PERFORMANCE AND STABILITY STUDY OF SOLID OXIDE FUEL CELL NANOCOMPOSITE ELECTRODES

By

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ABSTRACT

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As a chemical to electricity energy conversion technology, solid oxide fuel cells (SOFCs) must be operated at relatively high temperatures due to the high resistance of their electrodes. The low specific surface area caused by high sintering temperature during electrode fabrication, along with the poor catalytic ability of electrode materials, were the reason for the poor SOFC electrode performance. With the development of highly active electrode materials and new electrode synthesis methods like precursor solution infiltration, nano-sized, highly catalytically active materials like La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF), Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC) and Gd0_{.1}Ce_{0.9}O₂ (GDC) have all been successfully fabricated at relatively low temperatures. A new "nano-composite" structure for SOFC electrodes, where nano-sized electrode catalysts are added into micron-sized ionic conducting (IC) materials using precursor solution infiltration, has greatly improved the electrode performance and reduced the operating temperature for SOFCs due to the large number of active reaction sites for nano-sized electrode catalysts and the fast oxygen ion transport pathway provided by the sintered IC substrates.

Despite the improved electrode performance, lower operating temperatures are still desired so that cheaper materials for SOFC sealants and interconnects can be used, which will bring down the overall SOFC electricity generation cost. Moreover, long-term stability for these nanocomposite electrodes is still a problem. Even at reduced operating temperatures, particle coarsening and surface cation segregation were still reported for common SOFC electrodes, compromising their electrochemical performance over time.

For the work in this thesis, it is hypothesized that surface decoration methods can alter the electrochemical performance and long-term stability of SOFC nano-composite cathodes (NCCs) by changing their surface chemistry and structure. Electrochemical Impedance Spectroscopy analysis, as well as surface and composition characterization methods such as Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy analysis were conducted to test this hypothesis. Surface decoration methods like atomic layer deposition (ALD) and GDC pre-infiltration were conducted on LSCF-GDC NCCs. 1-5 nm ZrO₂ ALD overcoats reduced the degradation rate of LSCF-GDC NCCs without significantly altering their initial polarization resistance (R_P) , while GDC pre-infiltration reduced both the R_P and the degradation rate for LSCF-GDC NCCs. In both cases the decrease in SrCO₃ concentration was observed after aging, which cleaned up the LSCF surface and resulted in better stability. GDC pre-infiltration was also performed on SSC-GDC NCCs. With little SrCO₃ impurity phase formed during precursor solution firing, no R_P or durability enhancement effect was observed. Moreover, ALD and GDC pre-infiltration were performed together for LSCF-GDC NCCs. Higher degradation rates were observed compared with uncoated cells and the reason was believed to be the reaction between ZrO₂ overcoats and nanosized GDC particles during aging, which compromised their "SrCO₃ reduction" capability. Finally, precursor solution infiltration was used to fabricate SOFC anodes and symmetric anode tests showed lower anode R_P for the infiltrated anodes compared with commercial ones. Ni infiltration was also conducted on commercial Ni- (Y2O3)0.08(ZrO2)0.92 (YSZ) anodes and peak power density of the anode infiltration commercial SOFCs was significantly increased compared with uninfiltrated ones.

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1 Introduction and Literature Review

1.1 World Energy Problems

With the increase of the world's population and the development of world's economy, significant growth in word energy demand is expected over the next few decades. According to the International Energy Outlook published by U.S. Energy Information Administration, comparing with 2020, world energy consumption is expected to increase by ~43%, reaching 900 quadrillion Btu by the year 2050.¹ This increased energy demand, together with the ongoing call for the reduction of CO_2 emission to reach a carbon-neutral economy, stimulates the demand of new, more versatile energy generation/conversion technologies with higher efficiencies and less CO_2 emissions. Among all the potential candidates, solid oxide fuel cell (SOFC) technology has gained much attention and has the potential to become the next-generation environmentally friendly electricity generation method.

1.2 Solid Oxide Fuel Cell Technology Overview

Solid oxide fuel cells are solid-state devices that can convert chemical energy of the fuels directly into electricity. Figure 1.1 shows the schematic drawing for a typical SOFC single cell.² SOFCs consist of three major functional layers: cathode, anode and electrolyte. Cathode is a porous layer where oxygen gas gets reduced into oxygen ions. These oxygen ions diffuse into the porous anode layer through dense electrolyte layers due to the oxygen ion concentration gradient and react with the fuel or energy carrier. Electrons are generated and conducted from the anode to the cathode in the process. Compared with other chemical to electricity energy conversion technologies, the benefits of SOFCs include 1) high gravimetric and volumetric power density^{2,3}, 2) high chemical to electricity conversion efficiency (~60%⁴⁻⁶ when electricity alone is valued and up to 90%⁶ when waste heat is also included. As a comparison, the typical efficiencies of

large MW-scale coal-fired power plants are 45%-50%⁷. The efficiencies of coal-fired power plants with smaller MW scales are usually even lower), 3) the ability to produce electricity from a variety of fuels including hydrogen, ethanol, natural gas, biofuels,⁸ etc., 4) lower SO_x and NO_x emissions compared with conventional gas turbines (10 times lower when hydrocarbons are used as fuel and zero emission when hydrogen is used as fuel⁹). Moreover, SOFCs can also be operated in reverse in solid oxide electrolysis cell (SOEC) mode, where high-value fuels like hydrogen and syngas can be produced efficiently.¹⁰ Due to all these advantages, SOFCs have been developed and used for applications like automotive range extenders¹¹ and residential combined heat and power units.¹²



Figure 1.1 Schematic drawing of typical SOFCs.²

Unfortunately, the further commercialization of SOFCs is hindered by their high operating temperatures. Due to the low catalytic ability of the electrodes and low oxygen ion conductivity of the electrolytes, SOFCs have to be operated at relatively high temperatures (usually above $650^{\circ}C^{13}$). As a result, the use of low-cost SOFC stack components such as ferritic stainless steel

interconnects¹⁴ and polymeric sealing materials is limited due to the safety concerns and the diffusion-related degradation problem for SOFCs is more prevalent at these temperatures, which together increased the overall SOFC electricity generation cost.³ The long start-up time and structural instability caused by the high operating temperatures are also problematic for some SOFC applications. Therefore, the efforts have been made to explore new materials and better microstructures for SOFC electrodes and electrolytes so that the electrochemical performance and durability of SOFCs can be enhanced and the operating temperature reduced.

1.3 SOFC Materials and Microstructures

1.3.1 Electrolytes

The SOFC electrolyte is a dense layer sandwiched between cathode and anode and is responsible for conducting oxygen ions and separating the fuel of the anode side from the oxidant from the cathode side. Ideal SOFC electrolytes should have good stability at elevated temperatures, sufficiently high oxygen ion conductivity, low electronic conductivity and good chemical and CTE compatibility with both electrodes.¹⁵ Based on these requirements, a number of oxygen ion conductors have been investigated as the potential candidates for SOFC electrolytes, including doped fluorite structured electrolytes (Y₂O₃ stabilized ZrO₂ (YSZ),^{16,17} Sc₂O₃ stabilized ZrO₂ (ScSZ),^{18,19} Gd₂O₃ doped CeO₂ (GDC)^{20,21}), pyrochlore based electrolytes (Gd₂Zr₂O₇²²), Perovskite based electrolytes (La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} (LSGM)²³) and composite electrolytes.^{24,25}

Figure 1.2 shows the conductivities of various common materials used for SOFC electrolytes at different temperatures.²⁶ Overall, two strategies have been applied to lower the resistance of SOFC electrolytes. The first one is to utilize materials with higher conductivities. As the conventional choice of materials for SOFC electrolytes, YSZ has been widely used for commercial SOFCs. However, due to their high conductivities, materials like LSGM²⁷ and GDC²⁸

have become the more popular candidates for SOFC electrolytes, especially for the development of low-temperature SOFCs where high performance electrolytes are needed to reduce the SOFC operating temperature. Different doping elements for common oxygen ion conducting materials like zirconia and ceria have also been shown to affect their conductivities. As shown in Figure 1.2, ScSZ shows a higher conductivity than YSZ across all temperatures. Similar effect on oxygen conductivity was observed for ceria with single and multi-element dopants as well.^{29,30} The second strategy is to reduce the electrolyte thickness. As shown by the dotted lines in Figure 1.2, for an electrolyte layer of 10 µm thickness, a material conductivity of 0.01 S/cm is needed to reach a 0.1 Ω cm² electrolyte resistance. When the electrolyte thickness is reduced to 1 μ m, only 0.001 S/cm conductivity is needed to reach the same electrolyte resistance, which expands the number of potential candidates for high performance SOFC electrolytes. To fabricate these dense, thin electrolyte layers, fabrication methods like pulsed laser deposition (PLD)³¹ and sputtering³² have been developed. For the work presented in this thesis, GDC was used for all the lab-made electrolyte-supported symmetric electrode cells, and YSZ is used as the electrolyte material of commercial SOFC substrates for full cell tests. Electrolytes used for lab-made electrolytesupported symmetric cells were made by uniaxial pressing and high temperature sintering, with thicknesses of $\sim 500 \,\mu\text{m}$. For anode-supported commercial SOFCs, the electrolyte thickness is ~ 3 μm.



Figure 1.2 Conductivities of various electrolyte materials. The dotted lines represent the conductivity value necessary to reach a 0.1 Ω cm² resistance for thicknesses of 1 µm (top) and 10 µm (bottom).²⁶

1.3.2 Anodes

As the fuel electrode, SOFC anodes are where fuel oxidation reaction happens. At SOFC anodes, oxygen ions react with fuels while electrons are generated and transported to the cathodes through the outer circuit in the process, as shown in the half reaction (here hydrogen is used as fuel):

$$H_{2(g)} + O_{O(s)}^{X} \to H_{2}O_{(l)} + V_{O(s)}^{-} + 2e_{(s)}^{-}$$
^[1]

Therefore, fuel gas adsorption, oxygen ion transport and electron transport need to occur simultaneously for the reaction to happen. Since all these requirements are a lot to ask for in a single material, composite anodes with a mixture of metal (electron conductor) and ceramic (oxygen ion conductors) materials have been the common choice for SOFC anodes. The sites where the fuel oxidation reaction happens are thus called triple phase boundaries (TPBs), meaning

the boundaries where electron conductor (metals), oxygen ion conductor (ceramics) and fuel gas meet.

A good SOFC anode should possess high catalytic ability for fuel oxidation reaction, high electronic and oxygen ion conductivity, good chemical and CTE compatibility with electrolyte materials, porous structure to allow for the gas flow and large density of TPBs to facilitate the fuel oxidation reaction. Among all the candidates for SOFC anodes, metal-ceramic cermet-based anodes are the most intensively studied.

Since the first introduction by Liu et al. in 1995, Ni-YSZ composite anodes have been the most widely studied anode materials and are considered the standard SOFC anodes.³³ Decent anode performance has been reported for Ni-YSZ anodes. However, carbon deposition has been widely reported for Ni-YSZ anodes when hydrocarbons are used as fuels, where carbon products are deposited on the surface of Ni particles and anode pores during hydrocarbon fuel reforming due to the exceptional catalytic ability of Ni. This carbon deposition will compromise the fuel oxidation capability of Ni-YSZ anodes and block the fuel gas flow.^{34,35} Ni-YSZ anodes are also known to be sensitive to sulfur content in the fuel. Only ppm level of H₂S in the fuel could react with Ni and result in huge performance loss for Ni-YSZ anodes.^{36,37} Because of these disadvantages of Ni metal in Ni-YSZ anodes, other metals such as Cu and Co have been studied to replace Ni to form Cu -YSZ^{38,39} and Co-YSZ^{39,40} anodes. Other oxygen conductors with higher oxygen ion conductivities like GDC⁴¹ and SDC⁴² have also been studied as potential replacement for YSZ for SOFC anode applications in order to achieve better electrochemical performance. Moreover, instead of metal-oxide cermet, single-phase electron conducting oxides such as La₁- $_{x}Ca_{x}Cr_{1-x}Ti_{x}O_{3}^{43}$ and $Sr_{1.6}K_{0.4}FeMoO_{6-\delta}^{44}$ have also been studied. Their electrochemical performance, however, are generally inferior to Ni-YSZ anodes.

Besides materials selections, microstructures of SOFC anodes can also significantly affect their performance. As stated earlier, higher density of TPBs is preferred to facilitate the fuel oxidation reactions for the metal-ceramic cermet anodes, which means that considerations of anode particle size and distribution, metal/oxide ratio, porosity are needed to maximize the anode performance. Figure 1.3 shows the Ni-YSZ anode polarization resistance estimation at different temperatures for different particle sizes assuming the same particle size between Ni and YSZ using the transmission-line model.⁴⁵ To get 0.1 Ω cm² polarization resistance (*R_P*) below 700°C, particle size of less than 0.5 µm is required for Ni/YSZ. If the same *R_P* is to be achieved below 600°C, the particles need to be less than 0.1 µm.



*Figure 1.3 Ni-YSZ anode resistance vs particle size at different temperatures. Here Ni and YSZ are assumed to have the same particle size.*⁴⁵

SOFC anodes have been conventionally produced using high-temperature sintering, where anode materials are fabricated, mixed and sintered at high temperatures to make "connections". The anode particle coarsening during sintering, however, results in the increase of anode R_P . Therefore, new anode processing methods such as sputtering⁴⁶ and solution infiltration⁴⁷ have also been studied to reduce the processing temperature, decrease the particle size and increase the density of TPBs in the anodes. Figure 1.4 shows the SEM image of a Ni infiltrated Ni-SDC SOFC anode.⁴⁸ Ni precursor solution was infiltrated into SDC scaffold and nano-sized Ni particles can be observed after solution firing. Due to the increased TPB density, better electrochemical performance was observed. For the work presented in this thesis, electrochemical performance of Ni infiltrated Ni-GDC anodes were compared with commercial Ni-YSZ anodes using symmetric anode tests. Performance of SOFC full cells with Ni infiltrated commercial Ni-YSZ anodes were also evaluated.



Figure 1.4 SEM image of Ni infiltrated Ni-SDC anode structure.⁴⁸

1.3.3 Cathodes

SOFC cathodes have been widely considered as the primary source of overall cell polarization resistance, especially for conventional SOFCs at lower temperatures due to the large

activation energy of oxygen reduction reaction-related processes.^{3,13} Oxygen reduction reaction happens at the cathode, where oxygen gas get reduced into oxygen ions and diffuse across the electrolyte into the anode layer, as shown in the half reaction:

$$\frac{1}{2}O_{2(g)} + V_{O(s)}^{-} + 2e_{(s)}^{-} \to O_{O(s)}^{X}$$
^[2]

Therefore, ideal SOFC cathodes should have high oxygen reduction reaction catalytic capability, good electronic and oxygen ion conductivity, good CTE and chemical compatibility with the electrolyte layer. Moreover, large number of active sites are also preferred to facilitate oxygen reduction reaction at a higher speed.

Perovskite-related materials, including cubic perovskite materials, layered perovskite materials and Ruddlesden-Popper phase materials are the most widely studied materials for SOFC cathodes due to their exceptional oxygen surface exchange catalytic abilities.²⁶ Figure 1.5 shows the crystal structures of these materials. Cubic perovskite materials have an ABO₃ structure, where oxygen atoms and B-site transition metal form a 6-fold coordinated structure (BO₆) with A site alkaline earth or lanthanide ions on the vertices. Layered perovskite materials have an AA'B₂O₆ structure with alternating AO-BO₂-A'O-BO₂ layers. Ruddlesden-Popper structure can be written as A_{n+1}B_nO_{3n+1}, where AO-ABO₃ layered structure can be found in n layers of ABO₃ perovskite stacks.²⁶ Some of the most studied perovskite-structured SOFC cathode materials include La_{0.6}Sr_{0.4}MnO_{3.6} (LSM),^{49,50} La_{0.6}Co_{0.4}CoO_{3.6} (LSC),^{51,52} La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3.6} (LSCF),^{28,53,54} La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3.6} (LSFC),^{55,56} La_{0.6}Sr_{0.4}FeO_{3.6} (LSF),^{57,58} Sm_{0.5}Sr_{0.5}CoO_{3.6} (SSC),^{27,59,60} and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3.6} (BSCF).^{61,62} Most of these materials mentioned here (except for LSM) are mixed ionic and electronic conducting (MIEC) materials with good electronic conductivity and decent oxygen ion conductivity. These single-phase MIEC materials are preferred for SOFC

cathodes due to their relatively high oxygen ion conductivity (compared with conventional SOFC cathode materials such as LSM with little oxygen ion conductivity), which better facilities the oxygen reduction reaction by activating the whole material surface instead of limiting the reaction to the TPB between electron conducting cathode materials and the electrolyte.



*Figure 1.5 Crystal structures of cubic perovskite, layered (double) perovskite and Ruddlesden-Popper materials.*²⁶

Oxygen reduction reaction at the cathodes is a complicated process with several steps involved, including oxygen gas diffusion and adsorption, oxygen dissociation, oxygen reduction, charge transfer and oxygen ion diffusion.^{63,64} These complexities make it hard to obtain reliable reaction "parameters" such as diffusivity and surface exchange coefficient for the cathode materials. The different microstructures used in different studies also make it hard to directly compare the "catalytic ability" of oxygen reduction reaction between different SOFC cathode

materials in different studies. Therefore, studies like Baumann *et al.* developed an alternative SOFC electrochemical experimental system utilizing thin-film microelectrodes and obtained the surface exchange resistance (Rs) for different common SOFC cathode materials at different temperatures (as shown in Figure 1.6) using electrochemical impedance deconvolution, which will be discussed in detail in Section 2.2.⁶⁵ The Rs values reported here are expected to reflect only the "catalytic ability" of oxygen surface exchange reaction for these materials (no resistance related to interfacial reactions, electron conduction, etc.) due to the well-defined and reproducible cathode geometry. Arrhenius behavior was observed for all the materials studied for Figure 1.6 with different activation energies, showing different diffusion-related behavior. Different ratios of dopant elements are found to be able to alter the materials' overall catalytic ability, as shown by the different Rs values of the LSCF family. This Rs difference within the same family of materials is likely due to the different oxygen diffusion kinetics, surface exchange kinetics and oxygen vacancy formation energy caused by the difference in atomic radii and electronic structure between different cation elements.⁶⁶⁻⁶⁸



*Figure 1.6 Surface exchange resistance (Rs) for different cathode materials at different temperatures obtained from microelectrode electrochemical tests.*⁶⁵

Even for MIEC materials, their oxygen ion conductivities are still several orders of magnitude smaller than common oxygen conducting materials used for electrolytes. Therefore SOFC composite cathodes consisting of the mixture of both MIEC materials and ionic conducting (IC) materials are developed. The added IC materials provide a pathway for oxygen ion transportation within the cathode while the MIEC materials serve as the electron conductor and catalyst for the cathode oxygen reduction reaction. These additional fast oxygen ion pathways provided by IC backbone enhance the oxygen transportation capability of the cathode and thus reduce the overall cathode resistance. Similar to SOFC anodes, conventional SOFC composite cathodes are fabricated by mixing MIEC and IC powders and depositing the mixture on the electrolyte via various methods such as screen printing and spin coating before sintering.⁶⁹ The sintering temperature for the composite cathode fabrication is also usually high (over 1000°C) to make connections between cathode and electrolyte in order to avoid high grain boundary

resistances.⁷⁰ Figure 1.7 shows the microstructure of a LSFC-GDC composite cathode that was sintered at 1200°C for an hour.⁷¹ Fine and porous cathode microstructure was obtained with LSFC particle size of ~300 nm. Compared with single-phase LSFC cathode that was made similarly, R_P of the LSFC-GDC composite cathode decreased by ~80% at 500°C.



*Figure 1.7 Microstructure of LSFC-GDC composite cathode fabricated by 1200°C co-sintering for an hour.*⁷¹

For SOFC cathodes, more active surface area is usually preferred for more active reaction sites to facilitate surface oxygen exchange reactions. Among all the methods to achieve high surface area, reduction of catalyst particle size is a common way. Due to the high sintering temperatures used for conventional electrode fabrication methods, large catalyst particles are usually obtained. In order to achieve reduced particle size, an alternative low-temperature composite electrode fabrication method called precursor solution infiltration (also known as impregnation) was developed. In a typical infiltration process, catalytic materials (MIEC, IC or both) are introduced into a pre-sintered porous scaffold (MIEC, IC or MIEC/IC composite materials) by adding solvent solution containing precursor metal salt solutions of the catalytic materials into the scaffold before the subsequent drying and firing. Because the scaffold has been sintered to make "connections" between the electrode and electrolyte before the addition of cathode catalyst, relatively low firing temperature (usually below 850°C) is needed to decompose the precursors and form the catalyst, which leads to smaller particle size and higher specific surface area.⁷² Figure 1.8 shows the microstructure of LSF-YSZ composite cathode fabricated by infiltration. Mixed solution containing stoichiometric amount of lanthanum nitrate, strontium nitrate and iron nitrate are added into sintered YSZ substrates before fired at 850°C for an hour. ~100 nm LSF particles can be observed on the porous sintered YSZ scaffold.⁷³ Compared with Figure 1.7, cathode fabrication temperature reduction of ~350°C leads to a 67% particle size reduction. Since its initial development, precursor solution infiltration has been used to fabricate composite cathodes with various MIEC cathode materials such as $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3.6}$ (LSCF),^{28,53,54} Sm_{0.5}Sr_{0.5}CoO_{3.6} (SSC),^{27,59,60} and La_{0.6}Co_{0.4}CoO_{3.6} (LSC),^{51,52} and some of the best cathode performance has been achieved.^{52,54,59}



*Figure 1.8 Microstructure of LSF-YSZ composite prepared by precursor solution infiltration. Precursor solution was fired at 850°C for an hour.*⁷³

For MIEC infiltrated IC SOFC composite cathodes, multiple experimental as well as performance modeling studies have shown that the particle size of MIEC materials is directly related to the overall cathode performance. Specifically, Simple Infiltrated Microstructure Polarization Loss Estimation (SIMPLE) model has been shown to be able to predict the R_P of infiltrated SOFC composite cathodes.^{60,74,75} This model accounts for the oxygen surface exchange resistance of the MIEC materials, which is calculated using the loading level, particle size and material surface exchange resistance Rs, and the oxygen conduction resistance of the IC scaffold, which is calculated using the morphology of the scaffold (obtained from SEM analysis) and the material conductivity. The predicted Rp from this model has been proved to be in good agreement with the measured value for common MIEC infiltrated IC SOFC cathode like SSC-GDC NCCs and LSCF-GDC NCCs.^{60,74,75}

With the improved cathode performance, the operating temperature of SOFCs has greatly decreased to as low as ~650°C. Unfortunately, the good initial electrochemical performance of SOFC cathodes does not last. Significant performance degradation has been observed for some of the best performing SOFC cathodes, even at operating temperatures below 700°C.²⁸ Generally speaking, cathode particle coarsening, cation surface segregation and chemical reaction with impurities are three major sources of performance degradation over time for SOFC cathodes.²⁶

Particle coarsening means the size increase of catalyst particles over time, usually due to the decrease in total energy of the system and a reduction of total interfacial area. Given that particle size is directly related to specific surface area, particle coarsening can compromise the electrochemical performance of SOFC cathodes by reducing the number of active sites on the catalyst surface. A model describing the degradation behavior of LSFC-GDC NCCs was proposed by Shah et al, which established a relationship between the particle size increase of LSFC particles at different temperatures and the overall LSFC-GDC cathode R_P .⁷⁶ Different from the SIMPLE model mentioned above, this model only accounts for the resistance from MIEC materials and assumes that the cathode polarization resistance is linearly related to the MIEC particle length scale. Figure 1.9 shows the measured and fit R_P data of LSFC-GDC NCCs and the SEM images of the NCCs before and after aging. The model prediction of particle size increase after aging (38 nm to 60 nm) was consistent with the observed particle size change from SEM analysis, which suggest that LSFC particle coarsening is solely responsible for the degradation behavior observed. Similar SOFC cathode degradation caused by MIEC particle coarsening has been reported for other MIEC materials as well.⁷⁷ To alleviate the coarsening behavior, secondary materials with a more stable structure such as GDC²⁷ and ZrO₂ overcoats⁷⁸ have been added into the cathode to "constrain" the particle growth of the MIEC material.



Figure 1.9 (a) Experimental and fit R_P data for LSFC-GDC NCCs aged at different temperatures. (b) Fractured cross section images of LSFC-GDC NCCs before (top) and after (bottom) 850°C aging for 289 hours.⁷⁶

Cation surface segregation is often observed during aging for multi-cation SOFC cathode materials, where some cation elements diffuse towards the particle surface to release the local

elastic and/or electrostatic stress and form inactive impurity phases on the surface.^{79–82} Specially, Sr surface segregation has been widely reported for many Sr-containing MIEC materials including LSCF,⁸³ LSC,⁸⁴ and LSFC,⁸⁵ where concentration of Sr near the MIEC material surface increases with time and finally forms inactive species like SrO, Sr(OH)₂ and/or SrCO₃ on the surface. Since the oxygen surface exchange coefficients of MIEC materials are known to be very sensitive to surface structure and impurity concentrations,⁸⁶ the formation of these impurity phases will block active sites, compromise the catalytic activity of MIEC materials and thus cause SOFC cathode degradation.⁸⁷ Figure 1.10 shows the amount of soluble cation species (which represents the inactive species on the surface of LSFC caused by cation segregation) and the polarization resistance of porous LSFC cathode after 750°C aging for different durations. Significant concentration increase in soluble Sr content was observed after aging, suggesting increased amount of inactive Sr species on the surface due to Sr surface segregation during aging. This Sr surface segregation caused the degradation behavior for the porous LSFC cathodes, as shown by the increase in polarization resistance over time in Figure 1.10b.⁸⁸ In order to prevent or revert the Sr surface segregation, many approaches like application of small electrical DC potentials,⁸⁹ application of periodic large reverse DC bias⁹⁰ and depositing zirconia overcoats via atomic layer deposition (ALD)⁸³ have all been investigated, which all resulted in less Sr concentration on the MIEC surface and better long-term stability for the Sr-containing SOFC cathodes.



Figure 1.10 (a) The amount of cations dissolved in ultrapure water for cells aged at 750°C for different times and (b) Nyquist plots for porous LSFC cathodes after 700°C aging for different times.⁸⁸

Surface contamination due to chemical reaction with impurities usually refers to the hazardous reaction between cathode materials and volatile impurities from gas stream or SOFC stack components. Specifically, Cr and Si poisoning has been widely reported for SOFC cathodes. Volatile Cr species, which usually come from the Cr-containing metallic interconnects for SOFC stacks, react with cathode materials during operation and form Cr₃O₄, SrCrO₄ on the MIEC surface or result in Cr B-site substitution for MIEC cathode materials.⁹¹ Volatile Si species, on the other hand, usually come from the sealant for SOFC stacks and result in the formation of SiO₂ or Si(OH)₄ on the MIEC surface.⁹² These formed inactive species will form a passivating layer on the MIEC surface, block active sites and result in SOFC cathode degradation over time.

In the work proposed in this thesis, two common high performance SOFC composite cathodes, LSCF infiltrated GDC and SSC infiltrated GDC were studied. Different surface decoration methods like ZrO_2 ALD overcoating and GDC pre-infiltration were conducted on these cathodes and the reason for the observed change in their electrochemical performance and long-term stability was investigated. Due to the lack of SOFC interconnects or sealants used in this

work, only particle coarsening and Sr surface segregation were investigated as possible cathode degradation mechanism.

1.3.4 Common Cell Geometries

SOFC cells can be configured into different geometries based on the overall stack design. Cell shapes like tubular, planar, bell-and-spigot, banded and corrugated structures have all been designed, with distinct current paths and stack configurations for each design.^{69,93} Based on the mechanical support of each individual SOFC single cell, five different designs have been developed, namely electrolyte-supported, cathode-supported, anode-supported, porous substratesupported and interconnect-supported. The first three designs are usually called self-supporting structure while the last two designs are referred to as external-supporting structure.⁶⁹ Figure 1.11 shows the schematic drawings of the five different SOFC single cell designs. The support layer is usually much thicker (usually several hundred microns) than other SOFC components. Electrolytesupported design is widely used for symmetric cell tests, where the same electrode is present on both sides of the electrolyte. With this design, the electrolyte response can be calculated and subtracted from the cell performance, which makes this design especially helpful when only the electrode performance is of interest. However, electrolyte-supported cells are not widely used for SOFC full cell designs due to the low conductivity of the thick electrolyte layer. Cathode and anode-supported designs are considered to be more suitable for high performance SOFC full cell designs. External-supporting designs can utilize low-resistance materials as mechanical support (i.e. the thickest layer) to enhance the overall full cell performance, but will result in more complex stack designs and might introduce new source of contaminations for the SOFC electrolytes and electrodes. In this work, only planar configuration is used for all the experiments. Electrolytesupported design is used for symmetric cathode and anode tests, while anode-supported design is utilized for full cell testing.



*Figure 1.11 Schematic drawings of different SOFC cell designs based on different mechanical supports.*⁶⁹

1.4 Thesis Overview

SOFC technology is of great interest due to its advantages in power density, electricity generation efficiency and waste gas emission compared with other chemical to electricity conversion technologies. The poor electrode performance and unsatisfactory electrode long-term stability, however, hinders its further commercialization. Therefore in the work presented in the thesis, the electrochemical performance and long-term stability of the infiltrated SOFC electrodes are studied and surface decoration methods like ZrO₂ ALD overcoating and GDC pre-infiltration are conducted on different infiltrated cathodes to investigate their possible effect. Degradation mechanism and possible methods for electrochemical performance enhancement for infiltrated SOFC cathodes are also discussed, which hopefully shed light on the performance and

stability issues of SOFC electrodes that have been the research interest of SOFC community for years and advance the SOFC technology towards its further commercialization.

2 Experimental Methods

2.1 Cell Fabrication

2.1.1 Symmetric Cathodes for Electrochemical Tests

In this work, symmetric electrodes were used to evaluate the electrochemical performance of the electrode under open circuit voltage (OCV) conditions. The first step to fabricate symmetric cathodes was to fabricate dense electrolyte support using uniaxial pressing. ~1.2 g of GDC powder (Rhodia) was first pressed with a uniaxial press (Model 3851, Carver) in a 0.75-inch stainless steel die with ~40 MPa of pressure. The pressed GDC pellets were then heated to 1450°C with a 3°C/min heating rate and held at 1450°C for 20 hours before cooled down to room temperature with a 3°C/min cooling rate. Relative densities >93% was reached for all the GDC electrolyte pellets. These sintered GDC pellets were then sanded down to thickness of ~0.5 mm with 120 grit sandpaper.

Porous GDC scaffolds were then screen printed onto both sides of these sanded GDC pellets. GDC powder (Rhodia) was first coarsened at 800°C for 4 hours and then mixed with electronic vehicle (V-737, Heraeus) to produce a paste with a ~33 wt% loading level. The mixed paste was then screen printed onto both sides of the sintered GDC pellets. Here 12-inch by 12-inch, 80 mesh stainless steel screen was used. A circular pattern of 7.98 mm in diameter (0.5 cm² in area) in the center was designed for the screen used to simplify the cathode geometry. After each print, the cells were held in air for 5 min to let the ink flow before dried in the oven at 120°C for 5 minutes. Multiple prints were applied to reach the desired cathode thickness if necessary. The samples were then heated to 400°C with a 3°C/min heating rate, held at 400°C for an hour, ramped to 1100°C with a 5°C/min heating rate, held at 1100°C for 3 hours, and cooled down to room temperature with a 10°C/min

nominal cooling rate. The purpose of this heating procedure was to completely burn out the polymetric electronic vehicles and coarsen the GDC particles to form an inter-connected network of micron-sized GDC particles. The final thickness of the GDC scaffolds were measured with a profilometer (Dektak, Bruker) for the calculation of the catalyst loading level.

Next, precursor solutions were infiltrated into the GDC scaffolds. All precursor solutions (LSCF, SSC and GDC) were prepared by first dissolving ~3 wt% of the surfactant Triton-X 100 (Alfa Aesar) in MilliQ water before stirring for 10 minutes. For the fabrication of LSCF-GDC NCCs high-purity (>99.9% pure on a metals basis) $La(NO_3)_3 * 6 H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 * 6 H_2O$, and Fe(NO₃)₃*9 H₂O (Alfa Aesar) were dissolved into the solutions to form 1.5M LSCF nitrate solution with a 6:4:8:2 La:Sr:Co:Fe atomic ratio. These LSCF nitrate solutions were then pipetted into sintered GDC scaffolds. After each infiltration, each cell was held in air for 5 minutes to allow the solution to flow and then dried at 80°C in air for 5 minutes. Three infiltrations were performed to reach the desired 12 volume % infiltrate loading level. After each infiltration, the LSCF infiltrated GDC cells were heated to 700°C with a 10°C/min heating rate, held at 700°C for 1 hour and cooled down to room temperature with a nominal 10°C/min cooling rate. For SSC-GDC NCCs similar precursor solutions were made by mixing $Sm(NO_3)_3$, $Sr(NO_3)_2$, and $Co(NO_3)_2$ *6 H₂O (Alfa Aesar) in a 1:1:2 atomic ratio. The infiltration and firing processes were similar to LSCF-GDC NCCs. The firing temperature for SSC-GDC NCCs was set at 800°C in accordance with literature.⁶⁰ In some cells, GDC nitrate solution was infiltrated before the addition of MIEC catalysts. In this case of GDC pre-infiltrated cells, GDC precursor solutions, which were made by mixing Gd(NO₃)₃ and Ce(NO₃)₄ (Alfa Aesar) in a 1:9 ratio, were infiltrated into the scaffold, dried and fired before the addition of LSCF or SSC nano-particles via solution infiltration. The firing temperature for GDC infiltration was 700°C.

After infiltrate firing, (La_{0.8}Sr_{0.2})_{0.98}MnO_{3-x} (LSM) paste was printed on top of the infiltrated scaffold to form a porous LSM current collecting layer. LSM paste was fabricated by mixing LSM powder (Praxair) with the same electronic vehicle to produce an ink with a 33 wt% solids loading. The LSM paste was then screen printed atop each LSCF-GDC cathode with a 325 mesh stainless steel screen with a circular pattern 7.98 mm in diameter (0.5 cm² in area). After printing, the paste was allowed to flow in air for 5 min and dried in the oven at 120°C for 5 mins. The LSM coated LSCF-GDC cells were then heated up to 700°C with a 10°C/min heating rate, held for 1 hour at 700°C, and cooled down to room temperature with a nominal cooling rate of 10°C/min.

For some LSCF-GDC NCCs, ZrO₂ ALD overcoating was applied. First developed in the 1970s, ALD has been used to produce thin films from gas phase precursors with good conformality and process controllability. The control on the atomic level makes ALD ideal for producing extremely thin-film with complex nanostructures.⁹⁴ Figure 2.1 shows the schematic of a typical ALD cycle.⁹⁵ Sequential alternating pulses of two different gaseous chemical precursors are introduced and react with the substrate before flushed out with inert gas. Due to the self-limiting nature of the two "half reactions", the control of monolayer growth of thin films is made possible. The low deposition temperature for ALD process (usually below 350°C) also makes it ideal for nano-sized film fabrication without coarsening issues.


Figure 2.1 Schematic of a typical ALD process with a flow type reactor. (a) Substrate surface has natural functionalization has been functionalized. (b) Precursor A is pulsed and reacts with surface. (c) Excess precursor and reaction by-products are purged with inert carrier gas. (d) Precursor B is pulsed and reacts with surface. (e) Excess precursor and reaction by-products are purged with inert carrier gas. (f) Steps 2–5 are repeated until the desired material thickness is achieved.⁹⁵

Generally speaking, two different types of ALD reactors, namely the flow type (i.e. those where excess precursors are introduced and purged by inert gas) and the static type (i.e. those where excess precursors are evacuated by an external pump between cycles). Different overcoat morphologies has been reported in studies using different types of ALD reactors.^{96–98} For the work proposed in the thesis the ZrO₂ overcoats were applied to some of the LSCF-GDC NCCs using an ALD flow type reactor (Savannah 200 series, Ultratech). Pure tetrakis (dimethylamido) zirconium (IV) (>99.99%, Sigma-Aldrich) and deionized (DI) water were used as the Zr-precursor and oxidant, respectively. The respective temperature of the Zr-precursor and the reaction chamber were 75°C and 180°C. During an ALD cycle, the reactor chamber was first pumped down to 50 mTorr, the Zr-precursor was introduced into the chamber with a 0.4 second pulse, the Zr-precursor was allowed to permeate the cathode for 20 seconds, N₂ gas with a flow rate of 15 sccm was

introduced into the chamber to purge any residual Zr-precursor, the chamber was pumped down to 50 mTorr, deionized water was introduced for 0.015 seconds, and the chamber was held for 20 seconds to oxidize the precursor. This produced a ZrO₂ ALD deposition rate of 0.1 nm/cycle. The ALD overcoat deposition thickness was calibrated using a quartz crystal microbalance (QCM) technique. A QCM transducer unit (Sycon STM-2, Inficon) was used with a high temperature gold coated quartz crystal with a 6 MHz oscillation frequency.

Finally, to facilitate current collection Au paste (C5756, Heraeus) was screen printed on top of each LSM layer in a grid pattern using a 325 mesh.

2.1.2 Symmetric Cathodes for XPS Analyses

LSCF-GDC NCCs and SSC-GDC NCCs for XPS analyses were made in the same manner as those for electrical testing, except no gold or LSM current collecting layers were applied.

2.1.3 LSCF Pellets for XRD Analyses

LSCF pellets for XRD analysis were fabricated by firing LSCF nitrate solution at 700°C for an hour and pressing the obtained powder at ~120 Mpa for 5 minutes. The pellets were then sintered at 1000°C for two hours. After that, ~6 uL of LSCF nitrate solution was infiltrated into both sides of each pellets and fired at 700°C for an hour to produce nano-sized LSCF particles on top of the previously-obtained network of micro-sized LSCF particles. The possible reaction between LSCF and GDC during solution firing was also studied using XRD. In this case, LSCF precursor nitrate solution was fired on top of nano-sized GDC powder, which was observed by GDC nitrate precursor solution firing as well. After this, the mixed powder was pressed as fired similarly as LSCF pellets.

2.1.4 Symmetric Anodes for Electrochemical Tests

For symmetric Ni-YSZ cells, commercial Ni-YSZ paste (Fuelcellmaterials, Lewis Center, OH) was screen printed on both sides of the GDC pellets. 80 mesh, 12-inch by 12-inch stainless steel screen with a pass-through circular pattern of 7.98 mm in diameter was used for screen printing. After each print the cells were held in air for 5 minutes before left in the 120°C oven for 5 minutes for the paste to dry. Multiple runs were conducted to reach the desired anode thickness of ~40 µm. After screen printing the Ni-YSZ paste was then heated up to 400°C with a 3°C/min rate, held at 400°C for an hour, heated up to 600°C with a 3°C/min rate, held at 600°C for an hour, heated to 1100°C with a 5°/min rate and held at 1100°C for 3 hours to sinter before cooled down to room temperature. The thickness of the Ni-YSZ layers was measured by a profilometer (Dektak, Bruker, Billerica, MA). NiO nano-particles were added in some of the printed symmetric Ni-YSZ anodes by precursor solution infiltration. Nickle nitrate precursor solution was made by mixing high purity Ni(NO₃)₂·6H₂O (Alfa Aesar, Haverhill, MA) with Milli-Q water. The precursor solution was then pipetted into the Ni-YSZ anodes, held in air in 5 minutes and dried in the oven at 80°C for 5 minutes before fired at 700°C for an hour to form nano-sized NiO particles. Multiple solution infiltration processes were performed to reach a ~8 vol% loading level. Finally gold paste (C5756, Heraeus, West Conshohoken, PA) was printed on top of the anodes in a grid pattern to serve as the current collecting layer. Ni infiltrated GDC symmetric anodes were also fabricated, where same Ni precursor solution was infiltrated into GDC scaffold (made similarly as symmetric cathodes) and fired at 700°C for an hour, followed by the screen printing of gold grids.

2.1.5 Full SOFC Cells for Electrochemical Tests

For full cells testing, commercial Ni-YSZ anode/YSZ electrolyte/GDC interlayer/LSC cathode full cells (Fuelcellmaterials, Lewis Center, OH) were used as the commercial baseline

cells, while Ni-YSZ anode/YSZ electrolyte/GDC interlayer half-cells (Fuelcellmaterials, Lewis Center, OH) were used as the substrates for full cells with high performance LSCF-GDC NCCs. Screen printing and sintering of GDC scaffolds, cathode LSCF nitrate precursor solution infiltration and firing and the subsequent screen printing of LSM on top of LSCF-GDC NCCs were performed in the same way as symmetric LSCF-GDC NCCs. Nickle infiltration was also performed on some of the full cell anodes. Nickel nitrate precursor solution infiltration into the Ni-YSZ anodes and subsequent solution firing were performed in the same way as symmetric Ni-YSZ anodes mentioned above. Similarly, gold grid was printed as current collector.

2.2 Characterization Methods

2.2.1 Electrochemical Impedance Spectroscopy Measurements

NCC polarization resistance measurements were conducted via electrochemical impedance spectroscopy (EIS) measurements. As one of the most widely used electrochemical characterization methods, EIS measurement allows a small AC signal (usually below 100mV) to pass through the cell at different frequencies. Generally speaking the overall resistance for symmetric and full SOFC cells can be separated into ohmic resistance, which represents the resistance of oxygen ion conduction across the electrolyte, and the polarization resistance, which represents the resistance related to electrochemical processes in the cell. While oxygen ion conduction across the electrolyte dependence (no capacitance value), due to the fact that electrochemical processes in SOFCs are driven by currents, different frequencies. Therefore, overall resistance for SOFCs can often be simplified into the series of "resistor-capacitor" unit in parallel.⁹⁹ A simple equivalent circuit of full SOFCs is shown in Figure 2.2.¹⁰⁰ Because of the different capacitance values of different processes, resistance of different reaction

"steps" can be deconvoluted and identified from EIS plots (called Nyquist plots). Figure 2.3 shows a typical Nyquist plot of a micro LSCF electrode. Different arcs at different frequencies can be observed, representing different electrochemical processes in the microelectrode.⁶⁵



Figure 2.2 Equivalent circuit of a full SOFC including cathode impedance (Rc, Cc), electrolyte resistance (R_{ohm}) and anode impedance (Ra, Ca).¹⁰⁰



Figure 2.3 A Nyquist plot for LSCF microelectrodes at 750°C.⁶⁵

In the work proposed in the thesis, a two-point, push-contact setup with Pt contacting plates were used and impedance spectra were collected with 50°C temperature intervals using an impedance analyzer (IM6, Zahner). Cells were held for least 20 minutes at each temperature in

order to reach thermal equilibrium. Impedance data was collected between 0.1 Hz to 100 kHz with a 100 mV AC amplitude. Polarization resistances were determined from the separation between the two Nyquist plot x-intercepts, and the ohmic resistance (R_0) was determined from the high frequency Nyquist plot x-axis intercept. All testing temperatures were measured using a thermocouple next to the cell and the same test rig and furnace were used for all the electrical measurements reported here, in order to eliminate equipment-related temperature calibration errors. Symmetric cathodes were tested in static air while symmetric anodes were tested in 3% H₂ + 97% Ar gas mixtures. Flowing air was also used in the study to investigate the potential gas diffusing problem of LSCF-GDC NCCs. Moreover, some symmetric cathodes were tested under different oxygen pressures to investigate the different responses from the Nyquist plots. It was made possible by testing symmetric cathodes under 5% O₂ + 95% N₂, 20% O₂ + 80% N₂ and 40% O₂ + 60% N₂.

2.2.2 Current-Voltage Measurements

Current-voltage (I-V) measurement is another widely used electrochemical characterization method. In an I-V measurement linear bias are applied to the full cell and the current change is recorded. I-V measurement is helpful in identifying the cell voltage where peak power density can be reached, as well as in characterizing the full SOFC cell response under large current (as opposed to small AC current in EIS measurement). Figure 2.4 shows a current density vs voltage and power density plot for Ni-LSGM/LSGM/SSC-GDC full SOFC.²⁷ Generally, I-V curve can be divided into three regions, with first region (low current density) representing electrode resistance, second region representing electrolyte resistance and third region (high current density) representing gas diffusion resistance.



Figure 2.4 Current density vs voltage and power density plot for Ni-LSGM/LSGM/SSC-GDC full SOFC at 450°C, 500°C, 550°C and 600°C. H₂ was used as fuel at the anode and air as the oxidant at the cathode. ²⁷

In this work I-V measurement for full cells was conducted at 550°C, 600°C and 650°C with static air as oxidant on the cathode side and humidified hydrogen with a flow rate of 100 sccm as the fuel on the anode side. Full cells were sealed on top of a homemade stainless-steel test rig with silver paste (C8728, Heraeus, West Conshohoken, PA). Silver wires were used to conduct current.

2.2.3 Electron Microscopy Analysis

The morphology of the ZrO₂ overcoats in the LSCF-GDC NCCs were observed with a transmission electron microscope (TEM) (H-9500, Hitachi) operating at 300 keV. Samples for this analysis were prepared using a Focused Ion Beam (NB-5000, Hitachi) lift-out technique described previously in the literature.¹⁰¹

NCC microstructure was evaluated using scanning electron microscopy (SEM) (Auriga, Carl Zeiss). A 20 kV voltage beam was used with a ~3 mm working distance. Cells were broken in half and cross-sectional images for were taken near the cracks at the electrolyte-electrode interface to image the infiltrate particles, as described previously in literature.⁵⁴

2.2.4 X-ray Photoelectron Spectroscopy Analysis

Surface NCC elemental analysis was conducted via X-ray photoelectron spectroscopy (XPS) (Phi 5600, Perkin Elmer) analysis. An aluminum Ka X-ray source was used for XPS measurement at room temperature using a pressure of 10⁻⁹ Torr and a testing area of 1 mm by 3.5 mm. The relative atomic concentration the various elements and the Sr 3d peak deconvolution was conducted using the Multipak software. XPS survey scans were collected with a pass energy of 187.5 eV and a step size of 0.4 eV. Detailed XPS elemental scans were collected with a pass energy of 23.75 eV and a step size of 0.1 eV. For the detailed scans, multiple scans were conducted and summed together to obtain a good signal-to-noise ratio. For deconvolution of the Sr 3d peaks, the binding energy of all the Sr 3d peaks were calibrated by the C 1s photoemission peak of hydrocarbon impurities within the XPS found at 285.0 eV. Sr 3d peak was deconvoluted into two different sets of Sr peaks. Following past literature studies,^{78,102} the Sr 3d 5/2 and Sr 3d 3/2 doublets were attributed to "surface Sr" species like SrO, Sr(OH)₂ and/or SrCO₃, while Sr doublets with a lower binding energy were attributed to Sr in a perovskite crystal structure (Lattice Sr). The relative concentrations of the different Sr species were represented by the relative peak areas of their respective Sr doublets.

2.2.5 X-ray Diffraction Analysis

The phase purity of the LSCF powder, SSC powder, ZrO_2 overcoated LSCF pellets were evaluated via X-ray diffractor (XRD) (Miniflex II, Rigaku). General XRD scans were conducted for 2 θ angles of 20° to 80° with a sampling width of 0.05°/step and a scan speed of 1°/min. Detailed local XRD scans were conducted with a sampling width of 0.02°/step and a scan speed of 0.02°/min. A copper target and a nickel filter were used in all cases.

3 ZrO₂ ALD Overcoats as On-Board Sr Getter for Standard La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃-Gd_{0.1}Ce_{0.9}O₂ Nanocomposite Cathodes

3.1 Introduction

Solid Oxide Fuel Cells (SOFCs) are a promising next-generation energy conversion technology because of their high efficiency and high power density compared to other chemical to energy conversion technologies.²⁻⁶ Companies like Microsoft, Nissan, and Bosch are currently developing SOFCs for improved datacenter reliability/profitability/environmental friendliness,¹⁰³ high-energy density automotive range extenders,¹¹ and modular residential and industrial combined heat and power units,¹² respectively. Unfortunately, due to the poor oxygen surface exchange kinetics of SOFC electrodes, SOFCs can only be operated at high temperatures (typically 650-800°C) that cause long-term materials degradation and increase manufacturing costs.¹⁰⁴⁻¹⁰⁷ In an attempt to realize reduced SOFC operating temperatures, solution infiltration has received attention in the literature as a low-temperature cathode fabrication technique for producing high surface area SOFC cathodes.¹⁰⁸ During infiltration, precursor nitrate solutions seep into porous scaffolds and are heated to decompose the previously-dissolved nitrates. This process produces nano-sized mixed ionic and electronic conducting (MIEC) oxygen exchange catalysts such as $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF), 53,54,109 $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC), 27,59,60 and $La_{0.6}Co_{0.4}CoO_{3-\delta}$ (LSC),^{51,52} oftentimes within the pores of partially-sintered ionic conducting (IC) materials, like gadolinium doped ceria (GDC). By combining the good catalytic activity and electronic conductivity of MIEC materials with the high ionic conductivity of IC scaffolds, Nano-Composite Cathode (NCC) resistances of 0.1 Ω cm² have commonly been achieved at ~600°C.^{52,54,59} This performance is considerably better than that of traditional LSCF cathodes made from sintered submicron LSCF particles, which typically require ~750°C to reach 0.1 Ω cm².^{110–112}

Despite the reduced operating temperatures enabled by these high-performing SOFC cathodes, long-term NCC performance degradation can be problematic. For instance, previous studies have shown that even at low temperatures of 540°C and 600°C, LSCF infiltrated GDC cathodes exhibit polarization resistance (R_P) degradation rates of 49%/khrs⁵³ and 94%/khrs,⁵² which are much higher than the ~1 %/krs degradation rates observed for traditional LSCF cathodes made from sintered sub-micron LSCF particles.¹¹³

At high operating temperatures, the small infiltrate particle present in NCCs drive degradation via infiltrate particle coarsening.^{76,114,115} Specifically, La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃₋₈ (LSFC)-GDC NCCs aged at 850°C (corresponding to a LSFC homologous temperature $T_H = T$ (in K) / T_{Melt} (in K) of 0.52¹¹⁶) for 289 hours showed a greater than three-fold increase in R_P and an increase in the LSFC nano-particle size, from ~40 nm to >100 nm.⁷⁶ Similar coarsening behavior has been observed during aging for other common SOFC materials at temperatures where diffusion is active, i.e. at homologous temperatures greater than ~0.5¹¹⁷ such as LSC at 800°C ($T_H = 0.54$).¹¹⁴

Another major source of degradation for SOFC cathodes is cation segregation.^{79,87,118,119} MIEC oxygen surface exchange coefficients are very sensitive to surface structure and impurity concentration.⁸⁶ Specifically, for Sr-doped MIEC materials like LSCF, Sr has been shown to diffuse towards MIEC surfaces spontaneously over time at elevated temperatures. This Sr segregation, which occurs as the material attempts to minimize its elastic and electrostatic controlled strain energy^{79–81}, eventually results in the formation of SrO, Sr(OH)₂ and/or SrCO₃ that blocks active sites, compromises the catalytic activity of MIEC materials and thus causes cathode degradation.⁸⁷

For these reasons, multiple NCC cathode degradation mitigation attempts have focused on limiting infiltrate particle growth and Sr surface segregation. For instance, attempts to 1) apply intermittent DC biases intended to drive Sr back into the crystal lattice,⁸⁹ 2) develop A sitedeficient LSCF,¹²⁰ 3) develop of Sr-free cathodes,^{121,122} etc. have all been explored.

This chapter focused on using ALD zirconia overcoats to improve the degradation of LSCF-GDC NCCs, without significantly degrading their initial electrical performance. In recent years, ALD has been intensively studied as a surface modification technique to improve the electrical performance and long-term stability of SOFC cathodes. Aluminum oxide, 123,124 cerium oxide,¹²⁵ strontium oxide,¹²⁵ cobalt oxide,¹²⁶ and yttria doped zirconia¹²⁷ coatings several nanometers thick have all been deposited onto SOFC cathode materials. Although dense ZrO₂ overcoats have been reported to produce detrimental effects on SOFC cathode R_{P} , 96,97 porous ALD ZrO₂ overcoats produced by the incorporation and subsequent thermal decomposition of organics in the ALD coating have produced beneficial effects on SOFC cathode R_P and stability.⁹⁸ Specifically, Gong et al. showed that the ~20 nm thick, porous ZrO₂ ALD overcoats on micronsized LSFC | micron-sized GDC composite cathodes shown in Figure 3.1 reduced the 800°C open circuit cathode R_P degradation rate.¹²⁸ Decreases in the 700°C open circuit cathode R_P degradation rate were also observed for LSC infiltrated $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ (LSGM) with porous ~ 5 nm ZrO₂ overcoats.⁷⁸ In the present work, ZrO₂ overcoats of various thicknesses were deposited onto LSCF-GDC NCCs and the relationship between ZrO₂ overcoat thickness, initial 400-700°C performance, long-term 650°C stability, and degradation mechanism were examined for the first time.



*Figure 3.1 (a) Cross-sectional and (b) plan view High-Resolution Transmission Electron Microscopy (HRTEM) images of ALD ZrO₂ overcoats produced with the same recipes and equipment used in the present work. Note, (b) contains an Energy Dispersive Spectroscopy (EDS) analysis proving there are nano-sized pores in the ZrO₂ overcoats.*¹²⁸

3.2 Results and Discussion

Figure 3.2 shows Transmission Electron Microscopy (TEM) images for the 5 and 10 nm ZrO₂ coated 12 vol% LSCF (volume of LSCF infiltrate over volume of GDC particles)-GDC NCCs produced here after 1000 hours of 650°C aging. In all cases, geometrically conformal ZrO₂ overcoats were observed after 1000-hours of 650°C aging and the target thickness was successfully produced during the ALD fabrication process. Some discrete darker spots were observed in the ZrO₂ overcoat layers, which were attributed to different orientations of ZrO₂ or SrZrO₃ grains within the overcoat.¹²⁸ It is important to note that unprotected, post-Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) exposure to room-temperature air over several months resulted in amorphization of the ALD coating such as that shown in Figure 3.3. However, this amorphization may be the result of FIB-SEM beam damage, and given that the 650°C aging temperature utilized in the present work was higher than the ~500°C crystallization temperature

for nano-sized ZrO₂ films reported in the literature,¹²⁹ the ALD ZrO₂ overcoats produced here are expected to have fully crystallized during 650°C aging. TEM images shown in Figure 3.4 taken near the cathode/current collector interface and near the cathode/electrolyte interface indicate that the extreme ALD thickness variations with cathode depth (due to gas diffusion limitations of the ALD precursors within the cathode micropores) reported in the literature⁹⁸ were not present in the cathodes produced here.



Figure 3.2 TEM images for (a) 5 nm ZrO_2 and (b) 10 nm ZrO_2 coated LSCF-GDC NCCs after 1000 hours of 650°C degradation.⁸³



Figure 3.3 TEM images taken in the same spot for FIB-SEM sectioned 5nm ZrO₂ coated standard 12 vol% LSCF-GDC NCCs taken after 1000 hours of 650°C aging and approximately (a) three weeks after high temperature exposure and several days after FIB-SEM liftout, and (b) two more additional months of unprotected exposure to room-temperature air. Note that the ALD coating amorphized and expanded (perhaps due to atmospheric water attack) after FIB-SEM sectioning and multiple months of unprotected, room-temperature exposure to air.⁸³



*Figure 3.4 TEM images taken (a) near the cathode surface and (b) near the cathode/electrolyte interface for the sample in Figure 3.3 (b).*⁸³

Figure 3.5 shows representative EIS Nyquist plots for as-produced 12 vol% LSCF-GDC NCCs with 0, 1, 2, 5 or 10 nm of ZrO₂ overcoat at 500°C, 600°C and 700°C. All cells showed a

non-semi-circular arc at 500°C and two distinct arcs for both coated and uncoated cells above 600°C. The slight difference in R_0 between cells was attributed to the difference in electrolyte thickness between cells. The impedance spectra shapes observed here at various temperatures were similar to those observed in the literature for LSCF-GDC cathodes at similar temperatures.^{28,53,54}



*Figure 3.5 Representative Electrochemical Impedance Spectroscopy Nyquist plots for asproduced (a) 0 nm, (b) 1 nm, (c) 2 nm, (d) 5 nm, and (e) 10 nm ZrO₂ coated 12 vol% LSCF-GDC NCCs at 500°C, 600°C and 700°C.*⁸³

Figure 3.6 shows 650°C Nyquist plots for 10 nm ZrO₂ coated LSCF-GDC NCCs in either 50 sccm of air or 20% O₂+80% He before and after 500 hours of 650°C aging in air. These gas mixtures have the same oxygen partial pressure, but (due to the smaller effective cross-sectional area of He vs N₂) oxygen in 20% O₂+80% He has a 3.5 times higher oxygen diffusivity than in air.¹³⁰ Therefore, the great reduction in the size of the ~2 Hz arc with a switch from air to 20%

 O_2 +80% He indicates that this low frequency arc is due to gas transport through the micro-sized pores (*i.e.* GDC scaffold pores which were partially filled with LSCF after infiltration and firing) within the cathode. Hence, even though previous reports have assigned the low-frequency EIS arc to a surface oxygen exchange process and the high-frequency EIS arc to interfacial oxygen ion transfer process in literature cathodes,^{131,132} here the low-frequency arc was attributed to gas diffusion within the cathode micropores due to its response to changes in gas composition and its temperature-independent magnitude shown in Figure 3.5.



Figure 3.6 Representative 650°C Electrochemical Impedance Spectroscopy Nyquist plots for 10 nm ZrO₂ coated 12 vol% LSCF-GDC NCCs tested in flowing air and flowing 20% O_2 +80% He gas mixtures before and after 500 hours of 650°C aging.⁸³

Figure 3.7 shows a 400-700°C open-circuit R_P comparison for as-produced 12 vol% LSCF-GDC cathodes with 0, 1, 2, 5 and 10 nm thick ZrO₂ overcoats. All cells displayed Arrhenius behavior and no significant R_P variation was present with overcoat thickness (*i.e.* all the observed variations were within the standard deviation produced by taking measurements on at least three identically produced cells). The fact that the ALD overcoats made here did not significantly alter the NCC performance is consistent with 1) nano-pores within the ALD coating (such as those shown in Figure 3.1 and observed in other studies)¹³³ facilitating gas transport to the LSCF surface, and 2) the small ZrO₂ ALD overcoat volume not choking off gas permeation through the cathode micropores. A change in activation energy (represented by the slope of the Arrhenius R_P vs 1000/T plot) was observed for all cells at 650°C, where the activation energy changed from 0.9 eV-1.0 eV between 400°C and 650°C to 0.66 eV-0.69 eV from 650°C to 700°C. This activation energy transition has also been reported previously^{53,109} and is likely caused by the transition from the LSCF oxygen surface exchange reaction being the dominant process below 650°C, which has a reported activation energy of 1.0 eV-1.3 eV in the literature, ^{54,65,109,134} to gas diffusion within the cathode micropores being the dominant resistance at and above ~700°C.



Figure 3.7 400-700°C polarization resistance of 0, 1, 2, 5 and 10 nm ZrO_2 coated 12 vol% LSCF-GDC NCCs. The error bars equal the R_P standard deviation of at least 3 cells.⁸³

Figure 3.8a and 3.8b show the normalized 1000 hour, 650°C open-circuit symmetric cell polarization resistance and ohmic resistance, respectively, for 12 vol% LSCF-GDC NCCs with 0, 1, 2, 5 and 10 nm of ZrO₂ overcoat. In keeping with the data reported in Figure 3.7, an initial 650°C R_P of 0.09 +/- 0.03 Ω cm² was observed for all cells regardless of the ALD overcoat thickness. For uncoated LSCF-GDC NCCs a "break-in" region was observed with an accelerated R_P increase during the first 48 hours. This "break-in" effect has been also observed previously in the

literature¹⁰⁹ and has been attributed in the literature to the rapid initial surface Sr enrichment of LSCF as the surface evolves from its nonequilibrium, fired state.⁷⁶ The linearized 0-1000 hour degradation rate measured here for uncoated cells was 45%/khrs. In contrast, 1, 2 and 5 nm ZrO₂ coated cells displayed approximately linear degradation behavior over their entire first 1000 hours of 650°C aging, displaying linear degradation rates of 28%/khrs, 18%/khrs, and 12%/khrs, respectively. For 10 nm ZrO₂ coated cells, however, severe non-linear degradation was observed with a linearized 0-1000-hour degradation rate of 87%/khrs. As shown in Figure 3.8b, a linear ohmic degradation rate of 3 +/- 2%/khrs was observed for all cells, regardless of the overcoat thicknesses. This relatively small R_0 degradation was attributed to the possible formation of resistive phases such as SrZrO₃ or the accumulation of impurities at the LSCF-GDC interface, the LSCF-current collector interface, or the electrolyte grain boundaries.¹¹⁸ It is important to note that the overall degradation rates of SOFCs made with these, or other nano-composite cathodes, are likely to be much less than the cathode degradation rates reported here, because SOFC anode and interconnect-related resistances become more dominant as the cathode performance improves.



Figure 3.8 Normalized 650°C (a) polarization resistance and (b) ohmic resistance aging behavior of 0, 1, 2, 5, and 10 nm ZrO₂ coated 12 vol% standard LSCF-GDC NCCs.⁸³

Figure 3.9 shows scanning electron microscope (SEM) images for a) uncoated, asproduced LSCF-GDC cathodes, b) uncoated, 1000 hour, 650°C aged LSCF-GDC cathodes, and cf) 1000 hour, 650°C aged LSCF-GDC NCCs with ZrO₂ overcoats of different thicknesses. In all cases, the LSCF infiltrate particles had an average size of 45 nm +/- 15 nm. Although an accurate comparison of the average particle size between cells was difficult due to local particle size variations, Simple Infiltrated Microstructure Polarization Loss Estimation (SIMPLE) model^{60,74,75} predictions indicated that an average particle size increase from 45 nm to 90, 77, 69, 64 and 128 nm would have been required to produce the amounts of 1000-hour degradation shown in Figure 3.8 for the 0, 1, 2, 5, and 10 nm coated cells, respectively. Since these predicted particle size changes are all significantly larger than that shown in Figure 3.9, LSCF particle size coarsening was not concluded to be the main degradation mechanism. This is consistent with the low $T_H =$ 0.46 homologous temperature used for here for NCC aging, and the work of Wang *et al.* who used a FIB-SEM reconstruction to image the cathode structure before and after 800 hours of 800°C ($T_{\rm H}$ =0.54¹³⁵) aging and reported that Sr surface segregation, rather than microstructural changes, were the reason for LSFC cathode degradation.¹¹⁸



Figure 3.9 SEM images of a) as-produced, b) standard after 1000 hours at 650°C, c) 1 nm ZrO₂ coated after 1000 hours at 650°C, d) 2 nm ZrO₂ coated after 1000 hours at 650°C, e) 5 nm ZrO₂ coated after 1000 hours at 650°C and f) 10 nm ZrO₂ coated after 1000 hours at 650°C 12 vol% LSCF-GDC NCCs.⁸³

Figure 3.10 shows the 650°C EIS Nyquist plot for 10 nm ZrO₂ coated LSCF-GDC NCC aged at 650°C for 0, 100, 500 and 1000 hours. The largest differences between the as-produced and aged 10 nm ZrO₂ coated LSCF-GDC NCC were observed in the high frequency region of the EIS spectra, instead of the low frequency, 2 Hz, region assigned in Figure 3.6 to gas concentration polarization within the micro-sized NCC pores. This suggests that choking-off of the micro-sized NCC pores with aging was not the main degradation mechanism. (Note, since gas diffusion within the ALD nano-pores is likely controlled by interactions with the nano-pore walls (through a

Knudsen diffusion process) and/or advection,¹³⁶ instead of through gaseous diffusion impeded by collisions with other gas molecules, the variable atmosphere EIS tests reported in Figures 3.6 and 3.10 are not expected to yield information on the behavior of gas transport within the ALD nanopores).



*Figure 3.10 Representative Electrochemical Impedance Spectroscopy Nyquist plots for 10 nm ZrO*₂ *coated 12 vol% LSCF-GDC NCCs aged in static air for 0, 100, 500 and 1000 hours at 650°C. Note, each spectrum has been vertically offset by an amount proportional to its aging time.*⁸³

Figure 3.11 shows X-ray Photoelectron Spectroscopy (XPS) surface composition ratios as a function of ALD overcoat thickness before and after 1000 hours of 650°C aging. These ratios show a similar decrease in the La/Zr, Sr/Zr, Co/Zr, and Fe/Zr ratio as the ALD coating thickness in the as-produced cells is increased closer to the ~3- 5 nm XPS penetration depth.^{137,138} After aging, this same trend and the same approximate values were seen in the La/Zr, Co/Zr, and Fe/Zr ratios. However, the Sr/Zr concentration ratio clearly increased after aging, suggesting that some of the Sr diffused into, and/or chemically reacted with, the ZrO₂ overcoat during 650°C aging.



Figure 3.11 X-ray Photoelectron Spectroscopy determined (a) La/Sr, (b) Sr/Zr, (c) Co/Zr, and (d) Fe/Zr ratios for 12 vol% LSCF-GDC NCCs with 0, 1, 2, 5 and 10 nm ZrO₂ overcoat before and after 1000 hours of 650°C aging. Error bars represent typical XPS standard deviations of 5%.⁸³

Figure 3.12a, and the detailed XPS peak deconvolutions shown in Figure 3.12b-d on which it is based, show that the amount of what is called "surface Sr" in the literature (i.e. Sr that is not in a perovskite structure and resides in phases such as SrO, Sr(OH)₂ and/or SrCO₃),^{102,128} is significantly reduced with 650°C aging for cells with ZrO₂ overcoats a few nm in thickness (Unfortunately, this analysis could not be conducted on cells with thicker ZrO₂ overcoats due to the low intensity of the Sr 3d XPS peak). As might be expected due to the low ALD fabrication temperature of 180°C, no significant change was observed in the as-produced "surface Sr" concentration with different ALD coating thicknesses. These results suggest that the lower Figure 3.8 R_P degradation rates for the NCCs with 1-5 nm of zirconia overcoat may be due to the removal of "surface Sr" by the ZrO₂ overcoat.



Figure 3.12 (a) The fraction of Sr that is "surface Sr" (as opposed to "lattice Sr") as determined from XPS Sr 3d peak deconvolutions for the b) 0 nm, c) 1 nm, and d) 2 nm ZrO₂ coated 12 vol% LSCF-GDC NCCs before and after 1000 hours of 650°C aging. Error bars represent standard deviation of 10%. Dashed lines are guide to the eye.⁸³

Figure 3.13 shows X-ray diffraction (XRD) scans indicating that ZrO₂ ALD overcoats chemically react with Sr at 650°C to form SrZrO₃. Specifically, a new peak at ~31° appeared in the X-ray diffractograms of porous LSCF samples coated with 5 or 10 nm of ZrO₂ overcoat and aged for 500 hours at 650°C in air. This peak corresponds to SrZrO₃'s most intense peak, the (002) peak which occurs at ~30.8° (JCPDS 00-010-0268). (Note, these experiments were conducted without GDC due to the strong GDC (111), (220) XRD peak overlap occurring with LSCF at ~27 and 47 degrees).



Figure 3.13 X-ray diffractograms of (a) 5 nm and (b) 10 nm ZrO₂ overcoated LSCF pellets before and after 500 hours of 650°C aging, compared to the reference patterns for (c) LSCF (JCPDS 00-048-0124), (d) SrZrO₃ (JCPDS 00-010-0268) and (e) SrCO₃ (JCPDS 00-005-0418).⁸³

Figure 3.14 shows detailed X-ray diffraction scans indicating that all the SrZO₃ peaks that do not overlap with LSCF or SrCO₃ (i.e. those at ~54.8° and ~64.2°) are present in 500-hour, 650°C-aged samples with 10 nm thick ZrO₂ overcoats (and may be present in 500-hour, 650°Caged samples with 5 nm thick ZrO₂ overcoats). The formation of SrZrO₃ between Sr-containing SOFC cathode materials and zirconia is widely reported in literature at temperatures above ~1000°C.^{139,140} Therefore, its formation here at such a low temperature of 650°C is somewhat surprising. However, the likely non-equilibrium nature of a ZrO₂ overcoat made at 180°C, the fact that SrZrO₃ is thermodynamically favored over zirconia and strontium oxide,¹⁴¹ the short diffusion distances involved in completely reacting an ALD coating only a few nanometers thick, the large contact areas involved, and the intimate contact between the LSCF surface strontium and the conformal ZrO₂ overcoat likely all conspired to allow SrZrO₃ formation at this low temperature of 650°C.



Figure 3.14 Detailed X-ray diffractograms for 5 and 10 nm ZrO₂ coated LSCF pellets after 500hour aging at 650°C, compared to that of an uncoated, unaged LSCF sample and the reference patterns for LSCF (JCPDS 00-048-0124), SrZrO₃ (JCPDS 00-010-0268) and SrCO₃ (JCPDS 00-005-0418).⁸³

Figure 3.15 shows a schematic of the degradation mechanisms hypothesized to be active in the zirconia overcoated LSCF-GDC NCCs examined here. Based on the XPS data of Figures 3.11 and 3.12, and consistent with previous reports in the literature,^{79,86,87,118,119} the uncoated LSCF-GDC *R_P* degradation observed in Figure 3.8 was attributed to Sr surface segregation. In contrast, based on the XPS and XRD data of Figures 3.11-3.14, the lower Figure 3.8 *R_P* degradation rates of LSCF-GDC NCCs with 1-5 nm thick zirconia overcoats were attributed to SrZrO₃ formation improving LSCF performance via "surface Sr" clean-up more than it hurt LSCF performance through a reduction in exposed LSCF surface area (ZrO₂ expands from a unit cell that has a volume of 138 A³ and 4 Zr atoms (JCPDS 00-017-0923), to a unit cell that has a volume of 276 A³ and 4 Zr atoms when it reacts with Sr to form SrZrO₃ (JCPDS 00-010-0268).) The decreasing Figure 3.8 degradation rate with increasing 1-5 nm coating thickness was attributed to the additional "surface Sr" storage capacity of thicker overcoats. Further, due to the thin, substrateconstrained nature of these 1-5 nm ALD overcoats, it was hypothesized that the nano-pores within these 1-5 nm thick overcoats remained intact even after SrZrO₃ formation. In contrast, the higher Figure 3.8 R_P degradation rates of LSCF-GDC NCCs with 10 nm thick zirconia overcoats was attributed to extensive SrZrO₃ formation that inactivated a large percentage of the exposed LSCF surface by covering it directly with electrochemically-inactive SrZrO₃^{142–144} and/or choking off some of the ALD overcoat nano-pores. ALD Nanopore choking is likely promoted by the higher pore aspect-ratios found in thicker overcoats and the fact that SrZrO₃-induced volume expansion into the pores at the top of the coating becomes greater as the coating thickness increases (since the top of the coatings are less constrained by the substrate as the thickness increases).



*Figure 3.15 Schematic of the hypothesized degradation mechanisms for uncoated and ZrO*₂*-coated LSCF-GDC NCCs.*⁸³

3.3 Conclusions

In conclusion, improved polarization resistance stability was observed for LSCF-GDC nano-composite cathodes containing zirconia overcoats ≤ 5 nm in thickness. In contrast, decreased polarization resistance stability was observed for LSCF-GDC nano-composite cathodes containing zirconia overcoats 10 nm in thickness. XPS and XRD data suggested that these trends were caused by a competition between the "surface Sr" clean-up and the reduction in electrochemically active

LSCF surface area caused by SrZrO₃ formation at 650°C. Taken together, this work demonstrates that, if structured correctly, on-board Sr-getters can be used to improve the performance stability of SOFC electrodes. This work also demonstrates that, in some situations, SrZrO₃ can form at temperatures much lower than previously realized and is actually a good thing for SOFC performance.

4 The Impact of Gd_{0.1}Ce_{0.9}O₂ Pre-Infiltration on the Performance and Stability of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃-Gd_{0.1}Ce_{0.9}O₂ and Sm_{0.5}Sr_{0.5}CoO₃-Gd_{0.1}Ce_{0.9}O₂ Nanocomposite Cathodes

4.1 Introduction

SOFC cathodes have been widely studied over the years due to their poor oxygen exchange kinetics and the large activation energy related to oxygen reduction reactions, which makes cathode resistance more dominant at lower temperatures.^{13,145} As a low-temperature, nano-sized material fabrication method, precursor solution infiltration has been widely used for SOFC composite electrode synthesis.^{72,108} During a typical infiltration process, different soluble precursor solutions are mixed in the stoichiometric ratio and added to micron-sized porous substrates such as gadolinium doped ceria (GDC) before fired at relatively low temperatures (usually 700°C to 800°C) in air to form nano-sized cathode catalysts.^{27,53,54,59,60,109} Common mixed ionic and electronic conducting (MIEC) materials such as La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF),^{53,54,109} $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC),^{27,59,60} and $La_{0.6}Co_{0.4}CoO_{3-\delta}$ (LSC)^{51,52}, as well as ionic conducting (IC) materials^{146–148} and precious metals ^{149,150} have all been added into porous substrates to form the SOFC composite cathode structure. A typical MIEC infiltrated IC scaffold cathode structure is shown in Figure 4.1. Due to the high surface area achieved by the small catalyst particle sizes, polarization resistance (R_P) for SOFC cathodes saw a great reduction and the operating temperature for SOFC cathodes were reduced to ~600°C.^{52,54,59,148}



Figure 4.1 Schematic drawing of the typical SOFC NCC structure

In an attempt to further reduce the R_P for SOFC cathodes, co-infiltration of MIEC and IC materials have been developed by adding both nano-sized MIEC and nano-sized IC particles into micron-sized IC scaffolds through precursor solution infiltration. The combination of the good oxygen exchange catalytic ability and electronic conductivity of MIEC materials and the good ionic conductivity of IC materials, together with the large number of active sites provided by the high surface areas has greatly reduced the cathode R_P and achieved some of the lowest operating temperatures for SOFC cathodes. Specifically, Burye *et al.* added nano-sized GDC particles into GDC scaffold before LSCF nitrate precursor solution infiltration and successfully reduced the cathode operating temperature by ~80°C.¹⁰⁹ Zhan *et al.* also reduced the 500°C R_P of SSC-(La,Sr)(Ga,Mg)O₃ (LSGM) NCC by more than 50% with the addition of 30 wt% nano-sized samarium doped ceria (SDC) particles into SSC-LSGM NCCs using nitrate solution coinfiltration.²⁷ In both cases, the operating temperature (the temperature at which 0.1 Ω cm² cathode R_P was reached) for SOFC cathodes was reduced below 550°C. Improvement in the long-term stability for GDC pre-infiltrated LSCF-GDC NCCs has also been reported.⁸³

Unfortunately, the role that the nano-sized IC particles plays for co-infiltrated SOFC NCCs is still under debate. Burye *et al.* reported that the addition of nano-sized IC particles led to the particle size reduction for MIEC materials, where average particle size for nano-sized LSCF were

reduced by ~50% with the addition of GDC nano-particles. The increased LSCF surface area caused by this size reduction was considered to be the sole reason for the improved electrochemical performance observed.¹⁰⁹ Similar R_P reduction for SDC/SSC co-infiltrated SSC-LSGM NCCs was also attributed to the size reduction of SSC nano-particles due to the addition of SDC.²⁷ Alternatively, Zhang et al.⁸³ owed the performance improvement to the decrease of inactive SrCO₃ impurity phases on the LSCF surface. Moreover, no conclusion has been reached for the degradation mechanism for IC and MIEC co-infiltrated SOFC NCCs. Due to their high melting points, IC materials were postulated to be the "stabilizer" for the nano-sized MIEC particles and the enhanced stability for MIEC/IC NCCs compared with MIEC NCCs was attributed to the suppressed MIEC particle coarsening.¹⁵¹ In other reports, nano-sized IC materials were considered "Sr getters" and their "clean up" effect during aging was considered the reason for the improved stability.⁸³

Therefore, for the work included in this chapter GDC precursor solution pre-infiltration was conducted on LSCF-GDC NCCs and SSC-GDC NCCs. Different electrochemical activity and aging behavior was observed between the two different materials and the possible reason for it was investigated through XRD, EIS, SEM and XPS characterization.

4.2 **Results and Discussion**

Figure 4.2 shows the formation of different impurity phases during precursor solution firing between LSCF and SSC. Both LSCF and SSC powder were obtained from precursor nitrate solution firing outside GDC scaffold due to the XRD peak overlap, as stated in Chapter 3. While LSCF and SSC perovskite phases both dominated their respective formed infiltrate particles with relative concentration of more than 85% based on their respective most intensive XRD peak intensity ((104) for LSCF and (121) for SSC), different impurity phases were observed between

them. For LSCF, the impurity phase was identified solely as SrCO₃, while Co₃O₄, SrCoO₃, SmCoO₃, and SrCO₃ impurities were all observed for SSC, with relative concentrations of 9%, 12%, 12% and 4%, respectively. The formation of impurity phases during MIEC precursor solution firing has been reported before for materials like LSCF^{53,54,109} and SSC^{27,60} and was likely due to the difference in solubilities of different cation nitrates.



Figure 4.2 X-ray diffractograms of as-produced LSCF and SSC powder and reference XRD patterns. (LSCF JCPDS 01-073-7747, SrCO₃ JCPDS 00-005-0418, SSC JCPDS 00-053-01112, Co₃O₄ JCPDS 00-043-1003, SrCoO₃ JCPDS 00-049-0692, SmCoO₃ JCPDS 00-025-1071)

Figure 4.3 shows the different effect of GDC pre-infiltration on the 400°C-700°C R_P of LSCF-GDC NCCs and SSC-GDC NCCs. Arrhenius behavior was displayed regardless of the cathode materials. An activation energy change at ~650°C was observed for all cells where the activation energy changed from 0.9 eV-1.0 eV between 400°C and 650°C to 0.66 eV-0.69 eV from 650°C to 700°C. In Chapter 3 LSCF-GDC NCCs that were fabricated in the same way has shown the same activation energy change.⁸³ The change was attributed to the transition from LSCF oxygen surface exchange reaction and interfacial charge-transfer process dominating the overall

resistance below 650°C to gas diffusion within the cathode being the dominate process above 650°C. Given the same loading level and similar porous GDC microstructure between LSCF-GDC NCCs and SSC-GDC NCCs, here the reason for activation energy change of SSC-GDC NCCs was considered to be the same. Moreover, great R_P enhancement was observed for GDC pre-infiltrated LSCF-GDC NCCs compared with standard ones. For SSC-GDC NCCs, however, no significant change in R_P was observed with the GDC pre-infiltration.



Figure 4.3 400-700°C polarization resistance of (a) standard and 7.5 vol% GDC pre-infiltrated LSCF-GDC NCCs and (b) standard and 7.5 vol% GDC pre-infiltrated SSC-GDC NCCs. The error bars equal the Rp standard deviation of at least 3 cells tested.

Figure 4.4 shows the difference in Nyquist plots for standard and 7.5 vol% GDC preinfiltrated 12 vol% LSCF-GDC NCCs and SSC-GDC NCCs tested from 400°C to 700°C in static air. For both materials one arc was observed at lower temperatures (below 550°C and 600°C for LSCF-GDC NCCs and SSC-GDC NCCs, respectively) and an additional arc at ~2 Hz showed up at higher temperatures. These Nyquist plot shapes observed here at different temperatures were similar to those reported in literature for LSCF-GDC NCCs^{53,54,109} and SSC-GDC NCCs^{27,60} as well. Given the temperature independent nature of the ~ 2 Hz low-frequency arc and its response to oxygen with different diffusivity studied in Chapter 3, this arc was attributed to be related to gas-diffusion processes in the cathode. This assignment is also consistent with other reports for LSCF-GDC NCCs.⁸³ Moreover, consistent with Figure 4.3, significant R_P reduction was observed with GDC pre-infiltration for LSCF-GDC NCCs, while standard and GDC pre-infiltrated SSC-GDC NCCs show no major difference in R_P . The R_P reduction was mostly observed at high-frequency region of Nyquist plots for GDC pre-infiltrated LSCF-GDC NCCs.



Figure 4.4 Nyquist plots for standard and 7.5 vol% GDC pre-infiltrated (a)-(g) 12 vol% LSCF-GDC NCCs and (h)-(n) 12 vol% SSC-GDC NCCs from 400°C to 700°C. Difference in ohmic resistance (R_0) at the same temperature was less than 2% between standard and pre-infiltrated cells and was removed from the plots. Nyquist plots for GDC pre-infiltrated cells were also moved vertically for better visualization.

Figure 4.5 assigns the high, intermediate and low-frequency region of Nyquist plots of 12 vol% LSCF (SSC) -GDC NCCs to LSCF (SSC)/GDC interfacial resistance, LSCF (SSC) surface oxygen exchange resistance and gas diffusion related resistance, respectively, by testing them in O₂ and N₂ gas mixtures with 40%, 20% and 5% O₂ from 400°C to 700°C. The frequencies marked here are the same as those of Figure 4.4 at different temperatures. The slight difference (in magnitude and shift of frequencies for different arcs) between standard LSCF-GDC NCCs in Figure 4.4 and 20% O_2 + 80% N_2 LSCF-GDC NCC Nyquist plots in Figure 4.5 was likely due to the different testing environments (flowing gas vs static air) and cell to cell R_P variations. LSCF-GDC NCCs tested at different oxygen partial pressures show one non-semi-circular arc at 400°C and 450°C. At 500°C, one non-semi-circular arc was observed for LSCF-GDC NCCs tested with 20% and 40% O₂, while an additional arc was observed at low-frequency region (at ~2 Hz) for cells tested with 5% O2. This additional ~2 Hz arc was observed for all LSCF-GDC NCCs tested above 500°C and increased in magnitude when cells were tested at lower oxygen partial pressures. Given the fact that this ~ 2 Hz arc a) only showed up at higher temperatures (above 500°C), b) became more pronounced at low oxygen partial pressures and c) was temperature-independent at the same testing environment, this arc was attributed to the oxygen gas diffusion-related processes. This assignment for the ~2 Hz arc is consistent with Figure 4.4 analysis and was also reported in literature for LSCF-GDC NCCs before.⁸³ Note that for LSCF-GDC NCCs tested at 400°C and 450°C, given the large overall resistance, this ~2 Hz arc could not be observed from Nyquist plots (that is, "low-frequency region" does not exist for LSCF-GDC NCCs tested at 400°C and 450°C). Different from the ~2 Hz arc, both high and intermediate-frequency region reduced in size with the temperature increase. At the same temperature, high-frequency region remained almost unchanged with the change of oxygen partial pressure while the intermediate region showed great

oxygen partial pressure dependence. Between the two main sources of resistances for SOFC MIEC cathodes,¹⁵² oxygen surface exchange resistance is highly dependent on oxygen partial pressure while interfacial resistance is considered to be oxygen partial pressure independent.^{153,154} Hence in this work the high-frequency region was identified as the LSCF/GDC interfacial resistance and intermediate-frequency region was assessed to be LSCF surface oxygen exchange resistance. Given the similar response from SSC-GDC NCCs, same assignment of Nyquist response at different frequencies was made for SSC-GDC NCCs as well.

This identification of three different frequency regions for Nyquist plots was also validated in literature for SOFC MIEC thin film electrodes.^{155,156} Low-frequency response was attributed to gas diffusion losses caused by insufficient oxygen diffusion in the contact gold meshes and porous current collecting layers. This region was found to be only pronounced at low oxygen partial pressures and/or high temperatures and has weak temperature dependence. Intermediate-frequency region response was considered to be the cathode "chemical losses", which represents the resistance that is mainly related to oxygen surface exchange reaction. This region was highly sensitive to oxygen partial pressure. The high-frequency response was attributed to be interfacial resistance related, which had little oxygen partial pressure dependence. Intermediate and highfrequency regions were both highly temperature dependent. Therefore, given the fact that the main difference between standard and GDC pre-infiltrated LSCF-GDC NCCs in Figure 4.4 originated from the high-frequency region at all temperatures, the GDC pre-infiltration enhanced the electrochemical performance of LSCF-GDC NCCs by reducing their interfacial resistance without significantly affecting their oxygen surface exchange kinetics.


Figure 4.5 Nyquist plots for standard (a)-(g) 12 vol% LSCF-GDC NCCs and (h)-(n) 12 vol% SSC-GDC NCCs tested in 100 sccm flowing $40\% O_2 + 60\% N_2$, $20\% O_2 + 80\% N_2$, $5\% O_2 + 95\% N_2$ gas mixtures from 400° C to 700° C

Figure 4.6 shows the detailed XRD scans on LSCF powder fabricated on top of nano-sized GDC powder in order to study the potential reaction between SrCO₃ and GDC nano-particles during precursor solution firing, which would resulted in the formation of SrCeO₃. Separate detailed scans were performed between 20°-21.4°, 41°-43.6° and 51°-53°. These XRD 20 ranges were chosen to study the (011), (400) and (231) peaks of SrCeO₃. These are the only three SrCeO₃ peaks that do not overlap with GDC, LSCF or $SrCO_3$ peaks. Although a new peak showed up at about 42.4°, which was likely the (400) peak of SrCO₃, (011) and (231) SrCeO₃ peaks were not observed, potentially due to the huge XRD background (SrCeO₃ (011) peak, as shown in Figure 4.6a) or the neighboring major XRD peaks (the ~52.8° SrCeO₃ (231) peak might not show up due to the huge ~53.2° LSCF (122) peak, as shown in Figure 4.6c). The fact that some of the SrCeO₃ peaks did not show up might not be surprising due to the small volume fraction of the potential SrCeO₃ phase (SrCO₃ only took up ~6% of the total volume and it was hypothesized that only a portion of the SrCO₃ reacted with GDC to form SrCeO₃). It was concluded that no conclusive and definitive evidence was provided from these detailed XRD scans that suggested the formation of SrCeO₃.



Figure 4.6 Detailed XRD scans for both LSCF powder fabricated on top of GDC powder and pure LSCF powder fabricated outside GDC powder (SrCO₃ JCPDS 00-005-0418, SrCeO₃ JCPDS 01-074-8250).

Figure 4.7 shows the different degradation behavior between 12 vol% LSCF-GDC NCCs and 12 vol% SSC-GDC NCCs with and without 7.5 vol% GDC pre-infiltration. For LSCF-GDC NCCs, R_P degradation mitigation effect was observed for GDC pre-infiltration, where degradation rate for the first 500 hours dropped from 37% for standard LSCF-GDC NCCs to 6% for 7.5 vol% GDC pre-infiltrated ones. SSC-GDC NCCs, on the other hand, showed no major change in degradation behavior with GDC pre-infiltration, where a degradation rate of 20% was observed for standard SSC-GDC NCCs and 19% for GDC pre-infiltrated ones. Consistent with previous report,⁸³ relatively small 500-hour R_0 degradation of 2% ± 1% was observed for all LSCF-GDC and SSC-GDC NCCs. The R_0 degradation was attributed to the possible formation of resistive phases or the accumulation of impurities at the electrolyte grain boundaries.⁸³



Figure 4.7 Normalized polarization resistance and ohmic resistance comparison between standard and 7.5 vol% GDC pre-infiltrated (a) LSCF-GDC NCC and (b) SSC-GDC NCC during 500-hour aging at 650°C.

Figure 4.8 shows the Nyquist plots for standard and 7.5 vol% GDC pre-infiltrated 12% LSCF-GDC NCCs and SSC-GDC NCCs after 650°C aging for 0, 240 and 500 hours. For all the

cells aged here, increase in magnitude of both high-frequency and intermediate-frequency region was observed with time, which according to analysis in Figure 4.5 suggests that the degradation for LSCF (SSC)-GDC NCCs happens at both LSCF (SSC) surface and LSCF (SSC)/GDC interface.



Figure 4.8 Nyquist plots for (a)standard LSCF-GDC NCCs, (b) GDC pre-infiltrated LSCF-GDC NCCs, (c) standard SSC-GDC NCCs and (d) GDC pre-infiltrated SSC-GDC NCCs after 0, 240 and 500-hour 650°C aging in static air.

Figure 4.9 shows the SEM images for a) standard 12 vol% LSCF-GDC NCCs, b) 7.5 vol% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs, c) standard 12 vol% SSC-GDC NCCs and d) 7.5 vol% GDC pre-infiltrated 12 vol% SSC-GDC NCCs before and after 500-hour, 650°C aging. Interconnected nano-sized LSCF/SSC particles were observed on top of micron-sized GDC scaffolds. Direct particle size comparisons between cells proved to be difficult due to the local particle size variations for the same cell. For the potential particle coarsening of aged LSCF-GDC NCCs, particle size analysis was performed on at least 8 SEM images and at least 50 LSCF particles for as-produced and aged standard and GDC pre-infiltrated LSCF-GDC NCCs. Based on the analysis, no major LSCF particle size increase was observed for aged cells compared with as-produced ones (see Table 4.1 - 4.4 for detailed analysis). Therefore, it is concluded that particle coarsening is not the degradation mechanism for standard or GDC pre-infiltrated LSCF-GDC NCCs. Given the similar fabrication method and cathode morphology between LSCF-GDC NCCs and SSC-GDC NCCs, degradation for SSC-GDC NCCs was not caused by particle coarsening, either.



Figure 4.9 SEM images for (a) standard 12 vol% LSCF-GDC NCCs, (b) 7.5 vol% GDC preinfiltrated 12 vol% LSCF-GDC NCCs, (c) standard 12 vol% SSC-GDC NCCs and (d) 7.5 vol% GDC pre-infiltrated 12 vol% SSC-GDC NCCs before and after 500-hour, 650°C aging.

	Average Particle Size	Standard Deviation	Overall Particle
	(nm)	(nm)	Size (nm)
a	38.8	6.4	
b	38.6	5.9	
С	35.6	7.1	
d	35.3	11.0	27.0 ± 8.0
e	44.0	8.6	57.9 ± 6.0
f	38.5	7.0	
g	36.6	6.3	
h	35.7	7.3	

Table 4.1 SEM-Determined Particle Size Summary for Standard 12 vol% LSCF-GDC NCCs.

Table 4.2 SEM-Determined Particle Size Summary for 7.5 vol% GDC Pre-Infiltrated 12 vol% LSCF-GDC NCCs.

	Average Particle Size	Standard Deviation	Overall Particle
	(nm)	(nm)	Size (nm)
a	54.2	11.3	
b	38.6	6.7	
С	35.1	8.2	
d	38.2	8.1	38.1 ± 10.0
e	35.7	7.4	
f	37.1	6.7	
g	34.7	8.1	
h	31.2	4.3	

Table 4.3 SEM-Determined Particle Size Summary for Standard 12 vol% LSCF-GDC NCCs After 650°C Aging for 1000 Hours

	Average Particle Size	Standard Deviation	Overall Particle
	(nm)	(nm)	Size (nm)
a	49.8	8.1	
b	25.7	3.1	
с	36.2	4.6	
d	33.7	6.1	37.6 ± 8.6
e	40.4	3.4	
f	39.2	5.4	
g	42.9	6.1	
h	32.0	4.3	

	Average Particle Size	Standard Deviation	Overall Particle
	(nm)	(nm)	Size (nm)
a	40.2	7.8	
b	41.0	5.8	
С	36.6	5.0	
d	41.6	6.1	41.2 ± 7.0
e	42.5	9.0	
f	42.1	9.0	
g	42.0	6.4	
h	44.1	7.9	

Table 4.4 SEM-Determined Particle Size Summary for 7.5 vol% GDC Pre-Infiltrated 12 vol% LSCF-GDC NCCs After 650°C Aging for 1000 Hours

Table 4.5 shows the relative overall Sr concentration for standard and GDC pre-infiltrated LSCF-GDC NCCs ([Sr]/[La+Sr+Co+Fe]) and SSC-GDC NCCs ([Sr]/[Sm+Sr+Co]) before and after 650°C, 500-hour aging, determined by XPS detailed elemental scans. For as-produced LSCF-GDC NCCs, relative Sr concentration decreased significantly from 46% to 16% for LSCF-GDC NCCs with GDC pre-infiltration, while no similar change was observed for as-produced SSC-GDC NCCs. The relative Sr concentration decrease with the addition of nano-sized GDC particles indicates the removal of Sr species on the sample surface. Based on the SrCO₃ phase observed in as-produced LSCF powder shown in Figure 4.2a, it is hypothesized that the pre-infiltrated GDC particles resulted in the decrease of SrCO₃ for as produced LSCF-GDC NCCs. After 500-hour, 650°C aging, no major change in relative overall Sr concentration was observed for either LSCF-GDC NCCs or SSC-GDC NCCs. This is likely due to the combined effect of Sr surface segregation towards the sample surface and SrCO₃ species re-incorporating into the LSCF lattice way from the sample surface.⁸³

	LSCF-GDC	SSC-GDC
	[Sr]/[La+Sr+Co+Fe]	[Sr]/[Sm+Sr+Co]
As-Produced Standard	0.46	0.63
As-Produced GDC Pre-infiltrated	0.16	0.58
Aged Standard	0.45	0.63
Aged GDC Pre-infiltrated	0.13	0.64

Table 4.5 XPS-Determined Ratios of the Total Sr Concentration Relative to that of All the Other MIEC Cations on the Surface

Figure 4.10 shows Sr 3d peak deconvolutions for as-produced and GDC pre-infiltrated LSCF-GDC NCCs and SSC-GDC NCCs before and after aging and Table 4.6 summarizes the relative amount of "surface Sr" obtained from the Figure 4.10 Sr deconvolution. For as-produced LSCF-GDC NCCs, the addition of nano-sized GDC particles through GDC pre-infiltration greatly reduced the amount of "surface Sr", which represents the inactive Sr species such as SrO, Sr(OH)2 and SrCO₃.^{78,102} This "surface Sr" reduction, together with the SrCO₃ impurity phase observed in Figure 4.2 for as-produced LSCF powder and overall Sr concentration decrease in Table 4.5, suggests again that the reduction of interfacial resistance for GDC pre-infiltrated LSCF-GDC NCCs compared with standard ones shown in Figure 4.4 was attributed to reduction of SrCO₃ due to the addition of nano-sized GDC particles. This reduction cleaned up the LSCF/GDC interface and thus reduced the initial interfacial resistance for LSCF-GDC NCCs. On the other hand, because of the small amount of SrCO₃ impurities observed for as-produced SSC powder, only slight "surface Sr" reduction was observed with GDC pre-infiltration thus no major difference in initial R_P was observed between standard and GDC pre-infiltrated SSC-GDC NCCs. After 500hour, 650°C aging "surface Sr" content of GDC pre-infiltrated LSCF-GDC NCCs was still significantly smaller than that of standard LSCF-GDC NCCs, which shows that the "SrCO₃ reduction" effect of nano-sized GDC particles cleaned up LSCF surface over aging. Similar effect was not observed for SSC-GDC NCCs due to the difference in surface impurities, which likely caused the different degradation behavior shown in Figure 4.7.



Figure 4.10 Sr 3d peak deconvolutions for (a)standard LSCF-GDC NCCs, (b) GDC pre-infiltrated LSCF-GDC NCCs, (c) standard SSC-GDC NCCs and (d) GDC pre-infiltrated SSC-GDC NCCs before and after aging.

Table 4.6 XPS-Determined Percent of Sr Corresponding to "Surface Sr" Compared with Total Amount of MIEC Cations

	LSCF-GDC	SSC-GDC
	[Surface Sr]/	[Surface Sr]/
	[La+Sr+Co+Fe]	[Sm+Sr+Co]
As Produced Standard	0.29	0.38
As Produced GDC Pre-infiltrated	0.06	0.33
Aged Standard	0.23	0.42
Aged GDC Pre-infiltrated	0.08	0.43

4.3 Conclusions

In this work GDC pre-infiltration was performed on both LSCF-GDC NCCs and SSC-GDC NCCs and difference in initial R_P and degradation behavior was observed. Pre-infiltrated nano-sized GDC particles were shown to reduce the concentration of inactive SrCO₃ impurities on the LSCF surface, which cleaned up the LSCF surface during cell fabrication and aging. This "SrCO₃ reduction" effect was the reason for the improved R_P and stability for GDC pre-infiltrated LSCF-GDC NCCs. For SSC-GDC NCCs on the other hand, due to the lack of SrCO₃ impurity phase, no major R_P or durability enhancement of GDC pre-infiltration was observed. This work not only showed the possibility of improving both the initial electrochemical performance and long-term stability of LSCF-GDC NCCs, but also emphasized the importance role that surface chemistry for MIEC materials plays for the performance and durability of SOFC cathodes.

5 The Impact of ZrO₂ ALD Overcoats on Gd_{0.1}Ce_{0.9}O₂ Pre-Infiltrated La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃-Gd_{0.1}Ce_{0.9}O₂ Nanocomposite Cathodes

5.1 Introduction

Studies on improving the electrochemical performance of SOFC cathodes have seen great surge over the last several years and high performance infiltrated SOFC cathodes such as LSCF infiltrated GDC⁵³ and SSC infiltrated LSGM²⁷ has reached a polarization resistance of 0.1 Ω cm² below 550°C. These infiltrated SOFC cathodes have shown great potential towards the further development of SOFCs with intermediate operating temperatures. However, as stated earlier, longterm stability of high performance SOFC cathodes has been one of the limiting factors for the commercialization of SOFCs. Polarization resistance (R_P) degradation rates of 49%/khrs⁵³ and 94%/khrs⁵² have been reported for high performance LSCF infiltrated GDC electrodes, which are far above the preferred degradation rate for commercial SOFCs. In Chapter 3, 1-5 nm ZrO₂ ALD overcoats have shown to be able to improve the long-term stability of LSCF-GDC NCCs without altering their initial electrochemical performance. In Chapter 4 GDC pre-infiltration has successfully enhanced both the initial R_P and the long-term stability of LSCF-GDC NCCs. Both ZrO₂ overcoats and pre-infiltrated GDC nano particles can reduce the SrCO₃ impurities on the LSCF surface during aging, which clean up the LSCF surface and lead to the improved long-term stability of LSCF-GDC NCCs. Hence the hypothesis of the work contained in this chapter is to study the effect of the combination of ZrO₂ overcoating and GDC pre-infiltration on the electrochemical performance and stability of LSCF-GDC NCCs. 1 and 5 nm ZrO₂ overcoat was deposited on 7.5 vol% GDC pre-infiltrated LSCF-GDC NCCs. The initial electrochemical performance and long-term stability for these cells were evaluated and different electrochemical,

structural and surface characterizations were conducted to investigate the observed change in R_P and long-term degradation rates.

5.2 **Results and Discussion**

Figure 5.1 shows the R_P for GDC pre-infiltrated LSCF-GDC NCCs with different ZrO₂ overcoat thicknesses at different temperatures. Slight R_P reduction was observed for coated cells at temperatures below 550°C. Above 550°C, no significant R_P change was observed. Based on the Nyquist plot analysis shown in Figure 5.2 for standard, 7.5 vol% GDC pre-infiltrated and 5 nm ZrO₂ coated 7.5% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs at 400°C, 450°C and 500°C, different from the enhancement effect of GDC nano particles (discussed in Chapter 4), here significant change in the "intermediate frequency" region (below 7 Hz, 25 Hz and 68 Hz for cells tested at 400°C, 450°C and 500°C, respectively) was observed for 5nm ZrO₂ coated GDC pre-infiltrated LSCF-GDC NCCs compared with uncoated GDC pre-infiltrated cells. This region was analyzed in Chapter 4 to be related to surface oxygen exchange processes. Therefore, ZrO₂ overcoat enhanced the oxygen surface exchange processes for GDC pre-infiltrated LSCF-GDC NCCs at temperatures below 550°C.



Figure 5.1 Rp vs temperature for 7.5 vol% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs with 0, 1 and 5 nm ZrO₂ overcoats.



Figure 5.2 Nyquist plot analysis for standard, 7.5 vol% GDC pre-infiltrated and 5 nm ZrO₂ coated 7.5 vol% GDC pre-infiltrated LSCF-GDC NCCs at (a) 400°C, (b) 450°C and (c) 500°C.

Figure 5.3 shows the degradation behavior for 7.5% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs with 0, 1 and 5 nm ZrO₂ overcoats. Different from the degradation mitigation effect discovered for 1-5 nm ZrO₂ overcoats on standard LSCF-GDC NCCs, here uncoated GDC pre-infiltrated LSCF-GDC NCCs showed the lowest R_P degradation rate of ~10%/khrs, with 1 nm and 5 nm ZrO₂ coated GDC pre-infiltrated LSCF-GDC NCCs showing degradation rates of 22%/khrs

and 21%/khrs, respectively. Similar to ZrO_2 coated standard LSCF-GDC NCCs, no significant R_0 degradation was observed.



Figure 5.3 Normalized polarization resistance and ohmic resistance comparison between 7.5 vol% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs with 0, 1and 5 nm ZrO₂ overcoats over 1000 hours at 650°C.

Figure 5.4 shows the Nyquist plots after 0, 100, 500 and 1000-hour aging at 650°C for GDC pre-infiltrated LSCF-GDC NCCs with 0, 1 and 5 nm ZrO₂ overcoats. Similar to the Nyquist analysis performed in Chapter 4, all the Nyquist plots were divided into three different "frequency regions", with each frequency region representing a different electrochemical process related to the overall oxygen reduction reaction. Previous controlled atmosphere Nyquist analysis (discussed in Chapter 4) has shown that the high-frequency region was related to the interfacial resistance between LSCF and GDC and the intermediate-frequency region represented the oxygen surface

exchange process. The low-frequency region at \sim 2 Hz was proved to be related to gas diffusion. Based on this analysis, both degradation in interfacial process and oxygen surface exchange process happened during 650°C aging for all cells regardless of the overcoat thickness.



Figure 5.4 Nyquist plots for 7.5 vol% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs with (a) 0, (b) 1, (c) 2 and (d) 5 nm ZrO₂ overcoats after 0, 100, 500 and 1000-hour 650°C aging in static air.

Figure 5.5 shows the SEM images for as-produced GDC pre-infiltrated LSCF-GDC NCCs and aged GDC pre-infiltrated LSCF-GDC NCCs with 0, 1 and 5 nm ZrO₂ overcoats. Same with LSCF-GDC NCCs fabricated in a similar way shown in Chapter 3 and Chapter 4, inter-connected LSCF particles can be observed on top of sintered micron-sized GDC scaffold. Similar to standard LSCF-GDC NCCs discussed in Chapter 3 and Chapter 4, here no major LSCF particle size difference was observed between cells with different overcoat thicknesses. Comparing Figure 5.5a and Figure 5.5b, no particle coarsening was observed for GDC pre-infiltrated LSCF-GDC NCCs after 500-hour aging at 650°C either. Therefore, LSCF particle coarsening was not the major degradation mechanism for these GDC pre-infiltrated LSCF-GDC NCCs with different ZrO₂ overcoat thicknesses.



*Figure 5.5 SEM images for (a) as-produced standard, (b) aged standard, (c) aged 1 nm ZrO*² *coated and (d) aged 5 nm ZrO*² *coated 7.5% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs.*

Figure 5.6 shows the XPS surface composition ratios as a function of ALD overcoat thickness before and after 650°C aging for 1000 hours. For as-produced cells, the [La]/[Zr], [Sr]/[Zr], [Co]/[Zr] and [Fe]/[Zr] ratios decreased with the ZrO₂ overcoat thickness reaching the XPS penetration depth of ~3-5 nm.^{137,138} For 1 nm ZrO₂ coated GDC pre-infiltrated LSCF-GDC NCCs, significant increase in [cation]/[Zr] ratios was observed for all LSCF cations after aging. This is different from the similar analysis shown in Figure 3.11 for 1 nm ZrO₂ coated standard LSCF-GDC NCCs, where only [Sr]/[Zr] ratio increased significantly after aging. Moreover, the [La]/[Zr], [Sr]/[Zr], [Co]/[Zr] and [Fe]/[Zr] ratios for aged cells were all significantly larger than those for aged 1 nm ZrO₂ coated standard LSCF-GDC NCCs. For 5 nm coated cells, only slight increase was observed for all the aged cells compared with as-produced ones, presumably due to the detection depth of ~3-5 nm XPS penetration depth.^{137,138} This increase in all [cation]/[Zr] ratios for 1 nm ZrO₂ coated GDC pre-infiltrated LSCF-GDC NCCs suggests the possible reaction

between ZrO_2 overcoats and GDC nano particles, which reduced the thickness of ZrO_2 overcoats and caused the increase of relative concentration for all cations. The reaction between ZrO_2 and ceria has been widely reported in literature before.^{157,158} The significant amount of Sr on the sample surface for aged cells (reaching a [Sr]/[Zr] ratio of ~2.5) also indicates the accumulation of Sr species on the LSCF surface. This Sr accumulation was likely caused by the reduced "SrCO₃ reduction" capability of GDC nano particles, possibly caused by the reaction between ZrO_2 overcoat and GDC mentioned above. The compromise of "SrCO₃ reduction" capability was also hypothesized to be the reason for the higher degradation rate of ZrO_2 coated GDC pre-infiltrated LSCF-GDC NCCs compare with uncoated ones.



Figure 5.6 XPS determined (a) La/Sr, (b) Sr/Zr, (c) Co/Zr, and (d) Fe/Zr ratios for 7.5 vol% GDC pre-infiltrated 12 vol% LSCF-GDC NCCs with 0, 1 and 5 nm ZrO₂ overcoat before and after 1000 hours of 650°C aging. Error bars represent XPS standard deviations of 5%.

5.3 Conclusions

In this chapter both ALD ZrO₂ overcoating and GDC pre-infiltration were conducted on 12 vol% LSCF-GDC NCCs. Unfortunately, the addition of the two different Sr getters did not further improve the long-term stability of LSCF-GDC NCCs. While particle coarsening was still not considered to be the major degradation mechanism, increased amount of Sr was observed for ZrO₂ coated cells after aging. Meanwhile, all the [cation]/[Zr] ratios increased for aged cells compared with as-produced ones, which was different from what was observed for ZrO₂ coated standard LSCF-GDC NCCs discussed in Chapter 3. The reason for it was hypothesized to be the reaction between ZrO₂ overcoats and pre-infiltrated GDC nano particles, which led to the reduction of ZrO₂ thickness and at the same time compromised the "SrCO₃ reduction" capability of GDC nano-particles.

6 Precursor Solution Infiltration on SOFC Anodes and Its Effect on Full Cell Performance

6.1 Introduction

Solid oxide fuel cells (SOFCs) are an attractive power generation technology due to a number of advantages over other chemical to electricity conversion technologies, such as their high volumetric and gravimetric power density, high energy conversion efficiency, and fuel flexibility.^{2,3,6} A typical SOFC cell consists of three major components: cathode, electrolyte and anode. Due to the relative high activation energy of oxygen surface exchange related processes, SOFC cathodes have long been considered to be the most resistive layer for SOFCs, especially at reduced temperatures.^{3,13,32,64,108,145,159–171} Therefore much effort has been made to optimize the cathode microstructure as well as find more catalytically active SOFC cathode materials. Specifically, SOFC cathode materials have developed from conventional electron conducting perovskite materials like (La, Sr)MnO₃ (LSM)¹⁷²⁻¹⁷⁴ to highly active mixed ionic and electronic conducting (MIEC) materials like La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ (LSCF), ^{53,54,83,109} Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC), ^{27,59,60} and La_{0.6}Co_{0.4}CoO₃₋₈ (LSC).^{51,52} New electrode fabrication methods such as precursor solution infiltration have also been applied to make nano-sized catalysts for SOFC cathodes and the new nano-composite cathode (NCC) structure has further reduced the cathode R_{P} .^{72,108} Thanks to the performance improvement of cathodes, the operating temperature for SOFCs has reduced from ~1000°C to ~600°C. 52,54,59

Several recent reports, however, have shown that SOFCs with catalytically active cathodes experienced major change in full cell performance by modifying the anode materials and microstructures.^{175–177} In some reports EIS analysis on symmetric electrodes also suggested that SOFC cathode and anode have similar R_P .²⁷ The fact that the anode performance can potentially have great impact on the full cell performance not only calls for more attention to the previously somewhat neglected SOFC anode studies, but could also potentially change the way the SOFC community evaluates performance and stability for SOFC cathodes under current, where full cell performance and stability were considered the indicator of the performance and stability of the cathodes due to the belief that anode resistance and degradation are negligible.

Therefore, in order to re-evaluate the long-lasting belief that cathodes are the most resistive layer for SOFCs, I-V tests for commercial Ni-YSZ anode/YSZ electrolyte/GDC interlayer supported full cells with commercial LSC cathode and high performance LSCF-GDC NCCs were conducted at 550°C, 600°C and 650°C. Nano-sized NiO anode infiltration was also performed to investigate the effect of anode performance improvement on full SOFC cell performance. Moreover, EIS tests on symmetric uninfiltrated Ni-YSZ anodes, NiO infiltrated Ni-YSZ anodes and LSCF-GDC NCCs were also performed at 550°C, 600°C to investigate the open circuit voltage (OCV) R_P difference between commercial anodes and high performance cathodes.

6.2 Results and Discussion

Figure 6.1a and Figure 6.1b show the microstructures for commercial Ni-YSZ anode/YSZ electrolyte/GDC interlayer substrates with commercial LSC cathodes and high performance LSCF-GDC NCCs that were used for I-V analysis, respectively. For both cells a sintered ~15 μ m Ni-YSZ functional layer with fine structure was observed, supported by a thick, more porous Ni-YSZ support layer. The functional layer serves as the catalytic layer for the SOFC anode reaction while support layer transports electrons and allows for the gas flow. The ~3 μ m GDC interlayer between the cathode layer and the ~3 μ m dense YSZ electrolyte layer serves as a barrier to prevent the widely-reported reactions between La and Sr-containing cathode materials and YSZ electrolyte at high sintering temperatures during cell fabrication.^{139,140} Commercial LSC cathodes show sintered particles of ~200 nm in diameter while micron-sized GDC scaffold covered with nano-

sized LSCF particles was observed for LSCF-GDC NCCs. Figure 6.1c shows the high-resolution SEM image for the LSCF-GDC NCC structure. Interconnected nano-sized LSCF particles of ~ 50 nm in diameter were observed sitting on top of micron-sized sintered GDC scaffold. Here the nano-sized LSCF particles serve as high surface area, highly active oxygen reduction catalyst while sintered GDC scaffold offers fast oxygen ion conduction. Similar cathode structure was observed in literature for similarly made LSCF-GDC NCCs as well.^{53,54,83,109} Figure 6.1d shows microstructure for commercial Ni-YSZ anode with infiltrated NiO particles. Similar to LSCF-GDC NCC structure, NiO nano-particles ~50 nm were observed on the sintered Ni-YSZ scaffold.



Figure 6.1 Representative SEM images of (a) commercial full cell, (b) commercial anode/electrolyte substrate with homemade LSCF-GDC NCCs, (c) LSCF infiltrated GDC scaffold and (d) NiO infiltrated Ni-YSZ scaffold.

Figure 6.2 shows the potential, power density vs current density plots for (a) commercial Ni-YSZ anode/YSZ electrolyte/GDC interlayer substrates with commercial LSC cathode and high performance LSCF-GDC NCCs and (b) uninfiltrated and NiO infiltrated commercial Ni-

YSZ/YSZ/GDC substrate with LSCF-GDC NCCs at 550°C, 600°C and 650°C. OCV and peak power densities for the three cells at different temperatures were summarized in Table 6.1. Between commercial substrates with LSC cathodes and high performance LSCF-GDC NCCs (shown in Figure 6.2a), little difference in OCV or peak power densities were observed at all temperatures. The fact that changing the full cell cathode from commercial LSC to high performance LSCF-GDC NCCs resulted in little difference in I-V performance suggests that cathode performance did not have a major impact on the full cell performance. The increase in peak power densities at all these temperatures with the infiltration of nano-sized NiO catalysts into the anode shown in Figure 6.2b also suggests that the anode, rather than the cathode, is the most resistive, performance limiting layer for the full cell tested here. It is worth mentioning that increase in OCV was observed for NiO anode infiltrated commercial substrates with LSCF-GDC NCCs compared with uninfiltrated ones. This OCV increase with anode infiltration was attributed to the filling of pinholes in the YSZ electrolytes because of the infiltration of nickel nitrate solution.



Figure 6.2 Potential, power density vs current density plots for (a) commercial Ni-YSZ/YSZ/GDC substrates with commercial LSC and high performance LSCF-GDC NCC and (b) commercial and NiO infiltrated Ni-YSZ/YSZ/GDC substrate with LSCF-GDC NCC at 550°C, 600°C and 650°C.

Table 6.1 OCV and Peak Power Densities for All the Cells Tested in Figure 6.2 at 550°C, 600°C and 650°C

		550°C	600°C	650°C
Commercial substrate with	OCV (V)	1.06	1.05	1.04
commercial LSC cathode	Peak Power Density (W/cm ²)	0.21	0.41	0.54
Commercial substrate with	OCV (V)	1.06	1.04	1.03
high performance LSCF- GDC NCC	Peak Power Density (W/cm ²)	0.22	0.41	0.55
NiO infiltrated commercial	OCV (V)	1.11	1.10	1.09
substrate with high performance LSCF-GDC NCC	Peak Power Density (W/cm ²)	0.26	0.49	0.70

Figure 6.3a shows the OCV R_P improvement effect of NiO anode infiltration on symmetric Ni-YSZ anodes at 550°C, 600°C and 650°C. Both uninfiltrated and infiltrated symmetric anode

cells were tested in 3% H₂ balanced with argon. Despite the difference in H₂ concentration between EIS test (3%) and I-V test (97%) in Figure 6.2, the little difference in oxygen partial pressure makes the anode symmetric cell test an indicator of the anode OCV performance for full SOFC cells, as suggested in other literature as well.¹⁷⁸ One non-circular arc was observed for all cells at all temperatures. NiO infiltrated Ni-YSZ anodes saw a ~50% R_P decrease compared with uninfiltrated ones, which was consistent with the I-V performance improvement for NiO anode infiltrated full cells shown in Figure 6.2b. Similar to full cells, here the symmetric cell R_P reduction for NiO infiltrated Ni-YSZ was also attributed to the increased catalytic ability introduced by the additional nano-sized NiO catalyst. This R_P reduction also suggests that gas polarization resistance was not rate limiting for Ni-YSZ symmetric cells tested in 3% H₂. Figure 6.3b shows the OCV R_P for LSCF-GDC NCCs obtained from symmetric cathode tests at 550°C, 600°C and 650°C. Similar to literature reports for LSCF infiltrated GDC SOFC cathodes, two arcs were observed for cells tested at all three temperatures.^{53,54,83,109} High-frequency arc was considered to be cathode interfacial and surface oxygen exchange response while low-frequency arc was attributed to gasdiffusion related processes.⁸³ Comparing the R_P values from Figure 6.3a and Figure 6.3b, the R_P for uninfiltrated Ni-YSZ anode was 8-9 times higher than LSCF-GDC NCC R_P across all temperatures. This great difference in R_P again suggests that when high performance SOFC cathodes like LSCF-GDC NCCs are utilized for SOFCs, anodes are likely to be the most resistive layer.



Figure 6.3 Nyquist plots (a) commercial Ni-YSZ anode and NiO infiltrated commercial Ni-YSZ anode and (b) high performance LSCF-GDC NCCs at 550°C, 600°C and 650°C. The ohmic resistance for all the plots has been removed for better comparison.

6.3 Conclusions

In this chapter full SOFC tests were performed and showed that NiO anode infiltration improved the I-V performance for SOFC full cells while switching the SOFC cathode from the commercial LSC cathode to high performance LSCF-GDC NCCs showed no effect on their I-V performance. Moreover, commercial Ni-YSZ anode shows higher OCV R_P than LSCF-GDC NCCs from EIS tests on symmetric electrodes and similar to full cell performance, NiO anode infiltration reduced the OCV R_P for Ni-YSZ anodes. Taken these together, this chapter shows that contrary to the popular belief in the SOFC community that cathode is the most resistive layer for SOFCs, anode R_P can also be dominant among the SOFC components. Given that the dominant anode R_P would only be more problematic with the improvement of cathode and electrolyte performance, more attention should be paid on the improvement on SOFC anodes as well in order to achieve exceptional SOFC electrochemical performance.

7 Dissertation Conclusions and Future Work

In summary, the electrochemical performance and long-term stability for SOFC infiltrated nano-composite electrodes have been investigated and surface decoration methods such as GDC pre-infiltration and ZrO₂ ALD overcoating have been conducted on the infiltrated cathodes and shown impact on their performance and/or durability. The reason for the possible impact observed was investigated through various EIS, XPS, XRD and SEM analyses and possible mechanism of the electrochemical performance change and degradation behavior of these infiltrated nano-composite electrodes was proposed.

Specifically, ALD ZrO₂ overcoats of different thicknesses were applied on LSCF-GDC NCCs. While no major R_P change was observed for all the ZrO₂ coated cells from 400°C to 700°C, the long-term stability of these cells was shown to be greatly dependent on the overcoat thickness. 1-5 nm ZrO₂ overcoats enhanced the stability of LSCF-GDC NCCs while cells with 10 nm ZrO₂ overcoats resulted in higher degradation rate over the 1000-hour aging at 650°C. While SEM analysis showed no evidence of LSCF nano-sized particle coarsening, XPS analysis on aged cells showed increased amount of Sr signal on the sample surface compared with as-produced LSCF-GDC NCCs, and detailed XRD scan suggested the formation of SrZrO₃ phase for cells after 1000-hour aging at 650°C. It was thus proposed that ZrO₂ overcoats served as the "Sr getter" during aging and reacted with inactive Sr species (such as SrO, SrCO₃) that formed due to the Sr surface segregation. This reaction cleaned up the LSCF surface and caused the degradation rate decrease. With 10 nm ZrO₂ overcoats, too much SrZrO₃ started to accumulate on the surface of LSCF, blocking the active sites and possibly the gas diffusion, which resulted in the increased degradation rate.

In order to develop a more costly effective Sr getter and at the same time validate the proposed mechanism, GDC pre-infiltration was performed on LSCF-GDC NCCs and SSC-GDC NCCs. The added nano-sized GDC particles simultaneously improved the electrochemical performance and long-term stability for LSCF-GDC NCCs, while no change in either R_P or degradation rate was observed for SSC-GDC NCCs. XPS results showed the decrease in the concentration of inactive Sr species on the sample surface for GDC pre-infiltrated LSCF-GDC NCCs compared with standard ones. The inactive Sr species were identified as SrCO₃ and less SrCO₃ concentration was also observed for aged GDC pre-infiltrated LSCF-GDC NCCs. This "SrCO₃ reduction" was the reason for the improved initial performance and long-term stability for GDC pre-infiltrated LSCf-GDC NCCs. For SSC-GDC NCCs, however, besides SrCO₃, Co₃O₄, SmCoO₃ and SrCoO₃ phases also formed during solution firing and aging. Since GDC nano particle cannot reduced the concentrations these impurities, no impact on the R_P and degradation rate of SSC-GDC NCCs was observed. Moreover, Nyquist plot analysis was performed on both materials, where different temperature and oxygen pressure were used during electrochemical tests. Three different regions that represented three different oxygen reduction reaction processes were identified from Nyquist plots. Based on these assignments, the R_P enhancement effect for GDC pre-infiltration on LSCF-GDC NCCs was attributed to the interfacial resistance reduction, while both interfacial resistance and surface exchange resistance increased during aging.

To further improve the performance and stability of LSCF-GDC NCCs, 1-5 nm ZrO₂ overcoats were applied on GDC pre-infiltrated LSCF-GDC NCCs. Unfortunately, higher degradation rate was observed for coated cells compared with uncoated ones. XPS analysis showed slightly increased amount of La, Co and Fe and significantly more Sr on the sample surface of aged cells, while less Zr signal was observed for aged cells compared with as produced ones. This

suggested that there might be a reaction between pre-infiltrated GDC particles and ZrO₂ overcoat during aging, which compromised the "SrCO₃ reduction" capability of GDC nano particles and resulted in the accumulation of inactive Sr species on the LSCF surface. These inactive Sr species blocked the active sites and led to higher degradation rate for ZrO₂ coated GDC pre-infiltrated LSCF-GDC NCCs.

Finally, full cell tests were conducted on commercial Ni-YSZ/YSZ/GDC substrate with commercial LSC cathodes and lab-made high performance LSCF-GDC NCCs and no peak power density difference was observed. With some anode Ni infiltration, however, full cell peak power density increased by ~25%. It suggested that contrary to the popular belief, anode might be the most resistive layer of SOFCs, especially for SOFCs with high performance cathodes. Symmetric anode tests were also performed on both commercial Ni-YSZ anodes and lab-made Ni infiltrated GDC anodes. The lower R_P for Ni infiltrated GDC anodes not only showed the less-than satisfactory performance of commercial anodes, but also proved that precursor solution infiltration can also be used for fabricating high performance nano-composite anodes.

Based on the results from the work of the thesis, future work should focus on implementing the aforementioned "Sr getters" to full SOFCs and investigate their behavior under current. Under SOFC operation, currents will run through the whole cell, which might change the MIEC surface chemistry, cause particle coarsening due to high local current density and lead to unknown reactions between MIEC materials and the "Sr getters". Long-term tests for "Sr getters" decorated SOFCs under operation condition (with bias) can not only shed light on the possible unknown degradation behavior of these SOFC full cells, but also assess the possibility of commercialization of these "Sr getters". Moreover, based on the mechanism proposed in this work, other potentially more effective "Sr getters" might be discovered and developed, which might lead to even better long-term durability for SOFCs. Finally given the importance of high performance anodes based on the work of this thesis, nano-composite anodes with better materials and microstructures need to be studied to enhance the full cell performance. Similar to SOFC cathodes, the long-term stability of SOFC anodes also need to evaluated, and possible degradation mitigation measures for these high performance anodes need to be studied as well. BIBLIOGRAPHY

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