INVESTIGATION AND IMPROVEMENT OF SOFC COMPOSITE CATHODES

Fred Bidrawn
University of Pennsylvania, fbidrawn@seas.upenn.edu

Follow this and additional works at: http://repository.upenn.edu/edissertations

Recommended Citation

This paper is posted at ScholarlyCommons. http://repository.upenn.edu/edissertations/251
For more information, please contact repository@pobox.upenn.edu.
INVESTIGATION AND IMPROVEMENT OF SOFC COMPOSITE CATHODES

Abstract
The focus of this dissertation is on the preparation, performance, and long term stability of SOFC composite cathodes prepared by infiltration methods. The majority of the work that follows aims to improve the understanding of the processes contributing to cathode deactivation and to propose strategies to lessen the extent of this deactivation. Through this understanding of the factors governing cathode performance, improvements can be made in overall cathode performance which can in turn lead to lower operating temperatures.

The fuel cells used in this work were prepared by tapecasting and infiltration methods. Composite YSZ-perovskite electrodes were prepared by infiltration of stoichiometric ratios of perovskite precursor nitrate salts into a porous YSZ scaffold. First, the influence of ionic conductivity on the performance of solid oxide fuel cell cathodes was studied for electrodes prepared by infiltration of 40-wt% La0.8Ca0.2FeO3 (LCF), La0.8Sr0.2FeO3 (LSF), and La0.8Ba0.2FeO3 (LBF) into porous YSZ scaffolds. Although ionic conductivity varied by over an order of magnitude, no significant difference was observed in the performance of each material, suggesting that oxygen ion diffusion through perovskite film is not a rate limiting step for the oxygen reduction process within the cathode. Next, the effect of various infiltrated dopants on the performance of SOFC cathodes was examined. The addition of dopants had little influence on the 1123-K composite electrodes but all dopants tested improved the performance of the 1373-K, suggesting that the improved performance is related to structural changes in the electrode, rather than to improved catalytic properties or ionic conductivity. Based on these results, a model was developed to understand the performance of these electrodes. Two rate-limiting cases are considered for oxygen transfer into the YSZ fins: diffusion through the perovskite film or reactive adsorption of O2 at the perovskite surface. In agreement with the experimental results, an important implication from the model is that ionic conductivity of the pervoskite phase does not limit performance, for most commonly used perovskites, and that surface adsorption is likely limiting. Finally, strategies for improving cathode performance and stability are discussed.

Degree Type
Dissertation

Degree Name
Doctor of Philosophy (PhD)

Graduate Group
Chemical and Biomolecular Engineering

First Advisor
Raymond J. Gorte

This dissertation is available at ScholarlyCommons: http://repository.upenn.edu/edissertations/251
INVESTIGATION AND IMPROVEMENT OF SOFC COMPOSITE CATHODES

Fred Bidrawn

A DISSERTATION

in

Chemical and Biomolecular Engineering

Presented to the Faculties of the University of Pennsylvania

in Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy

2010

Supervisor of Dissertation

________________________________________
Raymond J. Gorte, Professor of Chemical and Biomolecular Engineering

Graduate Group Chairperson

________________________________________
Raymond J. Gorte, Professor of Chemical and Biomolecular Engineering

Dissertation Committee
John M. Vohs, Professor of Chemical and Biomolecular Engineering
Warren D. Seider, Professor of Chemical and Biomolecular Engineering
Christopher B. Murray, Professor of Chemistry and Materials Science and Engineering
Dedicated to my Mom and Dad

With Thanks to Professor Ray Gorte
ABSTRACT

INVESTIGATION AND IMPROVEMENT OF SOFC COMPOSITE CATHODES

Frederick Richard Bidrawn

Raymond J. Gorte

The focus of this dissertation is on the preparation, performance, and long term stability of SOFC composite cathodes prepared by infiltration methods. The majority of the work that follows aims to improve the understanding of the processes contributing to cathode deactivation and to propose strategies to lessen the extent of this deactivation. Through this understanding of the factors governing cathode performance, improvements can be made in overall cathode performance which can in turn lead to lower operating temperatures.

The fuel cells used in this work were prepared by tapecasting and infiltration methods. Composite YSZ-perovskite electrodes were prepared by infiltration of stoichiometric ratios of perovskite precursor nitrate salts into a porous YSZ scaffold. First, the influence of ionic conductivity on the performance of solid oxide fuel cell cathodes was studied for electrodes prepared by infiltration of 40-wt% La$_{0.8}$Ca$_{0.2}$FeO$_3$ (LCF), La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF), and La$_{0.8}$Ba$_{0.2}$FeO$_3$ (LBF) into porous YSZ scaffolds. Although ionic conductivity varied by over an order of magnitude, no significant
difference was observed in the performance of each material, suggesting that oxygen ion diffusion through perovskite film is not a rate limiting step for the oxygen reduction process within the cathode. Next, the effect of various infiltrated dopants on the performance of SOFC cathodes was examined. The addition of dopants had little influence on the 1123-K composite electrodes but all dopants tested improved the performance of the 1373-K, suggesting that the improved performance is related to structural changes in the electrode, rather than to improved catalytic properties or ionic conductivity. Based on these results, a model was developed to understand the performance of these electrodes. Two rate-limiting cases are considered for oxygen transfer into the YSZ fins: diffusion through the perovskite film or reactive adsorption of O$_2$ at the perovskite surface. In agreement with the experimental results, an important implication from the model is that ionic conductivity of the pervoskite phase does not limit performance, for most commonly used perovskites, and that surface adsorption is likely limiting. Finally, strategies for improving cathode performance and stability are discussed.
# Table of Contents

Chapter 1. Background 1

1.1 Motivation 1

1.2 SOFC Operating Principles 2

1.3 SOFC Thermodynamics 4

1.4 Three Phase Boundary Concept 6

1.5 Perovskite Cathode Materials 7

1.6 Preparation of Composite Cathodes 9

1.7 Degradation of Cathode Performance 11

Chapter 2. Experimental Methods 14

2.1 Fuel Cell Manufacture and Preparation 14

2.1.1 Tape Casting 14

2.1.2 Cell Assembly and Sintering 15

2.1.3 Cathode Preparation 16

2.1.4 Anode Preparation 17

2.1.5 Preparation for Testing 17

2.2 Cell Performance Measurements 18

2.2.1 V-i Performance Measurement 18

2.2.2 Electrochemical Impedance Spectroscopy 18

2.3 Composite Slabs 20

2.4 Perovskite Pellets 20

2.5 Total Conductivity Measurements 21
2.6 Ionic Conductivity Measurements 22
2.6.1 Blocking Electrodes 23
2.6.2 Oxygen Permeation Measurements 25
2.7 Surface Area Measurements 27
2.8 X-Ray Diffraction 27
2.9 Scanning Electron Microscopy 27

Chapter 3. Fabrication of LSM-YSZ Composite Electrodes by Electrodeposition 28
3.1 Introduction 28
3.2 Experimental 30
3.3 Results and Discussion 33
3.4 Conclusion 43

Chapter 4. The Effect of Ca, Sr, and Ba Doping on the Ionic Conductivity and Cathode Performance of LaFeO$_3$ 44
4.1 Introduction 44
4.2 Experimental 46
4.3 Results and Discussion 49
4.3.1 Ionic Conductivities 49
4.3.2 Cathode Performance Characteristics 51
4.3.3 Structural Characterization 54
4.4 Conclusions 61

Chapter 5. Dopants to Enhance SOFC Cathodes Based on Sr-Doped LaFeO$_3$ and LaMnO$_3$ 63
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>63</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>66</td>
</tr>
<tr>
<td>5.3 Results</td>
<td>68</td>
</tr>
<tr>
<td>5.3.1 Unpromoted LSF-YSZ and LSM-YSZ Electrodes</td>
<td>68</td>
</tr>
<tr>
<td>5.3.2 Effect of Additives on LSF-YSZ Cathodes</td>
<td>73</td>
</tr>
<tr>
<td>5.3.3 Characterization of LSF-YSZ Cathodes</td>
<td>79</td>
</tr>
<tr>
<td>5.3.4 Effect of Additives on LSM-YSZ Cathodes</td>
<td>80</td>
</tr>
<tr>
<td>5.4 Discussion</td>
<td>83</td>
</tr>
<tr>
<td>5.5 Conclusion</td>
<td>86</td>
</tr>
<tr>
<td>Chapter 6. Modeling Impedances of SOFC Cathodes Prepared by Infiltration</td>
<td>88</td>
</tr>
<tr>
<td>6.1 Introduction</td>
<td>88</td>
</tr>
<tr>
<td>6.2 Steady State Model</td>
<td>93</td>
</tr>
<tr>
<td>6.2.1 Structure of Composite Electrode</td>
<td>93</td>
</tr>
<tr>
<td>6.2.2 The Potential Within the YSZ Fin</td>
<td>94</td>
</tr>
<tr>
<td>6.2.3 Charge Flux Through the Perovskite Film</td>
<td>95</td>
</tr>
<tr>
<td>6.2.3.1 Diffusion Limited</td>
<td>96</td>
</tr>
<tr>
<td>6.2.3.2 Surface Reaction Limited</td>
<td>97</td>
</tr>
<tr>
<td>6.2.4 Analytical, Steady-State Solutions</td>
<td>100</td>
</tr>
<tr>
<td>6.2.4.1 Diffusion Limited</td>
<td>101</td>
</tr>
<tr>
<td>6.2.4.2 Surface Adsorption Limited</td>
<td>102</td>
</tr>
<tr>
<td>6.2.5 Effect of Perovskite Structure</td>
<td>104</td>
</tr>
<tr>
<td>6.2.6 Non-Steady State Solutions</td>
<td>105</td>
</tr>
</tbody>
</table>
List of Tables

Table 4.1  Peak positions for the (240) planes of doped LaFeO$_3$ samples. 46
Table 4.2  Total conductivities of the doped LaFeO$_3$ samples. 46
Table 4.3  Surface areas measurements of composite electrodes. 56
Table 5.1  Summary of effects of calcination temperatures and infiltrated materials on LSF-YSZ composite cathodes. 76
Table 5.2  Surface areas measured for LSF-YSZ composites with various calcination temperatures and additives. 78
Table 5.3  Summary of effects of calcination temperatures and infiltrated materials on LSM-YSZ composite cathodes. 82
Table 6.1  Material properties of doped LaFeO$_3$ and LaMnO$_3$. 111
Table 6.2  Structural parameters for a typical composite cathode. 111
Table 6.3  Example calculations based on the diffusion limited case at 973K. 112

List of Figures

Figure 1.1  Schematic diagram of a solid oxide fuel cell. 3
Figure 1.2  Perovskite lattice structure and oxygen conduction principle. 8
Figure 1.3  Degradation of a LSF-YSZ composite electrode over time. 12
Figure 1.4  SEM images of the LSF film on the YSZ scaffold. 13
Figure 2.1  A typical impedance spectrum from an SOFC. 19
Figure 2.2  Diagram of a four probe conductivity test. 22
Figure 2.3  Diagram of a standard blocking electrode system. 23
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>Diagram of the oxygen permeation system.</td>
<td>26</td>
</tr>
<tr>
<td>3.1</td>
<td>Deposition curves for pure DMSO and La and Mn solutions.</td>
<td>34</td>
</tr>
<tr>
<td>3.2</td>
<td>SEM of YSZ scaffold after electrodeposition in La or Mn solutions.</td>
<td>36</td>
</tr>
<tr>
<td>3.3</td>
<td>SEM of electrode after sequential electrodeposition of La and Mn.</td>
<td>39</td>
</tr>
<tr>
<td>3.4</td>
<td>EDX linescans of deposited species.</td>
<td>39</td>
</tr>
<tr>
<td>3.5</td>
<td>XRD data for electrodes prepared by impregnation and electrodeposition.</td>
<td>40</td>
</tr>
<tr>
<td>3.6</td>
<td>Impedance data for electrodes prepared by impregnation and electrodeposition.</td>
<td>42</td>
</tr>
<tr>
<td>3.7</td>
<td>V-i data for electrodes prepared by impregnation or electrodeposition.</td>
<td>42</td>
</tr>
<tr>
<td>4.1</td>
<td>Oxygen permeation of LBF pellet as a function of $PO_2$.</td>
<td>48</td>
</tr>
<tr>
<td>4.2</td>
<td>Ionic conductivities of the doped LaFeO$_3$ samples.</td>
<td>50</td>
</tr>
<tr>
<td>4.3</td>
<td>Impedance data for LaFeO$_3$ composite cathodes calcined to 1123 K.</td>
<td>52</td>
</tr>
<tr>
<td>4.4</td>
<td>Impedance data for LaFeO$_3$ composite cathodes calcined to 1373 K.</td>
<td>52</td>
</tr>
<tr>
<td>4.5</td>
<td>SEM images of LaFeO$_3$ composites calcined to 1123 or 1373 K.</td>
<td>56</td>
</tr>
<tr>
<td>4.6</td>
<td>Schematic illustrating the effect of higher temperature calcination.</td>
<td>60</td>
</tr>
<tr>
<td>5.1</td>
<td>V-i and impedance data for LSF-YSZ electrodes.</td>
<td>69</td>
</tr>
<tr>
<td>5.2</td>
<td>V-i and impedance data for LSM-YSZ electrodes.</td>
<td>70</td>
</tr>
<tr>
<td>5.3</td>
<td>SEM images of LSM-YSZ composites calcined to 1123 and 1373K.</td>
<td>74</td>
</tr>
<tr>
<td>5.4</td>
<td>Performance data for LSF-YSZ electrodes with various additives.</td>
<td>75</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>5.5</td>
<td>Performance data for LSF-YSZ electrodes with various additives.</td>
<td>75</td>
</tr>
<tr>
<td>5.6</td>
<td>SEM images of LSF-YSZ composites with various additives.</td>
<td>81</td>
</tr>
<tr>
<td>6.1</td>
<td>Schematic of composite cathodes prepared by infiltration.</td>
<td>89</td>
</tr>
<tr>
<td>6.2</td>
<td>Perovskite nonstoichiometry as a function of $PO_2$.</td>
<td>100</td>
</tr>
<tr>
<td>6.3</td>
<td>Representative potential step and current response profiles.</td>
<td>108</td>
</tr>
<tr>
<td>6.4</td>
<td>Corresponding Nyquist plot for the response data in Figure 6.3.</td>
<td>109</td>
</tr>
<tr>
<td>6.5</td>
<td>Impedance as a function of perovskite and YSZ ionic conductivity for the diffusion limited case.</td>
<td>114</td>
</tr>
<tr>
<td>6.6</td>
<td>Impedance as a function of sticking coefficient for the adsorption limited case.</td>
<td>114</td>
</tr>
<tr>
<td>6.7</td>
<td>Potential profile as a function of electrode thickness.</td>
<td>117</td>
</tr>
<tr>
<td>6.8</td>
<td>Calculated impedances based on the co-limited case.</td>
<td>119</td>
</tr>
<tr>
<td>6.9</td>
<td>Calculated capacitances based on the co-limited case.</td>
<td>119</td>
</tr>
<tr>
<td>6.10</td>
<td>Calculated frequencies as a function of zero-frequency impedance.</td>
<td>122</td>
</tr>
<tr>
<td>6.11</td>
<td>Calculated impedances as a function of perovskite reducibility.</td>
<td>122</td>
</tr>
<tr>
<td>7.1</td>
<td>V-i curves for H$_2$O-H$_2$ and CO$_2$-CO mixtures.</td>
<td>131</td>
</tr>
<tr>
<td>7.2</td>
<td>Impedance data for H$_2$O-H$_2$ and CO$_2$-CO mixtures.</td>
<td>131</td>
</tr>
<tr>
<td>7.3</td>
<td>V-i curves for various CO$_2$-CO compositions at 973 K.</td>
<td>134</td>
</tr>
<tr>
<td>7.4</td>
<td>V-i curves for various CO$_2$-CO compositions at 1073 K.</td>
<td>134</td>
</tr>
<tr>
<td>7.5</td>
<td>Power density data for various CO$_2$-CO compositions at 1073 K.</td>
<td>135</td>
</tr>
</tbody>
</table>
Chapter 1. Background

1.1 Motivation

Fuel cells hold the potential to provide a means of efficient, scalable, and environmentally friendly power generation. Unlike combustion engines which rely on the conversion of heat into mechanical energy and subsequently electrical energy, fuel cells are able to directly convert chemical energy into electrical energy. As a result, fuel cells are not limited by the Carnot cycle and are theoretically able to operate at much higher efficiencies than traditional combustion engines. Since fuel cells have no moving parts they have the potential for reliable power generation and long lasting performance.

A major advantage of Solid Oxide Fuel Cells (SOFCs) is that they are highly fuel flexible. Polymer membrane based fuel cells rely on the conduction of protons which requires that hydrocarbons must be reformed prior to use as fuel. Because SOFCs and are based on an O$_2^-$ conducting electrolyte, this allows the direct use of many higher hydrocarbons without a reforming step[90]. Although SOFC electrolyte materials require high operating temperatures in order to obtain sufficient conductivity[93], this excess heat can be used for steam turbine power generation.

When operated in reverse, SOFCs perform as Solid Oxide Electrolyzers (SOEs). SOEs are capable of higher electrolysis efficiencies compared to solution-based electrolysis cells, since they operate at high temperatures which lower both the equilibrium potential of the system, and the electrode impedances. The high-efficiency of solid-oxide steam electrolysis systems makes them attractive for the production of
hydrogen using renewable electrical energy sources such as wind and solar. In principle, SOEs are capable of reducing CO$_2$ to CO almost as easily as H$_2$O to H$_2$ [51]. This would provide an alternative to sequestration as a means to ameliorate the emission of CO$_2$ which is the primary greenhouse gas.

A major obstacle facing the commercial development of SOFCs and SOEs is the loss of power density due to inefficiencies of the electrodes. The focus of this dissertation is on the manufacture, characterization, and performance of SOFC and SOE air electrodes. By examining the processes that occur within the air electrode we hope to find ways to optimize performance and improve stability.

1.2 SOFC Operating Principles

A schematic of a typical SOFC is presented in Figure 1.1. Like all fuel cells, SOFCs consist of an electrolyte membrane, an anode, and a cathode. The unique and defining characteristic of an SOFC is that the electrolyte material is an ion-conducting ceramic[93]. Ideally, the electrolyte material used should possess very high ionic conductivity and negligible electronic conductivity at standard operating temperatures (~773-1073 K) and across a wide range of oxygen partial pressures. In order to adequately separate the fuel side of the SOFC from the air side, the electrolyte must be dense and leak free. Presently, the most commonly used electrolyte material is the oxygen ion conducting yttria-stabilized zirconia (YSZ). In addition to satisfying the above requirements, YSZ is also chemically stable and inert. Although some other materials possess greater ionic conductivity than YSZ, many of these begin to exhibit
electronic conductivity under the strongly reducing environment at the anode. At 973 K, YSZ has an ionic conductivity of 0.02 S/cm [8, 93]. In order to obtain an electrolyte resistance of less than .1 Ωcm$^2$, this requires that the electrolyte must be less than 20 µm thick.

During fuel cell operation, gas phase oxygen diffuses into the cathode where it is catalytically reduced into oxygen anions using electrons supplied through an external circuit. These oxygen ions are then conducted through the ceramic electrolyte by a defect hopping mechanism [1]. Upon arriving at the anode, the oxygen ions react with the supplied fuel, producing steam and/or carbon dioxide and liberating the electrons which
return to the cathode through the external circuit. When operating under fuel cell conditions, the cathode and anode half cell reactions for hydrocarbon fuels are

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

\[ C_nH_{2+2n} + (3n+1)O^{2-} \rightarrow nCO_2 + (n+1)H_2O + (3n+1)e^- \]  \hspace{1cm} \text{Equation 1.2}

During fuel cell operation, the driving force behind the oxygen ion diffusion is the difference in oxygen chemical potential between the air and fuel sides of the electrolyte. When an external potential is applied, the cell operates as a SOE, and the half cell reactions proceed in the reverse direction. Because the definition of a cathode is the electrode where reduction takes place and the anode is where oxidation takes place, during electrolysis the electrode that is exposed to O\(_2\) becomes the anode and the electrode that is exposed to the fuel becomes the cathode in an SOE. Therefore, when discussing SOFC and SOE together, it is sometimes convenient to refer to the electrodes as the “air” and “fuel” electrodes.

### 1.3 SOFC Thermodynamics

Since the electrons produced at the anode are at a higher potential than those consumed at the cathode they are therefore able to do work on an external circuit. In an ideal, reversible fuel cell, the work the electrons are capable of doing is equal to the Gibbs Free Energy of the oxidation reaction, \( \Delta G_{\text{rxn}} \), which is in turn related to the \( O_2 \) fugacities at the cathode and anode by Equation 1.3:

\[ \Delta G_{\text{rxn}} = RT \ln \left( \frac{P_{O_2,\text{anode}}}{P_{O_2,\text{cathode}}} \right) \]  \hspace{1cm} \text{Equation 1.3}
\(P(O_2 \text{ anode})\) is the fugacity established by equilibrium with the \(H_2\) and \(H_2O\) present in the anode compartment. Upon making this substitution and converting to electrical units, Equation 1.3 becomes the Nernst Equation:

\[
V_{\text{Nernst}} = V^\circ + \frac{RT}{nF} \ln \left( \frac{P_{H_2, \text{anode}} \cdot P_{O_2, \text{cathode}}^{\frac{1}{2}}}{P_{H_2O, \text{anode}}} \right)
\]

Equation 1.4

Here, \(V^\circ\) is the equilibrium potential at standard conditions, \(n\) is the number of electrons taking part in each half-cell reaction, and \(F\) is Faraday’s constant, the number of Coulombs in a mole of electrons.

For \(H_2\) oxidation at open circuit, the cell potential in real SOFCs and SOEs is usually very close to the Nernst Potential predicted by Equation 1.4. However, when there is current flowing through the cell, irreversible processes in the electrolyte and electrodes cause the cell potential to be lower, with the lost energy going to generate heat [93]. The losses in the electrolyte are simple to describe. Every material has an intrinsic conductivity, so that the area-specific resistance, \(R_E\), can be calculated from the conductivity and the thickness of the electrolyte [124]. The potential energy loss in the electrolyte for a current density, \(i\), is equal to \(iR_E\). This energy loss can be minimized through the by operating at higher temperatures and by using thinner electrolytes.

Because the electrodes are typically made from materials that have good electronic conductivity, \(i-R\) drops in the electrodes are typically small. However, mass transport of the gaseous reactants to the electrolyte interface and slow reaction kinetics for the electrode reactions can lead to potential drops, referred to as electrode
“overpotentials”, $\eta_{\text{anode}}$ and $\eta_{\text{cathode}}$. Therefore, the cell potential will vary with current density according to Equation 1.5:

$$ V = V_{\text{Nernst}} - (iR_E + \eta_{\text{anode}} + \eta_{\text{cathode}}) $$  

Equation 1.5

Losses due to the electrochemical reactions are very important in determining the performance of the cell but are difficult to describe. Since reducing these is the primary goal of electrode catalysis, we consider the physical situation in some detail in the next sections. The reader should recognize that our understanding of electrochemical processes in solid-oxide electrodes is incomplete, and that disagreements still exist among researchers in this area.

1.4 Three Phase Boundary Concept

From the reaction specified in Equation 1.1, it is apparent that gas phase oxygen, electrons, and oxygen ions must all be present simultaneously in order for oxygen reduction to successfully occur. This requires that there be points where the gas phase, the ionic conductor and the electronic conductor all come into contact. These points are commonly referred to as the three phase boundary (TPB) and in the strictest sense are the only sites where oxygen reduction can occur. If the cathode material has only electronic conductivity and the electrolyte has only ionic conductivity, the TPB only exists at the line of contact for the electrode, the electrolyte, and the gas phase [126]. In order to increase the number of TPB sites, ionic conductivity is often introduced into the cathode through the use of composites consisting of both the electronic conductor and an ionic conductor (typically the same as that used for the electrolyte). These composite cathodes
allow the oxygen reduction reaction to take place within the cathode rather than simply at the cathode-electrolyte interface as the YSZ within the cathode provides conductive channels allowing the oxygen ions to reach the electrolyte [41, 73].

It is important to note that the connectivity of all three phases is essential in order for the reaction site to be effective. If any of the three phases are unable to reach a particular TPB site, the reaction will be unable to proceed at that site. One major implication of this requirement is that the electrolyte material within the cathode will only be effective if it is satisfactorily sintered to the electrolyte. In order to successfully remove the grain boundaries between the electrode and the electrolyte, sintering temperatures of at least 1500 K are required [93].

1.5 Perovskite Cathode Materials

Perovskites are the most commonly used electronic conductors in SOFC composite cathodes and are preferred over Platinum due to their lower cost and better kinetic properties [1, 93]. The majority of the perovskites currently being used in composite cathodes have a perovskite crystal structure, \( \text{ABO}_3 \), as shown in Figure 1.2. Typically, a Lathanide series metal occupies the A site and a transition metal occupies the B site. The most commonly used perovskites are \( \text{LaMnO}_3 \), \( \text{LaFeO}_3 \), and \( \text{LaCoO}_3 \) based materials, all of which are mixed ionic and electronic conductors (MIECs).
Figure 1.2 Perovskite lattice structure and oxygen conduction principle [1]
The A site of the perovskite is often doped with an alkaline earth metal. Introduction of these lower valance dopants leads to the formation of oxygen ion vacancies and electron holes in order to maintain the charge neutrality of the lattice. These electron holes and oxygen ion vacancies lead to increases in the electronic and ionic conductivity of the perovskite [1]. Doping of the A site can therefore be used to tune the conductivity of the perovskite [8]. It has also been shown that oxygen ion vacancies increase with decreasing $P(O_2)$, as will be discussed more in depth in Chapter 5. In this work the majority of the prepared cathodes were composites of YSZ and La$_{0.8}$Sr$_{0.2}$MnO$_{3-\delta}$ (LSM) or La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ (LSF). In these expressions, the term $\delta$ accounts for the oxygen nonstoichiometry of the perovskite.

1.6 Preparation of Composite Cathodes

The conventional method for preparing composite cathodes typically involves the painting or screen printing of a slurry mixture of perovskite and YSZ powders onto a dense YSZ electrolyte [1, 93]. The cathode and electrolyte are then fired to the high temperatures required to sinter the YSZ. Because the perovskite within the cathode is subjected to the high sintering temperature, this method of cathode fabrication places several restrictions on the perovskite material used. The most important of these restrictions is that the perovskite must be thermally stable at high temperatures and must not undergo solid state reaction with the YSZ. It is also desirable that the perovskite used has a similar coefficient of thermal expansion (CTE) to that of YSZ. Because of its stability in the presence of YSZ [75], LSM is the most commonly used perovskite
material in traditionally prepared composite cathodes. However, LSM-YSZ composites show relatively poor performance at operating temperatures below 1000 K [138].

All of the composite cathodes discussed in this thesis have been prepared using an infiltration process rather than by the conventional co-sintering method [9, 32, 103]. Fabrication by infiltration consists of the formation of a porous layer of the electrolyte material along with the electrolyte. The porous layer is then used as a scaffold for the composite electrode and the perovskite material is deposited in subsequent steps. Cathode preparation by infiltration provides many advantages over the conventional method. [134] The most significant of these is that infiltration allows the sintering temperature of the YSZ to be separated from the calcination temperatures of the other cathode components. Additionally, cathodes prepared by infiltration are more tolerant of CTE mismatch and are able to achieve electronic connectivity of the perovskite at loadings below the theoretical percolation limit.

While electrodes prepared by infiltration are ideal for studying the fundamental relationships between the perovskite and the YSZ, their preparation can be tedious. Although several methods of infiltration, [44] such as the use of molten salts, have been demonstrated as feasible, the most commonly used method is wet impregnation. With wet impregnation, a solution of perovskite precursor nitrate salts is prepared and the porous YSZ scaffold is repeatedly saturated with the solution and calcined until the desired weight loading is achieved. Because the amount of perovskite precursor infiltrated during each step is limited by the pore volume and the solution concentration, as many as twenty steps are often required to achieve the desired weight loading [8].
This high number of calcinations steps is seen as limiting to the large scale manufacturability of the infiltration process.

1.7 Degradation of Cathode Performance

There is a great deal of flexibility in the choice of calcinations temperature when preparing composite cathodes by infiltration. Typically the minimum calcination temperature is the temperature required to form the perovskite phase, 1123 K for LSF or LSM. Previously it has been shown that the performance of LSF-YSZ composite electrodes calcined to 1123 K is unstable [137]. As shown in Figure 1.3, the total electrode impedance increases linearly during operation at 973 K. In this same study, it was shown that the characteristics of an LSF-YSZ composite electrode calcined to 1373 K were similar to those of the 1123 K composite after long-time operation.

The degradation of LSF-YSZ composites is often attributed to solid state reaction between the components. Subsequently, a number of groups have performed studies looking for solid state reactions between LSF and YSZ and have found no evidence for the formation of new phases below 1473 K [134]. The co-firing of LSF and YSZ to 1473 K has been reported to cause an expansion of the perovskite lattice, attributed to Zr incorporation into the lattice [118]. However, when purposefully infiltrating \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.9}\text{Zr}_{0.1}\text{O}_3 \) and calcining to 1123 K, the cathode performance was quite respectable and significantly better than that of a LSF-YSZ composite calcined to 1373 K [137].
The source of deactivation was also investigated using scanning electron microscopy (SEM) [137]. As shown in Figure 1.4, these SEM images showed significant sintering of the LSF crystallites. Following calcination to 1123 K, the LSF particles were approximately 0.05 µm in size. After 1700 hours of operation, however, these particles grew to an average particle size of 0.2 µm and formed a film over the YSZ scaffold. Similar aggregation and film formation of the perovskite was observed in the composite calcined to 1373 K.

Figure 1.3 Impedance results for a symmetric cell operating at 973 K as a function of time with LSF-YSZ composite air electrodes calcined to 1123 K. [137]
Figure 1.4 SEM images of (a) the porous YSZ scaffold, (b) LSF film on the YSZ scaffold after calcination at 1123 K, (c) LSF film after calcination at 1123 K and testing for 1000 hrs at 973 K, and (d) LSF film after calcination at 1373 K. [137]
Chapter 2. Experimental Methods

2.1 Fuel Cell Manufacture and Preparation

All of the work presented in this dissertation was carried out using electrolyte supported oxide SOFCs manufactured using tape casting and lamination techniques [9, 32, 103]. Any deviations from the methods described below will be detailed in the experimental section of the appropriate chapter.

2.1.1 Tape Casting

The tape that would become the electrolyte layer was prepared using

\[ \begin{align*}
30 \text{ g YSZ (TOSOH, TZ-8Y)} \\
13.5 \text{ g H}_2\text{O} \\
0.8 \text{ g D3005 (Rohm and Haas)} \\
7 \text{ g HA-12 (Rohm and Haas)} \\
9 \text{ g B-1000 (Rohm and Haas)}
\end{align*} \]

In the first step, the H\_2\_O and the dispersant, D3005, were mixed on a stirring plate for several minutes before the slow addition of the YSZ powder. This mixture was covered with foil and left stirring for 24 hours. The following day, the binder and emulsifier, B1000 and HA-12, were added. The mixture was weighed and left stirring, partially covered, for the next 24-48 hours, until \( \sim 7 \text{ g of water had evaporated.} \)

Once the appropriate amount of water had evaporated, the slurry was tape cast on to a mylar carrier film using a doctor blade and a tape-casting machine (Richard Mistler).
The thickness of the tape was controlled by the settings of the doctor blade. All cells prepared in this work consisted of a ~100 µm thick electrolyte layer. Once cast, the electrolyte tape was allowed to dry for at least 4 hours before handling.

The tape that would become the porous electrode layer was prepared using

\[ \begin{align*}
20 \text{ g YSZ (TOSOH, TZ-8Y)} \\
18.3 \text{ g of graphite (Sigma Aldrich)} \\
44 \text{ g H}_2\text{O} \\
3.6 \text{ g D3005 (Rohm and Haas)} \\
9.6 \text{ g HA-12 (Rohm and Haas)} \\
14.4 \text{ g B1000 (Rohm and Haas)}
\end{align*} \]

Similar to the method described for the electrolyte tape, the H\(_2\)O and D3005 were mixed on a stirring plate for several minutes before the slow addition of the YSZ and graphite powders. The mixture was left stirring for the next 24 hours. The following day, the B1000 and HA-12 were added and the slurry was left stirring for another 24 hours. The slurry was then tape cast using settings that would give a 50 µm porous layer after firing. Typically, the electrodes produced from the slurry composition were ~65% porous.

### 2.1.2 Cell Assembly and Sintering

Once both tapes had been cast and allowed to dry, discs were punched from each tape. The discs from the electrolyte tape were 13/16” in diameter and the discs from the porous electrode tape were 3/8” in diameter. One of the smaller porous discs was then placed on each side of the larger electrolyte disc, taking care to align the smaller
electrodes such that they were directly opposite on another. This assembly was then laminated using a hydraulic press at 343K and minimal pressure. Following lamination, the complete cells were placed into a furnace (Deltech) and sintered by heating in air to 1773 K for 4 hours. The heating rate was 2 K/min and the cooling rate was 3 K/min. After sintering, the cell diameter was ~1.4 cm and the electrode diameter was ~0.7 cm.

2.1.3 Cathode Preparation

The composite cathodes were prepared by repeated impregnation of aqueous nitrate salts solutions [44, 48]. As an example, to produce the LSF-YSZ composites, the porous YSZ was infiltrated with a solution of La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$ and Fe(NO$_3$)$_3$·9H$_2$O, at a molar ration of La:Sr:Fe = 0.8:0.2:1. In order to aid in the formation of the perovskite phase, the solution also contained citric acid (the Pechini method), with the concentration of citrate ions equal to that of the metal ions.

For all the cathodes used in this dissertation, the perovskite loading was fixed at 40 wt % because it had been previously determined that this amount was sufficient to achieve electronic conductivity throughout the electrode [40]. Because the amount of perovskite precursor that can be added in a single infiltration step is limited by the pore volume of the YSZ scaffold and the concentration of the nitrate solution, multiple impregnations were needed in order to achieve the desired weight loading [134]. Between each impregnation step, the electrode was calcined to 723 K for 30 minutes to remove the nitrate ions. Once the final weight loading had been achieved, the electrode was heated in air to their final calcination temperature, typically 1123 K or 1373 K.
Electrodes calcined to 1123K were heated at a rate of 30 K/min. Electrodes calcined to 1373 K were heated at a rate of 2 K/min. All electrodes were calcined for 4 hours.

2.1.4 Anode Preparation

In this dissertation, the anodes were prepared following the final calcination of the cathode. The majority of the anodes were prepared using a 50 µm porous layer [33, 71]. First, an aqueous solution containing Ce(NO$_3$)$_3$ was impregnated, followed by impregnation of an aqueous solution containing (NH$_3$)$_4$Pd(NO$_3$)$_2$. The final weight loadings for these anodes were 50-wt% ceria and 0.5-wt% Pd. The anodes were heated to 723 K between impregnation steps. Variations from this standard anode composition are detailed in the experimental section of the appropriate chapter.

2.1.5 Preparation for Testing

Following the completion of the cathode and anode, a loop of Ag wire was attached to each electrode using Ag paste. The cell was then sealed onto an alumina tube 1.0 cm in diameter with an alumina based sealant (Aremco VFG-552). The tube was then mounted onto a glass reactor and placed into furnace. The cells were heated in air to 973 K at 2 K/min with two hour dwells at 363 K and 540 K, following the curing procedure for the sealant. Thirty minutes prior to cell testing, the reactor was attached to a gas supply system and the anode was exposed to humidified (3% H$_2$O) H$_2$. 
2.2 Cell Performance Measurements

2.2.1 V-i Performance Measurement

The cell performance was evaluated using V-i curves. V-i curves show the voltage output of the fuel cell as a function of the current density. As stated in the previous chapter, fuel cells would ideally operate at the Nernst potential, but irreversible processes within the electrodes and electrolyte cause the cell potential to be lower. The cumulative impedance due to these processes is equal to the slope of the V-i curve.

The V-i curves in this dissertation were measured using a Gamry Instruments PC4/750 potentiostat with VFP600 software package. The ramp rate for the V-i measurements was -25 mV/s and the sample rate was 5 Hz. The V-I curves were measured from ~1.1 V to 0 V.

2.2.2 Electrochemical Impedance Spectroscopy

Although V-I curves can provide insight into fuel cell performance, they cannot be used to differentiate between the different various sources of loss within the cell. Electrochemical impedance spectroscopy (EIS) is a powerful technique that can provide information for identifying these different processes. Impedance measurements are typically made by applying a sinusoidal current perturbation, \( i(t) = i_0 \cos(\omega t) \), and measuring the systems phase-shifted, sinusoidal potential response, \( V(t) = V_0 \cos(\omega t + \phi) \). The impedance, \( Z = V(t)/i(t) \), is measured across a range of frequencies and presented on a Nyquist plot, as shown in Figure 2.1.
As mentioned previously, SOFC losses are due to inefficiencies of either the electrolyte or the electrodes. Because the conduction of ions through the YSZ electrolyte is considered a time independent process, this ohmic resistance corresponds to the high-frequency real-axis intercept. The low frequency real-axis intercept corresponds to the total resistance of the cell and therefore the time dependent impedance of the electrodes is measured by the distance between the two intercepts. Ideally, the response of each kinetic process within the cell is equivalent to that of a single, parallel R-C circuit: a single semicircle centered on the real axis of the Nyquist plot, with a diameter equal to the resistance, \( R \), and a peak frequency, \( f \), equal to \( 1/2\pi RC \). Actual measured impedance spectra, however, consist of many smaller overlapping arcs representing each of the various time dependent processes within the cell.
All impedance measurements in this dissertation were taken using a Gamry Instruments PC4/750 potentiostat with EIS300 software. The impedance spectra were taken with an AC perturbation of 10 mA rms at specified DC current values. The frequency was varied from 100 kHz to 0.01 Hz with 10 points per decade.

2.3 Composite Slabs

Perovskite-YSZ composite slabs used for surface area and conductivity measurements were prepared by infiltration methods similarly to the composite cathodes. Initially, a porous YSZ slab was using the same YSZ/graphite slurry described in Section 2.1.1. Instead of tape casting, the slurry was pored into a small cup and allowed to dry. The dried slurry was then cut into small rectangular bars and sintered to 1773 K for four hours. The resulting porous YSZ slabs were then infiltrated and calcined in the same manner as described previously for the composite cathodes.

2.4 Perovskite Pellets

Perovskite pellets used for ionic conductivity measurements were prepared using perovskite powders synthesized using the Pechini method. Aqueous solutions were prepared by mixing stoichiometric quantities of nitrate salts with citric acid, with the concentration of citrate ions equal to that of the metal ions. After drying these solutions, the solids were heated to 1123 K to form the perovskite phase. The perovskite powders were then uni-axially pressed into disks at a pressure of 1.8 metric tons for 60 s. Finally, the disks were sintered at 1773 K for 4 h in air. Finally, the pellets were milled to a
thickness of ~3 mm using a Struers MD-Piano grinding disc with 120 grit. Following sintering, the calculated density of each pellet was greater than 92 % of the theoretical density and XRD scans showed the perovskites to be single phase. YSZ pellets were prepared in a similar manner by pressing and sintering YSZ powder.

2.5 Total Conductivity Measurements

The total conductivity of a material or composite can be measured using a standard four probe system as shown in Figure 2.2. Typically, a small rectangular sample was prepared using a composite slab or a perovskite pellet that been milled to dimensions that were roughly 3 mm × 3 mm ×10 mm. Four Ag wires were then attached to the sample with Ag paste. One wire was wrapped around each end of the sample, and two were wrapped near the middle. The cross sectional area of the sample, $A_{CS}$, and the distance between the middle lead wires, $d$, were measured. The sample was then placed in a furnace and heated in air at 10 K/min. Finally, a current was supplied through the two outer lead wires and the potential was measured between the two inner lead wires. Using these values, the total conductivity of the sample was calculated using Equation 2.1:

$$\sigma_t = \frac{i \times d}{V(A_{CS})}$$

Equation 2.1
2.6 Ionic Conductivity Measurements

The measurement of the ionic conductivity of a MIEC material is nontrivial as standard four-probe conductivity measurements are unable to isolate the ionic conductivity from the typically much greater electronic conductivity. Ionic conductivities of MIEC are generally determined by one of three methods: through the use of blocking electrodes [107, 139, 153], by measuring oxygen permeation through a dense pellet, or by using secondary ion mass spectrometry (SIMS) to measure the diffusion of a tracer through the material [121, 122]. For the work in this dissertation, ionic conductivity measurements of various perovskites were attempted first through the use of blocking electrodes and ultimately were achieved through permeation measurements.
2.6.1 Blocking Electrodes

The use of blocking electrodes aims at suppressing the flow of electrons through the MIEC such that the only available charge carriers are oxygen ions. Ideally, the blocking electrode has an electronic conductivity that is significantly lower than the ionic conductivity of the MIEC [107]. A typical blocking electrode system is presented schematically in Figure 2.3. The MIEC test sample is placed in series with a purely ionic conductor and electrodes are attached to both the blocking electrode and the MIEC. A potential is then applied such that electrons are supplied to the blocking electrode and the resulting current across the entire system is measured. In theory, electrons are unable to pass through the blocking electrode and only oxygen ions are available for charge transfer through the MIEC. The measured resistance is then related to the ionic conductivity of the MIEC.

![Figure 2.3 Diagram of a standard blocking electrode system to measure ionic conductivity.](image-url)
Several attempts were made to measure ionic conductivity using blocking electrodes. Initially, a dense YSZ pellet was attached to a perovskite pellet using Ag paste and perimeters were sealed using a glass sealant (ESL Dielectric Composition Type 4461). Ag leads were attached to the exposed faces of each pellet using Ag paste. A similar system was prepared using a perovskite pellet sandwiched between two YSZ pellets. Finally, a microelectrode technique was attempted following the works of Zipprich et al [139, 153]. The tip of a YSZ rod was sharpened into a point and pressed into contact with the center of the perovskite pellet. The contact point between the YSZ tip and the perovskite was sealed with glass sealant. Ag leads were attached to the YSZ rod and the exposed face of the perovskite pellet using Ag paste. For each of the blocking electrode methods attempted, no meaningful conductivity data was obtained and in most situations the measured resistance was due to the ionic conductivity of the YSZ electrode.

While it is unclear why our attempts at using blocking electrodes were unsuccessful, it is known that the successful use of blocking electrodes ultimately depends on the conduction of oxygen ions across the interface between the blocking electrode and the MIEC [107]. Any porosity at this interface presents the opportunity for the oxygen ions to produce gas phase oxygen and electrons, defeating the purpose of the blocking electrode. Even if the interface is perfectly prepared, the chance exists that the oxygen pumped through the blocking electrode will accumulate at the interface rather
than pass through the MIEC. This will lead to a pressure buildup at the interface and ultimately the seal around the system will fail.

### 2.6.2 Oxygen Permeation Measurements

The system used for the oxygen permeation measurements is presented schematically in Figure 2.4 [8]. Initially, electrodes were painted on the inner and outer walls of a YSZ tube using Pt paste and Pt lead wires were attached. A perovskite pellet was then affixed to one end of the tube using glass sealant. The system was then heated to 923K at 2 K/min. Once the system had reached its final temperature, the open end of the YSZ tube was closed using a gas tight fitting.

The oxygen permeating through the perovskite pellet was measured by balancing the steady state permeation flux with the rate of oxygen pumped electrochemically through the YSZ tube via the Pt electrodes. Once the system had reached equilibrium, the potential across the Pt electrodes could be related to the oxygen partial pressure inside the tube and the current could be related to the permeation flux. For mixed conducting membranes [117], the permeation flux, $J_{O_2}$, is related to the bulk ambipolar conductivity, $\sigma_{amb}$, by Equation 2.2:

$$\sigma_{amb} = \frac{16F^2 \lambda}{R_g T} \left[ \frac{\partial J_{O_2}}{\partial \ln(pO_{2\text{air}} / pO_{2\text{in}})} \right]$$

Equation 2.2

In this equation, $pO_{2\text{air}} / pO_{2\text{in}}$ is the ratio of the oxygen partial pressures on either side of the perovskite pellet, $F$ is the Faraday constant and $\lambda$ is the specimen thickness. $\sigma_{amb}$ is the ambipolar conductivity of the perovskite as defined by Equation 2.3:
\[
\sigma_{amb} = \left( \frac{\sigma_i \sigma_{el}}{\sigma_i + \sigma_{el}} \right)
\]

Equation 2.3

where \(\sigma_i\) and \(\sigma_{el}\) are the ionic and electronic conductivities of the perovskite. Finally the ionic conductivity can be calculated from the ambipolar conductivity and the total conductivity \(\sigma_t\) using Equation 2.4:

\[
\sigma_i = \sigma_t \left[ \frac{1}{2} - \sqrt{1 - \frac{4\sigma_{amb}}{\sigma_t}} \right]
\]

Equation 2.4

In this dissertation, ionic conductivities were calculated from data in which the \(pO_2\) inside the system was varied between 2.5 and \(3.9 \times 10^{-2}\) atm.

**Figure 2.4** Diagram of the oxygen permeation system used to measure ionic conductivity.
2.7 Surface Area Measurements

BET surface areas were measured on rectangular composite slabs, prepared as described in Section 2.3, using the Kr isotherm at 78 K. The adsorption apparatus used in these measurements was self-built and is sensitive to surface areas as low as 0.002 m². Prior to measurement, the samples were degassed under vacuum at 573 K.

2.8 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) was used to identify the phases formed during cathode composite fabrication and to verify the absence of secondary phases. Typically, XRD scans were performed on actual composite cathodes after the final calcination and prior to the attachment of the silver lead wire. The phases of all composites were evaluated using a Rigaku D/Max-B Powder Diffractometer with a monochromated Cu Kα radiation source. Typically samples were scanned over a 2θ range from 20° to 60°. The scan was conducted with a sampling interval of 0.02° and a scan speed of 2°/min.

2.9 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was performed using a FEI Strata DB235 FIB and a FEI Quanta 600 FEG ESEM. The Quanta was equipped with an energy dispersive X-ray spectrometer (EDS) which was able to provide rapid qualitative estimates of chemical composition.
Chapter 3. Fabrication of LSM-YSZ Composite Electrodes by Electrodeposition

3.1 Introduction

As described in the previous chapters, the composite cathodes that will be discussed in this dissertation were prepared by infiltration of perovskite precursors into a porous YSZ scaffold after the scaffold had been sintered onto the YSZ electrolyte [15, 31, 72, 101]. The primary advantage of this method is that high temperatures can be used to sinter the YSZ component of the electrode to the electrolyte, while using lower temperatures for the perovskite component so as to avoid solid-state reactions with the YSZ and maintain the perovskite phase in nano-crystalline form [77].

Unfortunately, fabrication by infiltration is tedious due to the fact that multiple infiltration and calcination steps are required, which limits the commercialization of the process. The maximum amount of perovskite that can be added in a single step is equal to that which can be formed from the volume of liquid required to fill the pore volume of the YSZ scaffold. Therefore, it is easy to calculate that infiltration of 1 M solutions of La$^{+3}$ and Mn$^{+3}$ into a 65% porous scaffold will produce only 2.3-vol% LaMnO$_3$ [134]. Single-step infiltration of a 15-wt% solution of LaMnO$_3$ nanoparticles will produce an even lower loading of the perovskite [111, 112]. Even though less of the perovskite is required to achieve the percolation threshold in composites formed by infiltration [40], it seems apparent that loadings should at least approach the percolation threshold for normal composite electrodes, ~30-vol%.
Higher loadings of the conductive phase can be achieved in a single step by electrodeposition. For example, metal-YSZ composites with relatively high loadings of Cu, Co, or Ni have been prepared by electrodeposition of the metals onto porous YSZ scaffolds that had been coated with a thin layer of carbon to make them conductive [62]. While electrodeposition has not yet been used to synthesize perovskite-based electrodes, LaMnO$_3$ has been electroplated onto flat surfaces [92, 109, 128, 129]. Therefore, the present study set out to demonstrate that LSM-YSZ composites could also be produced in this way.

Ensuring that deposition occurs uniformly throughout the porous electrode, not simply on the external surface, is challenging; the necessary conditions for accomplishing this have been outlined in previous papers [35, 62]. Because most of the potential drop in electroplating occurs within a few nanometers of the solid surface [106], the potential in the fluid at the center of the micron-sized pores that make up the porous electrode must be uniform and similar to that of the bulk solution into which the porous substrate is immersed. This requires that the conductivity of the solution be high and that the concentration of cations in the solution be uniform throughout the bulk fluid and at the center of the pores [62]. In the absence of significant field gradients, the migration of ions into the pores from the external solution will be controlled primarily by molecular diffusion, since convection will be negligible in micron-sized channels. Therefore, it is necessary to control the concentration of the plating solution to maximize conductivity and to use low currents so that diffusion of ions into the pores is rapid compared to the rate of deposition.
This chapter will demonstrate that it is possible to use electrodeposition to achieve sufficiently high loadings of La and Mn so that a conductive electrode can be formed in a single electrodeposition step. Because we were unable to deposit La as a metallic species, the amount of La that we were able to deposit was limited by formation of an insulating film.

3.2 Experimental

The fuel cells used in this work were prepared from YSZ wafers that had a dense electrolyte layer separating two porous layers, as described in Chapter 2. The dense electrolyte layers were 100 µm thick and 1 cm in diameter, while the two porous layers were each 50 µm in thickness and 0.67 cm in diameter. Based on earlier work, the porous layers were known to be approximately 65% porous[7].

The cathodes of the fuel cells were synthesized by adding LSM (La$_{0.8}$Sr$_{0.2}$MnO$_3$) to one of the porous layers by either aqueous infiltration or electrodeposition. With aqueous infiltration, the cathodes were prepared following the procedure detailed in Chapter 2. Once the perovskite loading was 40-wt%, the cathode was calcined to 1373 K to form the perovskite phase.

When adding LSM by electrodeposition, it was first necessary to make the YSZ scaffold electronically conductive. This was accomplished by placing the sintered cell in flowing butane at 1123 K until approximately 2-wt% of conductive carbon had been deposited in the pores [62]. Assuming a density of 1 g/cm$^3$ for the carbon, 2-wt% corresponds to 15-vol% of the scaffold or 23% of the available pore volume within the
YSZ. The scaffold was not sufficiently conductive with less than 2-wt% carbon; depositing more than 2-wt% carbon resulted in significant filling of the YSZ pores, which limited the amount of material that could be added by electrodeposition. Following carbon deposition, a silver wire was attached with silver paste to the edge of the YSZ scaffold that would become the cathode. Candle wax was used to cover the silver wire and paste, as well as the opposing YSZ scaffold that would become the anode.

Before attempting to deposit La into the porous scaffold, experiments were performed on a flat stainless-steel foil in order to understand the nature of the deposits. Although there are reports that metallic La can be electrodeposited, even from aqueous solutions [27, 84], we found the process to be more complex. Our initial attempts to deposit La used aqueous solutions of La(NO$_3$)$_3$ containing sodium citrate, sodium tartarate, or EDTA; all of these produced a thin gel-like coating on the foil. The deposits were almost certainly La(OH)$_3$, as reported by Therese et al.[129], produced indirectly through the reduction of oxygen in the electrolyte [135]. Similar results were obtained using glacial acetic acid as the solvent. Finally, deposition was attempted using anhydrous LaCl$_3$ in DMSO (Fisher Scientific)[11, 20, 92, 150], DMF (Fisher Scientific)[88], and ethylenediamene (Alfa Aesar)[97]. The experiments carried out with DMSO were conducted in a dry box, under a N$_2$ atmosphere, after passing the DMSO through a bed of 4A molecular sieve. Although the use of dry organic solvents eliminated H$_2$ evolution at the electrode, the nature of the deposits was unchanged. For the present application, deposition of the hydroxide was considered acceptable.
Electrodeposition was accomplished using a two-electrode electrochemical cell with a Pt counter electrode. The Mn and La species were deposited separately using 0.1 M solutions of their respective nitrate salts in DMSO. For the composite La-Mn cell, deposition was performed consecutively, with the Mn deposited first because it deposited as a metal, immediately followed by La. In this study, all depositions were carried out galvanostatically, at a current density of 4.5 mA/cm². All deposition quantities in this paper were determined from measured weight changes in the sample. Once deposition was complete, the silver leads were detached and SrO was added by a single infiltration of Sr(NO₃)₂. Finally, the cells were calcined to either 1123 or 1373 K, temperatures that were sufficient to remove the deposited carbon and the candle wax.

For fuel-cell testing, ceria and Pd were infiltrated into the porous YSZ on the anode side, following the final calcination of the cathode side. A final composition of 50 wt-% CeO₂ and 0.5 wt% Pd, was used as described previously [7]. The final calcination temperature for the anode was 973 K. Cells were then mounted and tested at 973 K, with the anode in flowing, humidified (3% H₂O) H₂ and the cathode simply exposed to the laboratory air.

Following preparation of the various electrodes, characterization of the bulk phases was conducted using X-Ray Diffraction (XRD), while the morphology and uniformity of the deposits were examined by Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDX).
3.3 Results and Discussion

To determine the conditions for achieving homogenous deposition of each species, Mn and La were each electrodeposited onto separate, carbon-coated YSZ substrates. Figure 3.1 shows deposition curves for Mn and La, using 0.1 M nitrate solutions in DMSO. No current was observed for pure DMSO for potentials below 10 volts, while deposition on the fresh substrates occurred for both the Mn and La solutions beginning at ~3.5 V. However, for both Mn and La solutions, the deposition currents at a constant potential of 4.0 V were found to decrease with time over the period of several hours, well before the desired loadings of either component had been achieved, such that it was not practical to perform deposition in the potentiostatic mode. Therefore, deposition was performed galvanostatically with a current density of 4.5 mA/cm$^2$. As will be shown later, this current density was sufficiently low to allow uniform deposition throughout the porous scaffold and could be maintained to reasonable loadings for both Mn and La.

With Mn, the initial voltage was approximately 4 V and increased to ~5 V as the Mn deposited inside the electrode pores. Once the pore volume had been filled, the voltage increased rapidly, to above 10 V, and deposits began forming externally on the electrode surface. Internal Mn loadings as high as ~60-wt% Mn$_2$O$_3$ were obtained. The average Coulomb efficiency of deposition inside the electrode pores was approximately 30%.
The characteristics of La deposition were quite different. While the initial voltage required for 4.5 mA/cm² was also approximately 4 V, the voltage was found to rise and reach a plateau after 10 minutes at a value near 5 V. The loading at this point was equivalent to ~20-wt% La₂O₃, with an average Coulomb efficiency of 20%. Beyond this time, no further deposition occurred, either in the pores or on the external surface, even though the current remained constant. It is possible that particles of La(OH)₃ continued to form after this time but that they remained as colloidal particles in solution, external to the pore structure and separate from the sample.

We attempted to characterize the Mn and La by XRD immediately following the room-temperature deposition but the deposits were found to be amorphous. The cells were then calcined in air to 1123 K to remove carbon and oxidize the deposits to either Mn₂O₃ or La₂O₃. SEM micrographs of these oxidized deposits, taken at a depth of 40 µm
from the external surface of the scaffold and 10 µm from the dense electrolyte layer, are shown in Figure 3.2. For comparison purposes, Figure 3.2a) is an image of porous YSZ scaffold and shows that the scaffold is made up of relatively uniform pores, between 1 and 3 µm in size. With the addition of Mn, Figure 3.2b), the YSZ scaffold is covered with a layer of Mn₂O₃ particles, roughly 0.2 µm in size. The uniformity of the layer suggests that it was probably formed by oxidation of a thin film of the metallic Mn. The oxidized La deposits, Figure 3.2c), exist as clumps within the scaffold structure. This is consistent with the picture that La(OH)₃ particles form in solution near the surface and simply precipitate inside the channels.

Since it appears that Mn deposits in its metallic form as an even layer over the scaffold, the perovskites were prepared by electrodepositing Mn first, then adding the La. This allowed the conductivity of the scaffold to be maintained for the subsequent addition of La. The conditions used for sequential depositions were identical to that used for deposition of the individual components. A loading of 30-wt% LaMnO₃ was targeted, based in part on results obtained for electrodeposition of the pure compounds which suggested that this is the maximum realistic loading achievable for La and in part on the fact that this loading is sufficient to provide the necessary conductivity for infiltrated-LSM electrodes [40]. The voltage-time characteristics were in qualitative agreement with the results obtained for the pure compounds. For a constant current
Figure 3.2a. SEM image of a empty porous YSZ prior to electrodeposition.

Figure 3.2b. SEM images of a porous YSZ scaffold after electrodeposition in a solution containing 0.1M Mn(NO$_3$)$_3$ in DMSO Deposited species were fired to 1123 K immediately following deposition.
Figure 3.2c. SEM images of a porous YSZ scaffold after electrodeposition in a solution containing 0.1M La(NO$_3$)$_3$ in DMSO. Deposited species were fired to 1123 K immediately following deposition.

density of 4.5 mA/cm$^2$, the voltage rose continuously over the duration of the Mn deposition; when the sample was placed in the La-plating bath, the initial voltage was lower than the final voltage in the Mn bath but again rose to a plateau value, at approximately 6.5 V in this case.

Figure 3.3 shows an SEM micrograph of the YSZ scaffold after deposition of both Mn and La to a loading of 33-wt%, following calcination to 1123 K. The deposits are in the form of small nanoparticles, spread uniformly over the YSZ scaffold. The EDX line scan, shown in Figure 3.4, demonstrates that the La and Mn are present together, down to the interface with the YSZ electrolyte.

To confirm that the deposited species had formed the desired perovskite phase following calcination, XRD data were taken of the electrode prepared by
electrodeposition and compared to that of an LSM electrode prepared by infiltration to a loading of 40-wt% LSM. Both diffraction patterns were taken after calcination to 1373 K and are presented in Figure 3.5. Both patterns show a broad peak at approximately 32.5 degrees 2θ corresponding to the perovskite phase. The relative intensity of the perovskite peak to that of the YSZ peak was smaller for the composite prepared by electrodeposition, in part because the loading was lower. However, because salts added by infiltration tend to be pulled to the external surface of the scaffold during the drying process [61], it is also possible that the smaller intensity of the diffraction line following electrodeposition is due to the perovskite forming more deeply into the scaffold, closer to the electrolyte.

To determine how well composites formed by electrodeposition could perform as fuel-cell electrodes, otherwise identical fuel cells were prepared using electrodeposition and normal infiltration by nitrate salts. For these experiments, an aqueous solution of Sr(NO$_3$)$_2$ was introduced into the scaffold containing the electrodeposited La and Mn, prior to calcination, to produce a composition as close as possible to La$_{0.8}$Sr$_{0.2}$MnO$_3$, although it should be recognized that it is difficult to achieve the targeted composition precisely using electrodeposition. For both preparation methods, LSM-YSZ composites were calcined to 1373 K before adding 50-wt% ceria and 0.5-wt% Pd in the anode. The cells were then tested in humidified (3% H$_2$O) H$_2$ at 973 K, while holding the cathode in air.
Figure 3.3. SEM micrograph showing the porous YSZ scaffold following sequential electrodeposition in solutions of 0.1M Mn(NO$_3$)$_3$ in DMSO and 0.1M La(NO$_3$)$_3$ in DMSO, then calcined to 1123 K.

Figure 3.4. EDX linescans taken in the direction of the arrow shown in Figure 3. Species measured are (a) Zr, (b) La, and (c) Mn.
Figure 3.5. XRD data for LSM-YSZ composites prepared by (a) wet impregnation and (b) electrodeposition. Peaks marked by $\times$ correspond to YSZ. Peaks marked by $+$ correspond to undoped LaMnO$_3$.

Figures 3.6 and 3.7 provide a comparison of $V$-$i$ polarization curves and impedance plots for cells prepared by electrodeposition and normal infiltration. The results demonstrate that the performance of both LSM electrodes is essentially identical. Because the performance of LSM-YSZ electrodes changes after polarization$^7$, data are shown starting from open circuit and after shorting the cells for 2 h. Starting from open circuit, the $V$-$i$ relationships in Figure 3.6 are highly curved, with slopes decreasing with current density. After shorting for 2 h, the $V$-$i$ dependences are nearly linear. The impedance curves in Figure 3.7, measured at open circuit, before and after shorting, show that the ohmic losses are 0.45 Ω-cm$^2$ for the impregnated cell and unaffected by shorting. This value is in good agreement with the resistance expected for 100-µm YSZ.
electrolytes. The ohmic losses of the electrodeposited cell were slightly higher, at 0.65 Ω·cm², and decreased to 0.55 Ω·cm² after shorting. This increased ohmic loss is likely due to insufficient weight loading of the perovskite within the electrode. The most prominent effect of shorting was on the non-ohmic impedances, which decreased from 2.1 Ω·cm² to ~0.6 Ω·cm², with most of this coming from the LSM cathodes [34].

To demonstrate that it was not simply the silver paste that was acting as the cathode, we also tested a cell that was identical to the ones for which data are shown in Figure 3.6 and 3.7, except that no LSM was added on the cathode side. At 973 K, this cell exhibited an ohmic loss of 2.5 Ω·cm² and an impedance that was independent of current density. Assuming 2 Ω·cm² of the ohmic losses come from the empty YSZ scaffold, the conductivity of the 50-µm porous YSZ is calculated to be 0.0025 S/cm. This is a factor of 10 lower than that of non-porous YSZ at 973 K [8]. The result also demonstrates that the LSM added by electrodeposition must be providing conductivity to the electrode. Previous papers have discussed possible reasons for LSM activation by polarization and these will not be repeated here [38, 43, 113]. Of primary importance for the present study is that the LSM added by electrodeposition shows identical performance to normal infiltrated LSM.

While we chose to prepare LSM-YSZ electrodes in this present study, it should be apparent that electrodeposition could have been used to prepare electrodes with other compositions as well.
Figure 3.6. Impedance data measured at open circuit for cells with cathodes prepared by (♦) wet impregnation and (●) electrodeposition. Data are shown for both cells before (open symbols) and after (closed symbols) polarization by shorting the cells for 2 h. The data were obtained at 973 K and the spectra for the cell prepared by wet impregnation have been offset for clarity.

Figure 3.7. V-i polarization plots, measured at 973 K, for cells with cathodes prepared by (♦) wet impregnation and (●) electrodeposition. Data are shown for both cells before (open symbols) and after (closed symbols) polarization by shorting the cells for 2 h.
3.4 Conclusion

Previous work has shown that infiltration of perovskites or perovskite precursors into a YSZ scaffold can produce electrode materials with improved properties over traditional composites formed by sintering of mixed powders; however, the infiltration procedure must typically be repeated many times in order to achieve the necessary loading of the perovskite. In this chapter, we have demonstrated that it is possible to prepare similar perovskite-YSZ composites by electrodeposition with a single calcination step. The weight loading achieved in this study was limited by the fact that La deposited as a hydroxide and could be improved by electrodeposition of metallic La.
Chapter 4. The Effect of Ca, Sr, and Ba Doping on the Ionic Conductivity and Cathode Performance of LaFeO$_3$

4.1 Introduction

Since electrodes based on LSF deactivate after sintering at temperatures as low as 1000ºC [114, 116, 117], it is commonly assumed that similar solid-state reactions are responsible for deactivation in these electrodes as well. However, deactivation by formation of insulating materials may not apply to LSF. As mentioned in the introduction, XRD scans of LSF-YSZ composites calcined to high temperatures showed no evidence of secondary phase formation below 1673 K. Similarly, composites that were infiltrated with Zr-doped LSF showed excellent initial performance when calcined to 1123 K.

In a previous study of the stability of LSF cathodes prepared by infiltration into porous YSZ from our laboratory, deactivation correlated with a loss of LSF surface area and the formation of what appeared to be a dense film of LSF covering the porous YSZ [137]. Impedance spectra also showed that the ohmic resistance of deactivated cells remained unchanged, a strong argument against formation of insulating layers. Based on these observations, it was suggested that deactivation is either due to a decrease in O$_2$ adsorption rate (due to lost surface area) or to LSF forming an impenetrable barrier over the YSZ in the electrode. If LSF forms a dense layer, performance in the deactivated electrode could be limited by conduction of oxygen ions through the LSF.
Because the ionic conductivity of $\text{LaFeO}_3$ likely depends on the dopant, we decided to compare the performance of Ca-, Sr-, and Ba-doped $\text{LaFeO}_3$ (LCF, LSF, and LBF). Previous work in which Ca, Sr, or Ba was doped on the A sites of $\text{LaCo}_{0.2}\text{Fe}_{0.8}\text{O}_3$ suggested that the ionic conductivities would decrease with dopant in the following order: $\text{Sr} > \text{Ba} > \text{Ca}$ [82, 125]. Whether this ordering of the ionic conductivities with dopant can be applied to the $\text{LaFeO}_3$ is uncertain, as are the absolute ionic conductivities of doped $\text{LaFeO}_3$. For example, Wiemhofer et al. [139] have reported that the ionic conductivity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ at 973 K is $1.2\times10^{-5}$ S/cm, while Patrakeev et al. [105] reported an ionic conductivity of $3.4\times10^{-2}$ S/cm at 1023 K for this same material. A consequence of the higher conductivity reported by Patrakeev et al. would be to rule out the proposal that deactivation of LSF electrodes is associated with an impenetrable film, since the conductivity of YSZ at 1023 K is $2.9\times10^{-2}$ S/cm [109].

In this chapter, we set out to measure the ionic conductivities of LCF, LSF, and LBF and to determine the performance of electrodes made with these three materials. It will be shown that the ionic conductivities of the doped $\text{LaFeO}_3$ are low compared to that of YSZ and that the magnitudes of the ionic conductivities are as follows: LSF>LBF>LCF. For electrodes prepared by infiltration and calcination to 1123 K, the infiltrated perovskites are highly porous and electrode performance is similar for composites of YSZ with LSF, LBF, and LCF. However, when the infiltrated electrodes were calcined to 1373 K, the infiltrated perovskites formed dense films on the YSZ pores and the electrodes showed degradation in performance. This degradation, like the initial
performance, was the same for all dopants, showing no dependence on ionic conductivity.

4.2 Experimental

The samples used for measurements of both total and ionic conductivities were prepared from LCF (La$_{0.8}$Ca$_{0.2}$FeO$_3$), LSF (La$_{0.8}$Sr$_{0.2}$FeO$_3$), and LBF (La$_{0.8}$Ba$_{0.2}$FeO$_3$) powders that were synthesized in our laboratory using the Pechini method as described in Chapter 2 [48, 137]. X-ray diffraction showed that each of the materials was single phase. The positions of the (240) lines in the diffraction patterns, reported in Table 4.1, are consistent with doping of Ca, Sr, and Ba.

<table>
<thead>
<tr>
<th>$2\theta$ of (240) planes (degree)</th>
<th>LaFeO$_3$-d</th>
<th>LCF</th>
<th>LSF</th>
<th>LBF</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.40$^1$</td>
<td>57.74</td>
<td>57.68</td>
<td>57.28</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ Value reported from JCPDS 37-1493.

**Table 4.1.** Peak positions for the (240) planes of doped LaFeO$_3$ samples used in the ionic conductivity measurements.

<table>
<thead>
<tr>
<th></th>
<th>923 K</th>
<th>973 K</th>
<th>1023 K</th>
<th>1073 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCF</td>
<td>56.7</td>
<td>56.8</td>
<td>57.5</td>
<td>58.7</td>
</tr>
<tr>
<td>LSF</td>
<td>79.9</td>
<td>79.7</td>
<td>78.9</td>
<td>77.8</td>
</tr>
<tr>
<td>LBF</td>
<td>49.6</td>
<td>51.1</td>
<td>51.9</td>
<td>51.8</td>
</tr>
</tbody>
</table>

**Table 4.2** Total conductivities of the doped LaFeO$_3$ samples as a function of temperature.
Some disks were machined into bars, 3mm x 3 mm x 10 mm, and used to measure the total conductivities, $\sigma_t$, in air between 923 and 1073 K, using 4-probe measurements. The total conductivities of each material are listed in Table 4.2 and were found to be essentially independent of temperature over the measured range.

The ionic conductivities were determined by measuring the rate of oxygen permeation across the perovskite disks, following the method discussed in Chapter 2. Typical data relating the oxygen flux to the ratio of $P(O_2)$ across the membrane are shown in Figure 4.1 for three different temperatures with the LBF sample. The reproducibility of this data and the stability of the perovskites to reduction during the course of the measurements were demonstrated by cycling the $P(O_2)$ inside the apparatus and showing that the relationship between oxygen flux and the $P(O_2)$ remained unchanged. The linear relationship between the permeation flux and $P(O_2)_{\text{air}}/P(O_2)_{\text{ins}},$ along with the strong temperature dependence of the flux, provides proof that the membranes were free of pinholes. Furthermore, we ruled out the possibility that the permeation fluxes were limited by surface-exchange kinetics. First, the zero intercept in Figure 4.1 is inconsistent with surface-exchange limitations. Second, it has been estimated that the length scale for which the oxygen permeation flux is under mixed control of the surface exchange kinetics and bulk diffusion for LSF is approximately 0.3 mm[49], a factor of 10 less than the thicknesses of our samples. Finally, we measured the oxygen permeation rate of the LSF specimen, the one exhibiting the highest fluxes, after coating the surfaces with Pt and showed that the addition of catalyst had no effect on oxygen fluxes.
Fuel cells with composite cathodes formed by infiltration of LCF, LSF, and LBF into porous YSZ were prepared in a manner similar to that described in Chapter 2 for LSF [48, 137]. The LCF-, LSF-, and LBF-YSZ composite cathodes were synthesized by infiltration of aqueous solutions containing $\text{La(NO}_3\text{)}_3\cdot 6\text{H}_2\text{O}$, $\text{Fe(NO}_3\text{)}_3\cdot 9\text{H}_2\text{O}$, and either $\text{Ca(NO}_3\text{)}_2$, $\text{Sr(NO}_3\text{)}_2$, or $\text{Ba(NO}_3\text{)}_2$ at the proper molar ratios. Infiltration steps were followed by calcination to 1123 K to remove the nitrate and citrate ions; multiple impregnation steps (approximately 10 for LSF and LCF and 20 for LBF) were used to reach a final loading of 40-wt% of the perovskite. Finally, some of the composites were calcined to 1373 K for 4 h to simulate deactivation, since an earlier study of LSF-YSZ cathodes showed that this high-temperature treatment lead to similar performance changes as that observed after long-time fuel-cell operation [137]. The physical
characteristics of the cathode composites were examined by XRD, to ensure that the proper phases were produced, and by scanning electron microscopy (SEM).

The SOFC anodes used in this study differed slightly from those described in Chapter 2. These anodes consisted of a 10-µm, porous YSZ layer impregnated it with 40-wt% CeO$_2$ and 1-wt% Pd, using the corresponding nitrate salts. Based on earlier studies [33, 34], the performance characteristics of this anode at 973 K in humidified H$_2$ are described by an ohmic contribution of 0.08 Ω·cm$^2$ and a non-ohmic contribution of 0.1 Ω·cm$^2$ for current densities below 1 A/cm$^2$. Because we have found the use of reference electrodes to be unreliable [91], cathode performance in this paper was determined from the total-cell performance by subtracting the contribution of the above anode losses.

4.3 Results and Discussion

4.3.1 Ionic Conductivities

The ionic conductivities of the LCF, LSF, and LBF are shown as a function of temperature in Figure 4.2. As pointed out earlier, these values were measured with one side of the membrane at a P(O$_2$) of 0.21 atm and the other between 2.5 x 10$^{-2}$ and 3.9 x 10$^{-2}$ atm, so that the measurements were under conditions similar to that experienced by an SOFC cathode. The absolute values for the conductivities of LSF, 8x10$^{-4}$ S/cm at 973 K, lie between the previously reported values from Wiemhofer, et al [139], 1.2x10$^{-5}$ S/cm at 973 K, and Patrakeev, et al [105], 3.4x10$^{-2}$ S/cm at 1023 K. The differences in
previously reported values may be due in part to the fact that the measurements were all performed at different P(O_2). For example, Patrakeev, et al used the minimum in the total conductivity at low P(O_2) as the ionic conductivity, clearly conditions far from 0.21 atm.

It is of interest to compare the conductivity of LSF to that of Sr-doped LaCo_{0.2}Fe_{0.8}O_3 (LSCF) because LSCF is presently being used by a number of groups in SOFC cathode applications [25, 74, 115]. Because LSCF is also one of the materials under consideration for oxygen-separation membranes, it is not surprising that significantly higher conductivities are reported for this material. For example, the ionic conductivity of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3 is 0.076 S/cm at 1073 K [125], compared to the value of 0.0045 S/cm for LSF in our measurements. For SOFC applications, it is interesting to note that the conductivity of YSZ at 1073 K, 0.043 S/cm [109], falls between these values.

Figure 4.2  Ionic conductivities of the doped LaFeO_3 samples as a function of temperature.
Similar to what has been reported previously for Sr-, Ba-, and Ca-doped LaCo$_{0.2}$Fe$_{0.8}$O$_3$ [82, 125], LSF exhibited the highest ionic conductivity, followed by the LBF and LCF. This is likely related to Sr$^{+2}$ ions having the optimum size for movement of ions in the LaFeO$_3$ lattice. As expected, the ionic conductivities for each material exhibited an Arrhenius temperature dependence. The activation energies for ionic transport of LSF and LBF were nearly the same, 0.77 eV (0.779 eV for LSF and 0.763 eV for LBF), while the activation energy for LCF was significantly larger, 1.2 eV. These values are also in reasonable agreement with activation energies for ionic conduction determined with doped LaCo$_{0.2}$Fe$_{0.8}$O$_3$ [125].

4.3.2 Cathode Performance Characteristics

When the LSF, LBF, and LCF composites were calcined to only 1123 K, the fuel cells based on these cathodes showed cell potentials that decreased linearly with current density at 973 K. (These measurements were performed with the anode exposed to humidified H$_2$ and the cathode exposed to air.) Because of the linearity of the V-i curves, the open-circuit impedance plots in Figure 4.3 are sufficient to describe cell performance. The ohmic losses have been removed from the impedance curves because the electrolyte thickness varied between 100 and 125 µm; however, ohmic impedances were between 0.65 and 0.8 Ωcm$^2$ for each cell, values consistent with that expected for this electrolyte thickness at 973 K, plus the contribution of the anode [33, 34]. The data in Figure 4.3 show that the performance of each cathode was essentially identical, independent of which dopant was added to LaFeO$_3$. Each of the cells showed non-ohmic losses between
Figure 4.3 Open-circuit impedance data for cells made with LSF (■), LBF (●), and LCF (▲). The composite cathodes on each of these cells were calcined at 1123 K.

Figure 4.4 Impedance data for cells made with LSF (■), LBF (●), and LCF (▲). The composite cathodes on each of these cell were calcined at 1373 K. The filled symbols show data measured at open circuit while the open symbols were obtained at a current density of 100 mA/cm².
0.25 and 0.3 $\Omega\cdot\text{cm}^2$. Since the anode contributes approximately 0.1 $\Omega\cdot\text{cm}^2$ to this value [33, 34], each of the cathodes contributes between 0.15 and 0.2 $\Omega\cdot\text{cm}^2$. Previously, losses for LSF-YSZ cathodes, prepared by infiltration and calcined to 1123 K, had been estimated to be between 0.1 and 0.15 $\Omega\cdot\text{cm}^2$ for cathode-supported cells [48, 137]. The losses in this study were very similar.

When the composite cathodes were calcined to 1373 K, to simulate deactivation [137], the cell performances were much worse. (Note: The calcination to 1373 K was performed prior to adding the anode or Ag current collectors, so that performance differences can only be due to changes in the cathodes.) The decreased performances do not appear to be due to solid-state reactions between the perovskites and the YSZ. First, XRD measurements on the composites heated to 1373 K showed no evidence for new phases other than that of the perovskite and YSZ. Also, none of the composites showed evidence for a lattice expansion of the perovskite phase, a result which would indicate diffusion of Zr ions into the perovskite [118]. Finally, the ohmic losses for the cells heated to 1373 K were again between 0.65 and 0.8 $\Omega\cdot\text{cm}^2$, depending on the electrolyte thickness. A decreased conductivity of the perovskite phase or formation of new insulating phases would be expected to increase the ohmic losses.

Performance differences following the 1373-K calcination were associated with the non-ohmic components of the impedances, as shown in Figure 4.4. As with the cathodes calcined to 1123 K, the three doped-LaFeO$_3$ cathodes were nearly identical, with the the minor differences in impedance attributable to cell to cell variation. Also, the non-ohmic losses on each of the composite cathodes exhibited a strong dependence
on the current density after heating to 1373 K, similar to what had been reported earlier with infiltrated LSF composites [137]. The non-ohmic component of the impedance curve for each of the cells with the LSF-YSZ cathode decreased from ~3.0 Ω cm\(^2\) at open circuit to ~0.6 Ω cm\(^2\) at a current density of 100 mA/cm\(^2\).

### 4.3.3 Structural Characterization

As discussed above, we found no evidence by XRD that solid-state reactions are responsible for the changes in electrode performance following calcination to 1373 K. Therefore, to understand the reasons for the changes that were observed, we examined each of the perovskite composites using Scanning Electron Microscopy (SEM) and BET isotherms [46], before and after the high-temperature treatment, with the results shown in Figure 4.5 and Table 4.3.

Prior to the addition of the perovskites, the YSZ scaffold has relatively uniform pores, between 1 and 10 µm in diameter, as shown in Figure 4.5a) [137]. The surfaces of the pores are very smooth, with some areas showing well-defined crystallographic facets. After the addition of LSF, LBF, and LCF and calcination to 1123 K, Figures 4.5b), 4.5d), and 4.5f), the surface of the pores are coated with small, partially sintered, perovskite particles, approximately 0.05 to 0.1 µm in size. The sintering is more complete with the LBF sample, probably because this sample required more infiltration steps to achieve the 40-wt% loading, due to the low solubility of Ba ions. With each of the perovskites, the particles form a well connected network, which helps to explain the good conductivity of the infiltrated composite; but this network appears to have sufficient porosity to allow
oxygen to diffuse to the YSZ interface. The high porosity is also demonstrated by the BET measurements. While the initial YSZ scaffold had a specific surface area of 0.40 m\(^2\)/g, the surface areas of the infiltrated composites were significantly higher after calcination to 1123 K, ranging from 0.95 m\(^2\)/g for the LBF-YSZ composite to 1.69 m\(^2\)/g for the LSF-YSZ composite.

After heating the composites to 1373 K, the perovskite particles form dense films over the YSZ pore structure, as shown in Figures 4.5c), 4.5e), and 4.5g). That these films had low porosity was also established by the BET data. The surface areas of the composites ranged from 0.41 to 0.43 m\(^2\)/g, values that were similar to that of the initial YSZ scaffold.
Specimen & Surface Area
YSZ scaffold & 0.40 m$^2$/g  
LSF calcined at 1123 K & 1.69  
LBF at 1123 K & 0.95  
LCF at 1123 K & 1.59  
LSF at 1373 K & 0.43  
LBF at 1373 K & 0.41  
LCF at 1373 K & 0.43

Table 4.3 Surface areas measured from BET isotherms, performed using Kr at 78 K.

Figure 4.5a SEM micrograph showing the structure of the porous YSZ scaffold.
Figure 4.5b SEM micrograph of the electrode following infiltration of 40-wt% LSF and calcination to 1123 K.

Figure 4.5c SEM micrograph of the electrode following infiltration of 40-wt% LSF and calcination to 1373 K.
Figure 4.5d SEM micrograph of the electrode following infiltration of 40-wt% LBF and calcination to 1123 K.

Figure 4.5e SEM micrograph of the electrode following infiltration of 40-wt% LBF and calcination to 1373 K.
Figure 4.5f An SEM micrograph of the electrode following infiltration of 40-wt% LCF and calcination to 1123 K.

Figure 4.5g An SEM micrograph of the electrode following infiltration of 40-wt% LCF and calcination to 1373 K.
We suggest that the changes in the performance of the electrodes following calcination to 1373 K are associated with the formation of the dense film of the perovskite, but that the performance of the electrodes calcined to 1373 K is not significantly limited by ionic diffusion through that film. When the electrodes were calcined to only 1123 K, there is sufficient porosity for $O_2$ to diffuse close to the YSZ interface, where it can then react at three-phase boundary sites to form oxygen ions, which in turn are transported to the electrolyte by the YSZ scaffold. After calcination to 1373 K, the $O_2$ must react on the surface of the perovskite, with the ions diffusing through the perovskite film to the YSZ scaffold. However, since the performance of the various composites appear to be independent of the ionic conductivity of the perovskite, this suggests that the decline in performance may instead be related to the loss of adsorption sites. This morphological degradation mechanism is consistent with the absence of solid-state reactions.

Figure 4.6 A schematic illustrating the effect of higher temperature calcination on the infiltrated, doped LaFeO$_3$. The picture on the left represents the situation following calcination at 1123 K and the picture on the right represents 1373 K.
The changes in cathode morphology are illustrated schematically in Figure 4.6 and have a number of implications for stabilizing infiltrated electrodes based on LaFeO$_3$. First, one would expect to see significant improvements if the perovskite nanoparticles observed after 1123 K calcination could be maintained during long term operation. Previously, it has been observed that unlike LaFeO$_3$, species such as LaTiO$_3$ do not form films on YSZ after high temperature calcinations. Understanding the differences between these two materials could be the key to maintaining the pore structure that is present after low-temperature calcination of LSF-YSZ composites. If performance is indeed adsorption rate limited, another approach to achieving higher performance would be to prepare YSZ scaffolds with higher initial surface areas through the use of smaller pore formers in the initial slurry.

Perhaps the most important conclusion of this and a previous study of LSF-YSZ cathodes [137] is that the mechanism for deactivation of cathodes may well be different for different materials and well-established deactivation mechanisms for LaCoO$_3$-based electrodes may not apply to other systems. This opens up new strategies for the development of highly stable, high-performance SOFC cathodes.

4.4 Conclusions

In this chapter, it was shown that composite cathodes formed by infiltration of doped LaFeO$_3$ into YSZ tend to form dense perovskite films over the porous YSZ structure at higher calcination temperatures. The formation of this dense film corresponds to a decline in the performance of the electrodes. However, variations in the
ionic conductivity of the LaFeO$_3$ perovskites did not appear to have any affect on the performance of the composites calcined to either 1123 or 1373 K. Strategies for stabilizing the LSF-YSZ electrodes should target ways to avoid the formation of a thick layer of LSF near the three-phase boundary.
Chapter 5. Dopants to Enhance SOFC Cathodes Based on Sr-Doped LaFeO$_3$ and LaMnO$_3$

5.1 Introduction

There has been a considerable effort aimed at improving the performance of LSM-YSZ composites by adding catalytic or ion-conducting components to the composite electrode after it has been formed. The primary idea behind adding catalytic components is presumably to increase the rate of O$_2$ dissociation, while the addition of ionic or mixed-conducting materials should widen the three-phase boundary (TPB). Although there is still no consensus on what is the rate-limiting step that determines the impedance of LSM-YSZ cathodes, there are some intriguing observations that suggest that one can indeed enhance their performance by infiltration of a “promoter”, as discussed in the next paragraphs.

The addition of catalytic components has met with mixed success. While Uchida and coworkers found that the addition of Pt significantly enhanced the electrochemical performance of LSM-YSZ composites [132] and Erning, et al. reported similar enhancements through the addition of Pd [24], Haanappel and coworkers reported that neither Pd nor Pt had any effect on the performance of LSM cathodes [37]. Discrepancies also exist for claims about the effect of infiltrated cobalt oxide. Yamahara, et al. reported significant improvements in cathode performance following the addition of small Co$_3$O$_4$ nano-particles [142, 143]; Huang, et al. claimed that the incorporation of CoO$_x$ had no effect on LSM-YSZ cathode impedances [47].
There does seem to be agreement that the addition of mixed-conducting perovskites, either Sr-doped LaCoO$_3$ [13], Sr-doped SmCoO$_3$ [85], or Sr-doped LaFe$_{0.8}$Co$_{0.2}$O$_3$ [64], can decrease cathode overpotentials. While the reactivity of these perovskites with YSZ may preclude their being used in this application, the observation that the addition of relatively small amounts of these mixed-conducting perovskites can improve performance may indicate that they deposit preferentially at TPB sites in the LSM-YSZ composite and increase the width of those sites. Mixed conductivity at the TPB sites may also explain the improved performance of LSM-YSZ electrodes following the addition of Gd-doped ceria [56] or BiO$_x$ [59].

Catalysis and mixed conductivity do not explain electrode promotion with all additives. For example, one study reported that infiltration of Sr salts can improve LSM cathodes [80]. SrO is unlikely to be a catalyst for O$_2$ dissociation and the addition of SrO is not expected to significantly change either the electronic or ionic conductivity of LSM. Indeed, the segregation of Sr to the electrolyte interface is often thought to cause electrode deactivation [115]. Similarly, Mogensen, et al. found that adding either pure or doped ceria had a similar effect on cathode performance, even though the ionic conductivity of pure ceria should be much lower [98]. This group suggested that the improvement in LSM-YSZ electrode performance following the addition of nanoparticles might be due to gettering of impurities at the TPB sites.

A major complication in assessing how promoters change electrochemical properties is that electrode structure appears to play a very large role, not only in affecting performance, but also in determining whether or not additives will promote
performance. For example, one study of La$_{0.8}$Sr$_{0.2}$Cr$_{0.5}$Mn$_{0.5}$O$_3$ (LSCM) anodes fabricated by traditional ceramics-processing methods found that the addition of Pd had minimal effect on performance in H$_2$ [57], whereas studies of electrodes formed by infiltration of LSCM into porous YSZ demonstrated that the addition of even 0.5-wt% Pd increased the power density of cells by a factor of five [70]. Since the structure of LSCM-YSZ composites formed by conventional co-sintering of mixed powders is very different from that of composites formed by infiltration [68], we suggest that structural differences in the electrodes explain the apparent discrepancy.

Since variations in electrode structures may account for the differences that have been reported in the literature, regarding whether or not particular additives improve electrode performance, it seemed important to re-examine the issue of electrode promotion using a range of materials that have different properties with electrodes that have a common structure. In this chapter, we investigated the effect of additives on cathode composites formed from YSZ and either LSM or La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF). The LSM-YSZ and LSF-YSZ composite electrodes used here were prepared by infiltration of the corresponding nitrate salts into porous YSZ, so that all electrodes had a similar structure. As shown in the previous chapters, the electrochemical properties of LSF-YSZ and LSM-YSZ composites formed by infiltration are a strong function of calcination temperature [46, 137]; therefore, the effect of the promoters was examined on composites that were calcined to either 1123 K or 1373 K.

The specific additives that were incorporated into the LSF-YSZ and LSM-YSZ electrodes were Pd, CeO$_2$ (or Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$, SDC) YSZ, CaO, and K$_2$O. These materials
were chosen for their expected function (or lack thereof). Ceria is a good oxidation catalyst [131] and could provide both ionic and electronic conductivity, particularly if it is partially reduced at TPB sites. Pd is expected to be an outstanding oxidation catalyst but should have minimal effect on either ionic or electronic conductivity in the amounts incorporated in this study, 0.5 wt%. YSZ is an outstanding ionic conductor but should provide minimal electronic conductivity or catalytic activity over that of the composite electrode itself. CaO should have minimal effect on catalytic, electronic, or ionic-conduction properties. In the case of LSF, substitution of Ca for Sr in the perovskite lattices could reduce the ionic conductivity and therefore harm performance [8]. If anything, K$_2$O would be expected to hurt electrode performance. Finally, since the infiltration process itself could affect electrode structure, experiments were performed with both 0.1 N HNO$_3$ and NH$_4$OH solutions to test the effect that acidic and basic solutions might have on selective electrode dissolution.

A major conclusion of this chapter is that electrode promotion through the addition of catalytic and conducting components is associated with electrode structure, at least for the systems studied here.

5.2 Experimental

The fuel cell used in this study were all prepared in a similar manner, following the procedure described in Chapter 2. For this particular work, the dense electrolyte layers were approximately 100 µm thick for the series of cells made with LSF and 70 µm
thick for the series made with LSM. The porous layers were estimated to have a porosity of 65%, with a BET surface area of ~0.3 m$^2$g$^{-1}$ [8].

The composite cathodes were prepared via wet impregnation. Once the desired 40-wt% loading was achieved, the cells were then calcined to either 1123 or 1373 K to form the perovskite phases. After calcination, the precursor solution of one of the promoters was impregnated into the electrode and the sample was again calcined to either 973 or 1373 K.

For most of the cells, the anodes were added after the cathodes were prepared, by impregnating 50-wt% ceria and 0.5-wt% Pd into the porous layer opposite the cathode using the nitrate salts and calcination to 723 K as described in Chapter 2 [71]. On a few cells, the anodes were based on 40-wt% LSCM (La$_{0.8}$Sr$_{0.2}$Cr$_{0.3}$Mn$_{0.5}$O$_3$) with 5-wt% ceria and 0.5-wt% Pd, prepared as described elsewhere [68]. The performance characteristics of the LSCM-based anodes were essentially indistinguishable from those of anodes made with 50-wt% ceria. Although preparation of LSCM required higher temperatures, the ceria and Pd were again added after the cathodes were calcined to their final temperature. The impedance of both types of anodes is reported to be between 0.1 and 0.2 Ω·cm$^2$ [68, 71], independent of current density, when operated at 973 K in humidified (3% H$_2$O) H$_2$. 

67
5.3 Results

5.3.1 Unpromoted LSF-YSZ and LSM-YSZ Electrodes

While the characteristics of LSF-YSZ and LSM-YSZ electrodes formed by infiltration have been discussed elsewhere [46, 48], the results were reproduced for the present study so that the performance of electrodes with additives could be compared for the same YSZ scaffold structure. Fuel-cell data for cells made with LSF-YSZ cathodes, calcined to either 1123 or 1373 K, are shown in Figure 5.1.

The $V$-$i$ polarization curves in Figure 5.1a), obtained at 973 K with humidified $H_2$ as the fuel, show only slight curvature for the cell with the LSF-YSZ composite cathode calcined at 1123 K but significantly more curvature for the cell with the cathode calcined at 1373 K. This effect of calcination temperature is shown more dramatically by the open-circuit voltage (OCV) Cole-Cole plots in Figure 5.1b). The ohmic impedance, determined from the high-frequency intercept in the Cole-Cole plot, was $\sim 0.5 \ \Omega \cdot \text{cm}^2$ for both cells. This value is very close to the resistance expected for a 100-µm YSZ electrolyte [109]. The effect of increased calcination temperature was to increase the non-ohmic impedances, which are due to electrode losses and are calculated from the arc length in the Cole-Cole plots. The non-ohmic impedances at OCV
Figure 5.1a V-i polarization plots, measured at 973 K, for cells with LSF-YSZ electrodes calcined to 1123 K (▲) and 1373 K (●).

Figure 5.1b OCV impedance data for cells, at 973 K, with LSF-YSZ electrodes calcined to 1123 K (∆) and 1373 K (○). The spectrum for the 1123-K electrode has been offset for clarity.
Figure 5.2a V-i polarization plots, measured at 973 K, for cells with LSM-YSZ electrodes. Data are shown for composites calcined to 1123 K (●) and 1373 K (▲), starting from open circuit. Data are also shown for the cell with the composite calcined to 1373 K, after it had been shorted for 2 h (■).

Figure 5.2b OCV impedance of cells with LSM-YSZ cathodes calcined to 1123 (○) and 1373 K (Δ), before (open symbols) and after (closed symbols) polarization by shorting the cells for 2 h. The data were obtained at 973 K and the spectra for the 1123-K composites have been offset for clarity.
were approximately 0.35 Ω·cm² for the cell with the cathode calcined to 1123 K and 2.6 Ω·cm² for the cell with the cathode calcined at 1373 K. Assuming an anode impedance of 0.15 Ω·cm² as determined in previous studies [68, 71], most of the non-ohmic cell losses are associated with the cathodes. For the 1123-K, LSF-YSZ composite, the impedance is approximately 0.2 Ω·cm² and independent of current density. This is slightly higher than the impedance reported previously, 0.15 Ω·cm², possibly because the YSZ scaffold in the present study had a lower surface area [45]. For the 1373-K, LSF-YSZ composite, the impedance is approximately 2.4 Ω·cm² at OCV. Since the slope of the V-i polarization curve in Figure 5.1a) decreases with increasing current density, the cathode impedance must decrease with current density. The OCV impedance and current dependence for the cell calcined at 1373 K are essentially identical to what was reported in the previous chapter [137].

The characteristics of LSM cathodes formed by infiltration and calcined at either 1123 or 1373 K are shown in Figure 5.2. Figure 5.2a) provides the V-i polarization curves for cells operating at 973 K, while Figure 5.2b) shows the analogous OCV impedance data. Because the performance of LSM-YSZ electrodes changes after polarization [53, 55, 60, 89, 133], data were first obtained after holding the cells at open circuit overnight and with measurement of the V-i curve starting at open circuit. Then the cells were shorted for 2 h before again measuring the OCV impedance and V-i polarization curve. The cell with the 1123-K, LSM-YSZ cathode exhibited a relatively straight V-i relationship and was essentially unaffected by polarization. The total ohmic impedance was 0.35 Ω·cm², again in reasonable agreement with the resistance calculated
for the 70-µm YSZ electrolyte, while the total non-ohmic, OCV impedance was 0.7 to 0.8 Ω·cm², with ~0.6 Ω·cm² coming from the cathode. As in the case with LSF, this is slightly higher than the 0.4 Ω·cm² impedance reported previously for infiltrated LSM calcined to 1123 K [46], which is likely due to the lower surface area of the YSZ scaffold. The YSZ scaffold in that study was reported to have a greater surface area, 0.76 m²g⁻¹ versus 0.26 m²g⁻¹; and the performance of infiltrated electrodes has been shown to correlate with scaffold structure [45]. Finally, the impedance of the 1123-K, LSM-YSZ composite decreased by only 0.2 Ω·cm² after 2 h polarization.

The V-i relationship for the cell with the 1373-K cathode showed much greater curvature. While the ohmic losses for this cell were similar to that of the cell with the 1123-K cathode, the total OCV impedance was much higher, 2.6 Ω·cm². Another dramatic difference is that the 1373-K, LSM-YSZ electrode exhibited strong hysteretic behavior. After shorting this cell for 2 h, the total non-ohmic, OCV impedance dropped from ~2.3 Ω·cm² to less than 0.7 Ω·cm², a value very close to that obtained for the 1123-K, LSM-YSZ electrode. Furthermore, the V-i polarization curve shifted so that it nearly overlapped with that of the cell with the 1123-K cathode. This improved performance was reversible; when the cell with the 1373-K, LSM-YSZ cathode was left at open circuit overnight, the performance reverted back to that of the unpolarized cell.

Previous XRD data have demonstrated that solid-state reactions between LSM and YSZ are minimal at temperatures below 1373 K [46, 146]. Therefore, SEM measurements, shown in Figure 5.3, were performed to understand the effect of increased calcination temperature. Similar to what was observed with LSF in the
previous chapters, LSM formed small, interconnected particles in the pores of the YSZ after calcination at 1123 K, Figure 5.3a). After calcination to 1373 K, the LSM formed what appears to be a dense coating over the YSZ pores, Figure 5.3b). Given the low ionic conductivity of LSM [52], it is not surprising that a composite in which LSM coats the YSZ pores would have a short TPB and perform poorly. What is less clear is why the coated structure would be affected by polarization and the particle-filled pores would not. While there is still no consensus about what causes the hysteretic behavior in LSM cathodes [1, 134], the idea that the morphology of the LSM in the pores would affect this is consistent with a recent report suggesting that hysteresis is associated with movement of the LSM during oxidation and reduction [140].

5.3.2 Effect of Additives on LSF-YSZ Cathodes:

A variety of additives were incorporated into the LSF-YSZ electrodes and the results are summarized in Figures 5.4 and 5.5 and in Table 5.1. Figure 5.4 shows the V-i polarization curves for cells made with LSF-YSZ composites that were first calcined to 1373 K, then infiltrated with the salts needed to incorporate either 0.5-wt% Pd, 10-wt% YSZ, 10-wt% CaO, or 10-wt% K₂O, and finally re-calcined at 973 K. All of the cells showed significant improvement in impedance with the additives. For the cell with 10-wt% K₂O, the slope near OCV was similar to that of the cells with the other additives, but the impedance increased at higher current densities. The effect of additives is seen more clearly by focusing on the V-i polarization curves in the region near OCV, for which selected results are reported in Figure 5.5. The dramatic difference between...
**Figure 5.3a** An SEM image of the LSM-YSZ composite prepared by calcination at 1123 K.

**Figure 5.3b** An SEM image of the LSM-YSZ composite prepared by calcination at 1373 K.
Figure 5.4 Performance data for cells with an LSF-YSZ cathode that was calcined to 1373K after infiltration of either 0.5 wt% Pd (◊), 10 wt % YSZ (∆), 10 wt % CaO (□), and 10 wt% K$_2$O (○).

Figure 5.5 Performance data for cells with an LSF-YSZ cathode calcined to 1123 K (●), calcined to 1373 K (■), and calcined to 1373 K followed by infiltration of 0.5 wt% Pd (♦) and 10 wt % YSZ (▲).
<table>
<thead>
<tr>
<th>LSF Calcination Temperature (K)</th>
<th>Infiltrated Material and Wt-% Added</th>
<th>Second Calcination Temperature (K)</th>
<th>Non-Ohmic Impedance at OCV (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1123</td>
<td>None</td>
<td>None</td>
<td>0.35</td>
</tr>
<tr>
<td>1373</td>
<td>None</td>
<td>None</td>
<td>2.60</td>
</tr>
<tr>
<td>1123</td>
<td>10-wt% YSZ</td>
<td>973</td>
<td>0.30</td>
</tr>
<tr>
<td>1123</td>
<td>10-wt% YSZ</td>
<td>1373</td>
<td>3.30</td>
</tr>
<tr>
<td>1373</td>
<td>1.5-wt% YSZ</td>
<td>973</td>
<td>0.75</td>
</tr>
<tr>
<td>1373</td>
<td>10-wt% YSZ</td>
<td>973</td>
<td>0.70</td>
</tr>
<tr>
<td>1373</td>
<td>0.5-wt% Pd</td>
<td>973</td>
<td>1.25</td>
</tr>
<tr>
<td>1373</td>
<td>10-wt% CaO</td>
<td>973</td>
<td>0.70</td>
</tr>
<tr>
<td>1373</td>
<td>10-wt% K₂O</td>
<td>973</td>
<td>0.70</td>
</tr>
<tr>
<td>1373</td>
<td>10-wt% SDC</td>
<td>973</td>
<td>0.45</td>
</tr>
<tr>
<td>1373</td>
<td>0.1N HNO₃</td>
<td>973</td>
<td>2.60</td>
</tr>
<tr>
<td>1373</td>
<td>0.1N NH₄OH</td>
<td>973</td>
<td>2.65</td>
</tr>
</tbody>
</table>

**Table 5.1** Summary of effects of calcination temperatures and infiltrated materials on LSF-YSZ composite cathodes

with LSF-YSZ cathodes calcined at 1123 K and 1373 K is readily apparent in this figure. The addition of 0.5-wt% Pd or 10-wt% YSZ to 1373-K cathodes brings the initial slope closer to that of the 1123-K cathode but 1373-K cathodes with additives still exhibit somewhat poorer performance. Finally, even though the OCV impedances of the 1373-K cathodes were different following the addition of 0.5-wt% Pd (non-ohmic impedance of 1.25 Ω·cm²) and 10-wt% YSZ (non-ohmic impedance of 0.70 Ω·cm²), this had a relatively small effect on the overall V-i curves shown in Figure 5.5 because the impedances decreased with current density.

Because all of the additives, with the exception of K₂O, affected cell performance in a similar way, the results for the various cells that were tested can be characterized by
a single number, the total non-ohmic impedance at OCV. None of the dopants affected the ohmic impedances and only K$_2$O exhibited the deleterious behavior at higher current densities. In this study, the impedances were measured at 973 K, on similar cells with anodes that had an impedance of approximately 0.15 Ω·cm$^2$, as discussed in the previous section. Table 5.1 reports the initial calcination temperature of the LSF-YSZ electrodes, the amount and type of dopant, the calcination temperature used after incorporation of the dopant, and the total electrode impedance. For the cell with 0.5 wt-% Pd, Table 5.1 shows a non-ohmic impedance of 1.25 Ω·cm$^2$ near OCV. While this non-ohmic impedance is larger than the values seen for the other infiltrated cells, it still represents a dramatic improvement relative to the 1373-K, LSF-YSZ cell performance, as illustrated in Figure 5.5. That the non-ohmic impedance near OCV of the cell with Pd was larger than that of the other infiltrated cells could be due to the significantly lower weight loading of Pd compared to the amounts used with the other additives.

Only one 1123-K LSF-YSZ cell was tested after the addition of a dopant, 10-wt% YSZ in that case. While the non-ohmic impedance on this cell was slightly lower than that of the undoped cell, 0.30 versus 0.35 Ω·cm$^2$, the difference was so small that the significance of this improvement was unclear. A more interesting result was that obtained after the addition of 10-wt% YSZ onto the 1123-K composite, followed by calcination to 1373 K. It was expected that the YSZ would partially fill in the space between the LSF particles and modify film formation. Unfortunately, the non-ohmic impedance of this cell was similar to that of the undoped, 1373-K LSF-YSZ composite.
The data in Table 5.1 also highlight several other important observations. First, the greatest improvement in performance in our studies was achieved by adding 10-wt% Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (SDC). The non-ohmic impedance for that cell was only 0.45 $\Omega$ cm$^2$. Whether this is significant compared to the improvement with the addition of 10-wt% YSZ is uncertain. Second, only small quantities of dopant are required to enhance performance. The non-ohmic losses decreased to 0.75 $\Omega$ cm$^2$ after the addition of only 1.5-wt% YSZ. Finally, the enhanced performance achieved by infiltration of various compounds into the 1373-K LSF-YSZ electrode is probably not associated with the infiltration process itself. If the liquid used in the infiltration step were simply restructuring the LSF film, the infiltration of either a weak acid or weak base, 0.1 N HNO$_3$ and 0.1 N NH$_4$OH, should have modified the performance in a similar manner as that observed with the dopants. However, the infiltration of HNO$_3$ and NH$_4$OH, both of which will be completely removed following calcination at 973 K, had no effect on performance.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m$^2$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ scaffold</td>
<td>0.26</td>
</tr>
<tr>
<td>LSF-YSZ calcined at 1123 K</td>
<td>1.80</td>
</tr>
<tr>
<td>LSF-YSZ calcined at 1373 K</td>
<td>0.30</td>
</tr>
<tr>
<td>LSF-YSZ (1373 K) with 0.5 wt-% Pd (973 K)</td>
<td>0.46</td>
</tr>
<tr>
<td>LSF-YSZ (1373 K) with 10 wt-% CaO (973 K)</td>
<td>0.62</td>
</tr>
<tr>
<td>LSF-YSZ (1373 K) with 10 wt-% K,O (973 K)</td>
<td>0.60</td>
</tr>
<tr>
<td>LSF-YSZ (1373 K) with 10 wt-% YSZ (973 K)</td>
<td>2.56</td>
</tr>
<tr>
<td>LSF-YSZ (1373 K) with 10 wt-% YSZ (1373K)</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Table 5.2** Surface areas measured from BET isotherms using Kr at 78K
5.3.3 Characterization of LSF-YSZ Cathodes

XRD measurements were taken of LSF-YSZ cathodes calcined to 1123 and 1373 K and of 1373 K calcined samples infiltrated with the promoters used in this study. The XRD data obtained for the low and high temperature calcined samples were in agreement with results obtained in previous studies, showing most importantly that no phases were present other than those of the YSZ and the perovskite. With higher temperature calcination, the perovskite peaks narrowed which is consistent with the sintering of LSF into larger crystallites. None of the infiltrated species were observed in the XRD spectra, apparently due to the low weight loadings and broad diffraction lines. Since all of the dopants improved the performance of the 1373-K, LSF-YSZ composite, we examined several of the composites by SEM and Brunauer-Emmett-Teller (BET) isotherms to determine what changes occurred in the electrode microstructure following dopant incorporation. As reported in a previous work, the surface area of the LSF-YSZ cathode is highly dependent on calcination temperature. As shown in Table 5.2, the infiltration of LSF into the YSZ scaffold shows a significant increase in surface area when calcined to 1123 K, but this increased surface area is lost when the electrode is calcined further to 1373 K. When additional materials are infiltrated into the 1373-K, LSF-YSZ, there are again increases in surface area, although not to the levels measured in the 1123-K, LSF-YSZ cell, accept for when 10-wt% YSZ was added.

Micrographs of composites with 0.5-wt% Pd, 10-wt% YSZ, and 10-wt% CaO are shown in Figure 5.6. Figure 5.6a), the micrograph with 0.5-wt% Pd, suggests that the LSF film is relatively unaffected. The Pd is present as small, 0.1-µm particles on top of
the LSF film. This is consistent with the tendency of metals to interact weakly with oxides and the relatively large size of the Pd particles is simply due to the very low surface area of the LSF-YSZ composite. The micrograph in Figure 5.6b) shows that the composite with added YSZ has a very different appearance. In this case, the LSF film is covered by a rough film of the YSZ. Finally, the CaO deposits, shown in Figure 5.6c), appear as angular-shaped crystals over the LSF. Although the results are not reported here, structures similar to those observed in the YSZ and CaO infiltrated cells were seen in the cells infiltrated with SDC and K$_2$O, respectively. While these SEM images may not be depicting features at TPB sites, the micrographs in Figure 5.6 reveal no obvious commonalities between Pd, YSZ (SDE), and CaO.

5.3.4 Effect of Additives on LSM-YSZ Cathodes

In our studies of promotion in LSM-YSZ composites, we focused on improving the electrodes calcined to 1373 K. The effect of each promoter can again be described by the OCV impedance, measured before and after polarizing the cell, and is summarized in Table 5.3. As discussed earlier, the cell with the 1123-K, LSM-YSZ electrode exhibited a relatively low non-ohmic impedance of 0.8 Ω·cm$^2$ at 973 K and this decreased to 0.6 Ω·cm$^2$ after shorting the cell for 2 h. The cell with the 1373-K, LSM-YSZ electrode had a non-ohmic impedance of 2.3 Ω·cm$^2$ prior to polarization but showed a similar impedance, 0.7 Ω·cm$^2$, to that of the low-temperature composite after shorting.
Figure 5.6a An SEM image of the LSF-YSZ composite prepared by calcination at 1373 K with 0.5-wt% Pd.

Figure 5.6b An SEM image of the LSF-YSZ composite prepared by calcination at 1373 K with 10-wt % YSZ.
Figure 5.6c An SEM image of the LSF-YSZ composite prepared by calcination at 1373 K with 10-wt% CaO.

<table>
<thead>
<tr>
<th>LSM Calcination Temperature (K)</th>
<th>Infiltrated Material and Wt-% Added</th>
<th>Second Calcination Temperature (K)</th>
<th>Non-Ohmic Impedance at OCV (Ω·cm²)</th>
<th>Non-Ohmic Impedance at OCV After Polarization (Ω·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1123</td>
<td>None</td>
<td>None</td>
<td>0.80</td>
<td>0.60</td>
</tr>
<tr>
<td>1373</td>
<td>None</td>
<td>None</td>
<td>2.30</td>
<td>0.70</td>
</tr>
<tr>
<td>1373</td>
<td>10-wt% CeO₂</td>
<td>973</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>1373</td>
<td>10-wt% CeO₂</td>
<td>1373</td>
<td>2.50</td>
<td>1.35</td>
</tr>
<tr>
<td>1373</td>
<td>10-wt% YSZ</td>
<td>973</td>
<td>1.30</td>
<td>0.70</td>
</tr>
<tr>
<td>1373</td>
<td>0.5-wt% Pd</td>
<td>973</td>
<td>0.80</td>
<td>0.55</td>
</tr>
<tr>
<td>1373</td>
<td>0.1M NH₄NO₃</td>
<td>973</td>
<td>1.90</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 5.3 Summary of effects of calcination temperatures and infiltrated materials on LSM-YSZ composite cathodes
The addition of 10-wt% CeO$_2$ or 1-wt% Pd to the 1373-K composite decreased the OCV impedances dramatically. The total non-ohmic losses in the cell with 10-wt% CeO$_2$ decreased to 0.5 $\Omega \cdot \text{cm}^2$, which is only slightly higher than that of the cells with LSF-based electrodes, while the cell with 0.5-wt% Pd decreased to 0.8 $\Omega \cdot \text{cm}^2$. Both cells were also affected much less by polarization. The addition of 10-wt% YSZ also decreased the non-ohmic impedance, but only to 1.3 $\Omega \cdot \text{cm}^2$, and this cell was affected more strongly by polarization.

Unfortunately, calcination of an electrode with 10-wt% CeO$_2$ to 1373 K caused the impedance to increase to a value higher than the unpromoted case. The non-ohmic impedance of this cell increased to 2.5 $\Omega \cdot \text{cm}^2$ and shorting for 2 h reduced this to only 1.3 $\Omega \cdot \text{cm}^2$. In a study of the stability of LSF-YSZ electrodes formed by infiltration [137], it was argued that operation of an electrode for several thousand hours is equivalent to calcination for shorter times at 1373 K. If this is true for the ceria-doped LSM-YSZ electrodes, the improvement associated with the addition of ceria will not give stable performance. A similar point was made by Mogensen, et al., for conventional LSM-YSZ electrodes promoted by ceria [98].

5.4 Discussion

Several important observations can be taken from the data in this paper. First, even without the addition of promoters, LSF-YSZ and LSM-YSZ electrodes formed by infiltration exhibited a number of common features. For both cases, electrodes formed after low-temperature (1123 K) calcination were composed of fine perovskite particles
within the YSZ pore structure. These electrodes exhibited low impedances that are nearly independent of current density. After high-temperature (1373 K) calcination, both LSM and LSF formed films that appear to coat the YSZ pores. The impedances on the 1373-K electrodes were much larger at open circuit but decreased significantly with current density. The major difference between the LSM and LSF electrodes was that the high-temperature LSM exhibited hysteretic behavior, with the impedance decreasing dramatically after application of a current. Interestingly, the performance of the 1373-K LSM-YSZ electrode after activation was similar to that of the 1123-K composite. Since the conventional preparation of composite cathodes involves calcination at temperatures above 1273 K, it is possible that the relatively poor performance of LSF-based cathodes compared to ones based on LSM is due to the ability of LSM to improve under a load.

A recent study has argued that the non-stationary behavior of LSM-based electrodes is associated with formation of an LSM film under oxidizing conditions that can then break up under the reducing conditions imposed near TPB sites by a cathodic overpotential [140]. That picture is consistent with the morphological changes observed by SEM in the present study. Unfortunately, it was not simple to observe the formation of nano-pores following electrode polarization by SEM, since these would only be expected to form in the vicinity of the electrolyte interface, where the reducing conditions caused by polarization would be most severe. Still, circumstantial evidence – the fact that the 1123-K electrode shows performance characteristics similar to that of the electrode calcined at 1373 K after activation – points towards the importance of LSM morphology in determining properties. The relatively low calcination temperatures used
in the present study for even the “high-temperature” composites makes it less likely that formation of interfacial compounds is responsible for the observed behavior.

The bigger question concerns what the promoters are doing to enhance performance. The fact that Pd, CeO$_2$ (or SDC), YSZ, CaO, and K$_2$O are all capable of decreasing the electrode impedance of LSM and LSF cathodes argues that the effect is not primarily to enhance either catalytic or ionic conductivities. For example, if promotion were due to catalytic effects, Pd and CaO should have given dramatically different enhancements. The fact that the addition of each promoter to the 1373-K LSM and LSF electrodes caused the electrodes to exhibit a performance that approaches that of their 1123-K counterparts suggests that the addition of the promoters is somehow related to structure and possibly to the surface area of the cathode. Indeed, the only obvious correlation observed in the present study was between performance and electrode surface area. The fact that recalcination of the promoted electrodes to 1373 K caused them to revert back to their initial state is further evidence that enhanced performance is related to structure. Exactly how each of the modifiers affects the structure near the TPB sites is unclear at this point.

An important lesson to be taken from this study is that one should be careful in interpreting the results of studies in which a single modifier, or even a single class of modifiers is used, since a simple explanation for the observed results may not be applicable. If only species that were expected to be catalytic had been added, we would have concluded that the dopants had enhanced performance by increasing the oxidation rates of the cathode. Based on the fact that similar enhancements were obtained for Pd
and CaO, it seems unlikely that catalytic effects are responsible for our observations. An additional complication is that the influence of additives appears to depend on the initial electrode structure [57, 70]. This helps to explain some of the discrepancies in literature over whether certain dopants enhance performance or not. Finally, one very clear conclusion from this study is that our fundamental understanding of electrode processes in SOFC is insufficient. Despite the large body of work on SOFC cathodes [1], the main factors that limit performance are still uncertain.

5.5 Conclusion

The major conclusion of this chapter is that electrode promotion through the addition of catalytic and conducting components is associated with electrode structure, at least for the systems that were studied here. None of the additives studied had any effect on electrode performance for composites calcined at 1123 K, while enhanced electrode performance was observed with almost all of the additives, for both LSF-YSZ and LSM-YSZ electrodes, if the composites had first been calcined to 1373 K. Dopants that were not expected to enhance either catalytic or ionic-conductivity properties were equally effective to dopants that were. That enhancement is related to electrode structure helps to explain disagreements in the literature over whether certain additives decrease electrode overpotentials.

The results presented in this chapter further support the conclusions of the previous chapter: that electrode performance is not limited by the diffusion of oxygen ions through the perovskite film. Because the promoters were infiltrated onto the
perovskite film surface, the diffusion of the oxygen anions through the film should remain unchanged. This suggests that the decline in performance following high temperature calcination and the subsequent improvement in performance following the infiltration of promoters can be directly attributed to factors governing the oxygen reduction reaction itself rather than to diffusion through the perovskite film.
Chapter 6. Modeling Impedances of SOFC Cathodes Prepared by Infiltration

6.1 Introduction

As discussed in the previous two chapters, our understanding of the factors that lead to lower overpotentials in SOFC cathodes is still limited. For example, it is generally accepted that cathode performance should scale with the ionic conductivity of the cathode material [3, 26], despite evidence to the contrary, as discussed in Chapter 4. In another example, it is frequently assumed that cathode performance is limited by catalytic properties. However, Chapter 5 showed that even though the addition of various promoters has been reported to improve the performance of common cathode materials in some studies [24, 132], the enhancement appears to be due to structural changes in the electrode, rather than to any enhanced catalytic or ionic-conduction properties [7, 37]. Clearly, there is a need for an improved understanding of the factors that limit SOFC cathode performance.

A considerable number of modeling studies have been carried out to determine the factors that influence electrode properties [3, 6, 16, 18, 19, 28, 42, 66, 86, 100, 101, 110, 126, 141, 149]. In this chapter, we build on that background with an overall goal of calculating electrode resistances with at most one fitting parameter. In keeping with the work of the previous chapters, we have chosen to focus our modeling efforts on composites, using experimental parameters for $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (LSF) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) for the MIEC and yttria-stabilized zirconia (YSZ) for the electrolyte. The
properties of LSF, LSM, and YSZ are given in Table 6.1. The structure of the composite was chosen to model that of electrodes prepared by infiltration of the MIEC component into a porous scaffold of the electrolyte [46, 48, 54, 101, 134, 137]. These electrodes differ from traditional composites in that both the MIEC and electrolyte phases are well connected within the composite, even at loadings well below those necessary for percolation in random media [40]. However, the performance of electrodes formed by infiltration has many similarities to that of traditional composites [134], so that the ideas developed here likely apply to traditional composites as well.

The dependence of the morphology of the composite cathode upon calcination temperature has been described extensively in the previous chapters. Schematic diagrams of the composite structure are shown in Figure 6.1 and are similar to that used by others to model electrode performance [100, 101, 110, 126]. For this work, we assume that calcination at 1373 K gives rise to dense perovskite films (Figure 6.1b), while calcination at lower temperatures causes the perovskites to form smaller particles that cover the YSZ (Figure 6.1a) [30, 36, 149].

Figure 6.1. Schematic representation of the composite cathodes prepared by infiltration after calcination to (a) 1123K or (b) 1373K.
Although the performance characteristics of infiltrated LSM-YSZ and LSF-YSZ cathodes depend on whether they are best described by the structure shown in either Figure 6.1a or 6.1b, [7, 8, 137], cathodes with the film structure shown in Figure 6.1b do show reasonably low impedances at 1073 K [7, 8], despite the fact that, in the strictest sense, there are no three-phase boundary (TPB) sites available. Because modeling the structure in Figure 6.1b is significantly simpler, we will focus on this system and discuss the changes that would be expected if the perovskite phase were more particulate in nature. Although Figure 6.1a does not show the perovskite particles touching each other, we assume that they are connected electronically.

Considering the picture in Figure 6.1b, it is apparent that oxygen transfer from the cathode to the electrolyte will involve gas-phase diffusion of $O_2$ into the composite, electrochemical oxidation of the perovskite surface, diffusion of the oxygen ions through the perovskite film, and transport of ions down the YSZ fins, all taking place in series. In this paper we assume that gas-phase diffusion is sufficiently fast such that the $O_2$ concentration is independent of position. This is the usual case for all but the thickest electrodes operating at high current densities [29].

The step that is most difficult to describe is the oxygen reduction reaction at the perovskite surface. This is most often modeled using the Butler-Volmer Equation [50], which assumes that local field gradients are strong enough to perturb the energies of species along the reaction coordinate. The equation was derived to describe reactions that take place at metal surfaces in solution, where most of the potential drop occurs
across a double layer that is approximately 2 nm in thickness [106], so that field
gradients on the order of 1 V/nm are common. These are large enough to significantly
alter the reaction coordinate that describes the rate constant. The Butler-Volmer
Equation indicates that the rate constant should have an exponential dependence on
overpotential, so that the cell potential should decrease exponentially with current
density near open circuit.

It is not surprising that Butler-Volmer behavior is seen in proton exchange
membrane fuel cells (PEM-FC). With PEM-FC, the catalytic metals near the electrolyte
interface are effectively immersed in water so as to facilitate transfer of ions into the
electrolyte. The situation for SOFC electrodes is far less clear. First, there are many
eamples in the literature for which the electrode impedance is independent of current
density and is the same under cathodic and anodic polarization [7, 8, 10, 21, 46, 67, 102,
145] and this current independence has been observed in cells with electrolytes as thin as
15 µm [83]. While there are also many examples of nonlinear $V-i$ curves, it should be
notated that the overall shapes of these curve are often significantly different from that
predicted by Butler-Volmer [22, 81]. Furthermore, there are multiple possible
explanations for nonlinear $V-i$ curves, such as the hysteretic effects observed with LSM
composite cathodes[46]. Second, while field gradients exist in SOFC electrodes, the
length scale over which overpotential differences occur is likely much longer than 1 nm;
so that field gradients are likely small. Field gradients less than 0.01 V/nm will not
significantly affect the barrier height along the reaction coordinate for most reactions.
For these reasons, we propose an alternative model of cathode impedance that does not rely on Butler-Volmer kinetics.

As noted above, we consider two processes as being the most likely to limit the performance of the air electrode: Dissociative adsorption of gas-phase $O_2$ onto the perovskite surface and diffusion of oxygen ions through the perovskite film. Adsorption is treated as a reaction involving the dissociative adsorption of gas-phase $O_2$ onto oxygen vacancies on the surface of the perovskite, with the rate expressed in terms of a surface flux given by the Kinetic Theory of Gases and a reactive sticking coefficient. This sticking coefficient is the probability that an $O_2$ molecule which collides with an oxygen vacancy will then adsorb. Vacancy concentrations in the perovskite are determined from equilibrium data [1, 65, 94-96, 119, 120, 147], so that only the sticking coefficient, a number between 0 and 1, is unknown. Using the model structure presented in Figure 6.1b, electrode resistances are calculated based upon experimental parameters determined from characterization of actual cathodes prepared by infiltration. The effects of changing individual parameters are discussed and strategies for improving cathode performance are proposed.

A glossary of symbols and their definitions is presented at the end of this chapter. We will first present the steady-state models, then solve for the expected electrode resistances for cases where adsorption of $O_2$ is rate-limiting or diffusion of ions through the perovskite film is rate limiting. We will then estimate the capacitances that would be expected for the electrodes in non-steady-state measurements.
6.2 Steady-State Model

6.2.1 Structure of the Composite Electrode.

The cathode geometry presented in Figure 6.1b consists of a series of straight YSZ fins of height, $h$, and width, $w$, stemming from the solid YSZ electrolyte and extending to a distance $Z$ in the z-direction. Each fin is separated from the next by a distance, $L$. Although these fins are pictured as straight, we incorporate a tortuosity factor, $\tau$. This is in recognition of the fact that the YSZ scaffold of the actual cathode through which the ions will be diffusing could have a complex geometry and a length scale greater than $h$. This tortuosity effectively reduces the ionic conductivity of the YSZ fins by a factor of $\tau$ such that

$$\sigma'_{YSZ} = \frac{\sigma_{YSZ}}{\tau}$$

Equation 6.1

where $\sigma'_{YSZ}$ and $\sigma_{YSZ}$ are the effective and bulk ionic conductivities of YSZ, respectively. It is important to note that we are defining $\tau$ for the conduction of ions in the YSZ, not for diffusion in the gas phase.

The parameters defined here can be related to experimental parameters. For example, the tortuosity can be estimated from conductivity measurements on porous slabs. For straight YSZ fins, the conductivity would be that of bulk YSZ divided by $(1-p)$, where $p$ is the porosity of the YSZ scaffold. The width, $w$, of the fins is the characteristic size of the YSZ scaffold and can be estimated from the SEM images of the cathode microstructure. $L$, the characteristic repeat distance in the scaffold, can be related to $w$ and $p$ from Equation 6.2[126].
These parameters can also be related to the specific surface area of the YSZ scaffold, $S_g$, a parameter that can be measured using BET isotherms [46].

$$S_g = \frac{2}{w \rho_{ysz}}$$  \hspace{1cm} \text{Equation 6.3}

The perovskite phase is assumed to form a dense film of thickness $\lambda$ on the YSZ fins. This thickness can be calculated from the weight percentage of the infiltrated perovskite phase, $\theta$, the density of the perovskite, $\rho$, and the surface area of the YSZ scaffold[46].

$$\lambda = \frac{\theta}{(1 - \theta) \rho S_g}$$  \hspace{1cm} \text{Equation 6.4}

### 6.2.2 The Potential Within the YSZ Fin

When modeling the electric potential, $\Phi$, within the YSZ fins, we assume that the YSZ has uniform ionic conductivity, $\sigma_{YSZ}$, and negligible electronic conductivity. Because the height of the fins is much larger than the width, gradients in the $x$-direction are assumed negligible, as is ion flow through the perovskite film at the top of the fin. (This is essentially the fin approximation with an adiabatic tip.) Defining $i(y)$ as the current flowing down the fin at any position $y$ and $i''$ as the flux of charge coming into the fin through the perovskite film, the steady-state charge balance becomes Equation 6.5.

$$2Z \int_y^h i'' dy = i = -\sigma_{YSZ} W Z \frac{d\Phi}{dy}$$  \hspace{1cm} \text{Equation 6.5}
The electronic conductivity of the perovskite phase is assumed to be very large, so that the electrical potential of the perovskite phase is fixed. The boundary conditions for Equation 6.5 are then given by Equations 6.6 and 6.7, which simply state that the potential at the electrolyte interface is equal to the cathode overpotential and that there is no current flow from the top of the fin.

\[ \Phi|_{y=0} = \Phi_0 \]  

Equation 6.6

\[ \frac{\partial \Phi}{\partial y} \bigg|_{y=h} = 0 \]  

Equation 6.7

If we allow \( h \) to go to infinity, the condition in Equation 6.7 implies that \( h \) is greater than the thickness of the electrode active region, \( h_{AR} \), that part of the electrode in which essentially all of the oxygen reduction takes place. Previous work has shown the active region of some state-of-the-art cathodes to be as small as 10 µm [2, 151] although the thickness of the active region will be larger in poorer performing electrodes.

### 6.2.3 Charge Flux Through the Perovskite Film

To solve Equation 6.5, an expression is needed for \( i_S'' \), the current flux originating from ions coming through the perovskite film. We will consider two limiting cases: 1) The case where the perovskite surface is in equilibrium with the gas phase and oxygen ion diffusion through the perovskite is limiting; and 2) the case where diffusion through the perovskite film is relatively fast so that oxidation of the perovskite surface is rate limiting.
6.2.3.1 Diffusion Limited

The ion diffusion through the perovskite film is given by Equation 6.8 [8, 119].

\[ J_{O_2} = \frac{R_g T \sigma_{amb}}{16F^2} \ln \left( \frac{P_{O_2 \text{surf}}}{P_{O_2 \text{fing}}} \right) \]  

Equation 6.8

Here, \( P_{O_2 \text{surf}} \) and \( P_{O_2 \text{fing}} \) correspond to the oxygen fugacities at the film surface in contact with the atmosphere and with the YSZ fin, respectively. \( \sigma_{amb} \) is the ambipolar conductivity of the perovskite as defined by Equation 6.9 [8, 119].

\[ \sigma_{amb} = \left( \frac{\sigma_i \sigma_{el}}{\sigma_i + \sigma_{el}} \right) \]  

Equation 6.9

For materials with much higher electronic than ionic conductivities, as are the cases for LSF and LSM, the ambipolar conductivity is essentially equal to the ionic conductivity. For the case where diffusion of ions through the perovskite film is rate-limiting, \( P_{O_2 \text{surf}} \) is simply 0.21 atm. We assume equilibrium exists at the perovskite-YSZ interface, so that \( P_{O_2 \text{fing}} \) can be related to the potential within the YSZ fin using the Nernst equation.

\[ \Phi = \frac{R_g T}{4F} \ln \left( \frac{P_{O_2 \text{amb}}}{P_{O_2 \text{fing}}} \right) \]  

Equation 6.10

By combining Equations 6.8 and 6.10, the flux of oxygen ions through the perovskite film at any position can be directly related to the electric potential within the YSZ fin.

Finally, the oxygen flux can be related to \( i_s'' \) through Equation 6.11 [119]:

\[ i_s' = 4FJ_{O_2} \]  

Equation 6.11
6.2.3.2 Surface Reaction Limited

Although the dissociative adsorption rate of O$_2$ onto the perovskite surface could have been written in terms of surface-exchange rates, this formalism would not have allowed the rates to be expressed in terms of the oxidation state of the surface. Therefore, for the surface reaction-limited case, we assume that oxygen incorporation into the perovskite can be treated as a reaction between gas-phase O$_2$ and the oxygen vacancies in the perovskite lattice. If the vacancies are identical and independent of each other, the rate per area of surface will be proportional to the collision frequency between gas molecules and the surface and given by Equation 6.12:

$$r_{ads} = \frac{PO_{2, atm}}{(2\pi MR_g T)^{1/2}} \cdot S$$

Equation 6.12

Here, $S$ is the sticking coefficient, the probability that a molecule striking the surface will adsorb. Because a molecule must find a vacancy site in order to react, the sticking coefficient will depend on the vacancy concentration of the perovskite and a vacancy sticking probability, $S_0$.

For a perovskite of composition ABO$_{3-\delta}$, it is reasonable to suggest, as a first approximation, that

$$S = S_0 \left( \frac{\delta}{3} \right)$$

Equation 6.13

where $S_0$ is a constant at any given temperature and $(\delta/3)$ is the fraction of oxygen lattice sites that are vacant in the bulk. We are assuming here that only O$_2$ molecules impinging on unfilled lattice sites will be able to react with the surface. Although $S$ should probably depend on the square of the vacancy concentration for dissociative adsorption (i.e.
adsorption of an O\textsubscript{2} molecule will require two available sites, one for each oxygen atom.), we treat the dependence of \( S \) on the vacancy concentration as linear for simplicity in order to obtain an analytical solution. Although we recognize that oxygen adsorption rates in SOFC are more typically described using an exchange coefficient, \( k^* \), the advantage of using a sticking coefficient is that it allows us to define a rate constant, \( S_0 \), that is not dependent on \( PO_2 \). Furthermore, using the terminology of adsorption and catalysis provides connection with that vast literature, so that what is known from adsorption can be applied to electrochemistry. It is noteworthy that \( k^* \) has been shown to vary with \( PO_2 \) in ways that correlate with bulk oxygen vacancy concentrations in perovskite cathodes, an observation that supports the validity of the assumption made in Equation 6.13 [136].

At equilibrium, \( \delta \) will be a function of stoichiometry, temperature, and \( PO_2 \). For most materials of interest for SOFC cathode applications, \( \delta \) varies almost linearly with respect to \( \log(PO_2) \) over the range of interest for SOFC cathodes, \( 1 > PO_2 > 10^{-5} \) atm, as demonstrated by the thermodynamic data for LSM, LSF, and LSCo presented in Figure 6.2[94, 96, 119]. Therefore, we express the concentration of oxygen vacancies at the perovskite surface using Equation 6.14:

\[
\delta = m \log(P_{O_2}) + b
\]  
Equation 6.14

Here, \( m \) and \( b \) are the slope and intercept of a plot of \( \delta \) versus \( \log(PO_2) \). From Figure 6.2, it can be seen that \( m \) and \( b \) vary widely with perovskite composition. Upon combining Equations 6.12, 6.13, and 6.14, the adsorption rate can be expressed as follows:
When rates are limited by surface adsorption (i.e. Diffusion of ions through the perovskite film is relatively fast.), the surface vacancy concentration will be equal to that of the bulk and $PO_{2, surf}$ will be equal to $PO_{2, fing}$.

In the absence of ion flow (open-circuit conditions for the electrode), there will be an equilibrium vacancy concentration corresponding to the $PO_{2, atm}$ of the gas phase within the electrode. Because $O_2$ desorption must balance $O_2$ adsorption in order to establish this equilibrium, we define this equilibrium desorption as the adsorption rate at $PO_{2, atm}$. If we assume that lattice oxygen sites are equivalent and that changes in $\delta$ are small, it is reasonable to assume that the desorption rate, $r_{des}$, is constant and given by Eq. (16).

$$r_{des} = \frac{PO_{2, atm}S_0}{(2\pi MR_g T)^{1/2}} \frac{m \log(PO_{2, atm}) + b}{3} \quad \text{Equation 6.16}$$

As with the diffusion-limited case, the adsorption rate can then be related to the potential at any position along the YSZ fin and the net rate of adsorption can be related to $i_s''$ through Equation 6.17:

$$i_s'' = 4F(r_{ads} - r_{des}) \quad \text{Equation 6.17}$$
Figure 6.2 The $P_{O_2}$ dependence of the oxygen non-stoichiometry of (■) $La_{0.8}Sr_{0.2}$ $MnO_3$-[95], (●) $La_{0.6}Sr_{0.4}FeO_3$-[119], and (▲) $La_{0.3}Sr_{0.7}CoO_3$-[94].

6.2.4 Analytical, Steady-State Solutions

Because the net rate of oxygen adsorption at the gas-phase surface of the perovskite film must equal the flux of ions through the film, Equations 6.8 and 6.15 can be combined to solve for the oxygen fugacity of the perovskite at the gas-phase surface, Equation 6.18.

$$\log P_{O_2,surf} = \frac{A \ln P_{O_2,\text{fing}} - m \log(P_{O_2,\text{atm}})}{B \log e}$$

Equation 6.18

In this equation, there is no assumption as to whether the rate is limited by adsorption or diffusion; $A$ and $B$ are the prefactors for the diffusive flux and adsorption rate, respectively:
\[ A = \frac{R_s T \sigma_{\text{amb}}}{16F^2 \lambda} \]  

Equation 6.19

and

\[ B = \frac{S_0 P_{O_2, \text{atm}}}{(2\pi MRT)^{1/2}} \]  

Equation 6.20

The relative magnitude of \( A \) and \( B \) determines which process is rate limiting. If \( A \) is much larger than \( B \), \( PO_{2, \text{surf}} \) will become equal to \( PO_{2, \text{fing}} \) and surface adsorption is rate limiting. Conversely, if \( B \) is much larger than \( A \), diffusion is the rate limiting process and \( PO_{2, \text{surf}} \) will become equal to \( PO_{2, \text{atm}} \). We consider the analytical solutions for the expected electrode resistances for each of these limiting cases separately.

### 6.2.4.1 Diffusion Limited

By combining Equations 6.5, 6.8, and 6.11, the oxygen flux can be related to chemical potential at any given point in the YSZ fin, allowing one to solve for \( i_s' \) at any position along the fin, providing an expression for the amount of current entering the YSZ fin at a given point:

\[ i_s' = \frac{\sigma_{\text{amb}}}{\lambda} \Phi \bigg|_y \]  

Equation 6.21

Solving Equation 6.5 using the boundary conditions specified in Equations 6.6, 6.7 (with \( h=\infty \)), and 6.21 provides expressions for the potential and the total current within the YSZ fin. From these, the DC electrode resistance, \( R \), can be calculated from the ratio between the overpotential and the current. These solutions are shown in Equations 6.22 through 6.24.
\[
\Phi(y) = \Phi_0 \exp \left( -y \frac{\sigma_{amb}}{\frac{w}{2} \lambda \sigma'_{YSZ}} \right)
\]  
Equation 6.22

\[
i(y) = (1 - p) \sqrt{\frac{\sigma_{amb} \sigma'_{YSZ}}{\frac{w}{2} \lambda}} \Phi(y)
\]  
Equation 6.23

\[
R = \frac{1}{(1 - p)} \sqrt{\frac{w}{\frac{2}{\lambda} \sigma_{amb} \sigma'_{YSZ}}}
\]  
Equation 6.24

Although these results will be discussed more in depth later, it is worth noting that the dependence of the resistance upon \(\sigma_{amb}^{-1/2}\) is analogous to the result found by Adler and coworkers [3] when modeling the impedance of a porous layer of a mixed conducting material on a flat electrolyte.

6.2.4.2 Surface Adsorption Limited

The potential gradient within the YSZ fin for the case where surface adsorption is rate limiting can be obtained in the same manner as the diffusion-limited case, and the analytical solution takes a similar form. Combining Equations 6.10, 6.15, 6.16, and 6.17 with large \(A/B\) (such that \(PO_{2\text{surf}}\) equals \(PO_{2\text{fing}}\)) results in the following expression for \(i_S''\):

\[
i_S'' = E \left( mS_0 \right) \Phi_y
\]  
Equation 6.25
where $E$ is a simplifying collection of constants:

$$E = \frac{-16F^2 P_{O, atm} \log(e)}{(2\pi M)^{1/2} (R_g T)^{3/2}}$$

Equation 6.26

Substituting this expression into Equation 6.5 and again using the boundary conditions specified in Equations 6.6 and 6.7 (for $h=\infty$), we obtain expressions for the potential in the YSZ fin, the total current from each fin, and the overall electrode resistances, Equations 6.27 through 6.29:

$$\Phi(y) = \Phi_0 \exp \left( -y \frac{E \cdot mS_0}{\sqrt{\frac{3w}{2}} \sigma'_{YSZ}} \right)$$

Equation 6.27

$$i(y) = (1 - p) \sqrt{\frac{E \cdot mS_0 \sigma'_{YSZ}}{\frac{3w}{2}}} \Phi(y)$$

Equation 6.28

$$R = \frac{1}{(1 - p) \sqrt{\frac{3w}{2} \sigma'_{YSZ}}}$$

Equation 6.29

An important conclusion from this result is that the electrode resistance depends primarily on the slope, $m$, of the equilibrium, redox isotherm for the perovskite. This suggests that more reducible materials should show lower resistances.

For both the diffusion-limited case, Equation 6.24, and the adsorption-limited case, Equation 6.29, the electrode impedance depends on structural properties (porosity and fin size) and the dependencies shown are similar to those proposed previously by
Tanner, et al.[126] Both results also show an inverse square-root dependence of the electrode resistance on the ionic conductivity of the electrolyte scaffold. This suggests that the use of composites with an electrolyte of higher ionic conductivity (i.e. Gd-doped ceria) should decrease the impedance regardless of whether adsorption or diffusion is limiting. Finally, it is interesting to consider that the resistances obtained for both cases should not depend on the direction of the currents, so that impedances for electrodes operating cathodically or anodically should be the same, as we have already observed is often the case experimentally.

6.2.5 Effect of Perovskite Structure

It is interesting to consider the case where the perovskite particles are more particulate in nature, similar to that shown diagrammatically in Figure 6.1a, rather than film-like. Equations 6.5 through 6.7 which describe the potential in the YSZ fin would remain unchanged from the film case described above. Only the expression for $i_{s''}$ would be affected. Coming up with an expression for $i_{s''}$ in this situation is now more difficult. Considering just an individual perovskite particle on the YSZ surface, the picture is essentially that which is commonly used in modeling TPB sites [86]. There will now be sites where the perovskite particle, the YSZ, and the gas phase all come into contact. In principle, $O_2$ molecules could adsorb on the perovskite particles at sites far from the TPB sites and then diffuse to the YSZ interface, either through the bulk or along the perovskite surface.
For the case where adsorption of O$_2$ is rate limiting, the entire perovskite particle will be at the same chemical potential, determined by the potential of the YSZ at that position along the fin. The solutions given in Equations 6.27 to 6.29 would apply to this case, except that there would now be an increased surface area for adsorption. The surface area in the rate expression of Equation 6.12 is accounted for only in the perimeter of the YSZ fin. Depending on whether oxygen ions can be transferred between adjacent perovskite particles (Contact is required for electrical conduction.), the available surface area could be that of the particles in contact with the YSZ or could include particles that are only in contact with the YSZ through their interaction with other particles.

For the diffusion-limited case, the question is the relative importance of TPB sites compared to that of the bulk sites at the point of contact between the perovskite particles and the YSZ. For the “bulk” sites, Equations 6.22 through 6.24 still approximately apply, although the relevant length scale for diffusion, $\lambda$, would now be the particle size. For both the diffusion-limited and surface-adsorption-limited cases, the electrode impedances are expected to be smaller for the particulate case.

### 6.2.6 Non-Steady State Solutions

The framework developed in the previous sections can also be used to model the time response of the system to sudden changes in the cathode overpotential. Rather than using the steady-state approximation for the permeation flux through a thin perovskite film as specified in Equation 6.8, the flux entering the YSZ fin, which is related to $i_s$...
through Equation 6.11, can be expressed in terms of the oxygen-ion concentration gradient by the tracer self-diffusion coefficient, $D$, such that [1]

$$J_{O_2} = D \frac{\partial C(t)}{\partial x}$$

Equation 6.30

The ion concentration is a function of the stoichiometry parameter, $\delta$, as shown in Equation 6.31,

$$C = \frac{3 - \delta}{V}$$

Equation 6.31

where $V$ is the volume of the perovskite unit cell. The ionic conductivity can then be expressed in terms of the diffusion coefficient:

$$\sigma_i = -\frac{16F^2m\log(e)}{RTV} D$$

Equation 6.32

This relationship between $\sigma_i$ and $D$ differs slightly from that reported previously in the literature in that equilibrium conditions are included by including $m$ [119]. The time-dependent, oxygen-ion concentration profile within the film was then modeled using a one-dimensional form of Fick’s second law of diffusion [1],

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Equation 6.33

$J_{O_2}$ can again be expressed in terms of $i_s''$ through Equation 6.11. At the interface between the perovskite and the YSZ fin, a pair of matching conditions was used such that the chemical potential in the film and the fin were equal and that the fluxes of ions leaving the film and entering the fin were equal. At the perovskite surface in contact with the gas phase, net O$_2$ adsorption was again modeled according to Equation 6.15 and 6.16.
Electrochemical impedance spectroscopy (EIS) is a powerful technique that can provide information for identifying these different processes. These measurements can be performed either through sine wave testing or through current- or potential-step techniques, both of which provide identical information about the system being tested. Sine wave testing typically consists of applying a sinusoidal current perturbation and measuring the phase-shifted potential response of the system. The complex frequency domain impedance, \( Z(\nu) = \Phi(\nu)/i(\nu) \), is measured across a range of frequencies and presented on a Nyquist plot. Similarly, a potential step can be applied to the system while the current response is measured. Frequency domain data, identical to that which would be measured using sine wave testing, can then be obtained by performing a Fourier Transform of the time-dependent current and voltage profiles, \( i(t) \) and \( \Phi(t) \), followed by complex division [5, 63, 78, 148].

For the simulations in this work, we modeled the current responses to step changes in the cathode overpotential. For \( t < 0 \), the system was assumed to be at “open-circuit” voltage, with no overpotential applied to the YSZ fin. Because the system was considered at equilibrium, the vacancy concentration everywhere within the perovskite was set equal to \( C_0 \), the concentration of oxygen ions at \( PO_2 \text{ atm} \), corresponding to an overpotential of 0 V. Beginning at \( t = 0 \), the overpotential at the base of the YSZ fin was set equal to \( \Phi_0 \). Following this step change in potential, the current responses were calculated until new steady states were reached. Representative examples of the potential step, with a \( \Phi_0 = 0.01 \text{V} \), and the resulting current response are provided in Figure 6.3, as well as the corresponding Nyquist plot, shown in Figure 6.4. By integrating the current
response of the system over time, the capacitances were obtained. Because this model incorporated both oxygen adsorption at the perovskite surface and diffusion through the perovskite film, it allowed the calculation of resistances and capacitances for co-limited cases as well as the purely diffusion or adsorption limited cases addressed previously.

![Graph](image)

**Figure 6.3.** Representative time-profiles for the applied overpotential step function and the resulting current response for the non-steady state, co-limited model based on the parameters listed in Table 6.2 at 973K. This example case used $S_0=10^{-4}$ and $D=10^{-13}$ cm$^2$/s.
Figure 6.4. The corresponding Nyquist plot for the data presented in Figure 6.3.

6.3 Model Implications and Example Calculations

In this section, we examine the implications of this model for typical experimental conditions. Unless otherwise noted, all calculations use the thermodynamic and conductivity parameters presented in Table 6.1 and the structural parameters presented in Table 6.2.

6.3.1 Electrodes Based on Infiltrated LaFeO₃

Chapter 4 described a study in which LaFeO₃-based electrodes were synthesized with Ca, Sr, and Ba as dopants in order to examine the effect of changes the ionic conductivities [14]. A related study of infiltrated LaNi₀.₆Fe₀.₄O₃ and La₀.₉₁Sr₀.₀₉Ni₀.₆Fe₀.₄O₃ was carried out with the same YSZ scaffold and treatment conditions [79]. The impedances of these electrodes made with doped LaFeO₃ and
operating at 973 K in air were dependent on current density; at open circuit, the impedances of the electrodes calcined at 1373 K were \( \sim 3 \, \Omega \cdot \text{cm}^2 \). The impedances did not show the logarithmic dependence that would be expected for Butler-Volmer behavior [137] and the differences in the open-circuit impedances after calcination to 1373 K appear to be within the variability of different measurements [7, 8].

If the electrodes were limited by oxygen-ion diffusion through a dense perovskite film, the resistances can be calculated using Equation 6.24. Using the parameters from Table 6.1, the anticipated electrode impedances would vary from 0.06 \( \Omega \cdot \text{cm}^2 \) with LSF-YSZ electrodes to 0.3 \( \Omega \cdot \text{cm}^2 \) for the LCF-YSZ electrodes as shown in Table 6.3. Since one would expect this calculation to overestimate the resistance, given that the experimental perovskite films are almost certainly not perfectly dense, the fact that the measured impedances are significantly larger than the values predicted by the diffusion-limited calculation implies that diffusion limitations are likely not important. Another way of looking at the issue is to calculate what the ionic conductivity would have to be in order for the electrodes to exhibit an impedance of 3 \( \Omega \cdot \text{cm}^2 \). Based on Equation 6.24, the parameters in Table 6.2, \( \sigma_{\text{amb}} \) would have to be less than \( 10^{-7} \, \text{S/cm} \). Although doped LaFeO\(_3\) species have ionic conductivities much greater than this value, studies have shown LSM to have a significantly lower ionic conductivity[52]. This lower ionic conductivity suggests that LSM-YSZ electrodes may be limited by diffusion. This provides a possible explanation as to why LSM shows higher impedances compared to doped LaFeO\(_3\)[7, 89]. Figure 6.5 shows the resistance as a function of perovskite and YSZ ionic conductivity for the diffusion limited case as calculated by Equation 6.24.
<table>
<thead>
<tr>
<th>Parameter (Units)</th>
<th>Symbol</th>
<th>Value [Ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Sr$</em>{0.2}$FeO$_{3-\delta}$ (S/cm)</td>
<td>$\sigma_{amb}$ LSF</td>
<td>$8.3 \times 10^{-4}$ [8]</td>
</tr>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Ba$</em>{0.2}$FeO$_{3-\delta}$ (S/cm)</td>
<td>$\sigma_{amb}$ LBF</td>
<td>$3.1 \times 10^{-4}$ [8]</td>
</tr>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Ca$</em>{0.2}$FeO$_{3-\delta}$ (S/cm)</td>
<td>$\sigma_{amb}$ LCF</td>
<td>$3.8 \times 10^{-2}$ [8]</td>
</tr>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Sr$</em>{0.2}$MnO$_{3-\delta}$ (S/cm)</td>
<td>$\sigma_{amb}$ LSM</td>
<td>$4.0 \times 10^{-8}$ [52]†</td>
</tr>
<tr>
<td>Reducibility parameter of La$<em>{0.6}$Sr$</em>{0.4}$FeO$_{3-\delta}$</td>
<td>$m_{LSF}$</td>
<td>-.034 [119]</td>
</tr>
<tr>
<td>Reducibility parameter of La$<em>{0.6}$Sr$</em>{0.4}$FeO$_{3-\delta}$</td>
<td>$b_{LSF}$</td>
<td>.037 [119]</td>
</tr>
<tr>
<td>Reducibility parameter of La$<em>{0.8}$Sr$</em>{0.2}$MnO$_{3-\delta}$</td>
<td>$m_{LSM}$</td>
<td>-.0077 [95]</td>
</tr>
<tr>
<td>Reducibility parameter of La$<em>{0.8}$Sr$</em>{0.2}$MnO$_{3-\delta}$</td>
<td>$b_{LSM}$</td>
<td>-.039 [95]</td>
</tr>
<tr>
<td>Volume of LSF unit cell ($\text{Å}^3$)</td>
<td>V</td>
<td>60.5 [76]</td>
</tr>
</tbody>
</table>

**Table 6.1.** Material Properties of Doped LaFeO$_3$ and LaMnO$_3$. †Conductivity data for LSM is taken at 1073K.

<table>
<thead>
<tr>
<th>Parameter (Units)</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fin width (µm)</td>
<td>w</td>
<td>1</td>
</tr>
<tr>
<td>Electrode porosity</td>
<td>p</td>
<td>.66</td>
</tr>
<tr>
<td>Perovskite film thickness(µm)</td>
<td>$\lambda$</td>
<td>.26</td>
</tr>
<tr>
<td>Electrode thickness(µm)</td>
<td>h</td>
<td>50</td>
</tr>
<tr>
<td>Tortuosity factor</td>
<td>$\tau$</td>
<td>7</td>
</tr>
<tr>
<td>Ionic conductivity of YSZ at 973K (S/cm)</td>
<td>$\sigma_{YSZ}$</td>
<td>$2.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>Effective Ionic conductivity of YSZ at 973K (S/cm)</td>
<td>$\sigma'_{YSZ}$</td>
<td>$2.9 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

**Table 6.2.** Structural Parameters for Typical Composite Cathode.
If one assumes that the adsorption rate is limiting and that the vacancy concentrations at a given $PO_2$ are similar across this set of samples, Equation 6.29 can be used to estimate a sticking coefficient for the vacancy sites, $S_0$. As shown in Figure 6.6, using an electrode resistance of 3 $\Omega \cdot cm^2$ and the parameters in Tables 6.1 and 6.2, $S_0$ is calculated to be $\sim 10^{-4}$, a reasonable value for a reactive sticking probability. This, along with the fact that the resistances did not change with ionic conductivity in this series, suggests that the performance of the infiltrated LaFeO$_3$-based electrodes was limited by adsorption.

As noted previously, when modeling dissociative adsorption, $S$ is typically assumed to depend on the square of the vacancy concentration, effectively replacing Equation 6.13 with Equation 6.34:

$$S = S_0 \left( \frac{\delta}{3} \right)^2$$

Equation 6.34

Because the $\delta$ is of the order $\sim 0.1$ for overpotentials between 0.1 and 0.2 V in LSF, the presence of this additional term would requires that the value of $S_0$ increase by a factor of...
of 30 to obtain resistances of \( \sim 3 \, \Omega \cdot \text{cm}^2 \). It is also worth noting that the use of Equation 6.34 will also introduce a non-linearity into the resulting \( V-i \) curve. For example, when using a \( S_0 \) of \( 30 \times 10^{-4} \) and the parameters specified in Tables 6.1 and 6.2, the calculated resistances are \( \sim 3 \, \Omega \cdot \text{cm}^2 \) at an overpotential of \( 0.01 \, \text{V} \) and \( \sim 2 \, \Omega \cdot \text{cm}^2 \) at an overpotential of \( 0.25 \, \text{V} \). This suggests that dissociative adsorption may be a cause of the nonlinear \( V-i \) curves sometimes seen experimentally.

When calcined at only 1123 K, all of the LaFeO\(_3\)-based electrodes showed perovskite particles that were particulate in nature, rather than film-like, similar to that shown in Figure 6.1a. All of these electrodes exhibited a current-independent impedance of \( 0.2 \, \Omega \cdot \text{cm}^2 \) at 973 K [30]. As discussed earlier, the particulate nature of the infiltrated perovskites would be expected to affect both the diffusion-limited and the adsorption-limited case, so that this observation cannot be used to infer which process is limiting. However, if diffusion is not limiting for the electrodes calcined at 1373 K, diffusion limitations will certainly not be a factor for 1123-K electrodes, given that the length scale for diffusion will be much smaller.

### 6.3.2 Comparison of Sticking Coefficient to Alternate Rate Expressions

In SOFC, \( \text{O}_2 \) adsorption rates are most commonly presented in terms of the exchange coefficient, \( k^* \), or exchange current density, \( i_0 \), rather than a sticking coefficient. Values of \( k^* \) are typically determined from isotope exchange experiments [119] and can be related to oxygen adsorption through the relation:

\[
r_{\text{ads}} = k^* (C_{A0} - C)
\]

Equation 6.35
Figure 6.5  DC resistance as a function of perovskite and YSZ ionic conductivity for the diffusion limited case as calculated by Equation 6.24 using the parameters outlined in Table 6.2 and \( h=\infty \). The secondary axis illustrates the thickness of the active region for a given resistance using \( \sigma'_{YSZ}=0.0029 \) S/cm.

Figure 6.6  DC resistance as a function of perovskite and YSZ ionic conductivity for the diffusion limited case as calculated by Equation 6.29 using the parameters outlined in Table 6.2 and \( h=\infty \). The secondary axis illustrates the thickness of the active region for a given resistance using \( \sigma'_{YSZ}=0.0029 \) S/cm.
where $k^*$ has units of cm/s, and $C_{A0}$ is the oxygen concentration of the surface in equilibrium with the gas. Literature values of $k^*$ range from $\sim5 \times 10^{-4}$ cm/s at 973 K for La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ [65] to $\sim10^{-9}$ cm/s [17] at 973K for La$_{0.8}$Sr$_{0.2}$MnO$_{3-\delta}$. By substituting Equations 6.13 and 6.35 into Equation 6.12, and accounting for units, $S_0$ can be shown to be approximately 50 times $k^*$. It is interesting to notice that $k^*$ values reported in the literature correspond to $S_0$ values in the range of $10^{-2}$ to $10^{-7}$, which are in general agreement with the value of $S_0 = 10^{-4}$ coming out of our calculations.

Exchange current densities are sometimes used as fitting parameters in the Butler-Volmer expression and correspond to the forward and reverse reaction rate at equilibrium. By substituting Equations 6.13 and 6.14 into Equation 6.12 and assuming $PO_2 = PO_{2\text{atm}}$ at equilibrium, an $S_0$ value of the $10^{-4}$ can be shown to correspond to an $i_0$ of 1.3 mA/cm$^2$. This value is somewhat lower than the $i_0 = 300$ mA/cm$^2$ reported in the literature for LSF at 973K [152].

### 6.3.3 Thickness of the Electrochemically Active Region

The analytical solutions for the adsorption- and diffusion-limited cases were derived assuming the electrodes were infinitely thick. It is therefore of interest to relax the assumption of an infinitely thick electrode and determine the thickness of the active region, where the majority of the electrochemical reaction takes place. Equations 6.22 and 6.27 indicate that electrical potential within the YSZ fins decreases exponentially; when the electrical potential in the YSZ is zero, there is no potential driving force for oxygen transport through the perovskite. Defining $h_{AR}$ as the distance into the electrode
at which the potential is 10% of the total electrode overpotential, it can be shown through manipulation of Equations 6.22 and 6.24 or 6.27 and 6.29 that:

\[ h_{AR} = -\ln(0.1)\sigma_{YSZ}^{\prime} R(1 - p) \]  

**Equation 6.36**

For a measured impedance of 0.3 \( \Omega \cdot \text{cm}^2 \) using porosity values provided in Table 6.1, this equation predicts that the active region will be \( \sim 7 \) \( \mu \)m thick. This is in good agreement with literature reports that have determined the active region to be on the order of 10 \( \mu \)m thick [2, 151].

When the electrode thickness is less than \( h_{AR} \), the electrode impedance will be greater than that calculated from Equations 6.24 or 6.29, and Equation 6.5 must be solved with the appropriate value of \( h \) for the boundary condition in Equation 6.7. To demonstrate the effect that thinner electrodes can have, we present results from a calculation in which adsorption is assumed to be rate limiting, with \( S_0 \) equal to \( 10^{-4} \). Using the physical parameters listed in Table 6.2, the electrode impedance for an infinitely thick electrode is determined to 3.1 \( \Omega \cdot \text{cm}^2 \) and \( h_{AR} \) is found to be \( \sim 65 \) \( \mu \)m from Equation 6.36. Figure 6.7 shows numerically calculated results for the potential within the YSZ fins for electrodes having thicknesses of 20, 50, and 100 \( \mu \)m, assuming an overpotential of 0.2 V. For an electrode that is 100 \( \mu \)m thick, the potential profile is very similar to that which would be observed for an infinitely thick electrode and the electrical potential at the tip of the YSZ fin is approximately 0.02 V. The calculated impedance is identical to that obtained from Equation 6.29, 3.1 \( \Omega \cdot \text{cm}^2 \). For the 20- and 50-\( \mu \)m electrodes, the potentials within the electrode deviate from that of Equation 6.27
Figure 6.7 Potential profile within the YSZ fin for an applied overpotential of 0.2 V and electrode thicknesses, \( h \), of (■) 100, (●) 50, and (▲) 20 µm. Profiles are based upon the adsorption limited case with a \( S_0 \) value of \( 10^4 \) and the parameters listed in Table 6.2. Calculated impedances are provided for each electrode thickness.

but the calculated resistances, 3.33 and 5.42 Ω·cm\(^{-2}\), were significantly different only for the 20-µm electrode.

6.4 Non-Steady State Solutions

In the following sections, we used the time-dependent equations to examine the effects of \( D \) and \( S_0 \) on the electrode resistances and capacitances. The work in this section assumes an electrode thickness of \( h=50 \) µm.
6.4.1 Diffusion and Adsorption Co-Limited Impedances

To determine what the effect would be of having diffusion and adsorption be co-limiting, we calculated electrode resistances from the solution to the non-steady-state equations after long times. The results for typical experimental parameters from Table 6.2 are shown in Figure 6.8 as a function of the diffusion coefficients and sticking coefficients. As expected, for a given value of $D$, the diffusion-limited case gives the lowest possible impedance and this minimum value decreases as $D$ increases. Figure 6.8 also illustrates that for a given sticking coefficient, once the diffusion coefficient is sufficiently large and diffusion is no longer limiting, the impedance becomes independent of $D$.

6.4.2 Calculated Capacitances

Characterization of electrode performance by impedance spectroscopy measures the time response of the electrode to changes in the input. The capacitance of the electrode is measured in addition to the electrode impedance. To determine expected electrode capacitances for our model, we numerically calculated the current response to step changes in the overpotential from $\Phi=0$ V to $\Phi=.01$ V. This step change caused spikes in current density, which then relaxed to the steady-state currents expected for the steady-state electrode resistances. The area under the plot of current-versus-time was used to calculate the capacitance, similar to what would be done experimentally in current-interrupt measurements.
Figure 6.8 Calculated resistances as a function of diffusion coefficient and sticking coefficient for the non-steady state, co-limited model based on the parameters listed in Table 6.2. Symbols correspond to (■) the purely diffusion limited case, (○) $S_0=10^0$, (▲) $S_0=10^{-1}$, (◊) $S_0=10^{-2}$, (●) $S_0=10^{-3}$, and (□) $S_0=10^{-4}$.

Figure 6.9 Calculated capacitances as a function of diffusion coefficient and sticking coefficient for the non-steady state, co-limited model based on the parameters listed in Table 6.2 at 973K. Symbols correspond to (■) the purely diffusion limited case, (○) $S_0=10^0$, (▲) $S_0=10^{-1}$, (◊) $S_0=10^{-2}$, (●) $S_0=10^{-3}$, and (□) $S_0=10^{-4}$. 
Figure 6.9 shows the calculated capacitances as a function of both $D$ and $S_0$, again using physical parameters from Table 6.2. As with the calculated resistances in Figure 6.8, the purely diffusion-limited case provides the minimum capacitance value for a given $D$. For the cases where the adsorption rate becomes limiting, the calculated capacitance decreases as the sticking coefficient decreases. For a given $S_0$, the capacitance values are fairly constant and the adsorption and diffusion co-limited regions are not as easily identifiable as they were from Figure 6.8.

### 6.4.3 Analysis of Non-Steady State Solutions

From the results in Figures 6.8 and 6.9, it is possible to calculate the characteristic frequency for the electrode. Often, electrode impedances are modeled using equivalent RC circuits such that the characteristic frequency, $f$, can be related to the low-frequency intercept, $R$, and the electrode capacitance, $C_p$, by

$$f = \frac{1}{2\pi RC_p}$$

Equation 6.37

This characteristic frequency has been used to identify the process contributing to the impedance, with the assumption that larger frequencies correspond to electrochemical reactions and lower frequencies to diffusion processes. Figure 6.10 combines the data of Figures 6.8 and 6.9, showing frequency as a function of impedance. The uppermost curve, off of which the different branches emanate, corresponds to the purely diffusion limited case. Each of the branches from the main curve represents a particular value of
$S_0$; these branches deviate from the main curve at the point where adsorption becomes limiting for that particular $S_0$.

The characteristic frequencies in Figure 6.10 agree very well with the range of frequencies observed experimentally for infiltrated LSF-YSZ [137] and LSM-YSZ [46] electrodes. For calcination at 1123 K, the infiltrated LSF-YSZ electrodes exhibited an impedance of 0.2 $\Omega \cdot \text{cm}^2$ and a characteristic frequency of 400 Hz, which changed to 3 $\Omega \cdot \text{cm}^2$ and 4 Hz after calcination to 1373 K. A selection of experimentally measured frequencies and impedances are presented for comparison as individual data points in Figure 6.10.

However, one very interesting result from Figure 6.10 is that the characteristic electrode frequencies are very similar for the diffusion-limited and the adsorption-limited cases. In general, the frequencies for a given impedance differed by a factor of only two for the two different limiting cases. Closer inspection shows that this result should have been expected. For both diffusion and adsorption limits, the electrode capacitance results from diffusion of ions out of the perovskite film. In both cases, a step change in the overpotential requires diffusion of ions from that part of the perovskite that is in contact with the YSZ. The only difference between the two cases is that perovskite surface in contact with the gas phase remains unaffected in the diffusion-limited case but decreases over time in the adsorption-limited case. Therefore, an important consequence of the model is that the characteristic frequency does not allow one to argue which of these two processes is rate limiting.
Figure 6.10. Calculated resistances as a function of calculated characteristic frequencies for the non-steady state, co-limited model based on the parameters listed in Table 6.2 at 973K. Symbols correspond to (■) the purely diffusion limited case, (○) $S_0=10^0$, (▲) $S_0=10^1$, (◊) $S_0=10^2$, (●) $S_0=10^3$, and (□) $S_0=10^4$. Experimental data for (+) La$_{0.8}$Sr$_{0.2}$FeO$_{3-\delta}$ [137] and (×) La$_{0.8}$Sr$_{0.2}$MnO$_{3-\delta}$ [48] at 973K are presented for comparison.

Figure 6.11. Calculated resistances as a function of the perovskite reducibility parameter, $m$. Resistances were calculated using the non-steady state, co-limited model based on the parameters listed in Table 6.2 at 973K. Symbols provide examples of the (□) adsorption limited ($S_0=10^3$, $D=10^{-12}$ cm$^2$/s), (●) diffusion limited($S_0=10^2$, $D=10^{-13}$ cm$^2$/s), and (◊) co-limited cases($S_0=10^{-2}$, $D=10^{-12}$ cm$^2$/s).
6.4.4 Effect of Thermodynamics on Electrode Performance

It was shown in Equation 6.29 that the electrode impedance for the adsorption limited case depends on the slope, $m$, of the equilibrium, redox isotherm for the perovskite. Using the non-steady-state model, the effect of varying $m$ was examined for an adsorption limited, a diffusion limited, and a co-limited case. As shown in Figure 6.11, increasing values of $m$ lead to decreasing electrode resistances regardless of the limiting mechanism. This agrees with expectations from the steady-state solutions, since the substitution of Equation 6.32 into Equation 6.24 for the diffusion-limited case illustrates a dependence on $m$ similar to that seen in Equation 6.29 for the adsorption-limited case. This result suggests that highly reducible materials (i.e. LSCo) should provide superior performance for both the adsorption- and diffusion-limited cases. It is worth noting, however, that large values of $m$ and high ionic conductivities are often related.

6.5 Conclusions

In this chapter, we have modeled the electrode properties of electrodes formed by infiltration of perovskites into a porous layer of the electrolyte, followed by calcination to temperatures high enough for the perovskite to form a dense film of the electrolyte scaffold. Although the model is very simple, it captures the essential features that $O_2$ must adsorb onto the perovskite and then diffuse through the perovskite. By comparison with experimental data, the model shows that adsorption of $O_2$ onto the perovskite surface is likely rate limiting for perovskites with ionic conductivities greater than $10^{-7}$ S/cm, supporting the findings discussed in Chapters 4. According to the model, electrode impedances depend strongly on the ionic conductivity of the electrolyte scaffold, the
structure of the scaffold, and the slope of the perovskite oxidation isotherm. Finally, the characteristic frequency of the electrode cannot be used to determine whether diffusion or adsorption are rate limiting.

6.6 List of Terms

A  Diffusive flux prefactor
B  Adsorption rate prefactor
b  Reducibility parameter
C  Oxygen ion concentration within the perovskite film
C_{A0}  Oxygen ion concentration at equilibrium with gas phase O_{2}
C_0  Equilibrium oxygen ion concentration at atmospheric pressure
C_p  Electrode capacitance
D  Oxygen ion diffusion coefficient
\delta  Nonstoichiometry parameter
E  Simplifying collection of constants
F  Faraday constant
f  Characteristic frequency of the electrode
h  Electrode thickness
h_{AR}  Height of the active region
i(y)  Current density within the YSZ fin
i_s"  Charge flux entering the YSZ fin
i_0  Exchange current density
J_{O2}  O_{2} flux
k*  surface exchange coefficient
L  Length of repeating modeled unit
\lambda  Thickness of perovskite film
M  Molecular weight of O_{2}
m  Reducibility parameter
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PO_{2 \text{ atm}}$</td>
<td>Atmospheric $O_2$ partial pressure</td>
</tr>
<tr>
<td>$PO_{2 \text{ fin}}$</td>
<td>$O_2$ fugacity within the YSZ fin</td>
</tr>
<tr>
<td>$PO_{2 \text{ surf}}$</td>
<td>$O_2$ fugacity at the perovskite surface</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Electrical Potential</td>
</tr>
<tr>
<td>$\Phi_0$</td>
<td>Applied Overpotential</td>
</tr>
<tr>
<td>$R$</td>
<td>Zero-frequency impedance</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td>$r_{\text{ads}}$</td>
<td>$O_2$ adsorption rate</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of perovskite</td>
</tr>
<tr>
<td>$\rho_{\text{YSZ}}$</td>
<td>Density of YSZ</td>
</tr>
<tr>
<td>$S$</td>
<td>Sticking coefficient</td>
</tr>
<tr>
<td>$S_g$</td>
<td>Specific surface area</td>
</tr>
<tr>
<td>$S_0$</td>
<td>Sticking coefficient constant</td>
</tr>
<tr>
<td>$\sigma_{\text{amb}}$</td>
<td>Ambipolar conductivity of the perovskite</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>Ionic conductivity of the perovskite</td>
</tr>
<tr>
<td>$\sigma_{\text{el}}$</td>
<td>Electronic conductivity of the perovskite</td>
</tr>
<tr>
<td>$\sigma_{\text{YSZ}}$</td>
<td>Bulk ionic conductivity of YSZ</td>
</tr>
<tr>
<td>$\sigma'_{\text{YSZ}}$</td>
<td>Effective ionic conductivity of YSZ</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Tortuosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Percent weight loading of perovskite</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume of perovskite lattice</td>
</tr>
<tr>
<td>$w$</td>
<td>Fin width</td>
</tr>
<tr>
<td>$Z$</td>
<td>Characteristic length scale in z-dimension</td>
</tr>
</tbody>
</table>
Chapter 7. Efficient Reduction of CO\textsubscript{2} in a Solid Oxide Electrolyzer

7.1 Introduction

When the economy is based on renewable energy resources, such as wind and solar, the major source of H\textsubscript{2} for chemicals production and energy storage will be from electrolysis of water. The ability to reduce CO\textsubscript{2} efficiently by a similar process could also play a role in reducing greenhouse gas emissions and moving us towards a more sustainable economy[108]. CO produced in this manner could be used in chemicals production or reacted with H\textsubscript{2} to produce liquid fuels via the Fischer-Tropsch Reaction[4].

As mentioned in the introduction, SOEs are capable of higher water electrolysis efficiencies compared to solution-based electrolysis cells because they operate at higher temperatures (> 925 K). The higher operating temperatures result in a lower Nernst potential and in lower electrode overpotentials [104]. When performing electrolysis of steam, the electrode reactions are simply the reverse of those described previously by Equations 1.1 and 1.2. By analogy to the steam dissociation reaction, the reduction of CO\textsubscript{2} can also be carried out at the fuel-side electrode according to Equation 7.1.

\[
\text{CO}_2 + 2e^- \rightarrow \text{O}^{2-} + \text{CO}
\]  
Equation 7.1

It is noteworthy that the Nernst potentials for electrolysis of H\textsubscript{2}O and CO\textsubscript{2} are virtually identical.

There are a few reports in the literature for the electrochemical reduction of CO\textsubscript{2} to CO in SOE [123, 127, 144]. Most of these have focused on O\textsubscript{2} production for space
missions and have employed expensive bulk Pt electrodes that would not be practical for large-scale CO₂ electrolysis as would be required for sustainable chemicals and fuels production. Furthermore, the overpotentials for the Pt electrodes used in these studies were very high, so that the efficiency for CO₂ reduction was low.

In conventional SOEs used for steam electrolysis, the fuel-side electrode is a composite of Ni and YSZ [23, 39, 87], the same material that is used in SOFC for oxidation of H₂. In principle, Ni-YSZ electrodes can be used for CO₂ electrolysis [51] but they suffer from several important limitations. First, while Ni-YSZ electrodes are efficient for H₂ oxidation, electrode overpotentials for CO oxidation are much higher [14]. Indeed, a highly-optimized SOFC that was able to produce 1.8 W/cm² when H₂ was the fuel produced less than 0.3 W/cm² on a 44% CO-56% CO₂ mixture at 1073 K [58]. When SOFC are operated on syngas, a mixture of CO and H₂, the oxidation of CO proceeds primarily through the water-gas-shift reaction, CO + H₂O → H₂ +CO₂, with H₂ oxidation still being the primary electrochemical reaction [14, 58]. Second, there are concerns about the stability of Ni-YSZ composites in a CO-CO₂ environment. Ni carbonyls are highly volatile, making it important to choose operating conditions for which carbonyl formation is less favorable. Ni is also a superb catalyst for the Boudouard reaction, 2 CO → C + CO₂[99, 130], so that operation would be limited to higher temperatures and CO₂:CO ratios to avoid equilibrium conditions favorable for this reaction. Finally, Ni-YSZ composites are severely damaged by re-oxidation [12]. Since Ni would be oxidized by pure CO₂, it would be necessary to ensure that the feed to any
CO₂ electrolyzer contained sufficient CO or H₂ to make the gas composition reducing over all parts of the electrode.

Our groups have recently demonstrated that it is possible to achieve very high performance with an electrode made from 45-wt% La₀.₈Sr₀.₂Cr₀.₅Mn₀.₅O₃ (LSCM), 0.₅-wt% Pd, and 5-wt% ceria infiltrated into a porous YSZ scaffold [68]. In this composite electrode, LSCM provides electronic conductivity, YSZ provides ionic conductivity, and the Pd-ceria mixture enhances the catalytic activity for fuel oxidation. An SOFC with this fuel-electrode composition exhibited maximum power densities at 1073 K of 1.1 W/cm² and 0.71 W/cm² in humidified (3% H₂O) H₂ and methane, respectively, even though the cell had a relatively thick, 60-µm YSZ electrolyte. The composite electrode was also stable to oxidation and reduction cycles, showing conductivity under both oxidizing and reducing conditions. Finally, none of the materials used in LSCM-based electrode form vapor-phase carbonyls and none are good catalysts for carbon formation by the Boudouard reaction. These attributes make this electrode design a good candidate for use in a CO₂ SOE system.

In this chapter, we describe the performance characteristics for CO₂ electrolysis of an SOE with a fuel-electrode based on LSCM and an air electrode consisting of a LSF-YSZ composite. The results demonstrate that these electrodes are very efficient for the electrochemical reduction of CO₂.
7.2 Experimental

Cells were fabricated in a manner similar to that described in the previous chapters, though the procedure was modified slightly due to the use of a thinner electrolyte and an alternative anode composition. The porous layer on one side of the electrolyte was 300-µm thick YSZ (~65% porous) and was used as the scaffold for the air-side electrode, while the other porous layer was 60-µm thick YSZ (~65% porous) and was used as the scaffold for the fuel-side electrode. Porosity in the 300-µm layer was obtained using a mixture of graphite and polystyrene pore formers (the latter, was used to introduce larger pores), while the thinner porous layer used only graphite.

Once the porous-dense-porous wafers had been prepared, the addition of 45-wt% LSCM to the porous fuel-side layer was the next step in cell fabrication. The impregnating solution was prepared by adding $\text{La(NO}_3\text{)}_3\cdot 6\text{H}_2\text{O}$, $\text{Sr(NO}_3\text{)}_2$, $\text{Cr(NO}_3\text{)}_3\cdot 9\text{H}_2\text{O}$, and $\text{Mn(NO}_3\text{)}_2\cdot x\text{H}_2\text{O}$ to distilled water in the correct molar ratios, then mixing with citric acid to produce a solution with a citric-acid:metal-ion ratio of 2:1. After infiltrating the porous layer with this solution, the ceramic wafer was heated in air to 750 K to decompose the nitrate ions and the citric acid. This procedure was repeated until the desired weight loading of LSCM was achieved. Finally, the wafer was heated in air to 1473 K to produce the perovskite structure.

After forming the LSCM in the porous layer, the LSF-YSZ ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$) air-side electrodes were synthesized by impregnating the 300-µm thick layer with an aqueous LSF precursor solution, followed by calcination to 1123 K [137]. As has been demonstrated in the previous chapters, the impedance of LSF-YSZ electrodes prepared
in this way is between 0.1 and 0.15 Ω cm\(^2\) at 973 K and is independent of current density under both fuel-cell and electrolyzer conditions. Following the addition of LSF, 0.5-wt% Pd and 5-wt% of the mixed oxide, Ce\(_{0.48}\)Zr\(_{0.48}\)Y\(_{0.04}\)O\(_2\) (CZY), were added as catalysts to the LSCM-containing layer by addition of the nitrate salts and heating in air to 750 K. Pd supported on ceria-zirconia is known to be highly active for oxidation catalysis [131] and Y doping of the ceria-zirconia maintains the mixed oxide as a single-phase material following high-temperature treatments [69]. The addition of an oxidation catalyst was found to be essential for achieving high electrode performance [68].

The cell was prepared for testing as described earlier. The gas to the fuel-side electrode was either humidified (10% H\(_2\)O) H\(_2\) or a mixture of CO and CO\(_2\), with the concentration controlled by the relative flow rates of the gases. The air electrode was simply exposed to the ambient air.

### 7.3 Results and Discussion

A complete description of the LSCM-YSZ [68] electrode microstructure is given elsewhere. What this earlier work showed is that the infiltration process produces a remarkable morphology, with a thin porous layer of electronically-conductive LSCM covering the surface of the YSZ scaffold. Infiltration of the Pd/Ce\(_{0.48}\)Zr\(_{0.48}\)Y\(_{0.04}\)O\(_2\) catalyst into the LSCM pores then adds the necessary catalytic sites. This microstructure appears to be critical for achieving high performance by providing a mixed conducting substrate with a large, catalytically active, three-phase boundary. The electrode was demonstrated to be thermally stable on cycling up to at least 1173 K.
Figure 7.1 V-i polarization curves for 10% H$_2$O-90% H$_2$ (♦) and 10% CO$_2$-90% CO (●) mixtures at 973 K. Negative currents correspond to electrolysis of H$_2$O or CO$_2$. The cell composition was as follows: 40-wt% LSF in YSZ|YSZ(65 µm)|0.5-wt% Pd, 5-wt% CZY, and 45-wt% LSCM in YSZ.

Figure 7.2 Cole-Cole plots, measured at the open-circuit potentials, for 10% H$_2$O-90% H$_2$ (♦) and 10% CO$_2$-90% CO (●) mixtures at 973 K. The cell composition was as follows: 40-wt% LSF in YSZ|YSZ(65 µm)|0.5-wt% Pd, 5-wt% CZY, and 45-wt% LSCM in YSZ.
Figure 7.1 shows a comparison of the cell performance with the fuel-side electrode exposed to 90% H₂-10% H₂O and 90% CO-10% CO₂ mixtures at 973 K. In this figure, oxidation of H₂ and CO is indicated by positive currents and reduction of H₂O and CO₂ by negative currents. The cell potential at zero current was 1.05 V in H₂-H₂O and 1.07 V in CO-CO₂, which is close to the calculated Nernst potentials for these fuel compositions when the opposite electrode is exposed to ambient air. Because the feeds to the fuel side of the cell were dilute in both H₂O and CO₂, the overpotentials in electrolysis are higher than those under fuel cell conditions. With the H₂-H₂O mixture, a current density of 1.14 A/cm² was obtained at a cell potential of 0.5 V, while the corresponding electrolysis current density at 1.5 V was only 0.64 A/cm². With CO-CO₂ mixtures, the corresponding current densities at 0.5 and 1.5 V were 0.75 and 0.34 A/cm², respectively.

The corresponding open-circuit impedance spectra, Figure 7.2, provides insight into the origin of the overpotential losses while operating in the electrolysis mode. As expected, a significant fraction of the cell losses were ohmic and attributable to the i-R drop in the 65-μm YSZ electrolyte. The measured ohmic losses, determined from the high-frequency intercept with the abscissa, were 0.37 Ωcm² for operation in H₂ and H₂O and 0.35 Ωcm² for operation in CO and CO₂, in good agreement with the calculated resistance of 0.35 Ωcm² expected for the 65-μm electrolyte, using YSZ conductivities reported in the literature [109]. The non-ohmic losses, determined from the length of the arc under the impedance curves, were 0.19 Ωcm² for operation in H₂-H₂O and 0.6 Ωcm² for operation in CO-CO₂. Losses for the LSF-YSZ air electrode are estimated to be
between 0.1 and 0.15 Ωcm$^2$ at 973 K [137], suggesting that the fuel electrode losses in H$_2$-H$_2$O are approximately 0.1 Ωcm$^2$ and those in CO-CO$_2$ mixtures are 0.5 Ωcm$^2$.

Figures 7.3 and 7.4 show the V-i relationships for the cell during electrochemical reduction of CO$_2$ and oxidation of CO as a function of the CO:CO$_2$ ratio in the fuel at 973 and 1073 K, respectively. When pure CO$_2$ is fed to the fuel-side electrode, the open circuit potential is close to zero. (These are obviously conditions for which a Ni-YSZ electrode would undergo oxidation.) The cell potential rises to ~0.8 V as CO is produced by CO$_2$ reduction. At 1.5 V, the reduction current reaches 0.96 A/cm$^2$ at 973 K and 1.8 A/cm$^2$ at 1073 K. At 973 K for a CO$_2$:CO ratio of 9:1, the open-circuit potential is 0.87 V and increases with decreasing CO$_2$:CO ratio. The slope of the V-i curve remains nearly the same as that for pure CO$_2$, however, as long as there is sufficient CO$_2$ to avoid diffusional limitations. Diffusion limitations are almost certainly the reason for the increase in the slope at higher current densities. The nearly constant slopes, approximately 0.63 Ωcm$^2$ at 973 K and 0.36 Ωcm$^2$ at 1073 K, reflect the fact that the electrode impedances are nearly current-independent so long as diffusion of CO$_2$ (for CO$_2$ reduction) or CO (for CO oxidation) are not limiting. Because 65-µm YSZ electrolyte contributes to the increased slope of these lines, 0.35 Ωcm$^2$ at 973 K and 0.15 Ωcm$^2$ at 1073 K [109], significant improvements could be made by using a thinner electrolyte.
Figure 7.3 V-i polarization curves for mixtures of CO$_2$ and CO at 973 K. Negative currents correspond to electrolysis of CO$_2$. 100% CO$_2$-0% CO (♦); 90% CO$_2$-10% CO (■); 50% CO$_2$-50% CO (▲); 10% CO$_2$-90% CO (●). The cell composition was as follows: 40-wt% LSF in YSZ| YSZ(65 µm)| 0.5-wt% Pd, 5-wt% CZY, and 45-wt% LSCM in YSZ.

Figure 7.4 V-i polarization curves for mixtures of CO$_2$ and CO at 1073 K. Negative currents correspond to electrolysis of CO$_2$. 100% CO$_2$-0% CO (♦); 90% CO$_2$-10% CO (■); 50% CO$_2$-50% CO (▲); 10% CO$_2$-90% CO (●). The cell composition was as follows: 40-wt% LSF in YSZ| YSZ(65 µm)| 0.5-wt% Pd, 5-wt% CZY, and 45-wt% LSCM in YSZ.
Figure 7.5. The power density as a function of current density for the cell operating in the fuel-cell mode on CO-CO$_2$ mixtures at 1073 K: 90% CO$_2$-10% CO (■); 50% CO$_2$-50% CO (▲); 10% CO$_2$-90% CO (●). The cell composition was as follows: 40-wt% LSF in YSZ|YSZ(65 µm)|0.5-wt% Pd, 5-wt% CZY, and 45-wt% LSCM in YSZ.

It is interesting to consider how the LSCM-based electrode in the present study compares to the best Ni-YSZ electrodes. Since the only available CO$_2$ electrolysis data on cells with Ni-YSZ electrodes is for much higher temperatures, 1223 K [51], we instead compare the performance of our cells operating as a fuel cell. As mentioned earlier in this chapter, a highly-optimized SOFC with a Ni-YSZ anode and a 10-µm thick electrolyte produced less than 0.3 W/cm$^2$ on a 44% CO-56% CO$_2$ mixture at 1073 K, even though it was capable of producing 1.8 W/cm$^2$ on 100% H$_2$ at this temperature [58]. Figure 7.5, which shows the power density as a function of current density for our cell operating in the fuel-cell mode in various CO-CO$_2$ mixtures, demonstrates that our cell
achieved $0.45 \text{ W/cm}^2$ in a 50% CO$_2$-50% CO mixture at this temperature, even with a 65-$\mu$m electrolyte. Clearly, the performance of these LSCM-based electrodes in CO-CO$_2$ mixtures is excellent.

7.4 Summary

In this chapter, we have demonstrated that it is possible to reduce CO$_2$ electrochemically with an efficiency that is similar to that which can be achieved for H$_2$O electrolysis. This result suggests reduction of CO$_2$ by electrolysis in an SOE is feasible and could play a role in the development of sustainable and non-greenhouse gas emitting energy and fuel cycles which use renewable energy sources such as wind and solar to produce chemicals and liquid fuels.
References


25. Esquirol, A., N.P. Brandon, J.A. Kilner, and M. Mogensen, *Electrochemical characterization of La0.6Sr0.4Co0.2Fe0.8O3 cathodes for intermediate-


79. Lee, S., M. Bevilacqua, P. Fornasiero, J.M. Vohs, and R.J. Gorte, Solid oxide fuel cell cathodes prepared by infiltration of LaNi0.6Fe0.4O3 and La0.91Sr0.09Ni0.6Fe0.4O3 in porous yttria-stabilized zirconia. Journal of Power Sources, 2009. 193(2): p. 747-753.


82. Li, S.G., W.Q. Jin, P. Huang, N.P. Xu, J. Shi, Y.S. Lin, M.Z.C. Hu, and E.A. Payzant, Comparison of oxygen permeability and stability of perovskite type La(0.2)A(0.8)Co(0.2)Fe(0.8)O(3-delta) (A = Sr, Ba, Ca) membranes. Industrial & Engineering Chemistry Research, 1999. 38(8): p. 2963-2972.


