Improving Performance Of Infiltrated SOFC Cathodes Via Scaffold Engineering And Catalyst Surface Engineering

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Improving Performance Of Infiltrated Sofc Cathodes Via Scaffold Engineering And Catalyst Surface Engineering

Abstract
Solid Oxide Fuel Cells (SOFCs) are energy-generating devices operating at elevated temperatures. At their cathode sides, oxygen molecules reduce into oxygen ions and then transport to the anode side through a solid-state ceramic membrane (typically, Yttria-Stabilized Zirconia (YSZ)). At their anode side, the fuels react with the oxygen ions and then release electrons to the external circuit. Always, it is the cathode that has the slowest reaction kinetics, such it contributes the largest resistance in the entire device.

The state-of-the-art cathode materials are typically perovskite-phase ceramic materials, such as Strontium-doped Lanthanum Manganate (LSM), Strontium-doped Lanthanum Ferrite (LSF) and Strontium-doped Lanthanum Cobaltite (LSC). Conventionally, they are just printed to the well-sintered solid-state electrolyte surface and then sinter again to a medium temperature (~1373K) to build contact with the electrolyte. This brings multiple problems, such as solid-state reactions, bad mechanical properties, limited reaction sites, etc. To resolve these problems, infiltrated cathodes, which has nanoscale cathode materials distributed in a porous matrix of electrolyte, was developed at Penn. Cathodes made with this method have multiple advantages such as a significantly larger number of reaction sites, the avoidance of solid-state reactions, strong mechanical properties and the match of coefficient of thermal expansion.

However, although infiltrated cathodes exhibit significantly better performances than traditional printed cathodes, there is still room for improvement. An important concern about the infiltration method is manufacturability. A single infiltration step takes about 30 mins, and the infiltrated material per cycle is restricted by the volume of material that can be added. Normally, 30 wt% loading of the nanoparticles in the cathode matrix is necessary to achieve a good electronic conductivity, with only one thirds of the nanoparticles are there for the surface reaction kinetics. Therefore, to improve the manufacturability of infiltrated SOFC cathodes, one must develop an electronically conductive cathode at a low loading of the cathode nanoparticles. In our study, we have demonstrated a promising approach of using composite materials, such as LSF-YSZ and LSCrF-YSZ, instead of single-phase YSZ as the matrix material. This allows the cathode to have a better performance at low nanoparticles loading due to the incorporated electronic conductivity in the porous matrix backbone.

Another approach to improve the cathode performance is to increase the surface reaction kinetics of the infiltrated cathode materials. In this study, we used Atomic Layer Deposition (ALD), a thin-film growth technology capable of making atomic-level composition tuning, to reveal the desired surface composition of the perovskite-phase cathodes for the sluggish oxygen reducing process. It was discovered that for the ABO3 perovskites, an AO layer on top of BO2 layer configuration is desired for fast oxygen reducing kinetics and it is very likely due to the increase in surface oxygen vacancies. Computational study performed by our collaborator investigated the thermodynamic nature of this configuration and suggested its thermal instability, which was proved by further experimental evidence.

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ABSTRACT

IMPROVING PERFORMANCE OF INFILTRATED SOFC CATHODES VIA SCAFFOLD ENGINEERING AND CATALYST SURFACE ENGINEERING

Yuan Cheng

Raymond J. Gorte

John M. Vohs

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Chapter 1. Introduction

1.1 Motivation

Solid Oxide Fuel Cells (SOFCs) are an intriguing energy generating technology. They are high-temperature, solid-state devices that can convert chemical energy to electrical energy with high efficiency. They can use a variety of fuels, including hydrogen, biogas, and hydrocarbons, and can have efficiencies of over 50% when generating electricity [1-3]. Their reverse mode, Solid Oxide Electrolyser Cells (SOECs), can efficiently generate fuels, such as H2 and CO from water and CO2 [4-6]. Because of their potential, SOFCs are an attractive option for energy-efficient and low-carbon power generation. The global SOFC market has been growing for the past 5 years and is projected to reach USD 1.42 billion market size by 2025 [7].

Despite the promising future of this technology, there are still multiple opportunities to optimize and promote this technology. One major problem is the significant energy loss at the air electrode due to the sluggish reaction kinetics. The focus of this thesis is on understanding and re-engineering the air electrode in order to reduce the electrode loss.

1.2 SOFC Operating Principles

The primary components of an SOFC are the porous anode, the dense electrolyte and the porous cathode. Figure 1.1 illustrates the working principles of the fuel cell. On the
cathode side, gas-phase oxygen molecules dissociate on the cathode surface and combine with electrons to form oxygen ions. This half-cell reaction is represented in equation 1.1:

\[ O_2 + 4e^- \rightarrow 2O^{2-} \]  \hspace{1cm} 1.1

The oxygen ions are then transported though the electrolyte to the anode side. Fuel enters the anode and combines with the oxygen ions to form oxidized products, releasing electrons as shown in equation 1.2 and 1.3:

\[ H_2 + O^{2-} \rightarrow H_2O + 2e^- \]  \hspace{1cm} 1.2

\[ C_nH_{2n+2} + (3n + 1)O^{2-} \rightarrow nCO + (n + 1)H_2O + 2(3n + 1)e^- \]  \hspace{1cm} 1.3

The potential energy of the released electrons is higher than that of the electrons entering the cathode. These electrons can therefore perform work on an external circuit before returning to the cathode. SOFCs normally operate at elevated temperatures (i.e. 873 to 1073 K) in order for there to be fast ionic transport through the electrolyte and good surface reaction kinetics in the electrodes. The use of oxygen-ion conducting electrolytes allows SOFC to operate on any combustible fuel, such as H\textsubscript{2}, CO and hydrocarbons, if appropriate anode materials are used.
1.3 Voltage Losses in SOFCs

The output power of a cell is calculated from the product of the cell voltage and the output current. The theoretical maximum voltage a fuel cell can generate is determined by the Nernst equation (Equation 1.4), in which $\Delta G$ is the change in Gibbs Free Energy for the reaction of interest, $n$ is the number of transferred electrons in that reaction, $F$ is the Faraday constant, $R$ is the Ideal Gas Constant, $T$ is the absolute temperature, and the $P_i$ are the partial pressures of the products and reactants. Note that the potential can change due to the concentration of reactants, products, and temperature.

$$Nernst Potential = \frac{-\Delta G}{nF} - \frac{RT}{nF} \ln \left( \frac{\prod P_{Prod}}{\prod P_{React}} \right)$$  \hspace{1cm} 1.4
For an ideal process with no cell losses, the cell voltage will be equal to the Nernst Potential. However, there will be energy losses in any real-world process; therefore, the cell voltage will usually be lower than the Nernst Potential, although the cell voltage at zero current, the open-circuit potential, may approach the Nernst Potential in many SOFC. In all real cases, the cell potential will drop as current increases. Figure 1.2 shows the V-I characteristics of a typical operating cell. The cell voltage deviates increasingly further from the Nernst potential as the output current increases. While not a general principle, it is commonly observed that the cell voltage decreases almost linearly with current for SOFCs. In this case, the slope can be considered to be the total resistance of the cell.

![Figure 1.2: V-I characteristics of a functioning SOFC.](image-url)
There are a number of factors that can contribute to the total cell resistance. The resistance due to transport of the charge carriers, primarily the ions moving through the electrolyte, is always present and is referred to as the ohmic resistance. To minimize these losses, the electrolytes are usually prepared as thin films since the ohmic resistance is directly proportional to the electrolyte thickness. The resistances associated with the two electrodes are sometimes referred to as polarization resistances. There are two types of polarizations: activation polarization and concentration polarization. Activation resistances are related to the reaction kinetics of the surface reactions at both electrodes. Since the reduction of H$_2$ on the anode side is fast for the anode-supported, Ni-based cells that are most commonly used, it is usually the cathodic activation resistance that contributes the majority of the activation resistance. The concentration polarization is due to transport limitations of reactants to the electrode-electrolyte interface. Transport limitations are often important in working fuel cell at high fuel utilizations but are not typically important for lab-scale testing.

1.4 Electrochemical Impedance Spectrometry (EIS)

Although V-I polarization curves can measure the total resistance of a SOFC, they are not able to separate the resistances of the individual components of the cell. In order to test cathode performance, it is crucial to identify the cause of cell losses. For this purpose, EIS is employed to assist the diagnosis of cells. EIS records the sinusoidal current response of the system against a sinusoidal changing voltage to calculate the impedance of the system as a function of the frequency. The amplitude ratio and phase shift are the
impedance, $Z$, which can then be separated into a real part ($Z'$) and an imaginary part ($Z''$). By plotting $Z''$ vs. $Z'$ over a wide frequency range, a Nyquist plot is generated. One example is shown in Figure 1.3. The distance between the origin and each data point is the absolute impedance at that frequency.

![Figure 1.3: A typical SOFC Nyquist plot. The frequency of the different data points drops from 30000 Hz to 0.01Hz from left to right.](image)

In principle, a fuel cell can be modeled as a simplified equivalent circuit. The electrolyte losses are purely resistive and can be modeled as a simple resistor. Since the electrochemical reactions are frequency dependent, they are often modeled as a capacitor and resistor in parallel. The capacitor component models the electronic double layer formed
at the electrode-electrolyte interface, due to the polarization phenomenon. The resistance component models the sluggish surface reaction kinetics. A complete model of an SOFC is generated by assembling every component in series.

During an EIS test, time-dependent processes cannot be observed at high frequencies (the leftmost point in Figure 1.3). In the equivalent circuit representation, each capacitor acts as a short. When the frequency is almost zero (rightmost data point in the plot), one measures the total cell resistance (the slope of the V-i polarization curve). The capacitors in the equivalent circuit are essentially open circuits. The difference between the total cell resistance and the ohmic resistance is the polarization resistance, which is equal to the length under the arc in the Nyquist plot. With this powerful tool, one can distinguish between electrode and electrolyte losses.

1.5 State-of-the-art materials

1.5.1 Electrolyte Materials

A dense ion-conducting and electron-blocking ceramic electrolyte is essential to a SOFC. Yttria-Stabilized Zirconia (YSZ) is currently the industrial standard for this application. This fluorite-structured material is known for its relatively low cost, stability in both oxidizing and reducing environments, and high oxygen conductivity at medium-to-high temperatures. At the optimal Y-doping level, the ionic conductivity of YSZ at 973 K is 0.019 S/cm [8]. As with most oxides, it can undergo solid-state reactions with the perovskite-phase cathode materials that are commonly used. Some active cathodes, like
La_{1-x}Sr_xCo_{y}Fe_{1-y}O_{3-\delta} (LSCF) and La_{1-x}Sr_xCoO_{3-\delta} (LSCo), can form insulating phases at the interface with YSZ if co-sintered \cite{9-11}. Therefore, a thin and dense Gadolinium-Doped Ceria (GDC) layer is usually applied between the cathode material and the YSZ electrolyte as a barrier layer to prevent direct contact\cite{12,13,14}.

1.5.2 Anode Materials

A Ni-YSZ, ceramic-metallic (cermet) composite has become the standard high-performance anode material for H\textsubscript{2} fueled SOFCs \cite{15-18}. The cermet anode is typically prepared by pressing or tape-casting a mixture of YSZ and NiO powders. After high-temperature sintering, reduction of the NiO results in the Ni-YSZ cermet. In anode-supported cells, a layer of YSZ powder is usually deposited onto the NiO-YSZ mixture prior to sintering and the electrolyte and anode are then co-fired. The incorporation of YSZ in the cermet anode makes the anode Coefficient of Thermal Expansion (CTE) more closely match that of the electrolyte. It also provides pathways for oxygen-ion conduction from the electrolyte. Therefore, well-made porous Ni-YSZ cermet anodes can have a low resistance when used in anode-supported cells.

Although Ni/YSZ cermets work very well for H\textsubscript{2} fueled SOFCs, they cannot be used when hydrocarbon fuels are fed directly to the anode and suffer from redox instabilities. Because Ni tends to form carbon fibers when exposed to dry hydrocarbons, hydrocarbons must be externally reformed with steam to produce H\textsubscript{2} and CO before being fed to anode. Many coke-resistant anodes have been developed for direct hydrocarbon applications. For example, our lab had previously developed La_{1-x}Sr_xTiO_{3-\delta} (LST) \cite{19} and
La$_{1-x}$Sr$_x$VO$_{3.8}$ (LSV) $^{[20,21]}$ based, infiltrated anodes. These anodes are manufactured by impregnating a porous YSZ anode with a conductive electronic material, LSV or LST, together with catalytically materials such as ceria and Pd. The detailed instruction on infiltration process can be found in Chapter 2. These anode have been proven to be high-performance and coke-resistant.

1.5.3 Cathode Materials

It is commonly acknowledged that the cathode side has the largest resistance in anode-supported fuel cells. The conventional cathode material was a mixture of Strontium-doped Lanthanum Manganate (LSM) and YSZ, with LSM being the pure electron-conducting phase and YSZ being the pure ion-conducting phase $^{[18,22,23]}$. The oxygen-reduction reaction produces oxygen cations from the electrons and the oxygen molecules, which then pass into the electrolyte. Therefore, the reaction can only happen at three-phase-boundary (TPB) sites, which are those sites at the interface between LSM, YSZ, and the gas phase $^{[24]}$. LSM was chosen due to its moderate compatibility with YSZ at the cathode sintering temperatures. One way to make this cathode is to take a slurry mixture of LSM and YSZ and screen print it onto the sintered YSZ electrolyte. The cathode must then be sintered, typically at 1473 K, to prepare a good interface.

Cathodes made in this manner have some disadvantages $^{[24]}$. First, they have a high polarization resistance, typically greater than 0.4 $\Omega \text{cm}^2$ at 973 K. This is due to the randomly distributed reaction sites and the poor catalytic activity of LSM $^{[25]}$. Second, the sintering temperature is insufficient to form a robust connection between the cathode and the electrolyte, which leads to delamination after long-term operation. Unfortunately,
sintering at higher temperatures would cause LSM to react with YSZ and lead to an insulating layer.

Mixed-ionic-and-electronic (MIEC) cathode materials, like LSCo, La_{1-x}Sr_xFeO_{3-δ} (LSF) and LSCF, were developed as alternatives for dual-phase cathode materials [26–32]. Due to their mixed-conducting properties, the entire surface can be considered to be part of the TPB. A comparison of the reaction mechanism of a dual-phase cathode material and a MIEC cathode material is illustrated in Figure 1.4. The MIEC material clearly has a larger region for surface reactions than the dual-phase perovskite material. Because of this, the catalytic performance of these materials can be better than LSM-YSZ composites. However, the electronic conductivity of LSF is deficient and cobalt-containing materials can react with the YSZ electrolyte over time; therefore, high-temperature co-sintering is more of a problem than with LSM.
1.6 Printed SOFC cathodes vs. Infiltrated SOFC cathodes

Conventional SOFC cathodes are printed onto the sintered electrolyte as the last step during cell manufacturing. Due to the low reactivity of NiO and YSZ, the co-sintering of the anode-electrolyte dual-layer structure is usually performed first with Ni-YSZ based SOFC, with sintering performed at around 1673 K. After that, an ink consisting of the active cathode materials is printed onto the dense electrolyte surface, followed by medium...
temperature sintering at around 1373 K. There are issues associated with this process. First, the CTE of the deposited material must match that of the electrolyte, which limits the choice of materials that can be used in the cathode. Second, the best cathode materials undergo solid-state reactions with the YSZ electrolyte at the required sintering temperatures. Therefore, a barrier interlayer, typically GDC, is commonly applied between the cathode and the electrolyte. This interlayer not only adds to the ohmic resistance but is only partially able to block cation interdiffusion. Third, the sintering temperature must be a compromise between two competing processes. If the temperature is too low, contact between the cathode and the electrolyte is weak. But if the temperature is too high, the solid-state reaction between the deposited cathode material and the electrolyte can compromise the property of both parts. Therefore, printed cathodes often do not have good contact with the barrier layer.

Manufacturing SOFC cathodes via an infiltration method was developed here at Penn, initially as an attempt to avoid forming an insulating phase at the electrolyte interface during the high-temperature sintering process [24]. In this method, the dense electrolyte and a porous scaffold of the same material are formed together. Next, electronically conductive and catalytic materials are infiltrated into the scaffold, after which the resulting structure is calcined at a relatively low temperature (923 K to 1123 K) to form the catalytical perovskite phase. Details about this method will be discussed in the next chapter. Figure 1.5 shows a Scanning Electron Microscope (SEM) image of an infiltrated SOFC cathode. This approach minimizes solid-state reactions because different sintering temperatures are used for the scaffold and the infiltrated cathode materials. Since the scaffold is co-sintered to the electrolyte at high temperatures, the electrodes can have better mechanical stability. Unlike
cathodes prepared from mixed powders, composites prepared by infiltration are not random composites. One advantage of the non-random structure is that conductivity can be achieved with a lower mass fraction of the electronic conductor. Another is that the CTE in these non-random composites is closer to that of the electrolyte scaffold. Finally, the performance of infiltrated electrodes can be very good, both because the ion-conducting scaffold is well connected to the electrolyte and because the infiltrated phase can be nano-structured, providing for a high surface area and catalytic activity.

**Figure 1.5**: SEM of an LSF-YSZ infiltrated SOFC cathode. The bulk part is the YSZ scaffold and the nanoparticles are infiltrated LSM materials. Reproduced from reference [33].
1.7 Optimization opportunities for infiltrated SOFC cathodes

Cathodes formed by infiltration, which have nanoscale components dispersed in the porous YSZ electrolytes, exhibit significantly better performance than traditional screen-printed cathodes \(^{9,24,34,35}\). However, there is still room for improvement. In this thesis, I examined ways to improve both the scaffold component and studied how modification of the surface of the infiltrated component changes cathode performance.

1.7.1 Developing a Mix-Conducting Scaffold for Infiltration

An important concern about the infiltration method is manufacturability. A single infiltration step takes about 30 mins, and the infiltration amount per cycle is restricted by the volume of material that can be added \(^{24,36,37}\). For catalytic purposes, a few weight percent of the cathode component would be sufficient \(^{38}\); however, this level of loading is not sufficient to achieve the necessary electronic conductivity. Assuming that the YSZ scaffold will have a porosity of about 65\%, it is necessary to add about 30-wt\% (20-vol\%) of the conducting oxide in order to achieve sufficient electrode conductivity \(^{39}\). With solutions of nitrate salts, this typically requires at least 10 rounds of infiltration. Therefore, to improve the manufacturability of infiltrated SOFC cathodes, one must develop an electronically conductive cathode at a low loadings of the cathode components.

The general strategy we took is to prepare scaffold structure that were electronically conductive \(^{9-11}\). In this way, the amount of infiltrated material needed to generate
sufficient electronic conductivity was reduced. At the same time, it was necessary to have the scaffold have oxygen-ion conductivity, so that the dissociated oxygen ions can diffuse to the electrolyte interface. In addition, the scaffold material must be compatible with the electrolyte so that addition of a barrier layer was not needed. Adding an additional barrier layer would add an extra sintering step and extra ohmic resistance. Studies based on this strategy are discussed in Chapter 3-5.

1.7.2 Studying the desired surface composition of the infiltrated nanoscale perovskite materials

Another approach to improve the cathode performance is to increase the surface reaction kinetics of the infiltrated cathode materials. The kinetics of a surface reaction are related to both the total surface area and the number of reaction sites per surface area. Even though the infiltrated nanoscale perovskites already provide huge surface areas, the sluggish oxygen-reduction reaction often remains the largest resistance in the process. Therefore, in addition to increasing the surface area, it is also important to understand the surface compositions of these perovskites in order to maximize the surface reaction site density.

Since the reduction of oxygen molecules can only happen at the very surface of a cathode, it is crucial to tune the composition of the outermost layer of the perovskite. However, because this layer is in a different environment from that of the bulk, its composition could be different from that of the nominal composition of the infiltrated material after the calcination step. Therefore, it is not possible to control the surface composition by controlling the bulk composition.
Several groups have modified cathodes by infiltration with various metal oxides and have reported lower cathode impedances[^40,^41]. However, this method modifies two properties of the cathode at the same time: both the surface morphology and surface composition are changed. Therefore, it is not clear from these experiments which factor is responsible for the promotional effect. In addition, infiltration introduces particles, which do not uniformly modify the substrate surface. Therefore, we used Atomic Layer Deposition (ALD) to modify the surfaces of various cathodes, since this method changes only the surface composition without affecting the morphology or surface area.

An illustration of the ALD process used in our lab is shown in figure 1.6. During an ALD cycle, the surface is first exposed to an organometallic precursor molecule. The molecules react with the surface; but, since they do not react with themselves, the reaction is self-limited to one monolayer. After purging the excess precursors, the adsorbed molecules are oxidized. This process can be repeated to grow thicker films. This method was employed in our study to modify the composition of the outermost layer of the perovskite material, which is further discussed in Chapters 6 and 7.
Figure 1.6: An illustration of the ALD process. The light blue sphere is the target metal atom and the wavy orange band surrounding it represent the bulky ligands. A full ALD cycle consists of dose-purge-oxidation steps.
1.8 References


Chapter 2. Manufacturing Methods

2.1 Fabrication Procedure for Preparing Electrochemical Cells

2.1.1 Principles of Tape Casting

Tape casting is been a well-established industrial method for mass production of large-area, flat ceramic or metallic parts. An illustration of the tape-casting process is shown in Figure 2.1. The key component of this method is a uniform slurry, which consists of solvent, dispersant, binder, plasticizer, and metal-oxide powders \(^1\). The solvent is to dissolve all the organic components and form the main body of the slurry. The dispersant prevents the target particles in the slurry from agglomerating. The binder creates a polymer matrix to trap the particles after the solvent is removed, and the plasticizer provides the mechanical flexibility to the matrix. This uniform slurry is first poured into the reservoir. On one side of this reservoir, a tunable doctor blade is set to leave a certain open space for the slurry to exit. By drawing a mylar strip from under the doctor blade, a wet film of well-defined thickness is prepared. The wet film will then be dried to eliminate the solvents before the harvest of the dry tape. After this step, the dry tape can be cut into the desired shapes. Multiple tapes may be laminated to produce layered structures.
2.1.2 Dense electrolyte manufacturing using tape casting method

A thin and dense electrolyte is crucial for high-performance SOFCs. The tape casting method can be used to prepare thin ceramic films and for making layered structures; therefore, it is ideal for manufacturing planar fuel cells [2-5]. In order to yield a dense electrolyte, the powders for this application must be milled in order to produce uniformly sized particles. Our lab uses TZ-8Y YSZ powders from TOSOH, which have crystallite sizes of ~40 nm. However, since crystallites in these powders are often in the form agglomerates, it is still necessary to mill them before use. The milling is performed while the powders are mixed with an ethanol/xylene dual-solvent system, together with fish oil (dispersant), polyvinyl butyral resin B-98 (binder), and benzyl butyl phthalates and

**Figure 2.1:** An illustration of the tape casting process.
poly(ethylene) glycol (both are plasticizers), so that the particles remain well separated.

The mixture was typically ball milled for 48 hours to yield a uniform slurry before pouring into the reservoir for film manufacturing. The tape-casting procedure is described in the previous segment. After a dry tape is harvested, it can be cut into round pieces and then laminated with other tapes.

2.1.3 Porous electrode scaffold manufacturing using tape casting method

Most of the fuel cells used in my thesis used electrodes were prepared by infiltration. The starting step in this process required preparation of porous-dense-porous structures made from YSZ. The porous layers on either side of the dense electrolyte were used as electrode scaffolds, into which the electrode material was infiltrated, as described in Chapter 1. To prepare the porous-dense-porous structure, YSZ tapes with pore formers included were laminated to the central tape that did not have pore formers.

The recipe for the porous tapes was similar to that used for the dense tapes, except for the addition of pore formers. Several studies of pore formers were performed by earlier students, and it was suggested that both pyrolyzable pore formers and NiO (followed by acid etching) could be used to generate pores \(^6-^9\). In our case, we chose to use 43 wt% graphite powder to generate a 60-vol%, porous YSZ scaffold with pores of diameters around 1~2 micron. The tape-casting recipe was otherwise the same as that used for dense tapes and the slurry mixture was again ball milled for 48 hours to yield a uniform slurry before again being cast into a tape as described in section 2.1.1. Circular pieces of the resulting tape were then laminated onto either side of the electrolyte layer.
2.1.4 Cell Lamination and Sintering

After preparing the porous and dense tapes, a tri-layer structure of the porous-dense-porous tapes was made by lamination between two hot plates. It is important to keep the plate temperature above the glass-transition temperature of the binders, but below that which would cause thermal shock of the tape. The initial contact between layers was induced by applying moderate pressure, avoiding too high a pressure which can lead to undesired sticking or cracking. It is also recommended to use Mylar sheets in between the tapes and the heating pads to avoid sticking.

The final step for manufacturing the tri-layer ceramic structure involves high-temperature calcination. Due to the careful milling procedures used in our work, it was usually sufficient to calcine the structure at 1673 K 4 h. During the sintering step, zirconia plates were used to “sandwich” each sample in order to avoid contamination and curving. For the present work, the final structures were 1.5 cm$^2$ in area, with the porous electrode scaffold part is 0.35 cm$^2$ in area.

2.2 Impregnating Perovskite Materials via Infiltration Methods

A major advantage of electrodes prepared by infiltration of cathode components into a porous scaffold of the electrolyte is that the porous scaffold can act as an oxygen-ion conductor, so that oxygen ions generated deep in the cathode can be conducted to the electrolyte interface. However, the electrode must still be electronically conductive and be capable of catalyzing the dissociation of oxygen molecules. Therefore, the active electrode
materials must still be impregnated into the porous scaffolds. This is being done by infiltration. In our case, a solution of the nitrate salts was first prepared. For example, if the target material was to be LSCF, a saturated aqueous solution of $\text{La(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}$, $\text{Sr(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}$, $\text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$ and $\text{Co(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ with desired molar ratio was prepared. In each infiltration step, the scaffold was saturated with the solution at room temperature, after which the excess solution on the surface was removed. After allowing the cells to dry, they were heated to 873 K to decompose the nitrates. This procedure was repeated for the desired number of infiltration cycles. After the final infiltration step, the entire structure was heated to 1123 K to form the LSCF, perovskite phase.

The selection of calcination temperature is important for the infiltrated materials since the surface morphology of the calcined nanomaterials are sensitive to the preparation condition. In previous work, it was shown that the surface area of infiltrated LSM changed as a function of calcination temperature, with the surface area decreasing by a factor of four when the calcination temperature was increased from 1123 K to 1523 K \cite{10}. In addition to surface area reduction, high temperature treatment can also cause the solid-state reaction between the perovskites and the YSZ backbone, forming insulating phases \cite{11,12}. Therefore, it is important to avoid high-temperature calcination of the infiltrated materials. However, if the calcination temperature is too low, the electronically conductive perovskite phase will not be formed. Chelating agents, such as citric acid \cite{13}, are often added with the infiltrating salt in order to promote formation of the perovskites at lower temperatures. The chelating agents allow better mixing of the metal cations. For most of the studies used in this work, the condition that we choose (1123 K), adding these chelating agents is not necessary. Figure 2.2 shows the XRDs of infiltrated LSF, LSM.
and LSCo prepared with the methods and conditions. The XRD results demonstrate that one can form the perovskite phases without forming insulating phases. The surface area of the 30 wt% LSM infiltrated cathodes was measured to be 2.5 m² g⁻¹.
Figure 2.2: XRD result of the porous YSZ cathode infiltrated with LSM (a), LSF (b) and LSCo (c) after calcination at 1123 K. The perovskite phase peaks are labeled in red asterisks and the fluorite YSZ peaks are labeled with green triangles.
2.3 Atomic Layer Deposition (ALD)

As discussed in section 1.7.2, it is useful to study the effect of surface composition on the electrochemical performance of the infiltrated electrodes, independent of the surface morphology. Therefore, ALD was chosen to modify the surface composition. The home-built ALD setup is shown schematically in Figure 2.3. This setup was designed to allow two different precursors to alternatively react with the sample surface, with intermittent oxidizing steps.

![Figure 2.3: An illustration of the in-house built ALD system. Heating system is not shown in the figure.](image)

We found that there are three key design factors that were important for our process. First, it was important to be able to evacuate the sample so that we could use pressure-driven flow of the precursor molecules to saturate the sample. Since the vapor...
pressures of the precursors used in most of our work were below a few torr, even at elevated temperatures, this meant that the maximum base pressure for the sample chamber was 200 millitorr.

To achieve a sufficient vapor pressure of the precursor, it was necessary to heat the precursor. Furthermore, to avoid condensation, all of the tubing between the precursor and the sample had to be heated as well. Because chemical vapor deposition will occur at too high a temperature, there exists a temperature window for ALD \[14,15\]. Ideally, the sample temperature should be high enough to allow oxidation of the adsorbed precursor.

Finally, to avoid diffusional limitations with low-vapor-pressure precursors, the sample dimensions had to be sufficiently small and the exposure times sufficiently long. As suggested by Onn et al. \[16\], a higher precursor vapor pressure results in a larger driving force. In most of our trials, we used between 30 s and 2 min for each dosing and evacuation steps, depending on the surface area of the substrates.
2.4 References


Chapter 3. Preparation of SOFC Cathodes by Infiltration into LSF-YSZ Composite Scaffolds*

Summary

Fabrication of SOFC cathodes by infiltration of La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF) into porous scaffolds that were 50-wt% composites of La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ (LSF) and YSZ were investigated for purposes of reducing the number of infiltration steps required to make conductive electrodes. XRD patterns of porous, LSF-YSZ composites prepared by tape casting and calcined to 1723 K showed only fluorite and perovskite phases and were sufficiently conductive that 30-\(\mu\)m thick films attached to YSZ electrolytes did not substantially contribute to the ohmic resistance in symmetric cells or SOFC. Non-ohmic losses at 973 K were reduced from 1.4 \(\Omega\)cm$^2$ to 0.16 \(\Omega\)cm$^2$ by two infiltration cycles of LSCF.

3.1 Introduction

As mentioned in Section 1.6, Solid Oxide Fuel Cell (SOFC) cathodes are conventionally prepared from mixed powders of LSM and YSZ, often by screen printing the mixture onto the dense electrolyte$^{11}$. The performance of these composite electrodes is enhanced relative to that of the pure conductive ceramic because the ion-conducting component provides channels for transporting oxygen ions from the electrolyte to the

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surface of the electrode \[^2\]. However, manufacturing cathodes using infiltration method brings in multiple advantages \[^3,4,5\]. This method separates the calcination of the backbone material and the catalytic material, thus avoids the solid-state reaction. In addition to its initial intention, this non-random structure showed other advantages, such as great mechanic property, CTE match, high surface area and high catalytic activity. This allows the flexibility in infiltrated materials, including LSM, LSCo, LSF and LSCF.

A major issue with using infiltration methods to synthesize electrodes is that many steps are usually required to achieve the necessary loading of the electronically conductive phase \[^6\]. For example, past work on electrodes prepared by infiltration of La\(_{0.8}\)Sr\(_{0.2}\)FeO\(_3\) (LSF) into 65%-porous YSZ showed that the LSF loading needed to be at least 35-wt\% (20-vol\%) in order for there to be sufficient electronic conductivity for the ohmic resistance of the electrode to be negligible \[^7\]. A simple calculation of the LSF loading that can be theoretically achieved by filling the scaffold pores with a 1-M solution of La, Sr, and Fe, in the appropriate molar ratios, shows that a single infiltration step can only give 2.3-vol\% LSF. Even using molten nitrate salts \[^8\], the theoretical loading per step is less than 5-vol\%. It is important to notice that these calculations are based on filling the entire pore volume of the scaffold with the infiltrating solution. Because capillarity is a far greater driving force than evacuation, vacuum infiltration does not increase the amount of fluid that enters the pores and does not affect the required number of cycles, an observation that has also been verified experimentally \[^9\]. Although higher loadings could be achieved using a concentrated solution of oxide nanoparticles \[^8\], the ligands required to keep the nanoparticles suspended in solution are typically too large to significantly increase the loading per cycle.
Because the need for high loadings of the infiltrated phase is required to achieve electronic conductivity, it should be possible to obtain good performance with lower loadings if the scaffold is conductive. This approach has been used in the preparation of SOFC anodes by infiltration. In that case, the porous scaffold was a composite of La$_{0.7}$Sr$_{0.3}$TiO$_3$ (LST) and YSZ, two oxides that can be co-fired to high temperatures without causing solid-state reactions between the phases. Unfortunately, the conductivity of the porous LST-YSZ scaffold, by itself, was insufficient for good electrode performance. Enough conductivity could be achieved by infiltrating additional LST; however, electrodes prepared from the composite scaffold were still not as good as those obtained by simply infiltrating LST into a YSZ scaffold. Because LST is not a good ion conductor, it is likely that reduced ionic conductivity within the scaffold was responsible for the decreased performance.

In the present work, we set out to investigate the possibility of preparing infiltrated cathodes using a composite scaffold of LSF and YSZ. Previous reports have shown that LSF and YSZ are relatively unreactive towards each other. High-temperature sintering of LSF-YSZ mixtures has been reported to cause Zr to enter the perovskite phase, as evidenced by a shift in the LSF/perovskite lattice parameter; but, even after calcination of the mixtures to 1523 K, no additional phases were observed in this past work. Doped LaFeO$_3$ is also interesting because this material has a high ionic conductivity in addition to its electronic conductivity. It is commonly used in ceramic membranes as a Mixed Ionic and Electronic Conductor (MIEC) and one recent study reported that Ca-doped LaFeO$_3$ (LCF) has an ionic conductivity that is 50% higher than that of YSZ at 973 K.
In confirmation of the hypothesis, we demonstrate here that an LSF-YSZ scaffold can provide the electronic and ionic conductivity required for good cathode performance. Catalyst addition is required to reduce the non-ohmic losses in the electrode but reasonable performance can be achieved by using just one or two infiltration steps.

3.2 Experimental

The general scheme for making the cathodes used in the cells of this study has been shown in Figure 3.1. A green tape containing mixtures of LSF and YSZ, together with pore formers, was laminated onto a normal YSZ tape; and the two-layer structure was sintered to a temperature high enough to form a dense YSZ electrolyte, as described in Section 2.1. The porous LSF-YSZ scaffold was then infiltrated with aqueous solutions of the nitrate salts of La, Sr, Co, and Fe to form the LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$) phase after calcination to 1123 K. For symmetric cells, composite electrodes were formed on both sides of the YSZ electrolyte. For fuel-cell measurements, a porous YSZ scaffold was attached opposite the porous LSF-YSZ scaffold.
Figure 3.1: Schematic of the process used in making the composite electrodes.

Although the anode part is not showing in this figure, it has been demonstrated that a Ni-YSZ cermet anode can also be co-sintered with YSZ electrolyte.

The LSF powder used in the preparation of the composite scaffolds was synthesized by sol-gel methods. The appropriate amounts of $\text{La(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{Sr(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99.0%), and $\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, 98.5%) were dissolved in distilled water, along with the complexing agent, citric acid (Fisher Scientific, 1:1 ratio with the metal cations). This solution was then dried at 373 K, and the resulting gel was calcined in air at 1123 K to form the perovskite phase. YSZ was purchased from Tosoh (8-YSZ, TZ-8Y). Tapes for the LSF-YSZ composite scaffolds were prepared by mixing equal weights of LSF and YSZ, together with other components introduced in Section 2.1, using a recipe that is described in detail elsewhere $^{[16]}$. After ball milling the mixture for 48 hours, the resulting slurry was cast into a green tape.
Green tapes for the YSZ electrolyte and the porous YSZ scaffold were prepared in a similar manner and described in detail elsewhere [16].

For fuel-cell and symmetric-cell measurements, circular wafers were punched from the green tapes, and then laminated into a porous-dense-porous structure. Because there was a tendency for the LSF-YSZ tape to form a dense structure, we restricted the calcination temperature to 1623 K in this study, a temperature that was sufficient to make the electrolyte dense but low enough to avoid collapsing the pores in the LSF-YSZ scaffold. After calcination, the resulting dense layers were between 70 and 85 μm in thickness and 1 cm in diameter. The porous layers were approximately 35 μm in thickness and 0.7 cm in diameter. Fuel-cell anodes were fabricated from a porous YSZ scaffold by infiltrating La, Sr, and V salts to form a composite that was approximately 30-wt% LSV (La0.7Sr0.3VO3.85). Catalytic activity in these LSV-YSZ electrodes was incorporated by adding 1-wt% Pd and 5-wt% CeO2. Additional details of the anode fabrication are given elsewhere [17]. Cathodes were prepared from both porous LSF-YSZ and porous YSZ scaffolds by infiltration of aqueous solutions of LSCF, which has been discussed in Chapter 2.

Ag paste (Lot No. 1191013, SPI Supplies) and Ag wire were used for current collection in all cases. For fuel-cell measurements, the cells were attached onto an alumina tube using a ceramic adhesive (Ceramabond 552, Aremco). V-i polarization curves and impedance spectra for the fuel cells were measured using a Gamry Instruments potentiostat with the cathode exposed to ambient air and the anode exposed to humidified (3% H2O) H2. The impedance data were not time-dependent and there was no evidence for hysteretic behavior upon electrode polarization [18]. The crystal phases,
morphologies, and pore structures of the sintered tapes were analyzed using X-ray
diffraction (XRD) and scanning electron microscopy (SEM) (JEOL 7500F HRSEM).

3.3 Results

3.3.1 Compatibility of LSF and YSZ

To determine the reactivity of LSF with YSZ during calcination, composite LSF-
YSZ tapes were heated to various temperatures for 4 h and then examined by XRD to
determine the phases that were present. Results are shown in Figure 3.2. Even after
calcination to 1723 K, only peaks associated with fluorite and perovskite phases were
observed. A closer examination of the peaks near 30 and 32 degrees 2θ revealed that there
is a shift to lower angles of the perovskite peak at 32 degrees, beginning at 1623 K.
(Diffraction patterns obtained with graphite as an internal standard showed that the fluorite
peak did not shift.) The shift in the perovskite peak is consistent with Zr replacing some of
the Fe in the perovskite, as suggested in previous publications [12]. Increasing the
calcination temperature to 1723 K did not increase the shift in the diffraction peak,
implying that a saturation level of Zr doping had already been reached. It is worth pointing
out that one previous study intentionally prepared infiltrated cathodes with
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.9}\text{Zr}_{0.1}\text{O}_3$ in YSZ and demonstrated that the performance was similar to that
obtained with LSF in YSZ [13]. Therefore, Zr doping of the perovskite phase is likely not
catastrophic.
Figure 3.2: XRD patterns obtained on 50-wt% LSF-YSZ, mixed oxides as a function of calcination temperature. Only fluorite and perovskite phases were observed, even after calcination at 1723 K. The inset shows the peak positions for the fluorite (near 30°) and perovskite (near 32°) phases in more detail.

3.3.2 The interface between the LSF-YSZ cathode and the YSZ electrolyte

A cross-sectional SEM of the LSF-YSZ composite scaffold near the YSZ electrolyte interface is shown in Figure 3.3. The appearance of the porous-scaffold/dense-electrolyte interface is virtually identical to that of porous-YSZ/dense-YSZ interfaces
reported in other work [5]. The YSZ at the bottom is fully dense, while the LSF-YSZ scaffold has a “sponge-like” appearance, with pores ranging in size between 1 and 10 µm in diameter. The LSF-YSZ scaffold is well connected to the YSZ electrolyte and has a porosity around 60%.

**Figure 3.3:** An SEM image showing the interfacial region near the porous LSF-YSZ composite (at the top) and the dense YSZ (at the bottom). The sample was prepared by laminating a YSZ tape with a LSF-YSZ tape (containing graphite pore formers) and calcining this to 1623 K.
3.3.3 The EIS result of a cathode with a conventional YSZ scaffold

Results from impedance measurements performed at 973 K on a series of symmetric cells made from porous YSZ scaffolds are shown in Figure 3.4 and summarized in Table 3.1. The dense YSZ electrolyte layer was determined by SEM to be 70-µm thick in this series of cells. The values in the Nyquist plots have been divided by two to account for the two electrodes. In the absence of LSCF infiltration, both the ohmic and non-ohmic contributions to the impedance were very large, 2.5 Ωcm$^2$ and 2.0 Ωcm$^2$, respectively. The non-ohmic contribution is not meaningful in this case because the electrode is not sufficiently conductive but the ohmic losses can be compared to that expected for the 70-µm YSZ electrolyte. Based on the reported conductivity of YSZ at this temperature, 0.0197 S/cm$^1$9, half of the electrolyte contribution to the ohmic losses would be 0.18 Ωcm$^2$, so that most of the ohmic contribution comes from the porous YSZ layer. Using the ohmic component of the impedance data that is in excess of the 0.18 Ωcm$^2$ from the electrolyte, the conductivity of the 35-µm porous YSZ layer is determined to be approximately 0.0015 S/cm. Previous conductivity measurements performed on 65% porous, YSZ slabs were determined to be 0.001 S/cm$^7$. 
Figure 3.4: Nyquist plot showing the performance of symmetric cells with porous YSZ scaffolds at 973 K as a function of the number of LSCF infiltration cycles. The data is shown for cells with no added LSCF (■), after 2 cycles (▲), and after 8 cycles (●).

Infiltration with two rounds of LSCF, as described in the Experimental section, decreased both the ohmic and non-ohmic losses; however, the ohmic resistance per electrode, 0.33 Ωcm$^2$, was still 0.15 Ωcm$^2$ higher than that which would be expected for the electrolyte. Assuming the YSZ scaffold is 65% porous, 2 cycles should yield an LSCF loading just under 6-vol%. After 8 infiltration cycles, the ohmic resistance was 0.14 Ωcm$^2$. Based on weight changes, we estimate that the LSCF loading was 20-vol% after 8 cycles and this amount is sufficient to make the electrode conductive. The non-ohmic losses after 8 cycles, 0.15 Ωcm$^2$, were similar to values reported for electrodes prepared by infiltration of LSF in other publications \cite{7, 13}. In this case, infiltrated LSCF exhibited a performance almost identical to infiltrated LSF.
3.3.4 The EIS result of a cathode with a LSF-YSZ composite scaffold

![Nyquist plot](image)

**Figure 3.5:** Nyquist plot showing the performance of symmetric cells with porous LSF-YSZ scaffolds at 973 K as a function of the number of LSCF infiltration cycles. The data is shown for cells with no added LSCF (◼), after 1 cycles (△), and after 2 cycles (◇).

The analogous impedance data for a series of symmetric cells made using porous LSF-YSZ electrode scaffolds are reported in Figure 3.5 and Table 3.1. For this series of cells, SEM showed that the dense YSZ electrolyte layer was 80-µm thick. Even in the absence of any LSCF infiltration, the ohmic losses in these symmetric cells were only
slightly larger than that expected for the electrolyte. As shown in Figure 3.5, the ohmic resistance in the absence of LSCF was 0.21 Ωcm$^2$, compared to the expected value of 0.20 Ωcm$^2$ for this YSZ electrolyte thickness. The non-ohmic losses, 1.4 Ωcm$^2$, were large, as should be expected for a low-surface area, LSF-YSZ electrode formed by tape casting. The ohmic losses decreased to the expected value for the dense YSZ electrolyte after a single infiltration cycle but two infiltration cycles were required to reduce the non-ohmic contribution to 0.16 Ωcm$^2$. 
Table 3.1: Ohmic and Non-Ohmic Resistances for Symmetric Cells prepared by infiltration of LSCF into either porous LSF-YSZ composite scaffolds or YSZ scaffolds.

<table>
<thead>
<tr>
<th>Scaffold Composition</th>
<th>Infiltration</th>
<th>Ohmic Resistance @ 700°C (Ω cm²)</th>
<th>Non-Ohmic Resistance @ 700°C (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:50 LSF/YSZ Composite scaffold*</td>
<td>Bare Scaffold</td>
<td>0.21</td>
<td>1.44</td>
</tr>
<tr>
<td>1 Infiltration of LSCF</td>
<td></td>
<td>0.18</td>
<td>0.24</td>
</tr>
<tr>
<td>2 Infiltrations of LSCF</td>
<td></td>
<td>0.19</td>
<td>0.16</td>
</tr>
<tr>
<td>Pure YSZ scaffold*</td>
<td>Bare Scaffold</td>
<td>2.56</td>
<td>1.87</td>
</tr>
<tr>
<td>2 Infiltration of LSCF (10 wt%)</td>
<td></td>
<td>0.33</td>
<td>0.38</td>
</tr>
<tr>
<td>8 Infiltrations of LSCF (35 wt%)</td>
<td></td>
<td>0.14</td>
<td>0.14</td>
</tr>
</tbody>
</table>

* The thickness of the dense YSZ electrolytes were 70 µm in the series of cells made with the YSZ scaffold and 80 µm in the series with LSF-YSZ scaffolds. Because the impedances have been divided by two to account for the two electrodes, only half of the electrolyte resistance is attributed to each electrode.

3.3.5 Applying this novel cathode in a SOFC

In order to demonstrate that the good performance at open circuit in symmetric cells could be translated into a device, a fuel cell was prepared with a cathode consisting of an LSF-YSZ scaffold, infiltrated with two cycles of LSCF. The anode was prepared from
porous YSZ by infiltration with 30-wt% LSV, 1-wt% Pd, and 5-wt% CeO₂; and the electrolyte was again 70-μm thick, dense YSZ. Humidified (3% H₂O) H₂ was passed over the anode while the cathode was exposed to air. The V-i polarization curve and open-circuit impedance results at 973 K are shown in Figure 3.6. The open-circuit potential, 1.05 V, was slightly less than the Nernst Potential of 1.1 V; but the slope of the V-i polarization relationship was nearly independent of current density; and the cell achieved a maximum power density of 0.4 W/cm². The Nyquist plot indicates that ohmic losses in the cell were 0.37 Ωcm², which is close to the expected contribution from the electrolyte, 0.36 Ωcm². The non-ohmic losses were slightly greater than 0.3 Ωcm², with contributions from the anode and cathode probably about equal. Clearly, the data in Figure 3.6 are consistent with the cathode performance observed in Figure 3.5.
Figure 3.6: Electrochemical results for an SOFC at 973 K, made with a cathode prepared by infiltration of 2 LSCF cycles into a porous LSF-YSZ scaffold. The anode was 30 wt% LSV anode with 5 wt% ceria and 1 wt% Pd catalysts. V-i and P-i curves are shown in a). The open-circuit impedance spectrum is shown in b).
3.4 Discussion

The results obtained in this study have several important implications for producing high-performance SOFC cathodes. The first is that one can indeed produce cathodes by a single-step infiltration process if the scaffold is sufficiently conductive. In this case, the scaffold provides both ionic and electronic conductivity and the infiltrated phase provides the catalytic activity and surface area for the oxygen-exchange reactions. The nanostructure of the infiltrated phase is still likely to be unstable due to sintering [19] but recent results suggest that this problem can be solved. A paper by Gong, et al demonstrated that electrodes prepared by infiltration were dramatically more stable after they had been coated with a thin film of zirconia by Atomic Layer Deposition [20]. The authors suggested that the zirconia film stabilized the surface area and nanostructure of the infiltrated phase, thus maintaining the electrode performance. The combination of these two concepts could make infiltration methods practical for commercial processing.

Another important conclusion is that the co-firing of LSF and YSZ to high temperatures does not result in high-resistance, interfacial phases. The high electrode impedance that has been observed for LSF-YSZ electrodes after high-temperature treatments is likely caused by changes in the nanostructure and surface area, rather than by the formation of insulating phases at the LSF-YSZ interface [13]. It is common practice to incorporate a barrier layer of dope-ceria to prevent solid-state reactions between YSZ electrolytes and the perovskite phases used in electrodes [21]. This is clearly required for Co-containing perovskites but does not seem to be important for LSF. Although there is evidence that a doped-ceria barrier layer can lead to improved performance with LSF-based electrodes [22, 23], the doped ceria may be playing a role other than preventing interfacial
reactions. For example, doped ceria has a much higher ionic conductivity than YSZ and it has been shown that higher oxygen-ion conductivity for the electrolyte phase in composite electrodes leads to better cathode performance \cite{16}. Ceria is also a good catalyst and its addition to existing cathodes has been shown to improve performance \cite{24}.

Given that LSF and YSZ are relatively unreactive, it is interesting to ask whether LSF can replace doped ceria as a barrier layer for higher performance, Co-containing cathodes. A recent paper from Zhou, et al reported that doped-ceria interlayers can contribute to the ohmic resistance of a fuel cell \cite{25}. The authors concluded that this was due to migration of Zr into the doped ceria layer to form a less conductive phase. The fact that ceria-zirconia solutions have a lower ionic conductivity than YSZ has indeed been demonstrated \cite{26}. If a porous LSF-YSZ phase could act as a buffer layer in place of doped ceria, it may be possible to reduce this ohmic contribution.

Infiltration methods for cathode preparation are still relatively undeveloped. The present work, along with recent developments on the stabilization of nanostructures by ALD \cite{19}, demonstrates that it is still possible to introduce new concepts in this area to make this a practical approach for producing manufacturable and stable electrodes for SOFC.

3.5 Conclusions

No insulating phases are formed following calcination of LSF and YSZ mixtures to temperatures as high as 1473 K. Because of this, porous LSF-YSZ composites can be used as scaffolds to prepare SOFC electrodes by infiltration. Since the infiltrated phase is
only required for the catalytic reaction, good electrode performance could be achieved using only one or two infiltration cycles.

3.6 References


Chapter 4. Optimization of LSF-YSZ Conductive Scaffolds for Infiltrated SOFC Cathodes*

Summary

Porous composites of Sr-doped LaFeO$_3$ (LSF) and yttria-stabilized zirconia (YSZ) were investigated as conductive scaffolds for infiltrated SOFC cathodes with the goal of producing scaffolds for which only a few perovskite infiltration steps are required to achieve enough conductivity. While no new phases form when LSF-YSZ composites are calcined to 1623 K, shifts in the lattice parameters indicate Zr can enter the perovskite phase. Measurements on dense, LSF-YSZ composites show that the level of Zr doping depends on the Sr:La ratio. Because conductivity of undoped LSF increases with Sr content while both the ionic and electronic conductivities of Zr-doped LSF decrease with the level of Zr in the perovskite phase, there is an optimum initial Sr content corresponding to La$_{0.9}$Sr$_{0.1}$FeO$_3$ (LSF91). Although scaffolds made with 100% LSF had a higher conductivity than scaffolds made with 50:50 LSF-YSZ mixtures, the 50:50 mixture provides the optimal interfacial structure with the electrolyte and sufficient conductivity, providing the best cathode performance upon infiltration of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF).

4.1 Introduction

In the last chapter, it was suggested that the number of infiltration steps could be greatly reduced if the porous scaffold was itself electronically conductive \cite{1}. Infiltration is still required to add LSCF into the scaffold to carry out the oxygen-exchange reactions but the amounts required for the catalytic reaction can be much smaller. To implement this approach, it is necessary to find a conductive oxide that will not react with YSZ at the temperatures required to produce a dense electrolyte. Because Sr-doped LaFeO$_3$ (LSF) has been shown to be relatively unreactive with YSZ \cite{2,3,4} our group focused on preparing LSF-YSZ scaffolds for this application.\footnote{Co-firing LSF and YSZ did not lead to new phases but a shift in the lattice parameter for the perovskite phase suggested that some Zr was entering the perovskite lattice. Electrochemical cells produced with the LSF-YSZ scaffolds exhibited reasonable performance; however, some ohmic losses were observed prior to infiltration of additional perovskite, suggesting that higher conductivities would be desirable. Zr doping of LSF is known to decrease its electronic conductivity \cite{4} and this may be responsible for the low conductivity of the scaffold.}

In the present study, we have further explored the use of LSF-YSZ composites as scaffolds for SOFC cathodes and attempted to identify the optimal conditions for using this approach.
4.2 Experimental

La$_{x}$Sr$_{1-x}$FeO$_3$ (LSF) powders with various La:Sr ratios were synthesized via a standard sol-gel method, as detailed in the Experimental section of the last chapter. XRD analysis of the resulting powder showed only peaks characteristic of the perovskite phase. Throughout the remainder of this paper we will use the nomenclature LSF$_{nm}$, where n:m corresponds to the La:Sr ratio, to specify the composition of each LSF sample. For example, LSF$_{91}$ has a La:Sr ratio of 9:1. The YSZ powder was purchased from Tosoh (TZ-8Y) and contained 8\% Y$_2$O$_3$.

Mixtures of the LSF and YSZ powders were prepared using a roller ball mill. The desired amounts of each powder were placed into an HDPE bottle together with zirconia beads. Ethanol was added as a solvent and the powders were milled for 12 h. The ethanol was then removed and the powders milled for an additional 12 h. After drying, the mixed LSF-YSZ powders were used without further processing. Since the LSF-YSZ mixtures were to be co-fired with the green YSZ electrolyte during cell fabrication, we calcined samples of the LSF-YSZ mixtures to 1623 K for 4 h. After calcination, the samples were ground into fine powders and analyzed using XRD to determine the extent of solid-state reactions.

The total conductivities of dense, pure LSF and LSF-YSZ composite slabs were measured using the 4-probe method on slabs having dimensions of 7 mm x 3 mm x 1 mm. The slabs were prepared by pressing the LSF or mixed LSF-YSZ powders, followed by firing to 1623 K. The ionic conductivities of LSF$_{82}$ and a 40-wt\% LSF$_{82}$/60-wt\% YSZ composite were measured using a membrane reactor described in more detail in other publications \cite{5, 6, 7}. Briefly, dense pellets of the mixed-conducting oxides, 330-\textmu m thick
and 1-cm diameter, were prepared by sintering the pressed powders to 1623 K for 4 h. To minimize resistance to surface reactions, porous layers of LSF82, ~30 µm thick, were fastened onto both sides of the LSF82 pellet using xylene; and similar porous layers of LSF82-YSZ were fastened onto the composite pellet. For both pellets, the porous layer on one side was impregnated with two rounds of the nitrate salts of La, Sr, and Fe to enhance oxygen adsorption, while the porous layer on the other side was infiltrated with 1-wt% Pd and 5-wt% ceria using their nitrate solutions (tetraammineplatinum(II) nitrate, Alfa Aesar; and Ce(NO₃)₃·6H₂O, Alfa Aesar, 99.5%) to enhance reactions with CO. After mounting the pellets onto a YSZ tube so that the Pd-containing side could be exposed to flowing CO, with the other side exposed to air, oxygen-ion fluxes were determined from the rate of CO oxidation, measured using a gas chromatograph. Finally, the ionic conductivities were calculated from the oxygen flux and the chemical potential across the membrane, as described elsewhere [7].

The electrochemical cell manufacturing and testing methods are the same as described in Section 2.1 and Section 3.2.

4.3 Results & Discussion

4.3.1 Compatibility of Different LSF with YSZ

A major goal in this work was to increase the electronic conductivity of the LSF-YSZ scaffold so that infiltration of LSCF would be required for catalytic purposes only.
Because the conductivity of LSF increases with the level of Sr doping, we first examined the effect of Sr content on LSF-YSZ mixtures. Figure 4.1 shows a series of XRD patterns for mixtures of LSF and YSZ, after calcination to 1623 K. The line positions were referenced to an internal graphite standard and both the weight percent LSF and the La:Sr ratio were varied. The bottom pattern was obtained on a 50-wt% mixture of LSF82 and YSZ, prior to calcination, and shows features at 30.11 and 32.26 2θ corresponding to the (111) and (020) peaks of YSZ and LSF82, respectively. XRD patterns for physical mixtures of YSZ and LSF64 and LSF91 were essentially indistinguishable prior to calcination. Although the position of the (020) peak should change with La:Sr ratio, the shifts are small compared to the linewidth of the peaks shown here. None of the LSF-YSZ samples calcined at 1623 K showed evidence for new phases, but the peak positions for the perovskite phase shifted to lower angles in all cases. This result is consistent with previous reports for co-fired LSF-YSZ mixtures [2, 4]. The shift in the perovskite lattice parameter is believed to be caused by Zr cations dissolving into the perovskite lattice.
Figure 4.1: XRD patterns of LSF-YSZ mixtures after calcination at 1623 K for 4 h with different LSF:YSZ weight ratios (as indicated in the figure) and different La:Sr ratios in the LSF. The bottom pattern is that of a physical mixture of a 50-wt% LSF91-YSZ mixture prior to calcination. (a) shows the XRD patterns over a wider range of angles while (b) reports the same patterns in the region shown between the dashed lines in (a).
A closer look XRD patterns shows that the peak shift in the perovskite phase increases with Sr content. Considering only the 50-wt% LSF-YSZ samples, the (020) perovskite peak decreased to 32.12 degrees 2θ for the LSF91-YSZ sample, 31.96 degrees 2θ for the LSF82-YSZ sample, and 31.68 degrees 2θ for the LSF64-YSZ sample. The larger peak shift would suggest an increased level of Zr doping. When we increased the weight percent of perovskite in the LSF-YSZ mixtures to 70-wt% LSF, the position of the perovskite diffraction peak on the LSF91-YSZ and LSF82-YSZ samples did not change, suggesting that the two phases were essentially in equilibrium, with Zr doping having reached its saturation limit. For the 70-wt% LSF64-YSZ sample, the YSZ peak almost disappeared and the shift in the perovskite peak was significantly lower, implying that the YSZ phase had been almost completely consumed into the perovskite phase. This is again consistent with increased Zr doping for materials with higher Sr:La ratios.

4.3.2 Total Conductivity of LSF-YSZ composite as a function of Sr content

Ultimately, the goal in preparing LSF-YSZ composites is to increase the conductivity of the scaffold. The results from 4-probe conductivity measurements at 973 K of dense LSF and 50-wt% LSF-YSZ composites are shown in Figure 4.2 as a function of the La: Sr ratio. The conductivity of pure LSF decreases monotonically as the Sr content decreases, from approximately 160 S/cm for LSF64 to 25 S/cm for La0.95Sr0.05FeO3. However, the conductivities of the 50-wt% LSF-YSZ mixtures go through a maximum near the La: Sr ratio of 9. Furthermore, the conductivities of the composites are a small fraction of the pure LSF conductivities. Based on previous work with composites of Sr-
doped LaCrO$_3$ (LSCr) and YSZ \[^5\], a 40-wt%, random composite of a conductor and an insulator would have a conductivity approximately 5% of the pure electronic conductor. In the present study, a 50-wt% LSF64-YSZ composite exhibited a conductivity only 0.2% that of LSF64 and a 50-wt% LSF91-YSZ composite exhibited a conductivity that was 3% that of LSF91. These results imply that the Zr doping decreases the electronic conductivity of the perovskite and that the loss in conductivity decreases with Sr content.
4.3.3 Ionic Conductivity of LSF-YSZ composite as a function of Sr content

The scaffold ionic conductivity is another factor that influence electrode performance \cite{8, 9}. Both experiments and theory have shown that electrode impedances should vary with the inverse square root of this parameter if all other factors remain constant \cite{9}. In the present study, we measured the ionic conductivity of dense LSF82 and 40-wt% LSF82-YSZ composites using a membrane reactor to determine the effect of Zr dissolution into the LSF phase. Figure 4.3 shows the measured oxygen fluxes through LSF82-YSZ and LSF82 membranes as a function of temperature, with CO flowing on one
side of the membrane and the other side exposed to air. The oxygen fluxes were calculated from the CO conversion to CO$_2$, measured using a gas chromatograph. As discussed elsewhere [6,7], the total resistance of the mixed-conducting membrane to oxygen flow can be calculated from these measurements. By applying catalytic electrodes to the surfaces of the membrane, the surface resistances become small, making ion conduction the limiting factor.
Figure 4.3: Oxygen fluxes as a function of temperature measured in a membrane reactor using flowing CO on one side and air on the other. Data are shown for a) a dense, 40-wt% LSF82-YSZ membrane and b) an LSF82 membrane. Both membranes were 330 μm thick, with catalyst layer on both sides to reduce surface resistances.
The new data for the ionic conductivities of LSF82 and LSF82-YSZ at 973 and 1073 K are summarized in Table 4.1 together with previously reported data for the ionic conductivities of La$_{0.9}$Ca$_{0.1}$FeO$_3$ \[^6\] and the tabulated conductivity of YSZ \[^10\]. It is interesting to notice that, at 973 K, the ionic conductivity of LSF82, 0.072 S/cm, is about twice that of La$_{0.9}$Ca$_{0.1}$FeO$_3$, 0.03 S/cm. The major difference here is likely the higher dopant level in LSF82. Although it has been suggested that Sr-doped materials could have higher ionic conductivities than their Ca-doped analogs \[^{11,12,13}\], this does not appear to be the case.

Table 4.1: Ionic conductivities of dense materials used in this study. Results for the 40-wt% LSF82-YSZ composite and LSF82 were determined from oxygen fluxes measured in a membrane reactor. Data for LCF and YSZ were taken from references 9 and 14.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>40-wt% LSF82-YSZ (S/cm)</th>
<th>LSF82 (S/cm)</th>
<th>LCF91 (S/cm)</th>
<th>YSZ8 (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>0.006</td>
<td>0.072</td>
<td>0.03</td>
<td>0.019</td>
</tr>
<tr>
<td>1073</td>
<td>0.017</td>
<td>0.089</td>
<td>0.07</td>
<td>0.042</td>
</tr>
</tbody>
</table>

More significant for our purposes here, the ionic conductivity of the 40-wt% LSF82-YSZ composite at 973 K was only 0.006 S/cm, a value that is much less than that of either YSZ (0.019 S/cm) or LSF82. Interestingly, the ionic conductivity of a 40-wt%
LSCr-YSZ composite at 973 K was shown to be almost the same value, 0.0046 S/cm\(^5\).

Since the ionic conductivity of LSCr is likely negligible, most of the ionic conductivity in the LSCr-YSZ membranes was due to the YSZ. With LSF82-YSZ, the perovskite phase may be contributing but the low value suggests that Zr doping has significantly reduced the ionic conductivity of the perovskite phase.

4.3.4 Symmetric cell test results of cathode with different scaffolds

To determine the effect of scaffold properties on electrode performance, we compared symmetric cells made with pure YSZ scaffolds, with 50-wt% LSF91-YSZ composite scaffolds, and with pure LSF91 scaffolds. The scaffold made with pure LSF91 should have the highest electronic conductivity but could have a low ionic conductivity in the electrochemically active region since Zr doping near the electrolyte interface will be important. The pure YSZ scaffold likely has the highest ionic conductivity but negligible electronic conductivity, while the composite scaffold will be a compromise, at least with respect to electronic and ionic conductivities.
**Figure 4.4**: Nyquist plots of symmetric cells with different cathode scaffolds in air as a function of the number of infiltration rounds in the scaffold. Hollow symbols (O) are for cells with bare scaffolds and filled symbols are for cells with two rounds (▲) and eight rounds (●) of infiltration of LSCF. Data are shown at 973 K in (a) and 1073 K in (b).
Figure 4.4 (a) and 4.4 (b) show impedance data at 973 K and 1073 K in air for symmetric cells made from each of the scaffolds. Data were taken with zero, two, and eight infiltration cycles of LSCF. In the absence of infiltrated LSCF, all three cells exhibited ohmic resistances in excess of that expected for the YSZ electrolyte. (Because the Nyquist Plots have been divided by two to account for the two electrodes, the contribution from the 80-µm electrolyte is expected to be 0.2 Ω·cm² at 973 K and 0.1 Ω·cm² at 1073 K.) For pure YSZ at 973 K, the excess ohmic losses were nearly 2.5 Ω·cm² greater than the electrolyte resistance prior to infiltration. For the LSF91 and LSF91-YSZ scaffolds in the absence of infiltration, the ohmic resistances at 973 K were only 0.14 and 0.3 Ω·cm² in excess of the expected 0.2 Ω·cm². In the present study, the scaffolds were 35-µm thick and some of extra ohmic resistance could be reduced by using thinner scaffold layer. Since a typical electrode functional layer is less than one-third this value, thinner scaffolds could certainly be employed\textsuperscript{[14]}.

With the pure YSZ scaffold, two infiltration cycles of LSCF reduced the excess ohmic to 0.1 Ω·cm² above the expected electrolyte resistance at 973 K and 0.07 Ω·cm² at 1073 K. Eight infiltration cycles resulted in cells with the correct ohmic resistance. The non-ohmic losses in cells with eight infiltration cycles were less than 0.1 Ω·cm² at 973 K and 0.03 Ω·cm² at 1073 K. Similarly, infiltration of two and eight cycles of LSCF decreased the ohmic losses in cells with LSF91-YSZ and LSF91 scaffolds to the resistance of the electrolyte. However, while the non-ohmic losses in cells with the LSF91-YSZ scaffold decreased to values close to that achieved with the YSZ scaffold after eight
infiltration cycles, the non-ohmic losses with the LSF91 scaffold remained very large, ~2 Ω·cm$^2$ at 973 K.

4.3.5 Structural analysis of the scaffolds with SEM

In order to understand the possible reasons for the poor performance of cells prepared with LSF91 scaffolds, cross-sectional SEM images were taken of the electrolyte-scaffold interface on cells similar to those used in Figure 4.4. The images shown in Figure 4.5 demonstrate the likely reason for the poor performance of the cell with the pure LSF electrode scaffold. The image in Figure 4.5 a) is that of a cell with a pure YSZ scaffold. The electrode scaffold produced using graphite pore formers has uniformly distributed pores with diameters of ~2 µm, and the interface between the scaffold and the electrolyte shows good connectivity. The image in Figure 4.5 b) is that of a cell with a 50-wt% LSF91-YSZ scaffold. The scaffold structure again shows uniform pores but ones that are slightly larger, 5 to 10 µm in diameter. The scaffold-electrolyte interface again shows good bonding. These results are in contrast to what we observed for the cell with the pure LSF91 scaffold. As shown in Figure 4.5 c), this scaffold contained pores that were greater than 20 µm in diameter and the scaffold was poorly connected to the YSZ electrolyte. The poor connectivity with the electrolyte is an especially serious problem.
Figure 4.5: Scanning Electron Micrographs of co-fired scaffold-YSZ electrolyte interfaces. Data are show for (a) a pure YSZ scaffold, (b) a 50:50 LSF91-YSZ composite scaffold and (c) a pure LSF91 scaffold.

While it may be possible to engineer a better electrolyte-scaffold interface in cells with LSF scaffolds, there are fundamental issues that make this difficult. In order to form a good interface in laminated layers, the two layers need to shrink simultaneously during calcination. However, shrinkage and densification in pressed LSF pellets typically occurs at much lower temperatures, as low as 1273 K\[^{15}\], while temperatures in excess of 1623 K are typically needed to sinter YSZ\[^{16}\]. Therefore, the poor microstructure at the YSZ-LSF91 interface is likely due to this difference in the sintering rates for the LSF91 and YSZ. This conclusion is also supported by the SEM images which show that the pure
LSF91 scaffold (Figure 4.5 c) appears to have much larger grain sizes compared to what is observed in YSZ and YSZ-LSF91 composite scaffold.

4.4 Conclusions

While there is still much work to in order to understand the long-term stability of SOFC cathodes prepared by infiltration, the present study demonstrates that it should be possible to co-fire an electronically conductive scaffold based on LSF and YSZ together with a YSZ electrode, reducing the required number of calcination steps in cell fabrication. The use of these electronically conductive scaffolds decreases the number of infiltration steps required to prepare high-performance electrodes. Preparation of cathodes by infiltration into co-fired scaffolds should also eliminate the need for adding a barrier layer between the cathode and the electrolyte, which can also add to the cell resistance [17]. Therefore, infiltration into conducting scaffolds has the potential to be very attractive for improving SOFC performance and reducing the cost of cell fabrication.
4.5 References


Chapter 5. Cr-Doped LSF as A Zr-Excluding Component in Dual-Phase Cathode Scaffold*

Summary

Fabrication of SOFC cathodes by infiltration of LSCF into composite scaffolds were investigated. LSCrF-YSZ, was tested as potential SOFC cathode scaffolds for cells operating at 973 K. Although Zr migration in LSF-YSZ scaffold was discovered and determined to be harmful in the previous study, LSCrF-YSZ scaffold was able to eliminate Zr migration, but the poor sinterability of the LSCrF hindered sintering of the electrolyte. Although problems still exist, this scaffold showed improved performance at low LSCF loading due to the reduced ohmic loss.

5.1 Introduction

In the previous chapters, the compatibility of LSF and YSZ was extensively studied, and the optimized LSF composition was discovered for the composite application. However, the migration of Zr to LSF lattice was still not eliminated, therefore the ionic conductivity of the composite was compromised.

Sr-doped LaCrO$_3$ (LSCr) has good compatibility with YSZ and is widely used in interconnects and anodes $^{[1-3]}$. It is also a candidate for providing electronic conductivity

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for composite cathode scaffolds. Previous studies have shown that LSCr and YSZ do not react with each other at temperatures up to 1773 K, although it has the disadvantages of poor sinterability and low electronic conductivity. Several studies suggest, however, that substituting a portion of the Cr in LSCr with Fe (LSCrF) could help overcome these limitations \([4, 5]\). LSCrF also has some ionic conductivity which could be beneficial to cathode performance \([6]\).

In the present study we have, therefore, explored the use of LSCrF-YSZ as composite scaffolds for infiltrated SOFC cathodes. XRD was used to identify the conditions and compositions for which reaction between these perovskites and YSZ resulting in dissolution of some Zr into the perovskite phase can be avoided, and then evaluated the performance of infiltrated cathodes made using these materials.

5.2 Experimental

La\(_{0.8}\)Sr\(_{0.2}\)Cr\(_{x}\)Fe\(_{1-x}\)O\(_3\) (LSCrF) powders were synthesized in a similar manner as described in our previous study using Cr(NO\(_3\))\(_3\)-9H\(_2\)O (Alfa Aesar, 98.5%) as the Cr precursor. In the remainder of this paper we will use the nomenclature LSCrF## where ## represents the ratio of Cr to Fe in the B site. For example, LSCrF64 stands for La\(_{0.8}\)Sr\(_{0.2}\)Cr\(_{0.6}\)Fe\(_{0.4}\)O\(_3\). The YSZ powder was purchased from Tosoh (TZ-8Y) and contained 8% Y\(_2\)O\(_3\).

Mixtures of the perovskite and YSZ powders were prepared using a roller ball mill. The powders were placed into an HDPE bottle together with zirconia beads which were
used to facilitate the mixing process. Ethanol was added as a solvent and the bottle was rolled in the mill for 12 hrs. The ethanol was then removed and the bottle was rolled for an additional 12 hrs. After mixing the powders were dried and then used without further processing.

The cell manufacturing and testing methods were extensively discussed in previous chapters. Due to poor structural properties in the resulting cathode scaffolds, it was necessary to use less graphite pore formers in the LScrF-YSZ tapes compared to that in the LSF-YSZ tapes. Dense electrolyte tapes were made in a similar manner using tapes without pore formers. Detailed recipes for the porous and dense tapes can be found in previous publications [7, 8]. The sintered electrolytes were 1 cm in diameter and 100 μm thick for the cells in the LScrF-YSZ electrode scaffolds study.

In order to determine if reaction between the perovskite and YSZ occurred at the calcination temperature resulting in the formation of new phases at the interfaces between the two materials, slices of the green tapes were taken and calcined in the same manner as the symmetric cells. After calcination, the resulting chunks were ground into fine powders and then analyzed using XRD. As a reference, XRD patterns of unsintered perovskite-YSZ mixture were also collected.

5.3 Results and Discussion

5.3.1 Elimination of Zr incorporation with Cr doping into LSF
Figure 5.1 displays XRD data for LSCrF-YSZ mixtures as a function of the Cr B-site occupancy both before and after sintering at 1693 K for 4 h. The XRD patterns for the unsintered samples show an upward shift in the perovskite (020) peak with increasing Cr content. This is due to contraction of the unit cell as smaller \( \text{Cr}^{4+} \) ions are substituted for \( \text{Fe}^{4+} \) ions. For the LSCrF28 and LSCrF46 samples, upon sintering this peak undergoes a downward shift which as described above can be attributed to Zr dissolution into the perovskite. This shift, however, decreased with increasing Cr content and was absent for the LSCrF64 and LSCr samples, suggesting that reaction between these materials and the YSZ did not occur. While this suggests that LSCr would be a good choice for use in composite electrode scaffolds, one must recognize that it is difficult to sinter. LSCrF64 on the other hand may provide good phase stability with YSZ while having better sintering characteristics. For this reason we chose to further explore the use of this material in LSCrF-YSZ composite electrode scaffolds.
**Figure 5.1:** XRD data for LSCr\textsubscript{x}F\textsubscript{1-x}-YSZ mixtures at 1693 K. Room temperature patterns indicate the peak positions of the unsintered materials.
5.3.2 Conductivity of LSCrF-YSZ composites

Table 5.1 provides a comparison of the measured total conductivity at 973 K of LSF82 and LSCrF64 sintered at 1623 K and 1698 K, respectively. Note that while the LSF82 has a total conductivity of 80 S/cm, this drops to only 14 S/cm for LSCrF64; however, as shown in the table, this nearly 6-fold decrease upon Cr addition is not reflected in the conductivity of the LSF82-YSZ and LSCrF64-YSZ 50:50 composites which had conductivities of 0.8 and 0.75 S/cm, respectively. As shown above, the conductivity of the LSF82-YSZ composite is limited by the reaction between the two components that results in some Zr dissolution into the LSF. While this does not occur for the LSCrF64-YSZ composite, a similar conductivity is obtained due to the lower intrinsic conductivity of the LSCrF64.

Table 5.1: Conductivity test of La$_{0.8}$Sr$_{0.2}$Cr$_x$F$_{1-x}$ and La$_{0.8}$Sr$_{0.2}$Cr$_x$F$_{1-x}$-YSZ composites.

<table>
<thead>
<tr>
<th>X</th>
<th>$\sigma_{\text{Pure Phase (S/cm)}}$</th>
<th>$\sigma_{\text{Composite (S/cm)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td>0.6</td>
<td>14</td>
<td>0.75</td>
</tr>
</tbody>
</table>

5.3.3 Performance of LSCrF-YSZ composite scaffold

Impedance spectra for symmetric cells made with YSZ 100 μm electrolytes and pure YSZ or LSCrF64-YSZ electrode scaffolds are shown in Figure 5.2. Data is included for cells in which the performance of the electrodes have been enhanced by one, two, and ten
cycles of infiltration of LSCoF. A cell with the electronically conductive LSCrF64-YSZ scaffold with no LSCF infiltration had an ohmic ASR of 0.75 Ω cm² which is still larger than the theoretical contribution of the electrolyte but much better than that of the pure YSZ scaffold which has an ohmic ASR of 2.5 Ω cm². As shown in the figure, after one round of LSCoF infiltration, the ohmic ASR of the cells with the LSCrF64-YSZ and pure YSZ electrode scaffolds decreased to 0.35 and 0.43 Ω cm² respectively. Note, however, that while the LSCrF64-YSZ cell has a 0.08 Ω cm² lower in ohmic ASR, its non-ohmic ASR (Rₚ), 0.17 Ω cm², was 0.05 Ω cm² larger than that for the pure YSZ cell. This is likely due to the lower ionic conductivity of the LSCrF-YSZ scaffold. After another round of infiltration, both cells showed continued improvement in the ohmic and non-ohmic resistances with the LSCrF-YSZ cell having a 0.07 Ω cm² lower ohmic ASR. The non-ohmic ASR of the LSCrF-YSZ scaffold cell, 0.12 Ω cm², was more than twice that of the pure YSZ scaffold cell, 0.055 Ω cm². This difference in non-ohmic ASR unfortunately offsets the advantage that the composite scaffold has in ohmic resistance. Up to this stage, both cells have the same total resistance. After 10 rounds of LSCoF infiltration, the LSCrF-YSZ still had 0.03 Ω cm² extra ohmic ASR and 0.03 Ω cm² extra non-ohmic ASR compared to the pure YSZ scaffold cell. These together made the total ASR of LSCrF-YSZ scaffold cell ~0.06 Ω cm² larger than the LSCoF-infiltrated YSZ scaffold cell.
Figure 5.2: Nyquist plots for cells with LSCrF-YSZ scaffolds and pure YSZ scaffolds collected in air at 973 K. Red squares (□), green diamonds (◇) and blue circles (○) are for cells with one, two, and ten, rounds of LSCoF infiltration, respectively.

5.3.4 Structural defects of co-sintered LSCrF-YSZ composite scaffold

Unfortunately, the impedance data show that incorporating electronic conductivity into the electrode scaffold using LSCrF produced less improvement in the overall performance compared to a pure YSZ scaffold than expected. While the LSCrF-YSZ scaffold is less susceptible to Zr doping when sintered, it appears to have little advantage over the LSF91-YSZ scaffold described above. As was the case for the LSF91-YSZ...
scaffold, one must also consider how cell microstructure may be affecting performance. Figure 5.3 displays cross-sectional SEM images of cells with the LSF91-YSZ and pure YSZ scaffolds prior to infiltration with LSCoF. For comparison purposes an image for the LSF91-YSZ scaffold cell is also included. These images reveal several important differences between the cells. First the electrolyte layer for the cell with the LSCrF-YSZ scaffold is less dense than that in the other cells and contains numerous isolated pores (see images a, d). Since the electrolyte layers in the three cells were all cut from the same green tape, this cannot be due to cell-to-cell variability. We also note that this result was reproducible and observed in several other cells with LSCrF-YSZ scaffolds. While further study is needed to determine the exact cause for the pores in the electrolyte, it likely results from the poor sintering characteristics of the LSCrF which serves to inhibit complete densification of the YSZ electrolyte layer.
Figure 5.3: SEM images of (a) (d) a cell with LSCrF-YSZ scaffolds, (b) (e) a cell with pure YSZ scaffolds, and (c) a cell with LSF-YSZ scaffolds.
The extra ohmic resistance may also be due in part to the microstructure of the cathode. The pure YSZ cathode scaffold (images b, e) is composed of numerous 1-2 μm diameter fine pores with well-connected thin walls. This fine pore structure imparts high surface area and a high distribution of the infiltrated material. In contrast, both the LSCrF-YSZ (images a, d) and LSF-YSZ (image c) composite scaffolds contain larger pores (5-10 μm) with thick supporting walls. Together these features result in less active surface area and a poorer distribution of the infiltrated material. The former will adversely affect the non-ohmic ASR of the electrode, while the latter is likely to affect how well the infiltrated material is interconnected which could affect the ohmic ASR. These results illustrate the interplay between materials properties, microstructure, and morphology in influencing cathode performance. Optimization of all of these features is needed to improve both the manufacturability and performance of infiltrated SOFC cathodes that use composite scaffolds that contains both electronically and ionically conducting components.

5.4 Conclusions

Substituting a high fraction of the B-site Fe in the LSF with Cr helped alleviate the deleterious Zr incorporation reaction, but the poor sintering characteristics of this material caused other problems, such as incomplete densification of the co-fired YSZ electrolyte layer and a poor electrode microstructure.

The results of this study do, however, illustrate the promise of infiltrated cathodes that use a composite scaffold composed of a material optimized for ionic conductivity, such as YSZ, and a second component optimized for electronic conductivity, such as LSCrF or
LSF (previously studied). For these composite scaffolds, despite the issues mentioned above, good cathode performance was achieved with relatively few infiltration cycles of an LSCoF catalytic layer.

5.5 References

Chapter 6. Modification of LSF-YSZ Composite Cathodes by Atomic Layer Deposition*

Summary

Composite, Solid-Oxide-Fuel-Cell (SOFC) electrodes of La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF) and yttria-stabilized zirconia (YSZ) were prepared by infiltration methods and then modified by Atomic Layer Deposition (ALD) of ZrO$_2$, La$_2$O$_3$, Fe$_2$O$_3$, or LaFeO$_3$ films of different thicknesses to determine the effect of surface composition on cathode performance. Film growth rates for ALD performed using vacuum procedures at 573 K for Fe$_2$O$_3$ and 523 K for ZrO$_2$ and La$_2$O$_3$ were determined to be 0.024 nm ZrO$_2$/cycle, 0.019 nm La$_2$O$_3$/cycle, and 0.018 nm Fe$_2$O$_3$/cycle. For ZrO$_2$ and Fe$_2$O$_3$, impedance spectra on symmetric cells at 873 K indicated that polarization resistances increased with coverage in a manner suggesting simple blocking of O$_2$ adsorption sites. With La$_2$O$_3$, the polarization resistance decreased with small numbers of ALD cycles before again increasing at higher coverages. When La$_2$O$_3$ and Fe$_2$O$_3$ were co-deposited, the polarization resistances remained low at high film coverages, implying that O$_2$ adsorption sites were formed on the co-deposited films. The implications of these results for future SOFC electrode development are discussed.

6.1 Introduction

Atomic Layer Deposition (ALD) is attracting an increasing level of attention as a method for modifying SOFC electrodes because the surface composition can be modified with unparalleled precision \cite{111}. Uniform, atomic-scale films are formed in ALD by repeated cycles in which the surface is first allowed to react with an organometallic precursor, followed by a subsequent oxidation step. Since the reaction of the precursor with the surface is performed under conditions which limit the extent of reaction to one monolayer, the thickness of the final oxide film can be precisely controlled by the number of cycles.

In the case of SOFC cathodes, ALD has been used to improve both electrode stability and decrease impedance \cite{14}. For example, Gong, et al. reported that degradation rates for cathodes based on La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) decreased significantly after depositing a 5-nm ZrO$_2$ film\cite{3,4}. While they reported a slight increase in the initial electrode impedance, the performance of the ALD-modified electrode surpassed that of the unmodified electrode after less than 100 h and exhibited a much lower impedance after 900 h of operation at 1073 K. In another example of cathodes modified by ZrO$_2$ ALD films, the initial impedance of composite cathodes of Sr-doped LaMnO$_3$ (LSM) and yttria-stabilized zirconia (YSZ) actually decreased following deposition of films as thick as 60 nm \cite{5}.

However, studies in which electrodes were modified by ALD with other oxides have shown deleterious effects on performance. Yu, et al. examined submonolayer coverages of CeO$_2$, SrO, and Al$_2$O$_3$ on Sr-doped LaFeO$_3$ (LSF) cathodes and reported
that each of these blocked sites for oxygen adsorption\textsuperscript{[12]}. Likewise, Choi, et al. found that addition of CoO\textsubscript{x} layers onto La\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3} (LSC) cathodes increased electrode polarization by reducing the oxygen-exchange reaction\textsuperscript{[6]}. This latter study is particularly revealing because it had been previously reported that infiltration of CoO\textsubscript{x} nanoparticles could be used to decrease cathode polarization\textsuperscript{[13]}. Choi, et al. suggested that addition of CoO\textsubscript{x} by ALD differs from infiltration which produces inhomogeneous layers and because the infiltration process may induce changes in the cathode morphology\textsuperscript{[6]}. In principle, ALD allows catalytic materials to be added to the electrode surface as homogeneous layers, without changing the electrode morphology.

The properties of films prepared by ALD appear to depend on the specific deposition conditions that were used, especially when ALD is performed on porous materials. In the above examples of ZrO\textsubscript{2} films on SOFC cathode materials, the growth rates using tetrakis (dimethylamino)-zirconium (TDMZ) as the precursor were reported to be 0.57 nm/cycle\textsuperscript{[5]} and 0.67 nm/cycle\textsuperscript{[4]} at 583 and 573 K, respectively. In both cases, the ZrO\textsubscript{2} films were uniform throughout the porous electrodes but were themselves porous. Using the same precursor, Onn et al. reported ZrO\textsubscript{2} films deposited onto high-surface-area alumina formed dense, conformal films with a growth rate of 0.02 nm/cycle\textsuperscript{[14]}. Finally, Keuter, et al reported formation of dense ZrO\textsubscript{2} films on SOFC anode materials, with a growth rate of 0.1 nm/cycle, using a chemically similar precursor, tetrakis (ethylmethylamino)-zirconium\textsuperscript{[1]}. Major differences in the procedures used in these studies are the deposition temperatures and whether or not the precursors were exposed to the precursor in the presence of an inert carrier gas.
In the present work, we have investigated the effect of modifying an LSF-YSZ electrode with dense films of ZrO$_2$, La$_2$O$_3$, Fe$_2$O$_3$, and LaFeO$_3$, all formed by ALD. While each of the pure oxides appear to block O$_2$ adsorption sites on the cathode, we show evidence that LaFeO$_3$ films could form O$_2$ adsorption sites on the SOFC cathode.

6.2 Experimental

ALD was performed in a homebuilt system that has been described in detail in other publications [12,15–17]. The system is essentially an adsorption apparatus that can be evacuated with a mechanical pump to approximately 10$^{-3}$ torr. The system consists of separate chambers for the substrate and two precursors, separated by high temperature valves. Separate furnaces were placed around each chamber, as well as around the lines between the chambers, in order to control the temperature in each section. The evacuated sample could be exposed to one of the precursor molecules by simply allowing the vapor from the precursor chamber to flow into the sample chamber. Diffusion limitations in the porous samples were minimized by not having an inert carrier gas included with the precursor. After evacuation, the sample could then be oxidized by exposure to water vapor or O$_2$. The precursors used in the present study were tetrakis (2,2,6,6-tetramethyl-3,5-heptanedionato) zirconium (Zr(TMHD)$_4$, Strem Chemical, Inc.), tris(2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanum (La(TMHD)$_3$, Strem Chemical, Inc.), and ferrocene (Fe(Cp)$_2$, Sigma Aldrich). The deposition temperatures were chosen to be 573 K for Fe$_2$O$_3$ and 523 K for ZrO$_2$ and La$_2$O$_3$. Because the ligands for the La and Zr precursors could not be oxidized with O$_2$ or water at the deposition temperature, the
sample used in this study were removed from the system and oxidized in a muffle furnace at 773 K for 5 min after each deposition cycle. Later studies showed that the ligands could be effectively oxidized at the deposition temperature using NO₂ as the oxidant and that identical growth rates for ZrO₂ on γ-Al₂O₃ could be achieved by sequential dosing of the Zr(TMHD)₄, precursor and NO₂. As discussed in previous papers [15,16], varying the exposure times and pressures did not affect deposition rates for the conditions used in these experiments.

An attempt to observe changes in the sample by Scanning Electron Microscopy (SEM) following deposition of 100 cycles of La₂O₃ was unsuccessful. Therefore, ALD growth rates were determined by measuring weight changes per cycle on half a gram of γ-Al₂O₃ powder with a BET surface area of 130 m²/g [17]. These data are shown in Figure 6.1 for each of the precursors. To calculate film thicknesses, the films were assumed to cover the γ-Al₂O₃ surface uniformly and have their bulk density. Previously published microscopy results on γ-Al₂O₃ suggest that this is approximately correct [15, 16]. Based on these measurements, the growth rates were determined to be 0.024 nm ZrO₂/cycle, 0.019 nm La₂O₃/cycle, and 0.018 nm Fe₂O₃/cycle. To demonstrate that these growth rates are not strongly dependent on the substrate, measurements were also performed for Fe₂O₃ deposition on an LSF powder with a surface area of 6 m²/g. This showed a growth rate of 0.02 nm/cycle, a value essentially identical to that obtained on γ-Al₂O₃, but less accurate because of the lower surface area of the substrate. It is also worth noting that the growth rates for each of the oxides are similar to what is reported in some literature studies on nonporous substrates [18, 19].
LaFeO$_3$ films were grown by sequential deposition of La$_2$O$_3$ and Fe$_2$O$_3$, alternating between three cycles of La$_2$O$_3$ and one of Fe$_2$O$_3$ ALD cycle to ensure proper mixing of the stoichiometric amounts of each oxide. This ratio was obtained experimentally based on the molar growth rates per cycle of La$_2$O$_3$ and Fe$_2$O$_3$ on γ-Al$_2$O$_3$.

To demonstrate that the perovskite structure could be formed, X-ray Diffraction (XRD) patterns were measured following deposition of a 1-nm film (45 cycles of La$_2$O$_3$ and 15 cycles of FeO$_3$) on γ-Al$_2$O$_3$. Figure 6.2 shows XRD patterns of the LaFeO$_3$/γ-Al$_2$O$_3$ after calcination at 873 and 1073 K, together with the unmodified γ-Al$_2$O$_3$. Peaks associated with the perovskite phase are clearly visible after heating to 873 K. These peaks show greatly increased intensity after heating to 1073 K; however, because LaAlO$_3$ has a nearly identical diffraction pattern as LaFeO$_3$ and could form at this higher temperature [20], the pattern in Figure 6.2 c) could correspond to a mixture of LaAlO$_3$ and LaFeO$_3$. 

**Figure 6.1:** Growth rate as a function of number of ALD cycles on γ-Al$_2$O$_3$ for a) ZrO$_2$, b) La$_2$O$_3$ and c) Fe$_2$O$_3$. 
Figure 6.2: XRD patterns of the γ-Al₂O₃ sample before ALD modification and after depositing 45 ALD cycles La₂O₃ and 15 ALD cycles of Fe₂O₃. The XRD are of a) Fresh, unmodified γ-Al₂O₃; b) ALD-modified γ-Al₂O₃ after calcination to 873 K; c) the ALD-modified sample after calcination to 1073 K. Characteristic peaks for LaFeO₃ are marked by *, while obvious peaks associated with Al₂O₃ are marked by ●.
The effect of modifying electrodes by ALD was studied on symmetric cells with LSF-YSZ composite electrodes similar to cells used in previous studies \cite{21, 22}. The electrolyte-supported cells were prepared by infiltration of aqueous solutions of La, Sr, and Fe salts (La(NO$_3$)$_3$ · 6 H$_2$O (Alfa Aesar, 99.9%), Sr(NO$_3$)$_2$ (Alfa Aesar, 99%), and Fe(NO$_3$)$_3$ · 6 H$_2$O (Fisher Scientific, 98.4%) in a molar ratio of La:Sr:Fe = 0.8:0.2:1) into the porous layers of porous-dense-porous, YSZ wafers. Citric acid, in a 1:1 ratio with the metal cations, was used as a complexing agent with the metal salts in order to assist the formation of the perovskite phase at the calcination temperature of 1123 K. The porous scaffolds were approximately 60% porous and had a pore structure similar to that of a sponge, with average pore sizes of approximately 2 μm. The electrodes were loaded to a level of 35-wt% LSF. The thickness of the dense and porous layers in the cells were 100 and 35 μm, respectively; and the effective surface area of the scaffolds was 0.35 cm$^2$.

After ALD modification, the cells were not heated above 873 K in most cases and electrode performance was characterized using impedance spectroscopy at this temperature. This low temperature was chosen so as to avoid disrupting the ALD films. Silver paste was applied to each electrode for current collection; and impedance spectra were measured using a Gamry Instrument potentiometer, at open circuit, with a 1 mA AC perturbation. In order to achieve self-consistency in measuring the effect of each oxide film, a single cell was used for the entire series of measurements with that oxide. For example, in measuring the effects of ZrO$_2$ films on LSF-YSZ electrodes, impedance measurements were performed on the same cell, initially and after 0, 2, 10, 20, and 40 ALD cycles. In all cases, Ag paste was applied on the electrodes just before EIS test and removed carefully afterwards in order to perform subsequent ALD cycles. This allowed
us to avoid the effects of any small variations between different cells. Additional test was carried out to verify that the vacuum by itself has null effect on the cell performance. In this regard, a pristine cell with a known impedance spectrum was put under vacuum in ALD setup for half an hour. The conditions were kept similar to complete ALD cycle, but without exposure to the precursor. The impedance spectrum was unchanged after this test, demonstrating that other steps in the process did not affect the cell performance.

6.3 Result

6.3.1 Effect of ZrO$_2$ surface modification on LSF cathodes

To determine the effect ZrO$_2$ on the LSF-YSZ cathodes, impedance measurements were performed on symmetric cells after deposition of 0, 2, 10, 20, or 40 cycles by ALD. The samples were oxidized at 773 K after each deposition cycle; but the cells, at least at intermediate stages, were not heated to higher temperatures to avoid sintering of the film. For testing, the samples were simply ramped at 10 K/min to 873 K and impedance measurements were performed. The impedances, divided by two to account for the two electrodes, are shown in Figure 6.3. Spectra with the ohmic resistances included are given in Figure 6.3 a); Figure 6.3 b) shows the same data with ohmic losses removed. As expected, the addition of ZrO$_2$ did not significantly affect the ohmic resistance. The ohmic resistance for each of the cells was 1.2 Ω cm$^2$ (2x0.6 Ω cm$^2$). The resistance for an 80-µm, YSZ electrolyte is expected to be between 1.1 and 1.3 Ω cm$^2$, using YSZ conductivities from the literature$^{23}$. 
Figure 6.3: Nyquist plots of LSF-YSZ cathode symmetric cells before and after ZrO ALD treatment measured at 873 K. Black crosses (X), triangles (△), diamonds (◇), and squares (□) represents cells after 2, 10, 20 and 40 cycles of ZrO deposition, and red cycles (○) represent the pristine cell. Figure (a) shows the full-size plots and figure (b) shows only the non-ohmic resistance part.
By contrast, the effects of adding ZrO$_2$ on the non-ohmic losses at 873 K were significant. The non-ohmic losses in the pristine cell was 0.35 $\Omega$ cm$^2$, which is reasonably good cathode performance for a YSZ-based cell operating at this low temperature. The impedance increased in a regular manner with the addition of ZrO$_2$, to 0.4 $\Omega$ cm$^2$ after 2 ALD cycles and 0.52 $\Omega$ cm$^2$ after 10 cycles, then almost doubling to 0.7 $\Omega$ cm$^2$ after 20 ALD cycles and tripling to 1.2 $\Omega$ cm$^2$ after 40 cycles. Based on the growth rate of 0.024 nm/cycle, 20 and 40 ALD cycles form films that are only 0.5 and 1.0 nm thick, the equivalent of roughly 1 and 2 unit cells of cubic zirconia. Since previous work on essentially identical LSF-YSZ electrodes indicated that the performance of these cathodes is limited by O$_2$ adsorption$^{21}$, the fact that such thin ZrO$_2$ films have a large effect implies that the ZrO$_2$ must be covering the surface uniformly and blocking the adsorption sites for O$_2$. It is also worth noting that the amount of ZrO$_2$ that was added to the electrodes was very small in all cases. Assuming that the specific surface area of the LSF-YSZ electrode was 2 m$^2$/g $^{[21]}$, the weight of the electrode after 40 ALD cycles increases by only 1%.

Finally, to determine the thermal stability of the ZrO$_2$ films, the cell modified by 40 ALD cycles was heat to 973 K for 30 min and 1073 K for 1 min. This had no effect on impedance spectra measured at 873 K, demonstrating that at least the ZrO$_2$ films are reasonably stable.
6.3.2 Effect of Fe$_2$O$_3$ surface modification on LSF cathodes

Figure 6.4 shows the analogous results following ALD of Fe$_2$O$_3$ films on the LSF-YSZ electrodes at 873 K. The ohmic losses have been removed for clarity, since they did not change with the addition of Fe$_2$O$_3$. The initial non-ohmic impedance on this cell was 0.43 $\Omega$ cm$^2$ and this increased to 0.55 $\Omega$ cm$^2$ after 5 ALD cycles, 0.84 $\Omega$ cm$^2$ after 15 ALD cycles, and 1.32 $\Omega$ cm$^2$ after 65 ALD cycles. Since the growth rate for Fe$_2$O$_3$ was only 0.02 nm/cycle, the results again show that the Fe$_2$O$_3$ film must cover the surface uniformly. Given the similarity in the relationships between impedance and Fe$_2$O$_3$ and ZrO$_2$ film thickness, we suggest that both oxides increase impedance by simply blocking the surface and thereby limiting O$_2$ adsorption.
Figure 6.4: Nyquist plots of LSF-YSZ cathode symmetric cells before and after Fe$_2$O$_3$ ALD treatment measured at 873 K. Black triangles (△), diamonds (◇), and squares (□) represents cells after 5, 15, and 65 cycles of ZrO deposition, and red cycles (〇) represent the pristine cell. The impedance spectra have been offset for clarity.
6.3.3 Effect of La$_2$O$_3$ surface modification on LSF cathodes

The results for LSF-YSZ cathode modification by La$_2$O$_3$ ALD, reported in Figure 6.5, exhibit some interesting differences from that observed for ZrO$_2$ and Fe$_2$O$_3$. When the electrode was treated with small numbers of ALD cycles, the impedance improved. This result was highly reproducible and achieved on multiple cells. For the particular cell used in taking the data in Figure 6.5, the polarization resistance dropped from an initial value of 0.46 $\Omega$ cm$^2$ to 0.28 $\Omega$ cm$^2$ after 10 La$_2$O$_3$ ALD cycles. Additional ALD cycles caused the non-ohmic impedance to increase. Starting from the cell with 20 ALD cycles, the deterioration in performance with increasing number of cycles is similar to that observed with ZrO$_2$ and Fe$_2$O$_3$, given that the growth rate for La$_2$O$_3$, 0.019 nm/cycle, was slightly lower.
Figure 6.5: Nyquist plots of LSF-YSZ cathode symmetric cells before and after La$_2$O$_3$ ALD treatment measured at 873 K. The impedance spectra have been offset for clarity.

6.3.4 Effect of La$_2$O$_3$ and Fe$_2$O$_3$ surface modification on LSF cathodes

Figure 6.6 shows results from experiments in which both La$_2$O$_3$ and Fe$_2$O$_3$ were deposited together. While we expected to achieve the best results when La and Fe were deposited in the perovskite stoichiometric ratio, the results were more complex and favored having excess La. Again, the results in Figure 6.6 were reproduced on multiple cells. First, the polarization resistance of the pristine LSF-YSZ cell at 873 K was 0.44 $\Omega$ cm$^2$; and the performance improved, to 0.28 $\Omega$ cm$^2$, following the addition of 3 ALD cycles of La$_2$O$_3$. From the weight gain rate, it was estimated that the atomic growth rate
of Fe is three times of that of La. We then added 1 cycle of Fe$_2$O$_3$ to complete the
perovskite lattice but this increased the impedance to 0.37 $\Omega$ cm$^2$. Subsequent addition of
3 more ALD cycles of La$_2$O$_3$ reduced the impedance to 0.27 $\Omega$ cm$^2$. 
Figure 6.6: Nyquist plots of a LSF-YSZ cathode symmetric cell before and after La$_2$O$_3$ and Fe$_2$O$_3$ ALD treatment measured at 873 K. Labels on the right side of the curves show how many cycles of ALD have been performed on the cell. The impedance spectra have been offset for clarity.
Since 7 ALD layers is significantly less than a close-packed monolayer of the mixed oxide, the results to this point could be viewed as catalytic promotion of the initial LSF-YSZ electrode. To determine how a more complete overlayer would affect performance, we increased the coverages to a total of 15 La$_2$O$_3$ and 5 Fe$_2$O$_3$ layers, alternating between 3 cycles of La$_2$O$_3$ for each cycle of Fe$_2$O$_3$. This increased the polarization resistance to 0.57 $\Omega$ cm$^2$. The subsequent addition of 3 more La$_2$O$_3$ cycles decreased this to 0.47 $\Omega$ cm$^2$. As a final experiment, we added 22 more cycles of La$_2$O$_3$ and 3 more of Fe$_2$O$_3$ in order to achieve a final film with a La:Fe stoichiometry of 5:3. The final polarization resistance was 0.37 $\Omega$ cm$^2$.

The results in Figure 6.6 demonstrate that, for thicker oxide coverages, having both La and Fe at the surface together improves the performance of the cell compared to what would be observed with the individual oxides. Having either 40 La$_2$O$_3$ ALD cycles or 8 Fe$_2$O$_3$ cycles would lead to significantly decreased performance compared to the pristine cell, while the cell with co-deposited La$_2$O$_3$ and Fe$_2$O$_3$ exhibited an impedance lower than that of the pristine cell. However, it does not appear that the best performance is achieved with the ideal perovskite stoichiometry. All of the data following La$_2$O$_3$ and La$_2$O$_3$-Fe$_2$O$_3$ deposition suggest that having excess La near the surface is beneficial.
6.4 Discussion

The results of this study provide new insights into the use of ALD to modify the performance of SOFC cathodes. The fact that the impedance of infiltrated LSF-YSZ cathodes increased with an increased number of ALD cycles of ZrO$_2$ or Fe$_2$O$_3$ demonstrates that these oxides effectively block the oxygen adsorption/incorporation sites on the surface of the LSF. That the decrease in performance is severe for a total number of ALD cycles that produces films on the order of one nanometer thick also demonstrates that ALD can be used to deposit highly uniform layers on the surfaces of porous electrodes. Furthermore, the results obtained when alternating ALD cycles of La and Fe deposition demonstrate that the ALD method can be used to precisely grow uniform thin layers of perovskite oxides on cathode surfaces. This result is quite exciting because it provides for the possibility of optimizing the electrode performance through the use of perovskite layers with graded composition and/or through the growth of superlattices with two or more perovskite compositions.

The results for ALD deposition of La$_2$O$_3$ layers of the electrodes were more complex than those obtained for ZrO$_2$ or Fe$_2$O$_3$ and indicated that, for La$_2$O$_3$ ALD, there were at least two separate processes affecting the electrode performance. The increase in impedance at the higher La$_2$O$_3$ coverages can again simply be attributed to blocking of the surface oxygen adsorption sites by a thin, uniform film of La$_2$O$_3$. Since 100 ALD cycles corresponds to a film thickness of only 1.9 nm, the La$_2$O$_3$ layer appears to be very effective in blocking surface against O$_2$ adsorption. The more interesting process, however, occurs for less than 20 ALD cycles where the La$_2$O$_3$ coverage is less than or at
most one monolayer. For these conditions there is a noticeable decrease in the electrode impedance relative to that in the pristine cell. Based solely on the data collected in the present study, we can only speculate as to the origin of this effect. It is noteworthy, however, that the effect is highly reproducible and leads to a significant enhancement in electrode performance. It is likely that, for these ALD conditions, the electrode surface is covered with isolated La$_2$O$_3$ clusters or scattered atoms. Perhaps the enhanced performance is due to sites at the boundaries between these features and the underlying LSF having high activity for the oxygen reduction reaction.

Comparison of the results of this study to those in previous literature studies also demonstrate that the properties of ALD-modified cathodes depend highly on the procedures and conditions used to carry out the ALD growth. As pointed out in the Introduction, two previous studies reported uniform deposition of porous ZrO$_2$ films in porous electrodes, with growth rates of roughly 0.6 nm/cycle [4, 5]. In contrast, growth rates in our work were more than 20 times lower and the large effect of ALD modification on the electrode impedances implies the films must be reasonably dense.

To explain the differences, it is worthwhile to consider that Keuter et al., using a precursor of similar size to that used in our studies, calculated the expected growth curves for ZrO$_2$ to be ~0.1 nm/cycle, based on the maximum surface density of precursor molecules which may adhere to the surface [1]. Furthermore, since chemical vapor deposition (CVD) would not produce uniform films in a porous substrate, it seems unlikely that CVD was important in any of the published work. The main difference between our homebuilt ALD apparatus and most commercial units is that, following exposure of the samples to the precursor molecules, the excess molecules in our system
are removed by evacuation, rather than by flushing with an inert carrier gas. In porous materials, desorption rates are dramatically higher in vacuum compared to rates into a carrier gas [24]. Therefore, we suggest that at least some of the variability in the reported growth rates is related to how effectively excess precursor molecules are removed from the surface prior to the oxidation step in the cycle. Oxidation of a condensed layer of the precursors would lead to higher growth rates and films that are porous. There may be benefits to higher growth rates and porous films, but it is clearly important to have the ability to control the growth process.

There are important practical implications for using vacuum techniques in the performance of ALD. Gas-phase diffusion is very slow compared to Knudsen flow and deposition of uniform films on large-area electrochemical cells or powders is much more difficult in a flow system. It is for this reason that ALD on powders is often performed in a fluidized bed [25], a procedure that is unnecessary if adsorption is performed on an evacuated sample. While the flow system allows better separation of the precursor and oxidizer for more rapid cycling, which is important for producing thicker films, the pore dimension in high-surface-area materials strongly limits how thick films can be, so that large numbers of cycles are not necessary.

While not fully explored in the present study, ALD can be a very important scientific tool for understanding the role that surface stoichiometry plays in electrode performance. Unlike infiltration procedures, ALD does not change the surface area of the electrode [26], at least when conformal dense films are formed, so that performance can be more clearly linked to surface coverage. For example, deactivation in LSCF cathodes has frequently been associated with segregation of Sr cations [27–29]. The high degree of
compositional control provided by ALD of Fe$_2$O$_3$ may allow titration of the Sr in the form of SrFeO$_3$ and re-activation of the electrode.[30,31]

Finally, we suggest that ALD has great promise for producing electrodes with complex and potentially promising surface structures. Here, we demonstrated that both pure and mixed-oxide films can be grown, but more complicated structures can be imagined. For example, there may be advantages to depositing multilayered structures. Obviously, the topic is still in its infancy.

6.5 Conclusions

1. The procedures used to grow oxide films in SOFC electrodes can affect film growth rates and morphology. ALD films grown using vacuum procedures form conformal, dense films on the electrode surface.

2. ZrO$_2$ and Fe$_2$O$_3$ films increase the polarization resistances of LSF-YSZ electrodes, apparently by covering O$_2$ adsorption sites.

3. Low coverages of La$_2$O$_3$ decrease the polarization resistance of LSF-YSZ electrodes but high coverages again increase the polarization resistance by blocking O$_2$ adsorption sites.

4. Low polarization resistances can be maintained for relatively thick oxide films when La$_2$O$_3$ and Fe$_2$O$_3$ are co-deposited. However, excess La$_2$O$_3$ must be present for the optimal stoichiometry.
6.6 References


http://www.nature.com/articles/srep32997.


Chapter 7. Enhancing Oxygen Exchange Activity by Tailoring Perovskite Surfaces*

Summary

A detailed understanding of the effects of surface chemical and geometric composition is essential for understanding the electrochemical performance of the perovskite (ABO$_3$) oxides commonly used as electrocatalysts in the cathodes of ceramic fuel cells. Herein, we report how the addition of submonolayer quantities of A- and B-site cations affect the rate of the Oxygen Reduction Reaction (ORR) of Sr-doped LaFeO$_3$ (LSF), LaMnO$_3$ (LSM), and LaCoO$_3$ (LSCo). Density functional theory (DFT) calculations were performed to determine the stability of different active sites on a collection of surfaces. With LSF and LSM, rates for ORR are significantly higher on the A-site terminated surface, while surface termination is less important for LSCo. Our findings highlight the importance of tailoring the surface termination of the perovskite to obtain its ultimate ORR performance.

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7.1 Introduction

Enhancing oxygen reduction activity by controlling the surface chemistry of the perovskite-structured (ABO$_3$) mixed oxides used as cathodes in ceramic fuel cells has been a long-term goal for improving stability and performance. The surface composition (chemical and geometric) may not be the same as that of the bulk, and is often not known, due to segregation of the constituent cations during the high-temperature treatments required for cell manufacture $^{[1,2,3]}$. Therefore, it is not clear which surface structures should be targeted. Recent studies by Rupp et al. $^{[4]}$ and Rahmanipour et al. $^{[5]}$ have attempted to elucidate the nature of the active sites on La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ (LSCo) and La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ (LSF), respectively, by molecular engineering of the surfaces through controlled deposition of the component oxides; however, these studies have generated additional questions. For example, it was reported that the addition of an A-site oxide (SrO) diminishes the performance of LSCo $^{[4]}$, while the addition of La$_2$O$_3$ to LSF enhanced performance $^{[5]}$. In the work reported herein, we used combined experimental and theoretical studies to demonstrate that significant differences exist in the surfaces of LSF, LSCo, and La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ (LSM) that help to explain why these materials exhibit significantly different behaviors. Atomic layer deposition (ALD) of A and B site ions was used to provide atomic-level control of surface composition (see Figure 7.1) of real-world, high-performance cathodes and allowed us to investigate how the terminating sequence of the perovskite affects performance. Observation of significant changes in catalytic properties with changes in the sequence of the terminating atoms on LSF and LSM surfaces, coupled with density functional theory (DFT) calculations of the stability of each surface, was used to determine the optimal surface composition for these perovskites.
Figure 7.1: Schematic showing the different ALD-modified surfaces that were investigated in this study.

7.2 Methods

7.2.1 Experimental Methods

The effect of modifying electrodes via the ALD of oxide thin films was studied using symmetric cells with YSZ electrolyte and either La$_{1-x}$Sr$_x$FeO$_{3-\delta}$ (LSF), La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ (LSM) and La$_{1-x}$Sr$_x$CoO$_{3-\delta}$ electrodes. Each cell was constructed using a tri-layer YSZ scaffold consisting of a dense YSZ layer that was 80-μm in thickness, sandwiched between two porous YSZ layers that were 35-μm in thickness and 60% porous with an average pore
sizes of ~2 μm. The YSZ tri-layer scaffolds were produced using standard tape casting methods with carbon-based pore formers being used to impart porosity. Detailed descriptions of the synthesis of the YSZ tri-layer can be found in our previous publications [6, 7, 8]. LSF, LSM or LSCo were added to the porous electrode layers using the infiltration method discussed in previous chapters. XRD was used to confirm the formation of LSF, LSM or LSCo and to show that no other secondary phases were formed. Some dense LSF slabs were also fabricated for LEIS study. The LSF powders for making dense slabs were prepared via sol-gel methods using the solution. After harvesting, these powders were pressed into round wafers and then sintered at 1473 K for 2 hours to form dense wafers.

ALD of oxide thin films was performed using a homebuilt apparatus that has been described in Section 2.3. This system consisted of an adsorption apparatus that could be evacuated to approximately 0.02 torr with a mechanical pump. The system had a central chamber to hold the sample which could be heated by an external furnace. The precursors were contained in separate tubes connected to a dosing manifold that could also be heated by an external furnace. The first step in each ALD cycle consisted of evacuating the sample held at the desired temperature, followed by exposure to the precursor vapor. An inert carrier gas was not used in order to minimize any diffusional limitations that may affect adsorption of the precursor into the porous layers of the YSZ scaffold. After the sample was exposed to the precursor, the remaining unreacted precursor molecules were evacuated. After oxidation of adsorbed precursors in a muffle furnace at 773 K for 10 min, the process was then repeated as needed. The precursors used in this study were Sr(TMHD)₂, La(TMHD)₃, Pr(TMHD)₃, Ca(TMHD)₂, and Mn(TMHD)₃ (TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionato (TMHD⁻¹) and were purchased from Strem Chemical, Inc. The
deposition temperatures were 578 K for Ca(TMHD)$_2$, 583 K for La(TMHD)$_3$, 523 K for Mn(TMHD)$_3$, 523 K for Pr(TMHD)$_3$, and 603 K for Sr(TMHD)$_2$.

To determine the amount of oxide deposited per ALD cycle, gravimetric measurements as a function of the number of ALD cycles were made using a γ-Al$_2$O$_3$ powder (surface area = 120 m$^2$ g$^{-1}$) compressed into wafers. The ALD growth rates are reported as the number of metal cations per cm$^2$ per ALD cycle for each metal oxide in Table 7.1.

### Table 7.1: Growth rate for different ALD precursors

<table>
<thead>
<tr>
<th>Element</th>
<th>Precursor</th>
<th>Assumed Metal Oxide Composition</th>
<th>Growth Rate Per Cycle (metal atoms cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>La(TMHD)$_3$</td>
<td>La$_2$O$_3$</td>
<td>4.8$\cdot$10$^{13}$</td>
</tr>
<tr>
<td>Pr</td>
<td>Pr(TMHD)$_3$</td>
<td>Pr$_2$O$_3$</td>
<td>5.4$\cdot$10$^{13}$</td>
</tr>
<tr>
<td>Sr</td>
<td>Sr(TMHD)$_2$</td>
<td>SrO</td>
<td>5.3$\cdot$10$^{13}$</td>
</tr>
<tr>
<td>Ca</td>
<td>Ca(TMHD)$_2$</td>
<td>CaO</td>
<td>6.9$\cdot$10$^{13}$</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn(TMHD)$_3$</td>
<td>Mn$_2$O$_3$</td>
<td>5.1$\cdot$10$^{13}$</td>
</tr>
<tr>
<td>Zr$^*$</td>
<td>Zr(TMHD)$_4$</td>
<td>ZrO$_2$</td>
<td>5.1$\cdot$10$^{13}$</td>
</tr>
<tr>
<td>Fe$^*$</td>
<td>Ferrocene</td>
<td>Fe$_2$O$_3$</td>
<td>8.4$\cdot$10$^{13}$</td>
</tr>
</tbody>
</table>

*Data from a previous study performed in our lab$^{[5]}$}
Electrochemical Impedance Spectra (EIS) were measured on symmetric cells in air at 873 K using a Gamry Instruments potentiostat (1-mA AC perturbation). External electrical connections were made using silver paste and silver wires.

The Low Energy Ion Scattering (LEIS) was performed using a Qtac100 high sensitivity LEIS instrument with Ne\(^+\) as the probing ion. Initial LEIS experiments showed that the surfaces were contaminated with a carbonate layer most likely formed by reaction with CO\(_2\) in the ambient gas in the lab. This contaminant layer was removed by lightly sputtering with a 0.5 keV Ar\(^+\) ion beam (total ion flux to sample < 10\(^{15}\) cm\(^{-1}\)). For the porous infiltrated LSF-YSZ cathodes, due to the complexity of the surface morphology, only two cycles of 10\(^{14}\) cm\(^2\) 90° incident 0.5 keV Ne\(^+\) were performed to remove surface contamination. Comparing to the LEIS result of the fresh samples, the sputtering process boosted the total signal but not change the existence of the major peaks.

7.2.2 Computational Methods

To determine the stable surfaces of LSF under SOFC operating conditions, we calculated the Surface Gibbs Free Energy (SGFE) of the relevant surface terminations using spin-polarized Density Functional Theory (DFT)\(^{[9,10]}\). Due to the large La to Sr ratio in the samples considered in this study, the stable surface terminations of the (001) facet of LaFeO\(_3\) were taken as a representative model for LSF. In order to represent the different ALD modified surfaces of LSF investigated in this study, we consider a spectrum of different surface coverages ranging from sub-monolayer to beyond a monolayer coverage of AO units by modeling the stoichiometric BO\(_2\) and AO terminations, the AO terminations with defects, specifically with A, O and an AO unit vacancy, as well as the O- and A-
terminated AO surfaces of LSFO (001) (See Figure 7.8a for atomic structure). The different surfaces were modelled using either 2x2x7 or 1x1x7 symmetric slabs, with the middle 3 layers fixed to their bulk lattice positions, and a vacuum spacing of at least 10 Å was used to prevent interactions between periodic images. All calculations were performed using the Quantum Espresso software package \[11,12\] and setup using the Atomic Simulation Environment (ASE) \[13\]. Kohn-Sham wave functions were expanded using a plane-wave basis set with a kinetic energy cut-off of 500 eV. Ultrasoft pseudo-potentials were used to represent the core electrons \[14\]. The Brillouin zone was sampled using a (5x5x1) Monkhorst-Pack k-point grid \[15\]. Exchange and correlation were described at the Generalized Gradient Approximation (GGA) level using the Perdew-Burke-Ernzerhof (PBE) functional \[16\]. To account for the errors associated with the on-site Coulomb and exchange interactions, a Hubbard-U correction (GGA+U) with U = 5.3eV was applied on Fe \[17, 18\]. All geometries were considered optimized when the maximum force on each atom was less than 0.03eV/Å.

7.3 Results and Discussion

7.3.1 ALD modification of cathode surfaces

The symmetric button cells were prepared from yttria-stabilized-zirconia (YSZ), porous-dense-porous, tri-layer wafers consisting of a dense 80-μm-thick layer sandwiched between two 35-μm-thick, 60%-porous layers with 2-μm pores. 30 wt% LSF, LSM or LSCo was added to the porous layers using infiltration of aqueous salt solutions followed by annealing in air. Details of the cell manufacture are in previous publications \[6,19,20\] and
the supplemental information. Decoration of the perovskite surface with submonolayer amounts of A- or B-site cations was achieved using ALD with Sr(TMHD)$_2$, La(TMHD)$_3$, Pr(TMHD)$_3$, Ca(TMHD)$_2$, and Mn(TMHD)$_3$, (TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionato) precursors. Cation deposition rates per ALD cycle (measured gravimetrically using a high surface area alumina support) are given Table S1 and were between $5 \cdot 10^{13}$ and $8 \cdot 10^{13}$ metal atoms cm$^{-2}$, corresponding to $\leq 0.1$ monolayer per cycle, for each of the metal oxides.

Low-energy ion scattering (LEIS) provided a measure of the outermost surface chemical composition and was used to confirm the number of ALD cycles required to obtain a monolayer coverage. LEIS studies were performed on a porous LSF-YSZ electrode that was calcined to 1123 K and a dense LSF slab that had been annealed to 1473 K prior to ALD deposition. The LEIS spectrum of the pristine LSF slab, Figure 7.2a, exhibits the expected peaks for La, Sr, and Fe. The Sr peak is the most intense due to surface enrichment which is known to occur upon high-temperature annealing in air$^{[1,3,21]}$. Figure 7.2b shows the LEIS spectrum of this sample after 5 La$_2$O$_3$ ALD cycles. Note that this spectrum is now dominated by the La peak. Quantitative analysis of this spectrum indicates that the surface La cation (La$_2$O$_3$) coverage is somewhat less than a monolayer (ML), consistent with the ALD growth rate reported in Table S1 which predicts that 5 ALD cycles would produce a La cation coverage of $\sim 0.4$ ML (based on the cation density on LSF(100) which is $6.5 \cdot 10^{14}$ cm$^{-2}$). The LEIS data for the porous LSF-YSZ electrode prior to ALD modification (Figure 7.2c) shows that Sr segregation did not occur to an appreciable extent for the low-temperature synthesis conditions, resulting in a more stoichiometric LSF surface. Consistent with the LSF slab data and the gravimetrically-
measured growth rates, 10 La$_2$O$_3$ ALD cycles was sufficient to form a complete monolayer coating of La$_2$O$_3$ (Figure 7.2d).

**Figure 7.2:** LEIS spectra obtained from (a) a pristine LSF slab that had been sintered at 1473 K, (b) the sample in (a) after 5 La ALD cycles, (c) a pristine high-surface area infiltrated LSF-YSZ composite cathode that had been sintered at 1123 K and (d) the sample in (c) after 10 La ALD cycles.
7.3.2 Surface modification of LSF electrodes with A- and B-site cations

To investigate the effect of decorating the surface of an infiltrated LSF-YSZ electrode with La$_2$O$_3$, impedance measurements were made for symmetric cells after 5, 10, 20, and 55 La$_2$O$_3$ ALD cycles. These samples were oxidized in air at 773 K for 5 min after each ALD cycle, and the impedance spectra were collected with the cell exposed to air at 873 K. These data are displayed in Figure 7.3a (the ohmic part of each spectrum has been subtracted to facilitate comparison), and the electrode polarization resistance, $R_p$, extracted from these data are plotted in Figure 7.3c. After 5 La$_2$O$_3$ ALD cycles, corresponding to ~0.5 ML La$_2$O$_3$, $R_p$ decreased from that of the pristine cell, 0.48 Ω·cm$^2$, to 0.27 Ω·cm$^2$. As shown in Figure 7.4, this enhancement of electrode catalytic properties upon surface decoration with sub-monolayer amounts of La$_2$O$_3$ was observed for LSF electrodes prepared to have bulk compositions that were both A- and B-site deficient. Enhanced electrode performance was maintained after 10 La$_2$O$_3$ ALD cycles which gave an $R_p$ of 0.32 Ω·cm$^2$. However, additional La$_2$O$_3$ increased $R_p$ monotonically. After 55 cycles, corresponding to $2.8 \cdot 10^{15}$ La atoms·cm$^{-2}$, $R_p$ was 0.82 Ω·cm$^2$ which is more than twice that of the pristine cell.
Figure 7.3: Impedance spectra obtained from infiltrated LSF/YSZ composite cathodes as a function of the number of (a) La ALD cycles and (b) Sr ALD cycles. The polarization resistance, $R_p$, extracted from the impedance spectra as a function of the number of ALD cycles and number of metal atoms deposited for each sample is plotted in panel (c).
Figure 7.4: Effect of La$_2$O$_3$ ALD on infiltrated A-site deficient LSF (a), and B-site deficient LSF (b). Pristine cell performance is denoted as black squares (□). Red cycles (○) show the cell performance after 5 ALD cycles of La$_2$O$_3$.

The beneficial effect on catalytic properties and $R_p$ in the sub-monolayer regime was not limited to La$_2$O$_3$; and LSF surfaces decorated with other A-site perovskites elements, including Sr, Ca, and Pr, produced a similar effect. Figure 7.3b displays impedance spectra for an LSF-YSZ cathode as a function of the number of SrO ALD cycles;
and, similar to the observations with La$_2$O$_3$, $R_p$ was found to decrease from 0.55 Ω·cm$^2$ to 0.26 Ω·cm$^2$ after 10 ALD cycles (≤ 1 ML), then increase with further SrO deposition, reaching 0.85 Ω·cm$^2$ after 30 SrO ALD cycles. Figure 7.5 displays the analogous data for LSF cathodes decorated with Pr$_2$O$_3$ and CaO and shows the same trends in electrode performance with submonolayer coverages of these oxides. The effect of submonolayer-level surface modification of LSF with A-site cations is summarized in Figure 7.7 which gives the percentage change in the cathode area-specific resistance after 5 ALD cycles. In all cases, the decrease in $R_p$ following deposition of A-site cations was close to 50% in the submonolayer regime, with $R_p$ increasing once the ML coverage was obtained. It is noteworthy that, although Sr surface segregation is well known to have a deleterious effect on electrode performance $^{[1,4,22]}$, submonolayer addition of SrO significantly enhanced performance. ALD was also used to determine the effect of terminating the LSF surface with the B-site cations, Fe and Mn, and an inert oxide, Zr. Impedance data for Mn deposition is displayed in Figure 7.6, while data for Fe and Zr were reported elsewhere $^{[5]}$. Results are summarized in Figure 7.7 and show that terminating with these oxides decreases the catalytic activity of the electrode and increases $R_p$, regardless of the oxide coverage.
**Figure 7.5:** Effect of 5 ALD cycles of Pr$_2$O$_3$ (a), and CaO (b) on LSF cells. Pristine cell performance is denoted as black squares (□). Red cycles (○) show the cell performance after 5 ALD cycles of each metal oxides.
Figure 7.6: Effect of 5 ALD cycles of MnO$_x$ on LSF cells. Pristine cell performance is denoted as black squares (□). Red cycles (○) show the cell performance after 5 ALD cycles.

These results further demonstrate that the local atomic structure on the cathode surface plays a pivotal role in determining the catalytic activity for the oxygen reduction and incorporation reactions and thus the overall cathode performance. The fact that submonolayer amounts of La$_2$O$_3$ have the same enhancing effect on both stoichiometric and non-stoichiometric LSF cathodes further supports this and shows that, while the bulk composition may affect bulk electron and oxygen ion transport, sites on the surface that are highly active for the oxygen-exchange reaction are needed to obtain high cathode performance.
Figure 7.7: Effect of the addition of submonolayer amounts (5 ALD cycles) of A-site and B-site cations on the $R_p$ of infiltrated LSF/YSZ composite cathodes.

7.3.3 Thermal Stability Study of the AO-Terminated Perovskite Surface

DFT calculations, which have been successful in modeling the thermodynamic stability as well as ion transport in SOFC materials such as LaBO$_3$ [23], LSM [24], LSF [25] and LSCF [26], were performed to determine how surface non-stoichiometry might affect reactivity and whether the various surface terminations explored experimentally are stable. For these simulations, the (001) surface of LaFeO$_3$ was used as a prototypical perovskite surface. Figure 7.8b shows the calculated stability diagram at 1000 K and $P_{O_2}$ of 0.2 atm for the different LaFeO$_3$ surface terminations shown in Figure 7.8a. To determine the
stability of the different terminations, we considered their respective surface Gibbs free energies (SGFE) within the region defining the precipitation of bulk La$_2$O$_3$ and Fe$_2$O$_3$ as a function of the chemical potential of Fe in the system. We found that the stoichiometric BO$_2$ termination is thermodynamically the most stable surface under solid oxide fuel cell (SOFC) operating conditions (yellow vertical region in Figure 7.8b), indicating that the pristine samples used in the experimental studies were likely to be BO$_2$ terminated. As shown in Figure 7.3 and 7.8c, an improvement in cell performance was observed for systems with sub-monolayer coverages of La$_2$O$_3$ deposited using ALD. However, we found that while the stoichiometric AO- and O-terminated AO surfaces are relatively stable, the defective AO surfaces, particularly the ones with AO, A and O vacancies are all thermodynamically unstable under SOFC operating conditions. This is in agreement with the impedance data for an LSF electrode as a function of thermal cycling shown in Figure 7.8c, where the excellent performance obtained after 10 La$_2$O$_3$ ALD cycles goes back to that of pristine LSF upon heating at 973 K for 2 hrs. This suggests that the thermodynamically unstable defective surfaces are likely to be kinetically trapped phases, resulting in their eventual reconstruction to the stable stoichiometric BO$_2$ surface. It should be noted that preparing the system in one of these metastable, kinetically-trapped states is enabled by the nature of the ALD process, where control can be achieved to the level where the growth results in surfaces with non-uniform surface coverage. We, therefore, hypothesize that, although the surface modification as a result of the sub-monolayer coverage of La$_2$O$_3$ does not result in intrinsic thermodynamic stability, the improved cell performance may be attributed to the presence of kinetically-trapped surfaces with AO defects. Going beyond ML coverage of AO units results in reduced cell performance as
seen from Figures 6.3 and 6.8c. To model this, we considered the stoichiometric AO-terminated surface with an additional A unit consisting of an adatom adsorbed at the surface. We found that this system is thermodynamically the most unstable among the different surfaces considered under SOFC operating conditions. This suggests that going beyond a ML coverage, should result in a structure with several stoichiometric AO layers, which is thermodynamically more stable, as opposed to those with excess A on the surface. Interestingly, the fact that this is not observed with the thermal cycling, where further ALD modification upon restoration to the pristine cell at 973 K once again improves cell performance, suggests that two different mechanisms may be at play under different conditions.
Figure 7.8: Summary of DFT study of the stability of various terminations of LaFeO$_3$(001). The specific terminations that were studied are shown in (a) and the calculated surface Gibbs free energy for each termination as a function of the Fe chemical potential is plotted in (b), and (c) provides impedance spectra for a composite LSF/YSZ cathode as a function of La ALD cycles and annealing temperature for comparison with the stability calculations.
7.3.4 Observation of Similar Effect on A-cation Modified LSM Systems

To examine the generality of the beneficial effect of decorating LSF surfaces with submonolayer quantities of A-site cations, experiments were also performed for symmetric cells with infiltrated LSM-YSZ cathodes infiltrated to 1123 K. (Note: LSM-YSZ electrodes prepared by infiltration and calcined at 1123 K do not exhibit hysteretic behavior upon polarization [15].) Figure 7.9a shows impedance spectra collected in air at 873 K for one of these cells as a function of the number of La$_2$O$_3$ ALD cycles. The trends in these data are similar to those observed for LSF in Figure 7.3, with $R_p$ decreasing significantly up to monolayer La$_2$O$_3$ coverage and then increasing with further La$_2$O$_3$ addition. As shown in Figure 7.9a, the pristine LSM-YSZ electrode had an $R_p$ of 1.4 $\Omega \cdot \text{cm}^2$ which decreased to 0.55 and 0.35 $\Omega \cdot \text{cm}^2$ after 5 and 10 La$_2$O$_3$ ALD cycles, respectively, before gradually increasing with additional La$_2$O$_3$. Impedance data obtained from an LSM-YSZ electrode before and after 5 ALD cycles of SrO, Pr$_2$O$_3$, and Mn$_2$O$_3$ are shown in Figure 7.10. These results are again similar to that reported above for LSF with sub-monolayer films of the A-site oxides, SrO and Pr$_2$O$_3$, both causing $R_p$ to decrease by ~40%. In contrast, 5 MnO$_x$ ALD cycles had a small effect on $R_p$ (Figure 7.10c).
Figure 7.9: Impedance spectra obtained from (a) infiltrated LSM/YSZ and (b) LSCo/YSZ composite cathodes as a function of the number of La ALD cycles. The polarization resistance, $R_p$, extracted from the impedance spectra as a function of the number of ALD cycles and number of metal atoms deposited for each sample is plotted in panel (c). To facilitate comparison, data for LSF/YSZ composite electrodes (from Figure 7.3) is also included in this plot.
The fact that the same performance trends were observed for ALD-modified LSF and LSM surfaces is quite interesting. LSM is known for being a relatively poor cathode due to its lack of ionic conductivity \cite{28,29,30}. However, as shown in a modeling study by Bidrawn \textit{et al.}, cathodes prepared by infiltration into porous YSZ scaffolds do not require high ionic conductivity from the perovskite since the ionic conductivity is provided by the scaffold \cite{31}. These calculations suggested that, for electrodes prepared by infiltration, ionic conductivity of the infiltrated phase does not limit performance as long as the ionic conductivity is above about $10^{-7}$ S·cm$^{-1}$ (973 K). Therefore, the poor performance of the pristine infiltrated LSM cathode used here is likely due to slow surface kinetics. It was possible to increase oxygen surface exchange so as to decrease the cathode impedance to 0.35 Ω·cm$^2$ at 873 K. Furthermore, only 5 ALD cycles of the B-site oxide, MnO$_x$, onto LSF doubled $R_p$. These data suggest that pristine LSM is also BO$_2$ (MnO$_2$) terminated, resulting in sluggish rates for the surface oxygen exchange reaction. Therefore, an AO-terminated surface is also catalytically beneficial for LaMnO$_3$ systems.
Figure 7.10: Effect of 5 ALD cycles of Pr$_2$O$_3$ (a), SrO (b), and MnO$_x$ (c) on LSM cells. Pristine cell performance is denoted as black squares (□). Red cycles (○) show the cell performance after 5 ALD cycles of each metal oxides.
7.3.5 Surface modification of LSCo with A-site cations

Finally, ALD modification of LSCo-YSZ electrodes was also investigated. In this case, enhancement of cathode performance was not observed upon addition of submonolayers of La$_2$O$_3$, a result that is consistent with the recent study by Rupp et al.\cite{4}. As shown in Figure 7.9b, the $R_p$ of pristine LSCo was $0.40 \ \Omega \cdot \text{cm}^2$ and was unaffected by the ALD deposition of up to 1 ML of La$_2$O$_3$. Higher La$_2$O$_3$ coverages decreased cathode performance, as expected. For LSF and LSM, the experimental and theoretical results all point to the requirement to have highly-defective, A-site terminated surfaces for achieving high catalytic activity for the surface oxygen exchange reaction. We achieved this using ALD to add submonolayer amounts of the A-site cations to select materials and surfaces. By necessity, such surfaces contain a high concentration of oxygen vacancies which are most likely the active sites for oxygen adsorption. LSCo, however, is much more easily reduced compared to LSM and LSF\cite{32,33,34}, and, therefore, it intrinsically contains a higher concentration of oxygen vacancies and other defects prior to A-site modification. Indeed, this is most likely the reason why LSCo is one of the best cathode materials for SOFC operation at intermediate temperatures\cite{35}; in effect, LSCo already has the optimal surface structure. In the submonolayer regime, the addition of more AO units merely maintains the defect concentration, while multi-layer AO addition ultimately blocks the active sites leading to an increase in $R_p$. 
7.4 Conclusions

In summary, we have demonstrated that ORR rates on perovskite-based SOFC cathodes are strongly affected by the terminating sequence and geometry at the surface. ORR rates are greatly enhanced on LSF and LSM by addition of sub-monolayer quantities of A-site cations, likely because this enhances the surface oxygen vacancy concentration. LSCo is much less sensitive to surface modifications because of its intrinsically higher surface vacancy concentration. These findings call for a better control of the synthesis of the perovskite surfaces at the atomic-scale to obtain SOFC materials with optimal performance.

7.5 References


Chapter 8. Conclusions

Normally, the cathode part of an SOFC has the largest resistance in the whole cell. Infiltrated cathodes, which have nanoscale perovskite materials impregnated in a porous scaffold of ionic conductors, show multiple advantages over traditional printed cathodes, such as well-defined structures, the absence of insulation phases, significantly higher surface area, better mechanical strength, etc. An infiltrated cell can be manufactured in two steps, with the first step being tape-casting and sintering, and the second being infiltration. The detailed manufacturing process was described in Chapter 2. However, the wide use of infiltrated cathodes still faces multiple challenges, such as the tedious infiltration process and a lack of understanding about desired surface composition.

The tedious infiltration process has to do with the need for enough electronic conductivity in the cathode. Normally, a YSZ-based infiltrated cathode must have more than 30 wt% conductive perovskite loading, which corresponds to more than 10 infiltration cycles. However, only the first 10 wt% is there to increase the surface reaction rate, and the rest of the perovskites are there to facilitate electron conduction. Our approach to resolve this problem is trying to incorporate electronic conduction path in the cathode backbone, so that less infiltrated material is needed. As an initial demonstration of this idea, a cathode with an LSF-YSZ composite scaffold was introduced in Chapter 3. The manufacturing process is almost identical as a traditional cell with a YSZ scaffold, just to replace half of the YSZ powders with La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ (LSF) powders. LSF was examined to have reasonable chemical compatibility with YSZ (no insulation layer formation), but some migration of Zr from YSZ to LSF still occur. The resulted cathode, even without any
infiltration, showed significantly improved electronic conductivity comparing to that of a pure YSZ scaffold. Due to this advantage, a 10 wt% La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF) perovskite loaded LSF-YSZ composite cathode had a lower cell resistance than that of a traditional YSZ scaffold with the same perovskite loading.

In order to thoroughly understand the factors governing the manufacturing of a good LSF-YSZ composite scaffold, a more fundamental study about the composite material was performed in Chapter 4. It was first discovered that the formation of LSF-Zr solid solution is dictated by the Sr dopant level in LSF. The total conductivity of the composite showed a volcanic pattern as a function of Sr dopant in LSF, which peaked at 10% Sr in LSF. It was also discovered that the oxygen ion conductivity of the composite material is less than that of either LSF or YSZ, probably due to the formation of Zr-doped LSF. Therefore, it was suggested that using 10% Sr in LSF is optimal for the composite scaffold application. The performance of cathodes manufactured with an LSF scaffold, an LSF-YSZ composite scaffold, and a YSZ scaffold, were investigated. With this study, it was discovered that the tested LSF-YSZ composite material, although already outperformed the traditional YSZ scaffolds, still have room to optimize, due to its large pore size. A such scaffold with finer pores, eg. ~1 μm diameter pores as those with YSZ scaffolds, could yield even better performance.

As mentioned, one problem with LSF-YSZ composite scaffolds is the interdiffusion of Zr into LSF. Therefore, it would be crucial if one can prevent this from happening. In Chapter 5, it was successfully achieved with Cr doping into LSF. It was discovered that, if the B-site of LSF is replaced with 60% Cr, this structure can exclude any further Zr incorporation. As expected, this composite scaffold had a significantly
improved electronic conductivity. However, the poor sinteribility of this new material led to a poorly-sintered electrolyte and large cathode pore sizes. Still, this material is promising if one can overcome these manufacturing problems.

In addition to scaffold engineering, another method to improve the cathode performance is to discover the favored surface composition for oxygen reduction reactions. A fundamental study of the surface composition without changing the surface area was initially performed on LSF using Atomic Layer Deposition (ALD) method. It was discovered that the deposition of ZrO$_2$ on LSF can only cause surface blocking effects, since this material cannot catalyze the oxygen reduction reaction. Another surface modification of LSF with Fe$_2$O$_3$ showed the same outcome as ZrO$_2$, suggesting that the surface Fe$_2$O$_3$ was not responsible for direct catalyzing the reaction. However, surface modification of LSF with La$_2$O$_3$ show another pattern. With the deposition of monolayer amount of La$_2$O$_3$, the surface kinetics increased by 100%. However, further deposition made the performance worse. This suggests that for LSF perovskite, a La-rich surface is ideal for oxygen reduction.

Inspired by this phenomenon, a further study on the general effect of A-site and B-site surface modification on LSF was performed in Chapter 7. In this study, we characterized the surface of as-prepared LSF perovskite and confirmed that both A-site and B-site elements appear on the surface. After 10 cycles of La, it was found out that the surface had been uniformly coated with La$_2$O$_3$ without the appearance of other elements. The submonolayer-level surface modification with all the A-site elements, including La, Pr, Sr, Ca, showed surface improving effect. On the other hand, surface modification with Fe, Zr and Mn showed surface blocking effect. This trend had been reproduced on
La$_{0.8}$Sr$_{0.2}$MnO$_{3-\delta}$ (LSM), but not on La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ (LSCo). Since the major difference between LSCo and LSM is that the former has a much larger surface vacancy density than the later, it was concluded that an A-site rich surface of the perovskite has a much larger surface vacancy density, and it was the increment in the surface vacancy density of LSF that enhanced the oxygen reduction reaction kinetics after monolayer-level surface modification with A-site metal oxides.