3.1(c). After the purging of Precursor A is complete, Precursor B is pulsed through the chamber, shown in Figure 3.1(d). As before, Precursor B contains functional groups that react selectively and exclusively with the functional groups attached to Precursor A. Thus, a monolayer of Precursor B is deposited on top of Precursor A, such that all reaction sites become occupied and no accumulation occurs on top of the monolayer. The remaining byproducts and Precursor B molecules are purged from the chamber with inert gas, as shown in Figure 3.1(e). For a binary system, the purging of Precursor B would mark the end of one single cycle. For ALD processes, the number of cycles controls layer thickness, so cycles
can be repeated until the desired thickness is reached. Typical ALD deposition rates are generally less than one Å/cycle, and depending on the specific process, can vary between 100-300nm/hr [22,23].

To further illustrate the ALD process, a common process for SOFC application is the deposition of YSZ thin films electrolytes. This can be achieved by alternating deposition of precursors yttria ($Y_2O_3$) and zirconia ($ZrO_2$). As mentioned in Section 2.2.1, the optimal composition or YSZ contains 8 mol% yttria. This composition can be accurately achieved with ALD by pulsing the precursors in specific ratios [24]. This observation leads to another important advantage of ALD: composition control. The nature of the ALD process allows for the deposition of thin films with highly tunable compositions, allowing for deposition of many different types of metal and metal-oxide materials. A more comprehensive review of ALD applications in SOFC development will be given in the next chapter.
Chapter 4

LITERATURE REVIEW

4.1 Sintering Aid Optimization

An important step in the SOFC fabrication process is sintering, whereby the electrode or electrolyte material is heated to high temperature (800-1600°C) to facilitate grain growth and interconnectivity. Grain size has been shown to have a significant impact on cell performance, and grain interconnectivity is important for maximizing pathways for ion and electron conduction, thereby minimizing cell resistance [17]. Much research effort has been put forth to improve the sintering behavior of electrode and electrolyte materials at lower sintering temperatures, allowing for co-sintering of electrode/electrolyte materials, thereby facilitating commercialization of SOFC technology. In many studies, this is accomplished by adding a small amount of Co−, Cu−, Fe−, or Mn-oxides to the electrode or electrolyte materials. In the current study, cobalt oxide is studied as a sintering aid for LSCF-GDC cathode materials, and therefore the effects of cobalt oxide on the sintering properties of materials will be reviewed.

The majority of SOFC sintering aid research has been dedicated to improving the sintering behavior of electrolyte materials such as GDC and YSZ. Yoshida et. al. [25] decreased the sintering temperature of samaria-doped ceria by 200°C by adding 1 at% $\text{Co}_3\text{O}_4$, showing that addition of cobalt oxide significantly enhanced grain growth for doped-ceria electrolyte materials. Silva et. al. [26] showed that addition of 1 mol% Co to 8YSZ powder (8 mol% yttria) reduced electrolyte sintering temperature by 100°C and improved densification of the electrolyte. Mai et. al. [13] sought to decrease the sintering temperature of the GDC interlayer for YSZ/GDC/LSCF SOFCs, since it had been shown previously that high sintering temperatures can cause formation of a solid solution between YSZ and GDC, resulting in a lower ionic conductivity at the interface [27,28]. The authors concluded that although addition of cobalt oxide to the GDC layer improved sinterability and densification of the interlayer, cracks developed in the layer due to high shrinkage relative to the YSZ electrolyte. Fagg et. al. [29] showed that addition of 2 mol% cobalt oxide to fluorite material $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ allowed for a 500°C decrease in sintering temperature, with dense layers consisting of sub-micron grains to be formed at 1000°C. The study showed that addition of cobalt oxide as a sintering aid increased electrical conductivity by two to three times, which was likely due to the
formation of Co-rich grain boundary layers. Additionally, the authors concluded that the presence of cobalt oxide significantly improved oxygen surface exchange. 

Ran et. al. [30] studied the effect of the addition of cobalt oxide as Co$_2$O$_3$ on mixed ionically/electronically conductive cathode material Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF). The authors showed that the electrical conductivity of BSCF was significantly improved by adding 5 wt% Co$_2$O$_3$ to the electrode material before sintering. This was caused by the reduction of Co$_2$O$_3$ to Co$_3$O$_4$ during sintering, which led to incorporation of Co into the B-site of BSCF with the formation of A-site cation deficient BSCF (it has been shown that A-site deficiency influences sintering activity and Sr depletion stability for perovskite materials) [13]. Chen et. al. [12] optimized the concentration of Co$_3$O$_4$ as a sintering aid for BSCF cathodes, measuring the performance of electrodes with 0-40 wt% Co$_3$O$_4$. They found that the electrical conductivity of the cell was maximized by using 10 wt% Co$_3$O$_4$, with a value of 70 S cm$^{-1}$ at 700$^\circ$C, as compared with 40 S cm$^{-1}$ for a pure BSCF electrode. The authors concluded that the increase in electrical conductivity was due to a synergistic effect between the BSCF and Co$_3$O$_4$. Additionally, it was shown that the addition of 10 wt% Co$_3$O$_4$ minimized the area-specific resistance (ASR) of the cell, with the value decreasing from 0.091 $\Omega$ cm$^2$ at 600$^\circ$C for pure BSCF to 0.049 $\Omega$ cm$^2$ for BSCF + 10 wt% Co$_3$O$_4$. The impedance spectra for this study showed that both the charge transfer resistance and surface diffusion resistance were minimized with the BSCF + 10 wt% Co$_3$O$_4$ cathode; thus, the authors concluded that both the charge transfer process and surface diffusion process were improved by using the proper amount of Co$_3$O$_4$. Zhang et. al. [31] used Co$_3$O$_4$ as a sintering aid for Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (SSC) cathodes, and varied the sintering aid concentration from 0-50 wt% to optimize cell performance. The authors found that the cell impedance was minimized for 40 wt% Co$_3$O$_4$, showing 0.058 $\Omega$ cm$^2$ at 600$^\circ$C, as compared with 0.204 $\Omega$ cm$^2$ for a pure SSC cathode.

Chen et. al. [15] investigated the use of Co$_3$O$_4$ to lower the sintering temperature of LSCF cathodes, so that sintering could be carried out at a sufficiently low temperature to prevent insulating phase formation occurring between the LSCF electrode and YSZ electrolyte. Co$_3$O$_4$ content in this study was fixed at 5 wt%. From a microstructural standpoint, LSCF + Co$_3$O$_4$ cathodes showed much better particle interconnectivity and mechanical strength than pure LSCF electrodes sintered at the same temperature. Electrochemical performance was also improved by addition of Co$_3$O$_4$ to LSCF; pure LSCF cathodes showed a polarization resistance of 0.129 $\Omega$ cm$^2$ and ohmic resistance of 2.418 $\Omega$ cm$^2$ at 700$^\circ$C, whereas LSCF + 5 wt% Co$_3$O$_4$ cathodes had polarization resistance of 0.071 $\Omega$ cm$^2$ and ohmic resistance of 2.356 $\Omega$ cm$^2$. The significantly reduced polarization resistance was explained by the much-improved particle interconnectivity for the Co$_3$O$_4$ samples. The authors concluded that Co$_3$O$_4$ is an excellent choice of sintering aid for LSCF cathodes, allowing the electrodes to be properly sintered at sufficiently low temperatures to
prevent undesirable reactions between LSCF and YSZ. Additionally, it was shown that $Co_3O_4$ could be used as a successful sintering aid for BSCF, SSC, SScC, and PBC electrodes.

In summary, much research has shown that cobalt oxide is an effective sintering aid for ceramics, electrolyte materials, and electrode materials. It promotes grain growth and interconnectivity, and allows for lower sintering temperatures for SOFC materials. It has been shown to improve electronic conductivity and catalytic activity in several SOFC electrode materials, thereby lowering cell impedance and improving overall performance. Although sintering aid optimization studies have been conducted for several SOFC cathode materials, the current state of literature is missing a sintering aid optimization for LSCF-based cathodes, and more specifically, LSCF-GDC composite cathodes.

4.2 Layer Thickness Optimization

Recall that the cathode electrodes used in this study consist of two layers: the composite LSCF-GDC functional layer, and the pure LSCF current collecting layer. The purpose of the layer thickness optimization study was to explore the relationship between the thickness of each of the electrode layers and the resulting cathode performance, quantified by the magnitude of the cell ohmic resistance $R_{ohm}$ and polarization resistance $R_p$.

Virkar et. al. [32] studied the effect of cathode thickness for LSM-YSZ composite cathodes, varying electrode thickness from 0-85 µm and measuring the resulting charge transfer resistance. It was shown that $R_{ct}$ decreases asymptotically with increasing cathode thickness, reaching a limiting value with a thickness of approximately 45 µm. They hypothesized that increasing the electrode thickness increased the triple phase boundary area, thereby increasing the number of reaction sites for oxygen reduction and ion/electron transfer. The charge transfer resistance decreased by nearly an order of magnitude with increasing layer thickness, from 1.2 Ω cm$^2$ to 0.14 Ω cm$^2$ at 800°C. However, the 85 µm thick cathode showed slightly worse performance than the 45 µm cathode, possibly due to either increased difficulty for oxygen gas permeating the cathode, or due to small cracks observed in the cathode microstructure at very high electrode thickness. Juhl et. al. [33] studied the effect of functional layer thickness on the charge transfer resistance for bilayer LSM-YSZ/LSM cathodes. In this study, the current collecting pure LSM layer thickness was fixed at 40 µm, and the functional layer thickness was varied between 2-12 µm. It was shown that the charge transfer resistance decreased with increasing thickness of the cathode functional layer, from approximately 76 Ω cm$^2$ for a 2 µm functional layer to approximately 10 Ω cm$^2$ for a 12 µm functional layer at 700°C. Again, this was attributed to an increase in the triple phase boundary area of the electrode. Furthermore, they showed that the polarization resistance is much
more sensitive to changes in electrode thickness at intermediate temperatures than at high temperatures.

Qiang et. al. [34] used an LSCF cathode with a thin GDC layer separating the electrode from the YSZ electrolyte, and studied the effect of varying the cathode thickness on the polarization resistance and ohmic resistance of the cell. In this study, electrode thickness was controlled by varying the number of screen printed layers, with the cathode thickness varying from $15 \pm 7 \mu m$ to $66 \pm 7 \mu m$. The study found that the polarization resistance decreased slightly from $15 \mu m$ thickness to $28 \mu m$ thickness, and then increased sharply with further increases in electrode thickness, having a minimum polarization resistance of approximately $0.18 \Omega \ cm^2$ at $800^\circ$ for the $28 \mu m$ cathode. The authors concluded that increasing cathode thickness increased the triple phase boundary areas, allowing more reactions to take place across the length of the cathode, therefore decreasing the polarization resistance. However, they concluded that increasing thickness past a certain point (in this case, $28 \mu m$) would have a detrimental effect on polarization resistance, since a very thick electrode would create longer paths for ion diffusion and could hinder gas permeability. These findings are somewhat inconsistent with previous layer thickness studies performed on LSM cathodes, which showed that the polarization resistance asymptotically decreases with increasing cathode thickness, showing only slightly higher values than at intermediate thicknesses. This discrepancy could be due to different electrode materials between the studies, and to different operating temperatures (recall that a previous study showed that the electrode thickness/polarization resistance correlation is highly dependent on operating temperature). Additionally, this study found that the ohmic resistance of the cell was relatively insensitive to electrode thickness between 15-43 $\mu m$. However, the ohmic resistance increased dramatically for an electrode with a 66 $\mu m$ thickness. The authors concluded that because of the mismatch in thermal expansion coefficients between the LSCF electrode and YSZ electrolyte, there may have been significant adhesion problems at the electrode/electrolyte interface, causing a higher contact resistance at the interface, and thus leading to a large increase in ohmic resistance. In summary, this study showed that an electrode thickness of $28 \pm 7 \mu m$ (three screen printed layers) showed the best performance.

Haanappel et. al. [35] optimized electrode thickness for bilayer LSM-YSZ/LSM electrodes. In this study, both the functional layer (FL) thickness and the current collecting layer (CCL) thickness were optimized. This was done by holding constant the thickness of the FL and varying the CCL thickness, measuring the impedance of the cell at each of the different thicknesses. Once the CCL thickness was optimized, the FL thickness was varied while the CCL was kept constant, and electrochemical measurements were taken at each thickness. The results showed that for the CCL, the polarization resistance decreased as the layer thickness increased, from $0.630 \Omega \ cm^2$ for a 10-20 $\mu m$ electrode to $0.486 \Omega \ cm^2$ for a 50-60 $\mu m$ electrode, at $700^\circ C$. 

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Further increases in CCL thickness had a negative effect on polarization resistance, showing 0.531 Ω cm² for a 70-75µm electrode. The authors concluded that for a small CCL (small in relation to the distance between contact points of the current collecting mesh), current may not be collected from the entire FL/CCL interface, and therefore the CCL must exceed a minimum thickness to ensure total utilization of the surface area of the interface. Additionally, the study showed that the electrode performance is highly dependent on the FL thickness. Previous studies have shown that for LSM/YSZ electrodes, a FL thickness smaller than about 11µm severely hinders cell performance, due to limited percolations of electrons and ions for very small FL thicknesses [33,36]. Thus, this study explored FL thicknesses of 10µm or larger, and found that increasing FL thickness beyond 10µm increases the cell impedance, likely due to longer pathways for gas diffusion.

Many authors have studied the effect of cathode layer thickness on cell performance for pure LSM and composite LSM-YSZ electrodes. However, few layer thickness studies have been conducted for LSCF electrodes, and no studies exist which explore the effect of varying layer thickness for both functional layer and current collecting layers for bilayer LSCF-GDC/LSCF electrodes. Thus, one of the purposes of the current study is to fill the gap in the current research by exploring the layer thickness/impedance relationship for LSCF-based composite cathodes.

4.3 ALD Applications for SOFCs

Electrolytes are a major cause of ohmic losses and severely limit SOFC performance. As noted in Section 2.2.1, the ohmic resistance of an SOFC is highly dependent upon electrolyte thickness; thus, much research has been conducted to minimize electrolyte thickness, and several studies have shown that thin film electrolytes such as YSZ and GDC deposited by atomic layer deposition significantly improve performance as compared with conventionally deposited electrolytes [24,37–39]. Additionally, ALD has been used to modify the surface of SOFC electrolytes to improve performance. Fan et. al. [40] showed that the cathode/electrolyte interfacial resistance could be dramatically decreased by depositing an ultra-thin layer of yttria-doped ceria (YDC) between the YSZ electrolyte and Pt cathode. ALD has also been successfully used to deposit standalone SOFC electrodes. Several sources cite the use of ALD to deposit thin film Pt layers to be used as highly catalytic SOFC electrodes [38,41,42]. Holme et. al. [42] attempted to deposit LSM cathodes using ALD for low temperature micro SOFCs. Although the LSM cathode was successfully deposited, the performance was much worse than comparable LSM electrodes deposited using other methods.

Several studies have shown that surface processes such as adsorption of molecular oxygen onto surface vacancy sites are the most probable rate limiting step for
perovskite cathode materials such as LSCF, and that these processes can be improved by using various surface modification techniques [43–47]. In addition to electrolyte and electrode deposition, ALD has also been used more recently to modify existing electrodes to improve performance and durability. Gong et. al. [48] investigated the use of ALD to improve durability of LSCo-LSGM composite cathodes. It was shown that the cathode exhibited excellent durability over 4000 h of operation by depositing a thin layer of $\text{ZrO}_2$ via ALD, with the polarization resistance increasing about 18 times more slowly than the untreated sample. The authors conclude that the addition of a $\text{ZrO}_2$ overcoat suppressed particle agglomeration and surface Sr-segregation, which are major causes of cell degradation. Although the benefits of $\text{ZrO}_2$ were not completely apparent at first, it was shown that extended heat treatment caused the $\text{ZrO}_2$ layers to become more porous and mixed conducting, which caused the ORR activity to improve significantly over time. Although $\text{ZrO}_2$ deposition by ALD improved performance for LSCo cathodes, Rahmanipour et. al [49] found that $\text{ZrO}_2$ deposition actually blocked active reaction sites for LSF cathodes, dramatically hindering performance.

Yu et. al. [50] evaluated the effect of $\text{CeO}_x$ deposition by ALD on the performance of LSF, LSCo, and BSCF cathodes. It was shown that ceria particles preferentially reacted with oxygen vacancies on the surface of the LSF cathode, impeding oxygen adsorption and therefore significantly increasing the electrode impedance. This conclusion was confirmed by ceria deposition on BSCF and LSCo cathodes; BSCF has a much higher concentration of oxygen vacancies at the surface, and LSCo oxygen vacancies are comparable to that of LSF. Consequently, BSCF was much more tolerant to ceria deposition, showing a lesser decrease in performance, and LSCo showed a decrease in performance that was similar to LSF.

Gong et. al. [51] investigated ALD deposition of $\text{ZrO}_2$ onto LSCF-GDC composite cathodes. The authors found that the ALD treatment lowered the cathode polarization resistance by 3 times, lowered the ohmic resistance by 1.5 times, and improved long-term durability by 4 times. They concluded that this was due to increased porosity, increased ionic conductivity, and suppressed surface Sr-enrichment by the $\text{ZrO}_2$ overcoat. Sholklapper et. al. [52] showed that LSCF cathodes infiltrated with YDC dramatically increased the ionic conductivity of the electrode, causing a decrease in ohmic resistance for the infiltrated electrode as compared with a pure LSCF electrode. Although the YDC deposition was not by ALD, it is relevant since the current study focuses on ALD deposition of YDC for LSCF and LSCF-GDC electrodes. At the time of this writing, there are no studies which investigate the effect of YDC-ALD treatment on LSCF or LSCF-GDC cathodes; thus, it is the purpose of the current study to fill this gap in the current literature.
Chapter 5

EFFECT OF SINTERING PROCESS WITH \( CO_3O_4 \) ON THE PERFORMANCE OF LSCF-BASED CATHODES FOR SOLID OXIDE FUEL CELLS

5.1 Introduction

Solid oxide fuel cells (SOFCs) are considered to be promising solid-state electrochemical devices that can convert chemical energy into electrical energy with a high efficiency, and can operate on a number of fuels [53,54]. One of the major bottlenecks in commercializing SOFCs is based on the fact that conventional systems operate at high temperatures (800-1000°C), which results in high cost and poor reliability [55]. To overcome these issues, the development of intermediate temperature SOFCs (IT-SOFCs) operating between 500-800°C has been extensively studied [56–58]. \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \) (LSCF) has been regarded as the most suitable candidate as a cathode material for IT-SOFCs as it shows better electrochemical activity for oxygen reduction at intermediate temperature than the conventional LSM electrodes [59–63]. As its ionic conductivity is compromised significantly at a reduced temperature due to its high activation energy for oxygen transport, it is often mixed with oxygen ion-conducting particles such as gadolinia-doped ceria (GDC) [16].

The key characteristics of a good cathode are sufficient porosity, large surface area, fine grain size, and good adhesion between particles [16]. As will be discussed later in this report, a high sintering temperature results in a larger grain size of the electrode decreasing the electrochemically active area, which is a major drawback of high temperature sintering along with the zirconate formation [64–66]. The downside of sintering at lower temperatures is weak interfacial adhesion, which could lead to poor connectivity and delamination. Therefore, it is important to optimize the microstructure by controlling the grain size and ensuring strong adhesion between particles and different layers simultaneously. A widely used approach to tackle this challenge is to use a metal oxide-based sintering aid [12,67,68].

The main aim is to study the effect of \( CO_3O_4 \)-based sintering aid concentration and its selective application to each cathodic layer on the microstructure and electrochemical performance of LSCF-based cathodes through a low temperature sintering process (850°C). Surprisingly, to the best of our knowledge, these effects have not been reported although the use of \( CO_3O_4 \) as a sintering aid is not new.
5.2 Experimental
5.2.1 Cell Preparation

Cells consisted of GDC interlayer, LSCF-GDC functional layer, and LSCF current collecting layer. Slurries were made for each layer, consisting of terpineol as a solvent, ethyl cellulose as a binder, $\text{Co}_3\text{O}_4$ (BET surface area: 40-70 $\text{m}^2/\text{g}$; particle size: $<50$ nm) as sintering aid, and Hypermer KD-1 as dispersant (Croda). For GDC slurry, terpineol was first mixed with Hypermer KD-1 at 60°C for 5 h. GDC nanopowder (surface area: 30-40 $\text{m}^2/\text{g}$; d$_{50}$ particle size: 0.1-0.4 $\mu$m; FuelCellMaterials) and ethyl cellulose were added and mixed at room temperature overnight. Final slurry was composed of 40 wt% terpineol, 10 wt% Hypermer KD-1, 2 wt% ethyl cellulose, and 48 wt% GDC nanopowder. GDC slurry was screen printed onto both sides of 8 mol% YSZ electrolyte substrate (270 $\mu$m thickness, FuelCellMaterials), dried at 80°C for 1 h and sintered at 1150°C for 5 h. For sintering, the sample was heated to 500°C at 2 °C min$^{-1}$, and held at 500°C for 30 min to facilitate binder burn off. Sample continued heating at 3°C min$^{-1}$ to sintering temperature, and cooled at 3°C min$^{-1}$ after sintering.

For LSCF and LSCF-GDC slurries, $\text{Co}_3\text{O}_4$ nanopowder was first dissolved in ethanol with LSCF ($\text{La}_{0.8}\text{Sr}_{0.20})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (surface area: 13-18 $\text{m}^2/\text{g}$; particle size (D$_{50}$): 0.4-1.0 $\mu$m; FullCellMaterials) or LSCF-GDC hybrid powder (LSCF:GDC = 50:50 wt%), and was mixed in planetary ball mill at 1100 rpm for 1 h. Mixture was dried at 70°C, and the resulting powder was crushed with pestle and mortar. Hypermer KD-1 was dissolved into terpineol as described. Cathode powder was mixed with solvent/dispersant mixture and binder, and slurries were ball milled for 4 h at 1100 rpm. Final slurries were composed of 35 wt% terpineol, 5 wt% Hypermer KD-1, and 4 wt% ethyl cellulose. $\text{Co}_3\text{O}_4$ concentration varied from 0-12 wt%, and LSCF or LSCF-GDC concentration varied from 44-56 wt%. LSCF-GDC functional layer was screen printed on top of GDC interlayer and dried at 80°C for 1 h. LSCF layer(s) were screen printed on top of LSCF-GDC functional layer, and dried at 80°C for 1 h. Completed symmetric cells were sintered at 850°C for 2 h, with the same heating profile as described.

5.2.2 Electrochemical and Microstructural Characterization

After sintering, samples were loaded into an inconel SOFC test station. Pt mesh was used as a current collector (250 $\mu$m nominal aperture, Goodfellow.com), and a 5 kg weight was placed on top to ensure good contact between electrode and mesh. Dry $\text{O}_2$ was fed to both electrodes at 50 sccm. Samples were heated to operating temperature at 3°C min$^{-1}$, and held for at least 40 min before testing. EIS was performed with 20 mV ac perturbation from 7 MHz to 50 mHz (Bio-Logic SP-240). A Zeiss Gemini 500 FEG-SEM was used for microstructural characterization at 3 kV operating voltage.
Figure 5.1: SEM images and EIS results of cells sintered at two different temperatures. (a-b) Top-view images of cells looking into their CL surfaces (left) and cross-sectional images (right) of cells sintered at (a) 850°C and (b) 1100°C without sintering aid. (c) Impedance spectra obtained in the open circuit voltage (OCV) condition at 700°C.

5.3 Results and Discussion

The images of Figure 5.1(a-b) are top-view SEM micrographs of cathode surface sintered at 850°C and 1100°C, respectively. All samples studied in the report are symmetric cells with a GDC interlayer, an LSCF-GDC functional layer (FL) and an LSCF current-collecting layer (CCL) on both sides of a commercial YSZ substrate. The LSCF sintered at 1100°C exhibits a significant mud-cracking, unlike those sintered at 850°C. The cross-sectional images (on the right side of Figure 5.1(a-b)) also show that the high temperature sintering caused cracks in the GDC interlayer, whereas the interface with a 850°C sintering process maintained the well-defined geometry of GDC interlayer. The crack development is ascribed to the discrepancy in the rate of sintering process and the amount of densification between layers. On the other hand, it is clearly visible from the high-magnification images that the high temperature sintering caused a significant grain growth unlike 850°C sintering. These observations regarding crack development and grain growth reemphasize the critical necessity of a low temperature sintering for the cathode. The cross-sectional images also present that the cathode layers (both FL and CCL) sintered at 1100°C became 2-3 times thinner than those sintered at 850°C, indicating a significant densification of cathode layers by the high temperature sintering.

EIS was performed on the symmetric cells to compare different electrodes, and to quantify ohmic and electrode polarization impedances. The spectra consist of a high-frequency induction attributed to the electrical probes, the ohmic resistance ($R_{ohm}$) roughly corresponding to the high frequency intercept with the real axis, and the electrode polarization impedance represented by the diameter of arc appearing at
a lower frequency. The electrode polarization impedances of all the samples studied have a characteristic frequency of 9 kHz, indicating an oxygen reduction reaction (ORR) limited by the charge transfer process [69]. In comparison with the SEM images, the high polarization resistance of the sample sintered at 1100°C could be related to the much larger grain size and lack of micropores due to densification. The high frequency arc (with a characteristic frequency of 9 kHz) of the sample became significantly larger (0.27 Ω cm²) than those sintered at 850°C. This is in line with the grain growth because this is directly related to the loss of electrochemically active area. In addition, the appearance of a second arc with a low characteristic frequency of 200 Hz corroborates a diffusion limited process caused by the aforementioned cathode densification [70].

The effect of sintering aid was studied by varying Co₃O₄ loading of cathode from 0 to 12 wt%. Each sample was composed of the same weight percentages of Co₃O₄ in its FL and CCL, and sintered at 850°C. Figure 5.2(a) shows the EIS spectra and resulting ohmic and electrode polarization resistances as a function of Co₃O₄ wt% (inset). As shown, both ohmic and electrode polarization resistance are sensitive to the sintering aid content. Both resistances exhibit a highly coupled behavior, having 4-5 wt% of Co₃O₄ as their optimum dose. As the characteristic frequencies of these cathodic polarization arcs are between 8-10 kHz, these resistances can also be referred as charge transfer resistance (R_{ct}). R_{ct} decreased from 0.163 to 0.062 Ω cm², and R_{ohm} decreased from 2.66 to 2.24 Ω cm² by adding 4 wt% Co₃O₄. A partial explanation about the decrease in R_{ct} and R_{ohm} with Co₃O₄ loading up to 5 wt% can be found in Figure 5.2(b-c). By adding 4 wt% Co₃O₄, the overall grain size was maintained small and uniform after sintering. An improved connection between electrode particles and/or better bonding between layers can be additionally expected by adding Co₃O₄. A Co₃O₄ dose larger than 5 wt%, however, became detrimental to both ohmic transport and electrode reaction kinetics. All the samples did not develop pronounced cracks, nor did they exhibit any delamination/crack at the cathode-interlayer interface regardless of Co₃O₄ content from 0 to 12% (images not presented), unlike the sample sintered at 1100°C. Therefore, the increase of R_{ct} and R_{ohm} with an excessive Co₃O₄ dose (> 5 wt%) can be ascribed to a formation of an ion-transport barrier between particles and/or a blockage of electrochemically active surface areas. As Co₃O₄ is known to be a good catalyst for ORR [71], the former is considered as a more probable case.

Up to now, both FL and CCL were applied with the same percentages of Co₃O₄ in each sample. Fig. 10(a) shows EIS spectra obtained from the cells where Co₃O₄ was applied selectively (to both, either or neither FL or CCL) to better reveal the role of Co₃O₄. First, R_{ct} values of the two cells with 4% Co₃O₄ in FL were similar to each other (B: 0.065 and C: 0.059 Ω cm²) and much lower than those from the other cells (A: 0.16, D: 0.14 and D': 0.38 Ω cm²). The slightly smaller R_{ohm} of Cell B (compared to Cell C) by adding 4% Co₃O₄ to the CCL can be
Figure 5.2: (a) Impedance spectra of cells sintered with different Co$_3$O$_4$ concentrations (0-12%) at 850°C. Measurements were performed at 700°C in the OCV condition. Inset: The resulting effect of Co$_3$O$_4$ dose on the Faradaic resistance and ohmic resistance. An equivalent circuit of $L-R_{ohm}-(R_{ct}/Q)$ was used to fit the impedance data where Q is a constant phase element and L is an inductor. (b-c) SEM micrographs of LSCF sintered at 850°C with 0 and 4 wt% Co$_3$O$_4$.

ascribed to a better sintering of CCL and resulting improved trans-particle charge transport. However, a 4% Co$_3$O$_4$ addition to CCL did not always warrant a lower $R_{ohm}$ as exemplified by Cells D and D’, in which Co$_3$O$_4$ is added to CCL but not to FL. Cell D’ revealed pronounced mud-cracks as shown in the inset of Fig. 10(c), which propagated to the interface between its FL and GDC interlayer resulting in a very high $R_{ohm}$. This should be due to a significant thermal stress caused by much more facilitated sintering (and thus more shrinkage) of CCL compared to that of the neighboring layer. The high $R_{ohm}$ of Cell D, even larger than Cell A with 0% Co$_3$O$_4$ in both layers, is also attributed to the thermal stress and partial crack development. On the other hand, Cell C, in which Co$_3$O$_4$ was added to FL only, did not develop considerable cracks likely because addition of Co$_3$O$_4$ to the FL compensated for the rapid shrinkage of the CCL (Figure 5.3(b)). (Note that the degree of sintering is known to be more pronounced in LSCF than in GDC [72].) From these observations, it is concluded that the addition of Co$_3$O$_4$ has a dominant impact on charge transfer kinetics in FL and a moderate impact on the electronic transport in CCL. It is also reminded that local thermal stress development should be a key consideration when adding sintering aid.
Figure 5.3: (a) Nyquist plots from four different cells with $Co_3O_4$ concentrations of either 0 or 4 wt% in their FL and CCL. Cells D and D’ were fabricated using the same recipe, but Cell D’ exhibits much higher resistances due to crack developments shown in (c). Measurements were performed at 700° in OCV condition. (b-c) Cross-sectional SEM images of (b) Cell C, and (c) Cell D’.

5.4 Conclusions

The present study investigated the impact of sintering process on the microstructure and performance of LSCF-based cathodes. The influence of sintering temperature was confirmed to be significant, in that a sintering at 1100°C caused a severe agglomeration and crack development detrimental to the cathodic performance while a sintering process at 850°C preserved the small grain sizes and microstructural integrity with superior performance. The effect of $Co_3O_4$ addition on ohmic and charge transfer resistance was subsequently studied with a range of $Co_3O_4$ concentration of 0-12 wt%. The results show that ohmic and charge transfer resistances are highly coupled with $Co_3O_4$ concentration, with an optimum concentration of 4-5 wt%. The improvement with the $Co_3O_4$ addition up to 5 wt% is likely due to improved bonding between and within the layers, but the poorer performance with higher doses may be observed because redundant $Co_3O_4$ starts to act as a barrier against fluent charge transport between particles and layers. It is also noted that the $Co_3O_4$ addition exhibits a dramatic impact on charge transfer kinetics in the LSCF-GDC composite layer and a moderate impact on the electronic transport in the current-collecting LSCF layer. The importance of considering local thermal stress development is also noted when adding $Co_3O_4$. 
Chapter 6

LAYER THICKNESS OPTIMIZATION FOR LSCF-GDC/LSCF CATHODES FOR SOLID OXIDE FUEL CELLS

6.1 Introduction

Many microstructural characteristics have been shown to affect the performance of solid oxide fuel cell cathodes, including electrode porosity, density, tortuosity, particle interconnectivity, and electrode layer thickness. The purpose of the current study is to investigate the effect of functional layer (FL) and current collecting layer (CCL) thickness on the ohmic and polarization resistance of bilayer LSCF-GDC/LSCF cathodes. Several studies have investigated the effects of varying layer thickness for other cathode materials, such as LSM, LSM-YSZ composite cathodes, and pure LSCF cathodes [32–36]. However, many of the findings across different studies are inconsistent or contradictory, and at the time of this writing, no study has been conducted to investigate the effect of varying thickness for LSCF-GDC composite cathodes, nor does a study exist which examines thickness optimization for bilayer LSCF-GDC/LSCF cathodes. For the LSCF-GDC functional layer, it is expected that the polarization resistance will be very sensitive to layer thickness, and that increasing the thickness beyond 10-15 $\mu$m will have a detrimental effect on the resistance [33,35]. No previous studies were found which investigated the effect FL thickness on ohmic resistance. All FL thicknesses used in this study were greater than the minimum value of 10 $\mu$m found in other studies [33, 36]. FL thickness has generally been shown to have a large effect on polarization resistance, but it is expected that increasing FL thickness beyond the minimum recommended thickness will have little effect on the ohmic resistance of the cells. For the current collecting LSCF layer, most studies have shown that cell impedance tends to decrease asymptotically as the layer thickness increases. It has been shown that if the spacing between adjacent wires in the current collecting mesh is much larger than the CCL thickness, then most of the ohmic resistance will occur in-plane, as opposed to through the thickness of the CCL [35]. Therefore, since the mesh spacing in this study is relatively large, it is expected that the ohmic resistance will continue to decrease as the thickness of the CCL increases. Additionally, increasing CCL is expected to improve polarization resistance due to extension of the triple phase
boundary (TPB) area [35]. However, at least one study has shown an optimized layer thickness of 30µm for pure LSCF cathodes, with electrode impedance increasing sharply with further increases in layer thickness [34]. Therefore, the effect of layer thickness for the current collecting LSCF layer is difficult to hypothesize, but it is expected that performance is likely to improve with increasing layer thickness.

6.2 Experimental

Electrode and electrolyte slurries were made using the same method as described in Section 5.2.1. One layer of GDC was deposited on either side of a YSZ button cell (250-300µm thickness, FuelCellMaterials.com) using the screen printing method. GDC layer was sintered at 1150°C, with heating at 2°C/min up to 80°C, drying for 1 hour at 80°C, heating at 2°C/min to 500°C, held at 500°C for 30 minutes to burn off organic binder, heated at 3°C/min to sintering temperature, held at sintering temperature for 5 hours, and cooled at 3°C/min. Two sets of cells were made: Set A for optimization of current collecting layer thickness, and Set B for functional layer thickness optimization. For Set A, a total of four cells were made. Each cell in Set A was screen printed with one LSCF-GDC functional layer, and then dried at 80°C for 1 h. After drying, 1-4 LSCF current collecting layers were screen printed on top of the FL. CCL thickness was controlled by number of screen printed layers. Samples were sintered at 850°C for 2 h, with the same heating profile as described above for GDC interlayer. Sintered samples had FL thickness of 25±5µm and CCL thicknesses ranging from 20-70µm.

Two samples were fabricated for cell Set B, for optimization of FL thickness. LSCF-GDC functional layers were screen printed on top of the sintered GDC interlayer. Samples were screen printed with either one or two functional layers, with drying at 80°C in between screen printed layers. As with Set A, FL thickness in set B was controlled by number of screen printed layers. Samples were sintered at 850°C, with same temperature profile as in Set A. Sintered samples had CCL thicknesses of 35µm, and FL thicknesses ranging from 25-55µm. Impedance spectra and SEM images for all cells in the study were obtained using the same methods and equipment as described in Section 5.2.2. Cell impedance was measured at 700°C, and only OCV conditions were investigated in this study.

6.3 Results and Discussion

6.3.1 Effects of Current Collecting Layer Thickness Variation on Cell Impedance

Figure 6.1(a) shows the impedance data for cells of various current collecting layer thicknesses. The effect of increasing layer thickness on the ohmic resistance of the electrode is illustrated in Figure 6.1(b). Note that 1 CCL corresponds with 20µm thickness, 2 CCL corresponds with 35µm, 3 CCL corresponds with 55µm, and 4 CCL corresponds with 70µm thickness. For a thin CCL (20µm thickness), the
Figure 6.1: (a) Impedance spectra for cells with LSCF current collecting layer thickness varying from 20-70µm, LSCF-GDC functional layer thickness fixed at 25±5µm. Cells were sintered in air at 850°C, and impedance spectra was taken at 700°C, OCV condition; (b) Ohmic and polarization resistance vs current collecting layer thickness, obtained from the spectra in (a)

Ohmic resistance is very high, approximately 5.58 Ω cm². The resistance decreases sharply when the CCL thickness is increased to 35µm, reaching a value of 2.12 Ω cm². Further increases in layer thickness have a much smaller effect on ohmic resistance, with a 55µm layer having ohmic resistance of 1.96 Ω cm² and a 70µm layer having a slightly higher resistance of 2.06 Ω cm². This behavior agrees well with the study performed by Haanappel et. al. [35], which showed that the ohmic resistance for LSM cathodes decreased dramatically for CCL thicknesses between 45-60µm, and that further increases in cell thickness had minor effects on the resistance. The limiting thickness values in the present study were different (35µm as opposed to 50µm for the Haanappel study), since different cathode materials were used in the previous study, and also because the nominal aperture of the Pt mesh used in this current study was relatively large (250µm). A small CCL thickness does not allow for complete utilization of the FL/CCL interface, whereas a larger thickness allows for total utilization of the interface, and allows for an increased number of pathways for ion/electron transfer. The slight increase in ohmic resistance for the very thick CCL can be attributed to small inconsistencies in the impedance measurements, or more likely caused by cracking occurring in the electrode, as shown in Figure 6.2. For very large electrode thickness, the difference in thermal expansion between the electrode and electrolyte becomes more pronounced, leading to high thermal stresses in the cathode. Figure 6.2(a-b) shows significant cracking at the surface of the electrode, and at the electrode/electrolyte interface. This same behavior was
seen for very thick electrodes in previous studies, and had a similar effect on ohmic resistance [32,35].

Figure 6.2: (a) Top view of sample with 4 current collecting layer coats (70µm CCL thickness) showing surface cracks; (b) cross-sectional view of (a), showing delamination at the electrode/electrolyte interface

Figure 6.2(b) illustrates how the polarization resistance of the electrode was affected by increases in the CCL thickness. The trend is similar to the effect of increasing layer thickness on ohmic resistance: a sharp decrease in polarization resistance is observed between 20-35µm CCL thickness, and the polarization resistance is relatively insensitive to further increases in layer thickness. This trend agrees well with a similar study performed by Virkar et. al. [32], which investigated FL and CCL layer thickness variations for bilayer LSM-YSZ/LSM electrodes. Since LSCF is a mixed ionic/electronic conducting material, the decrease in polarization resistance by increased CCL thickness is due to an increase in active reaction sites caused by the extension of the triple phase boundary area. For a very thick CCL (70µm, 95µm total electrode thickness), a significant increase in polarization resistance is observed. The same observation was made by Virkar et. al. and Qiang et. al. for LSM-based electrodes [32,34]. One possibility is that a very high CCL thickness creates a longer path for oxygen diffusion; since polarization resistance is correlated with oxygen diffusion and adsorption, it follows that an extremely large CCL could increase polarization resistance for this reason. Additionally, the sample with the largest CCL thickness experienced some cracking and delamination due to thermal stresses, as shown in the SEM images in Figures 6.2(a-b). This cracking of the electrode would also cause an increase in polarization resistance, as observed in previous studies [32].
6.3.2 Effects of Functional Layer Thickness Variation on Cell Impedance

Figure 6.3(a) shows the impedance spectra for cells with functional layer thickness varying from 25-55 µm, with current collecting layer thickness fixed at 35±5µm, and Figure 6.3(b) summarizes the effects of increasing FL thickness on ohmic and polarization resistance. Polarization resistance was shown to increase significantly with increasing FL thickness, from 0.05 Ω cm$^2$ for a 25µm thick FL to 0.16 Ω cm$^2$ for a 55µm layer. In theory, a thicker FL should extend the triple phase boundary area, creating more reaction sites and therefore decreasing polarization resistance. However, it is shown here that if the FL is too thick, further increases in thickness have a continuously detrimental effect on the polarization resistance of the cell, due to a longer path for ion diffusion and gas permeation. These findings are consistent with previous studies conducted on LSM-based cathodes with LSM-YSZ functional layers [33, 35, 36]. However, it should be noted that a more thorough investigation of the effects of FL thickness on cell impedance should also include thinner layers, starting at less than 10µm. The screen printing method used in this study for layer deposition allows for minimum layer thicknesses of about 20-25µm. Therefore, a future study should either utilize a different electrode deposition method such as plasma spray deposition, or should explore the use of electrode slurries with lower viscosity to allow for better thickness control.

Figure 6.3: (a) Impedance spectra for functional layer thickness variation study. Cells were sintered in air at 850°C, and impedance spectra was taken at 700°C at OCV conditions. LSCF-GDC functional layer thickness ranged from 25-55µm, with LSCF current collecting layer thickness fixed at 35±5µm; (b) Ohmic resistance and polarization resistance vs functional layer thickness, obtained from the spectra in (a)

The effect of FL thickness on the cell ohmic resistance is illustrated in Figure 6.3(b). Between 25-40µm, the ohmic resistance was essentially unaffected by the increasing thickness of the functional layer, increasing from 2.05 Ω cm$^2$ for a 25µm
layer to only 2.08 for a 40\(\mu\)m layer. This small difference is likely due either to small variations in CCL thickness between the samples, or to slight inconsistencies in the impedance measurements. This finding is consistent with the hypothesis that the changes in functional layer thickness beyond 10-15\(\mu\)m should have little effect on the ohmic resistance. However, for a larger FL thickness of 55\(\mu\)m, the ohmic resistance increased dramatically from 2.08 to 2.48 \(\Omega\) cm\(^2\). After examination of the microstructure via SEM, significant cracking was seen in the electrode, similar to the cracking for a thick CCL shown in Figure 6.2. It should be noted that the total electrode thickness for the sample shown in Figure 12 is around 95\(\mu\)m (5 total coats, 1 FL and 4 CCL). This is approximately the same thickness as the sample in this discussion, with 3 FL and 2 CCL. Therefore, when the total electrode thickness approaches 100\(\mu\)m, the thermal stresses (caused by the electrode and electrolyte expanding at different rates) result in cracking and/or delamination of the electrode, which has a detrimental effect on the ohmic and polarization resistance of the electrode. Other studies have reported similar behavior for electrodes in the same thickness range [32, 35].

6.4 Conclusions

In this study, symmetric cells were made with bilayer LSCF-GDC/LSCF cathodes. The effect of the LSCF-GDC functional layer thickness and the LSCF current collecting layer thickness on cell impedance were investigated. Ohmic resistance and polarization resistance decreased asymptotically as the CCL thickness was increased, but for different reasons. The observed decrease in ohmic resistance was ascribed to a full utilization of the FL/CCL interface and by an increase in the number of electronic and ionic pathways in the electrode. However, a very large CCL thickness caused an increase in ohmic resistance, due to cracking and delamination in the electrode, which was a result of pronounced effects of thermal expansion mismatch between the LSCF-based cathode and the YSZ electrolyte. The decrease in polarization resistance is ascribed to an extension of the triple phase boundary area, and therefore by an increase in the number of reaction sites on the surface of the electrode material. However, in addition to cracking and delamination, a very thick CCL is expected to result in longer pathways for oxygen permeation, which had a detrimental effect on the polarization resistance of the cathode. Both observations confirmed findings from previous studies performed on various electrode materials [32, 34, 35]. For the FL thickness variation, polarization resistance increased with increasing layer thickness, which agreed with observations made in a previous study by Haanappel et. al. for LSM-YSZ/LSM cathodes [35]. The increase in FL resulted in a longer path for ion diffusion and oxygen permeation, both of which hindered the electrode performance. The nature of the electrode deposition process used in this study did not allow for deposition of layers thinner than 20-25\(\mu\)m; a future study should include investigation of FL thicknesses on the order of 10\(\mu\)m, so that an
optimal FL thickness can be determined. In terms of ohmic resistance, it was shown that the ohmic resistance of the cell was relatively insensitive to changes in FL thickness for thicknesses between 25-40µm, as expected. However, an increase in ohmic resistance was observed as the FL thickness reached 55µm (with a total electrode thickness of approximately 95µm). SEM images revealed significant cracking in the electrode, similar to the cracks observed in the sample with a large CCL thickness (having about the same total electrode thickness). Therefore, it can be concluded that the total electrode thickness should not approach 90-100µm, since the expansion of the electrode relative to the electrolyte will cause cracking, hindering the performance of the cell. The best cell performance in this study was observed with an electrode having a FL thickness of 25µm or less and a CCL thickness between 35-55µm (2-3 screen printed layers).
7.1 Introduction

The oxygen reduction reaction occurring at the solid oxide fuel cell cathode is much more sluggish than the hydrogen oxygen reaction occurring at the anode, and is generally considered to be the rate-limiting factor for SOFC performance \[44\]. Therefore, much research effort goes into improving ORR kinetics, often using surface treatment or modification of the SOFC cathode material. ALD has emerged relatively recently as a method of depositing highly uniform layers of a variety of materials with thickness control on the angstrom scale. In terms of ALD applications for SOFCs, much research involves deposition of ultra-thin electrolyte layers such as YSZ, or deposition of electrodes such as Pt \[24, 37–42, 73\]. More recently, however, ALD has been used for surface treatment of a variety of cathode materials. While the impacts of ALD treatment on cathode durability have been mostly promising, its effects on cathode performance are somewhat controversial. Multiple studies have shown that ALD treatment on SOFC cathodes have been effective in suppressing particle agglomeration and surface Sr-enrichment, which are major causes of SOFC cathode degradation, and has also had positive impacts on cathode ohmic and polarization resistances \[48, 51\]. However, several studies have shown that ALD treatment can cause physical blocking or preferential reactions with active oxygen reaction sites on the cathode surface, dramatically hindering cell performance \[50, 74\].

It is the purpose of the current study to investigate the effect of the deposition of ionically conductive yttria-doped ceria (YDC) on LSCF-based cathodes. We study ALD functionalization in the hope of suppressing particle agglomeration, stabilizing surface chemistry, and forming an additional surface/interfacial path for oxygen species. At the time of this writing, equipment for long-term durability testing is in the final stages of development, and therefore durability is not available for this study. Thus, the current study will focus only on the effects of ALD surface treatment on initial cathode impedance.
7.2 Experimental

7.2.1 Cell Fabrication

Electrode and electrolyte slurries were fabricated as described in Section 5.2.1, with sintering aid content of 4 wt% for both LSCF and LSCF-GDC slurries. GDC layers were screen printed on either side of the commercially available YSZ electrolyte (270 µm thickness, FuelCellMaterials.com). GDC interlayers were sintered in air at 1150°C for 5 h. Heating profile for sintering was as follows: samples were heated 2°C/min to 80°C, and held for 1 h for drying. Heating was continued at 2°C/min to 500°C, and held for 30 min to facilitate burn off of organic binder. Heating was resumed at 3°C/min to sintering temperature, and cooled at 3°C/min after sintering. Interlayers had 5-7 µm thickness after sintering.

Two sets of cells were made: one set consisted of a GDC interlayer, LSCF-GDC functional layer, and two LSCF current collecting layers. The other set consisted of only a GDC interlayer and three LSCF current collecting layers. For the first set, one layer of LSCF-GDC was screen printed on top of the GDC interlayer, and subsequently dried at 80°C for 1 hour, with 2°C/min heating and 3°C/min cooling. After drying, yttria-doped ceria (YDC) was deposited onto the functional layers with varying thicknesses via ALD (see Section 7.2.2 for details). The second set of samples were fabricated in the same way, the only difference being that the LSCF-GDC functional layer was replaced by an LSCF layer for the second set of samples. At the completion of ALD treatment, two LSCF current collecting layers were screen printed on top of the ALD-treated layer, with drying at 80°C in between the printing of each layer. Samples were subsequently sintered at 850°C for 2 h, with the same sintering profile as for the GDC interlayer. Sintered electrodes had functional layer thicknesses of approximately 25-30 µm and current collecting layer thicknesses of approximately 45-50 µm.

7.2.2 YDC Deposited by ALD

For the YDC-ALD deposition, precursors were tris-(i-propylcyclopentadienyl) cerium (99.9%-Ce), and tris-(methylcyclopentadienyl) yttrium (Y(MeCp)3). During deposition, the chamber was held at 250°C, and each precursor was kept at 152°C. Deposition pressure was 0.4 Torr for oxidant (deionized water), 0.16 Torr for cerium, and 0.2 Torr for yttrium. N2 was used for purging, which was fed into the chamber at 0.12 Torr with a flow rate of 3 sccm. Oxidant pulses were 0.4 s, cerium and yttrium pulses were 1 s, and chamber purge was 40 s. Each YDC super cycle consisted of a total of 7 cycles, with a 6:1 ratio for CeO2:Y2O3. Growth rate was approximately (0.5 nm)/(super cycle).

7.3 Results and Discussion

Figure 7.1(a) shows the impedance spectra for the bilayer LSCF-GDC/LSCF cathodes, with the functional LSCF-GDC layer treated with varying thicknesses
Figure 7.1: (a) Impedance spectra for bilayer LSCF-GDC/LSCF samples, LSCF-GDC functional layer treated with YDC deposition by ALD. Samples were sintered at 850°C in air, and impedance spectra was obtained at 700°C, OCV conditions; (b) ohmic and polarization resistance vs number of ALD cycles for the spectra presented in (a) of YDC deposited by ALD. The ohmic resistance and polarization resistance as a function of number of ALD cycles are summarized in Figures 7.1(b). Figure 7.2 summarizes the effect of YDC functionalization on the ohmic and polarization resistance of pure LSCF cathodes, with the first cathode layer treated with YDC.

In terms of ohmic resistance, a similar trend is observed in both sets of samples, with the resistance for 3 ALD cycles being higher than for the bare samples, but subsequently decreasing with increasing number of cycles. Previous studies report similar behavior; in two separate studies, Gong et. al. [48, 51] deposited ZrO$_2$ via ALD onto composite mixed ionic/electronically conducting SOFC cathodes, and found that although the impedance of the cell after ALD treatment was initially higher than the untreated cell, the impedance lowered during operation (after 100 h) to values much lower than impedance values for the untreated cell. This was ascribed to increased porosity and increased ionically conductive behavior of the ALD-deposited layer after a prolonged heat treatment. Therefore, although the results of the current study show an inverse relationship between YDC thickness and ohmic resistance of the cell, it seems that some prolonged heat treatment will be necessary to fully realize the effects of the treatment. At the time of this writing, we are building test equipment that is capable of prolonged SOFC testing, but the equipment is still in the final stages of development, and so durability results are unavailable. Future work will include subjecting the cells with YDC-deposited functional layers to prolonged heat treatment/testing, so that the benefits of the ALD treatment can be further investigated.

In terms of polarization resistance, LSCF samples and LSCF-GDC/LSCF
Figure 7.2: Ohmic resistance and polarization resistance vs number of ALD-YDC cycles for LSCF samples, with first cathode layer functionalized with YDC treatment. Samples were sintered at 850°C in air, and impedance spectra (not shown) were obtained at 700°C, OCV conditions.

samples both exhibited an increase in polarization resistance as the YDC thickness increased. Yu et. al. [50] reported that ALD deposition of ceria onto perovskite LSCF cathodes caused a preferential reaction to occur between the ceria and the oxygen vacancies on the surface of the cathodes, severely hindering oxygen adsorption and resulting in an increase of polarization resistance. In addition, several studies have reported ALD modification of SOFC cathodes caused a physical blocking of the active sites on the electrode surface, having a negative effect on the polarization resistance of the cathode [50, 74]. YDC deposition by ALD includes the deposition of ceria, so it can be concluded that the ceria either reacted with the oxygen vacancies or caused a physical blocking of the reaction sites on the surface of the LSCF, causing the increase in polarization resistance illustrated in Figures 7.1 and 7.2. Additionally, the aforementioned ALD-ZrO₂ studies showed an initial increase in polarization resistance, which subsequently decreased with prolonged heat treatment [48]. Some further investigation will be needed to conclude whether prolonged heat treatment after ALD deposition will subsequently improve the polarization resistance, or whether the ALD deposition negatively affects performance by interfering with oxygen adsorption on the electrode surface.

7.4 Conclusions

LSCF cells and bilayer LSCF-GDC/LSCF cells were fabricated using the screen printing method. The innermost layers on the cathode (LSCF layer for LSCF cells, LSCF-GDC layer for bilayer cathodes) were treated with various thicknesses
of yttria-doped ceria deposited by atomic layer deposition. For both sets of cells, the ohmic resistance initially increased with 3 cycles of ALD treatment, but subsequently decreased with increasing YDC deposition thickness. This behavior has been observed in the literature with $\text{ZrO}_2$-ALD treatment of LSCO-LSGM composite cathodes and LSCF-GDC composite cathodes, and it is probable that prolonged heat treatment is needed for the effect of YDC deposition of ohmic resistance to be fully realized. For both cell types used in this study, polarization resistance increased with deposition of YDC. According to previous studies, it is most likely that the ceria deposited during the ALD process preferentially reacted with active oxygen vacancies on the LSCF surface, severely hindering oxygen adsorption and therefore causing increases in ohmic resistance. It is also possible that the deposited YDC physically blocked these reaction sites, which would also cause the observed increase in polarization resistance. Some further investigation is needed to pinpoint the cause of the decrease in performance. In addition, some prolonged durability testing is needed to fully realize the positive effects of the ALD treatment, for which we lacked the proper equipment at the time of this writing.
Chapter 8

CONCLUSIONS AND FUTURE WORK

This paper outlined the need for clean and sustainable energy, and introduced solid oxide fuel cells (SOFCs) as a possible addition and/or replacement for the fossil fuel-based infrastructure. An overview of SOFC operation was given, followed by a description of materials that are generally used for cell fabrication. The characterization methods used in this study were outlined, followed by a review of the current state of research for the topics that were investigated. These topics include: optimization of sintering aid content and the resulting effects on performance for LSCF-based cathodes, investigation of the effects of functional layer and current collecting layer thickness on the performance of LSCF-based cathodes, and the effects of surface modification of LSCF-based cathodes by atomic layer deposition. Following the literature review was an in-depth explanation of each of the three studies. Motivation was given for conducting each of the research studies, experimental methods were described, and the results were presented and interpreted.

For the sintering aid optimization, bilayer LSCF-GDC/LSCF cathodes were fabricated with sintering aid concentration in each layer (functional layer and current collecting layer) varying from 0-12 wt%. It was shown that $Co_3O_4$ is a highly effective sintering aid for LSCF and LSCF-GDC composite cathodes, dramatically improving particle connectivity and grain growth during the sintering process. It was shown that changes in sintering aid content had a large impact on the charge transfer kinetics of the LSCF-GDC functional layer, and had only a moderate impact on electron transport in the current collecting LSCF layer. It was concluded that a 4-5 wt% concentration of $Co_3O_4$ in both the functional layer and the current collecting layer was most effective in improving cathode performance.

The layer thickness optimization investigated the effects of varying the layer thickness for both the functional layer and current collecting layer for bilayer LSCF-GDC/LSCF cathodes. CCL thickness was varied from 20-70µm, and FL thickness was varied from 25-55µm. The results of the study showed that both the ohmic resistance and the polarization resistance of the cell asymptotically decreased as the layer thickness of the CCL was increased. The decrease in ohmic resistance with increasing CCL thickness was caused by maximum utilization of the FL/CCL interface, and by improved charge transport due to the increase in pathways in the
current collecting layer. These results were consistent with the majority of previous studies conducted using other cathode materials. The decrease in polarization resistance with increasing CCL thickness was caused by an increase in the triple phase boundary area of the electrode, which increased the number of reaction sides for oxygen adsorption and charge transfer. Again, these findings agreed well with previous studies. It was shown that increases in the FL thickness had a negative effect on the polarization resistance, due to longer pathways for ion transport and oxygen permeation. The lowest polarization resistance was observed for the smallest FL thickness of 25 µm, but it is hypothesized that further decreasing the FL thickness may improve cell performance. The optimum performance should be found at a FL thickness where the overall kinetics of ORR limited by the availability of electrochemically active sites (adsorption site and TPB area) is well balanced with the charge transport kinetics (resistance against charge and charge diffusion). Because of the nature of the electrode deposition method used in this study, a 25 µm FL was the minimum possible layer thickness, but a further study should be conducted using either a different deposition method that allows for more precise thickness control, or the viscosity of the electrode slurry should be decreased to allow for deposition of thinner layers. For very large FL thickness and CCL thickness, cracks and delamination were observed in the microstructure, severely hindering cell performance. It can be concluded that as the total electrode thickness approaches 90-100 µm, the thermal expansion of the electrode relative to the electrolyte becomes significant enough to cause physical damage to the electrode, and that electrode thickness should be kept as low as possible to prevent this. In this study, the optimized electrode giving the lowest impedance had a FL thickness of 25 µm and a CCL thickness of 35-55 µm.

The final study investigated the performance effects of depositing yttria-doped ceria onto LSCF and bilayer LSCF-GDC/LSCF cathodes via atomic layer deposition. For the two sets of cells fabricated in this study, YDC was deposited onto the innermost electrode layer (LSCF layer for the pure cathodes, and LSCF-GDC layer for the bilayer cathodes). For the bilayer cathodes as well as the pure LSCF cathodes, it was found the ohmic resistance of a YDC-deposited cell was initially higher than that of a bare cell, but that ohmic resistance subsequently decreased with further YDC treatment. This behavior has been observed in previous studies which explored deposition of other materials via ALD onto different cathode materials. The previous studies showed that while the ohmic resistance initially increased, significant decreases were observed after prolonged operation. Therefore, it was concluded that prolonged heat treatment would be needed to fully realize the benefits of YDC deposition onto LSCF-GDC composite cathodes. Additionally, the results showed that the YDC treatment generally had a negative effect on the polarization resistance for both LSCF and bilayer LSCF-GDC cathodes. This can be explained by a preferential reaction between the ceria and the LSCF cathodes that has been observed in previous studies using other A-site deficient perovskite
cathode materials deposited with ceria-based materials via ALD. Because of these preferential reactions, fewer active sites are available for oxygen adsorption, causing an increase in the polarization resistance of the cell. Therefore, it can be concluded that while ALD treatment is potentially beneficial for LSCF-based cathode performance, a material should be used that does not contain ceria, so that these unwanted reactions can be avoided.

Much future work is needed for the ALD study. Firstly, according to previous studies, ALD modification seems to have a most profound effect after extended operation, and in addition to improving initial performance, should dramatically improve cell durability. At the time of this writing, much work has been put into designing and building an SOFC test station capable of prolonged operation. However, the test station is in the final stages of development, and so durability data was not available for this study. The immediate next steps should be investigating the effects of YDC treatment on the durability and degradation rate of LSCF-based cathodes. Additionally, it was hypothesized that the ceria used in this study may have poisoned the cells, causing a dramatic increase in polarization performance after ALD treatment. Some different materials such as $ZrO_2$ should be further investigated as replacements for ALD modification of LSCF-based electrodes.
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