MICROSTRUCTURAL ENGINEERING OF COMPOSITE CATHODE SYSTEMS FOR INTERMEDIATE AND LOW-TEMPERATURE SOLID OXIDE FUEL CELLS

By

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To my mother Maria, father Frank, and inspiration Tonya
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Solid oxide fuel cells (SOFCs) are electrochemical devices with the potential to generate power at high efficiency with little environmental impact. However, in order to improve their commercial appeal, operating temperatures must be lowered from the 800-1000 °C temperature range to 500-700 °C and below. Due to the high bond strength of oxygen molecules, the kinetics of oxygen reduction are orders of magnitude slower than those of fuel oxidation. Consequently, much research in the reduced-temperature SOFC field is aimed at enhancing cathode performance.

A composite cathode makes use of an electronic conducting phase as well as an ion conducting phase in order to spread the 3PB reaction zone beyond the cathode/electrolyte interface. Silver-stabilized bismuth oxide composite cathodes exhibit low resistance to oxygen reduction due to a combination of high catalytic activity for oxygen reduction of both phases, as well as high ionic conductivity of the bismuth oxide phase.

Isothermal comparisons were made between pure silver cathodes, silver-yttrium stabilized bismuth oxide (YSB) cathodes, and silver-erbium stabilized bismuth oxides (ESB) at 650 °C. The performance of all cathodes was shown to degrade with time. Cathode area specific
resistance (ASR) of both the Ag-YSB and Ag-ESB electrodes increased by around 70%, while the pure Ag system experienced a near fourfold increase during the same length of time under open circuit conditions. In light of the electrochemical, microstructural, and chemical evidence presented, it was concluded that electrode microstructural evolution due to growth, agglomeration, and coalescence of the silver phase, rather than chemical reactivity of the bismuth oxide phase, was responsible for the observed degradation in electrochemical performance.

Attempts were made to reduce the microstructural evolution of the silver phase in Ag-ESB20 composites by introduction of small particles (nano-size 8YSZ or vibratory-milled ESB20 particles) into the electrode. The addition of 5 vol% 8YSZ nano powders significantly improved unbiased electrode stability by 97 %, and reduced the initial, zero time ASR value by 31 %. Similar results were obtained when YSZ-free electrodes were prepared from ESB20 powders composed of particles hundreds of nanometers in size as opposed to electrodes prepared from ESB20 powders composed of micron-sized particles—the zero time ASR value was reduced by 25 %, and ASR vs. time slope during unbiased testing of the silver-ESB20 system at 650 °C was reduced by 95 %. The ASR vs. time slopes during testing under a 250 mV external applied bias were lowered by 50 % using the smaller ESB20 particles due to suppression silver phase electro-migration.

Porous composite electrodes consisting of BRO7 and ESB20 were also synthesized and characterized using impedance spectroscopy on symmetrical cells. Using a combination of compositional and microstructural optimization, a minimum electrode ASR of 0.73 Ωcm² and 0.03 Ωcm² was achieved at 500 °C and 700 °C, respectively, making it one of the lowest resistance cathode materials reported to date at such low temperatures.
There is an expanding list of reasons to explore alternatives to conventional energy generation methods (namely coal-fired steam turbines and gasoline-powered combustion engines). From an ecological standpoint, there has been a longstanding need to reduce the polluting byproducts of conventional energy generation. Greenhouse emissions from automobiles and power plants have long been suspected of contributing to global climate change. Particulate matter exhausted from buses and larger vehicles can penetrate into the lungs, causing respiratory and cardiac disease. From an economic standpoint, worldwide demand for energy continues to rise as more and more nations, notably China, join the ranks of the industrialized countries. Also, the cost of oil is subject to global political landscapes—the dramatic upswing in gasoline and diesel fuel prices during winter and early spring 2000 were the direct result of an intentional reduction in crude oil production by OPEC. This exemplifies how sensitive oil prices are to a relatively small (about 4\%) reduction in supply, and given that oil is a finite resource, this signifies what may happen as supplies eventually begin to dwindle. From a socio-political standpoint, there has been a lot of tension regarding the foreign policies of oil-consuming nations, as evidenced by frequent protests and even wars. Lowering the global dependence on oil might reduce such tension. Yet despite all of this, changes to energy generation methods throughout the world have been exceedingly slow, as evidenced by the internal combustion Otto cycle engine, which has been used in automobiles for more than a century.

Obviously, the concept of alternative energy is not new. Many different sources of energy exist (or are proposed) that can supplement, and have the potential to replace, conventional generation methods. Popular examples include solar radiation, wind motion, and fusion energy. Each of these technologies has its own set of problems that have plagued its commercial
inception, but much research is being conducted to overcome these problems. Presently, it is unknown which of these sources, if any, will realize the greatest share of the commercial energy market in the coming decades. What is certain, however, is that the market for alternative highly efficient, eco-friendly energy production technologies is expanding.

There is a general push towards higher efficiencies. Current combustion-powered automobiles have an overall efficiency of about 20%\(^2\). That is, only 20% of the thermal energy content of the gasoline is converted into useful mechanical work and the rest is wasted. Higher efficiencies translate into reduced energy costs per unit of work done.

Fuel cells, another alternative energy technology, have received growing interest in recent years. The fuel cell, an invention credited to Grove in 1939,\(^3\) is a device that converts the chemical energy of fuels directly into electricity and heat by electrochemically combining the fuel and an oxidant gas via an ion-conducting electrolyte. The need for direct combustion is eliminated, giving fuel cells much higher conversion efficiencies than conventional thermo-mechanical methods (Figure 1-1).\(^4\) As a result, fuel cells have the added advantage of lower CO\(_2\) emissions per unit of power output compared to conventional technologies.\(^5\) Moreover, the production of NO\(_x\) and SO\(_x\), the main components of smog and acid rain, are expected to be 90% lower than in conventional pulverized coal plants\(^5\)—the NO\(_x\) and SO\(_x\) emissions from a 100 kW Siemens Westinghouse SOFC system were both reported to be less than 1 ppmV.\(^6\) Fuel cell power generation is virtually noise-free and can be tailored for standalone, off-grid applications, eliminating the need for, and losses associated with power transmission lines. Additionally, fuel cells have the potential to be used for combined heat and power (CHP or cogeneration) applications. This further increases efficiency by utilizing the thermal energy that is produced.
generating electricity. The current trend to deregulate the production of electric power will serve to promote CHP, thus furthering the marketability of fuel cells.

There are several different kinds of fuel cells in development. The main difference between each is the material used for the electrolyte, and consequently the operating temperature ranges and thus plausible market applications. Solid oxide fuel cells (SOFC) utilize a fast oxygen ion-conducting electrolyte, which is capable of supporting a high flux of oxide ions ($O^{2-}$) while in the solid state. A great deal of heat is produced during the energy production process. This heat can be utilized to partially reform common hydrocarbon fuels—gasoline, diesel, and alcohol—internally without combustion, unlike the case of polymer electrolyte membrane fuel cells (PEMFC) where external partial combustion reformers are required to produce hydrogen gas. The CO gas created during the reforming process is consumed as an additional fuel (unlike the case of PEMFC where CO gas is a catalyst poison). The generated heat can also be utilized for CHP applications. These points add to the efficiency of SOFC. Also, SOFC are made from inexpensive ceramic materials, and don’t require precious metal catalysts like platinum (which is required for lower temperature fuel cells). For these reasons, some experts predict that solid oxide fuel cells will be the eventual winner in the automotive market.\(^4\)

There is one major drawback of SOFC that has hurt their viability in this market. The high operating temperatures (800-1000°C) of current SOFC technology would require extended startup times—a period of fuel burning is needed to reach these operating temperatures. High operating temperatures are also responsible for sealing problems and expensive interconnect and balance-of-plant materials for SOFC stacks. Additionally, high temperature operation can induce thermal stresses at electrolyte-electrode interfaces, as well as cause interdiffusion between cell components.\(^7\) Most of these problems will be solved if the operating temperature can be
lowered to around 500ºC.\textsuperscript{8} An added bonus of lowered operating temperatures is the possibility of direct oxidation of methane without carbon deposition, which would eliminate the need for fuel reforming.\textsuperscript{9} For these and other reasons, the movement to lower the operating temperature of SOFC has intensified. However, the barriers to low operating temperatures are significant.

To gain a better insight into lowering the operating temperature of SOFC, one must first understand the construction of SOFC, the various reactions and losses that occur in the different components of SOFC, as well as explore some of the progress already made by researchers.
2.1. Basic Principles of SOFCs

Solid oxide fuel cells are capable of operating over a wide range of temperatures. Intermediate temperature SOFCs (IT-SOFCs) operate in the range from 500 °C to 700 °C. A typical single SOFC [Figure 2-1] is composed of a dense ceramic oxide electrolyte separating two porous electrode catalysts—a cathode on the oxidant (air) side and an anode on the fuel side. Oxygen molecules are fed to the cathode where it combines with electrons (supplied from the electrocatalyst in the cathode which is electrically connected to an external circuit) and is reduced into oxygen ions, which are injected into the electrolyte (Eq. 2-1a), where the subscripts ‘c’ and ‘e’ stand for cathode and electrolyte, respectively. Note that at times it is more convenient to think of the process of oxygen ions moving through the electrolyte as the equivalent process of oxygen vacancies (which can be considered simply as point defects in a periodic oxide lattice where a normally occupied oxygen site is left vacant) migrating from the anode side towards the cathode side, depicted in Eq. 2-1b using Kröger-Vink notation. That is,

\[ O_{2e} + 4e^- = 2O^{2-} \quad (2-1a) \]

\[ \frac{1}{2}O_2 + 2e^- + V_o^- = O^{+}_o \quad (2-1b) \]

The electrolyte conducts the ions, but blocks electrons. The oxygen ions emerge on the anode side of the electrolyte where they react with fuel (H₂ and CO) to form H₂O, CO₂ and electrons,

\[ 2O^{2-} + H_{2a} = H_2O + 4e^- \quad (2-2) \]

\[ 2O^{2-} + CO_a = CO_2 + 4e^- \quad (2-3) \]

where the subscript ‘a’ stands for the anode.
Electrons produced during the reaction are released to the electrocatalyst in the anode (which is also electrically connected to the external circuit). Thus the circuit is complete and useful work can be done in the external circuit. The gradient in oxygen concentration (or oxygen partial pressure or oxygen chemical potential) across the electrolyte provides the driving force for all of these electrochemical processes. Thus, SOFCs are considered oxygen concentration cells with a theoretical reversible voltage (or electromotive force, emf), $E_{th}$, given by the Nernst equation

$$E_{th} = \frac{RT}{4F} \ln \left( \frac{pO_{2c}}{pO_{2a}} \right)$$

(2-4)

where $R$ is the gas constant, $T$ is the absolute temperature, $F$ is Faraday’s constant, and $pO_{2a}$ and $pO_{2c}$ are the partial pressures of oxygen at the anode and cathode, respectively. The coefficient ‘4’ in the denominator represents the number of electrons transferred per mole of oxygen molecules reacted in the cell. As already stated, air is usually fed as the oxidant to the cathode side, thus $pO_{2c}$ is 0.21 atm. The oxygen partial pressure on the anode side for any particular fuel can be predicted using the Gibbs free energy change equation

$$\Delta G^0_T = \Delta H^0_T + T \Delta S^0_T = -RT \ln (K_{eq})$$

(2-5)

where $\Delta H^0_T$ is the heat change and $\Delta S^0_T$ is the entropy change of the fuel gas reaction at any anode temperature, $T$. $K_{eq}$ is the equilibrium constant for the fuel gas reaction. For many laboratory SOFC experiments, the fuel is hydrogen gas bubbled through water at room temperature. The fuel gas reaction is

$$H_{2(g)} + \frac{1}{2} O_{2(g)} = H_2O_{(g)}$$

(2-6)

and the mass action expression is
Rearrangement and substitution of Eq. 2-7 into Eq. 2-6 yields

\[
pO_2 = \left( \frac{pH_2O}{pH_2} \right)^2 \exp \left[ \frac{2(\Delta H_f^O + T\Delta S_f^O)}{RT} \right] \tag{2-8}
\]

The vapor pressure of water at any bubbler temperature, \( T_{\text{bub}} \) as well as the heat and entropy change values, \( \Delta H_f^O \) and \( \Delta S_f^O \), are readily available in tabulated form.\(^{11,12} \) Assuming no water condensation occurs in the gas delivery system between the water bubbler and the SOFC anode, the expression for \( pO_2 \) in Eq. 2-8 can be substituted for \( pO_{2a} \) in the Nernst Equation (Eq. 2-4) to predict the theoretical Nernst potential at any cell temperature. Plots of \( pO_{2a} \) and Nernst potential versus cell temperature using hydrogen fuel bubbled through water at 25 °C are shown in Figure 2-2. To increase theoretical cell voltage and power output, multiple cells are usually combined in series into a ‘stack’ with adjoining anodes and cathodes separated by an interconnect material (Figure 2-3).

No cell is perfect—that is the cell voltage during operation is always lower than the theoretical Nernst value (Fig. 2-4). As current is drawn to the load, the cell voltage is reduced due to various electrochemical losses. For an SOFC with an ionic transference number, \( t_i=1 \) (discussed below in Section 2.2), cell polarization or overpotential, \( \eta \), is the difference between theoretical and operating voltages. The total cell polarization can be considered the sum of three individual contributions—resistance (ohmic) polarization \( (\eta_\Omega) \), charge transfer (activation) polarization \( (\eta_A) \), and diffusion (concentration) polarization \( (\eta_D) \).

\[
\eta_{\text{tot}} = \eta_\Omega + \eta_A + \eta_D \tag{2-9}
\]
Ohmic polarization is caused by resistance to the flow of ions in ionic conductors and electrons in electronic conductors, and by contact resistances between cell components. As the name implies, these potential losses are directly proportional to the amount of current passing through the cell.

Activation polarization ensues whenever reacting chemical (including electrochemical) species are involved. An activation energy barrier must be overcome in order for the reaction to proceed. This results in a potential drop which may be regarded as the extra potential necessary to overcome the energy barrier of the rate-determining step of the reaction, and is related to the current passing through the cell by the phenomenological Butler-Volmer relation (discussed below in Section 2.4). In the electrode reactions (Eq. 2-1 through 2-3), the activation polarization is due to the transfer of charges between the electronic and ionic conductors. For this reason this overpotential is often termed charge-transfer polarization.

Concentration polarization occurs when reacting species are supplied to reaction sites slower than they are consumed, or when reaction products are not removed fast enough so that they block the reaction sites. This effectively results in lower concentrations of reactant species at the reaction sites (lower oxygen partial pressures at the cathode or lower partial pressures of fuel at the anode) than in the bulk of the gas stream and leads to a concomitant reduction in voltage. This type of loss becomes significant when large amounts of current are drawn from the cell, and in some cases a limiting current is reached where the concentrations of gases are unsustainable (approach zero at the reaction sites) causing fuel cell operation to cease.

While these losses cannot be completely eliminated, they can be minimized by proper choice of materials and by microstructural engineering of each cell component.
2.2. Dominant Component Losses

2.2.1. The Electrolyte

The dominant polarization losses in SOFC electrolytes are ohmic losses caused by the resistance to ionic conduction. In fact, the main contribution to the ohmic polarization of a SOFC is due to the electrolyte.\(^\text{13}\) As stated earlier, the role of an SOFC electrolyte is to conduct oxygen ions from the air side of the cell towards the fuel side. Good electrolyte materials have high ionic conductivity (low resistivity) for oxygen ions (or equivalently oxygen vacancies), and low electronic conductivity (to prevent internal short-circuiting and thus reduced cell performance) under an applied field. That is, ideally, the electrolyte should have an ionic transference number equal to unity,

\[
t_i = \frac{\sigma_i}{(\sigma_i + \sigma_e)}
\]

(2-10a)

where \(t_i\) is the ionic transference number, \(\sigma_i\) is the ionic conductivity (S/cm), and \(\sigma_e\) is the electronic conductivity (S/cm). This results in a deviation from theoretical Nernst potential, allowing \(t_i\) to be measured using

\[
t_i = \frac{E_O}{E_N}
\]

(2-10b)

where \(E_N\) is the theoretical Nernst potential, discussed above, and \(E_O\) is the actual cell open circuit potential (OCP). A material that has a low migration enthalpy for oxygen vacancies (or ions) in its lattice will have high ionic conductivity.\(^\text{14}\) The mobility of vacancies or ions within a lattice is affected, for example, by the spacing between ions in the lattice (which is related to the lattice parameter of the lattice), the binding energy between counterions and oxygen ions (which is dependant on the type of cations in the lattice), and also what are known as defect associates, which are caused by bonding between these defect species. The concentration of defects also

\[\]
affects the ionic conductivity. Oxygen ions move by jumping into an oxygen vacancy. If only one vacancy were available for such a jump, only one ion could move at a time. By increasing the number of oxygen vacancies, the number of mobile ions also increases and thus the ionic conduction is increased. However, at a certain concentration the defects can begin to interact, and these interactions tend to lower ionic conduction.

One crystal structure that is seen repeatedly in SOFC electrolytes is the cubic fluorite structure (Figure 2-5). A variety of oxides can exist in the fluorite structure (AO\textsubscript{2}), such as zirconia (ZrO\textsubscript{2}), ceria (CeO\textsubscript{2}), and bismuth oxide (Bi\textsubscript{2}O\textsubscript{3}). The configuration of the two sublattices and its “open” or “spacious” nature allow for relatively facile defect migration in fluorite oxides. For many of these materials however, the cubic fluorite structure is a high-temperature polymorph. For example zirconia undergoes a cubic-tetragonal transition below around 2400°C, and bismuth oxide undergoes a transition from cubic to monoclinic around 730°C.\textsuperscript{15} It has been shown that the cubic fluorite structures of these materials can be maintained down to room temperature by doping with various trivalent (and divalent) transition metal and rare-earth oxides. Typically, dopant cations with ionic radii larger than that of the host cation are more effective in stabilizing the cubic fluorite phase—smaller dopant cations tend to distort the lattice more than larger ones.\textsuperscript{16} In addition to imparting structural stability to these materials, these oxides may also serve to improve ionic conduction by virtue of the requirement that the lattice be electronically neutral. That is, the aliovalent dopant cations (Re\textsuperscript{3+}), which substitute the host cations (A\textsuperscript{4+}), have a net negative charge compared to normal lattice positions. However during this substitution process the lattice must maintain charge neutrality. Two of these negative charges can be compensated for by the creation of a vacant oxygen site (or oxygen vacancy), which has a +2 charge. In Kröger-Vink notation the dopant incorporation reaction is
Thus, the stabilized material is also imparted with a certain amount of oxygen vacancy defects, which (up to a point) increases ionic conduction. One can see from this that the electrolytic behavior of a material can be improved by optimization of the type and concentration of dopant cations in the lattice.

The conventional SOFC electrolyte, yttria-doped zirconia (YSZ), has an operating temperature around 1000°C. As the operating temperature is lowered, ohmic losses across the solid electrolyte increase. These losses can be minimized by reducing the distance that ions and vacancies need to travel, i.e. by reducing electrolyte thickness, and by choosing a material that has higher ionic conductivities than YSZ. Several physical and chemical techniques can be used to deposit thin-film electrolytes on to anode substrates including vapor deposition, slip casting, and electrophoretic deposition. Significant reductions in electrolyte resistances have been achieved by use of anode-supported thin-film electrolytes. Two alternative materials which have shown improved performance over YSZ are doped ceria and stabilized bismuth oxide.

At intermediate temperatures (~500-750 °C), stabilized bismuth oxides show some of the highest ionic conductivities among all studied fast ion conducting oxides (Figure 2-6). This is attributable to the inherent nature of its lattice structure. Because bismuth is a trivalent cation, and because it can be stabilized in the cubic fluorite form, bismuth oxides intrinsically have ¼ of the regular fluorite anion sites vacant. Consequently, there is a large excess of equipotential lattice points among which the anions (oxygen ions) can be distributed, which in effect leads to the observed high conductivities. Stabilized bismuth oxide thus has the potential to provide high power densities at low temperatures. However use of this material in fuel cell electrolyte
applications has been limited because it becomes unstable in reducing conditions such as those experienced at fuel cell anodes.23

While the ionic conductivity of stabilized ceria is less than that of stabilized bismuth oxide, it has also shown great potential to replace YSZ in fuel cell electrolyte applications.8,24 However ceria also has limitations at reducing conditions. The electrolytic domain of 10 mol% and 20 mol% GDC persists until ~10^{-15} atm at 800 °C and ~10^{-20} atm at 700 °C.25 Below these pO2 values, some of the Ce^{4+} ions take on an electron and are reduced to Ce^{3+}, creating Ce^{-}\text{Ce}^{3+} defects (also known as small polarons). These defects can be conducted through the electrolyte by a hopping mechanism from Ce^{-}\text{Ce}^{3+} sites to Ce^{3+}\text{Ce}^{3+} sites. This results in n-type conduction, lowered ionic transference number, short-circuiting of the cell and thus reduced cell efficiency. This leads to further problems when reducing electrolyte thickness to lower ohmic losses. When mixed conductivity is present, any electronic leakage current will increase as electrolyte thickness is decreased.8

2.2.2. The Electrodes

The dominant losses in the electrodes of SOFC are activation polarization and concentration polarization. Activation polarization is typically more of an issue in cathodes due primarily to the kinetics of the oxygen reduction reaction (attributable to the high bond strength present in oxygen molecules), which is several orders of magnitude slower than the reactions involving fuel oxidation.26-32 The dissociated chemisorption of H2 in a typical SOFC anode, for example, is a non-activated process.32 That is there is no barrier to the dissociation of a hydrogen molecule into two separate adsorbed atoms on (open, atomically rough faces of) the catalyst surface (typically Ni). At the cathode, the dissociative adsorption of oxygen is a thermally activated process.33 As the operating temperature is lowered, the rates of chemical
reactions drop dramatically, and activation polarization at the cathode becomes an even larger issue. Thus anode-supported cells have gained wider acceptance than cathode-supported cells in low-temperature SOFC research. This use of thick anodes results in longer diffusion lengths, and concentration polarization can become an issue, especially at high current densities. It should be noted that an analysis of isothermal transport of gaseous species through porous electrodes, based on commonly used anode and cathode gases, suggests that for comparable porosities and electrode thickness, the concentration polarization effects should in general be lower on the anode side. A complete polarization model of SOFC has been developed and the various loss mechanisms for an anode-supported cell are shown against a power density curve in Figure 2-7. These curves were generated using data extracted from literature that focused on cells that operated at 800°C. It should be noted that the values used for exchange current densities, electrolyte conductivity and thickness were among the highest values obtained from the literature. Based on the fact that the cell voltage reaches zero before an anodic limiting current is reached, the authors conclude that the anode limiting current density will not be reached under normal operating conditions. In addition, experimental studies have shown that the low-current interfacial resistance was 70-85% of the total cell resistance from 550°C to 800°C, and still played a major role in limiting cell performance at higher current densities. For these reasons, development of highly active cathodes, based on improvements in materials and microstructures that are thermally and chemically compatible with adjacent stack components are critical to the successful operation of low temperature SOFC.

2.3. Classes of Cathode Materials

The oxygen reduction reaction (Eq. 2-1) is the net reaction of interest for all SOFC cathodes. There are a series of steps involved in the reduction mechanism which depend on the type of cathode used. The cathode resistance emerges from these processes. In order to improve
the performance of cathodes for low temperature SOFC, whether by optimizing microstructure or composition, one must understand the various possible steps involved in this overall reaction. A review of three basic categories of porous cathode materials—single phase electronic conducting cathodes, dual phase electronic and ionically conducting cathodes, and single phase mixed ionic and electronic conducting (MIEC) cathodes—is given below to help gain insight into these processes. The review will include sections covering the mechanism for oxygen reduction, experimental (and theoretical) results, and methods for the determination and enhancement of the rate-limiting step of the reduction reaction. The experimental methods mentioned in this section are discussed in some detail in Appendix A of this dissertation.

2.3.1. Single-Phase Electronic Conductor

The most conventional type of cathode is a porous single-phase electronic conductor. Traditional cathodes for YSZ electrolytes such as platinum (and other noble metals), and the electronically conducting ceramic material, La$_{1-x}$Sr$_x$MnO$_{3+\delta}$ (LSM; $\delta$ is the average number of vacant oxygen sites per unit cell, or more simply, the oxygen nonstoichiometry, which ranges from +0.01 to +0.06 at 1000 °C and 700 °C, respectively, in air, for the typical composition $x=0.2$)\textsuperscript{35}, fall into this category. This particular construction restricts the oxygen reduction reaction (Eq. 2-1) to one-dimensional regions where the three phases—gas phase (pores), electrode phase, and electrolyte phase—meet, or three-phase boundaries (3PB). In this case, one can visualize that such 3PB are limited to the electrode/electrolyte interface (Figure 2-8).

The gas phase supplies the oxygen species, the electrode phase supplies the electrons and catalyzes the reaction, the oxygen-deficient electrolyte phase provides the vacant sites into which the ionic oxygen species are injected. Generally, the reaction mechanism for this type of cathode involves gaseous oxygen molecules diffusing through the pores (or they may dissociate and adsorb onto the surface of the cathode and diffuse along the pore walls) toward the reaction sites
(3PB), where charge transfer occurs and oxygen ions are injected into the electrolyte. Naturally, the reaction cannot occur on a one-dimensional line. Before combination with an electrolyte oxygen vacancy, it is expected that some diffusion of oxygen ad-atoms over the electrode and electrolyte surfaces takes place, but this reaction zone is expected to be very narrow. LSM cathodes have been particularly useful for these conventional SOFC due to their relatively low cost (compared to noble metal catalysts) and their thermal and chemical compatibility with YSZ electrolytes. In fact, the LSM cathode/YSZ electrolyte combination is the most widely studied system in the SOFC field. Such cathode materials have proven effective for SOFC operating at high temperatures (greater than 1000 °C) where reaction kinetics are fast. However, for cells that are to operate at lower temperatures the polarization losses in these cathode materials become so large that practical power densities cannot be achieved. A great deal of materials engineering has thus been necessary in order to overcome these losses.

2.3.2. Dual-Phase Composite Cathodes

One of the means to this end has been the development of porous dual phase composite cathodes where one phase is a purely electronic conductor and the other phase is a purely ionic conductor. The rationale for the use of this type of cathode is that it allows the reaction zone to spread from the cathode/electrolyte interface into the cathode (Figure 2-9). The length and density of the 3PB is increased, i.e., more sites are available for the charge transfer reaction. The general reaction mechanism is essentially the same as described above for purely electronic conducting cathodes except that the diffusion distances for the oxygen species to the 3PB reaction sites are shorter for dual phase cathode materials. Also, there is an additional path for transport of oxygen species—bulk diffusion through the ionically conducting phase.

The composition, including the materials used for each constituent phase and the relative amounts of each phase, is a key factor in determining the performance of these dual phase
composite cathodes. Consideration must be given to ensure that the individual phases within the composite electrode are continuous in order to create a path for the transport of the respective species—one phase for electrons, one phase for ions, and pores for gases. According to the effective medium percolation theory (EMPT), in order for a randomly distributed solid phase to be continuous, its volume fraction should exceed 1/3 of the total volume of the composite, including porosity. In addition, the cathode must be chemically and thermally compatible with the electrolyte. For this reason, the ionic conducting phase is usually chosen to be the same material as the electrolyte. The choice of the electronically conducting phase has a large effect on the inherent catalytic activity of the composite cathode towards the oxygen reduction reaction. This phase must be compatible with the ionically conducting phase for structural stability and to keep the intrinsic interfacial resistances between these two phases low. Common examples of this type of cathode include LSM/YSZ, and Ag/YSB (yttria stabilized bismuth oxide).

2.3.3. Single-Phase Mixed Ionic and Electronic Conductors (MIECs)

One class of SOFC cathodes that is growing in popularity includes single-phase oxides that exhibit mixed ionic and electronic conductivity. The most frequently used and versatile crystal structure in this category is the ABO₃ perovskite structure (Figure 2-10).

Typical host lattices of perovskites used for SOFC cathode applications are composed of a trivalent lanthanide cation on the A-site and a transition metal cation on the B-site. Electronic conduction is possible due to the multivalent nature of the B-site cation. If the cation has an affinity towards increasing its valence state (say, from +3 to +4), p-type electronic conduction can occur by an electron-hole hopping mechanism (also a small polaron mechanism). In contrast, if the cation has a tendency to want to lower its valence state (from +3 to +2, for example), n-type electronic conduction can also occur via a small polaron electron hopping mechanism. Note that this latter example can also have the effect of creating oxygen vacancies.
in order to charge-compensate the lattice, while the former example can have the opposite effect of oxygen vacancy annihilation. Oxygen mobility through vacancies provides the basis for ionic conductivity in these perovskite materials. Another way defects may be introduced is by doping the A-site cation with a divalent cation, typically Sr$^{+2}$ or Ca$^{+2}$. In air and at low cathodic overpotentials, the perovskite material is nearly stoichiometric, hence charge compensation for negative defects caused by substitution of divalent (e.g., Sr) cations for the trivalent (e.g., La) cation is mostly obtained by formation of electron holes. Under conditions of reasonably high cathodic overpotential, the pO$_2$ local to the reaction sites is lowered, and as a result of defect equilibrium requirements, oxygen vacancies concentration is increased.

The presence of these electronic and ionic defects broadens the electrochemically active region of the cathode to a much larger surface area—the oxygen reduction reaction is no longer limited to regions close to the triple phase boundaries. In other words, since both electrons (or electron holes) and oxygen vacancies are mobile defects in a MIEC cathode, it is possible for oxygen to be reduced at the gas/MIEC interface according to (Eq. 2-12a) or (Eq. 2-12b).

\[
\frac{1}{2} O_{2(g)} + 2e_{(\text{MIEC})}^- + V_{O_{(\text{MIEC})}} = O_{O_{(\text{MIEC})}}^x \quad (2-12a)
\]

\[
\frac{1}{2} O_{2(g)} + V_{(\text{MIEC})} = O_{O_{(\text{MIEC})}}^x + 2h_{(\text{MIEC})} \quad (2-12b)
\]

Furthermore, an additional path through which oxygen species may be supplied to the cathode/electrolyte interface—bulk transport through the electrode by vacancy jumping. At reasonable cathodic overpotentials (noted above), this oxygen flux through the electrode is likely to be increased. Consequently, MIEC cathode materials typically exhibit lower polarization and have improved performance compared to the other classes of cathodes already discussed. The reaction path for oxygen reduction in such MIEC cathodes has been described as including...
(1) oxygen diffusion in the gas phase, (2) oxygen adsorption-desorption on the MIEC cathode surface with charge transfer and oxygen incorporation at the MIEC cathode surface, (3) surface diffusion of the adsorbed oxygen on the MIEC surface, (4) bulk diffusion of oxygen ions in the MIEC cathode, (5) oxygen ion transfer at the cathode/electrolyte interface, and (6) charge transfer and incorporation of the adsorbed oxygen at the 3PB (Figure 2-11).

With some groundwork laid, some of the experimental and theoretical results and comparisons between the performances of different SOFC cathode materials will now be discussed.

2.4. Cathode Materials – Conventional and State-of-the-Art

The rate at which charge transfer reactions occur at the electrocatalyst/electrolyte interface is often expressed by the aforementioned Butler-Volmer equation, which relates this current density, \(i\), to the activation overpotential, \(\eta_{\text{act}}\), by

\[
i = i_0 \left\{ \exp\left(\frac{\alpha n F \eta_{\text{act}}}{RT}\right) - \exp\left[\frac{-(1-\alpha)nF\eta_{\text{act}}}{RT}\right]\right\}
\]

(2-13)

where \(i_0\) is the exchange current density, \(\alpha\) is the transfer coefficient, \(n\) is the number of electrons participating in the electrode reaction. \(F, R,\) and \(T\) were defined in Section 2.1. At sufficiently low current densities, Eq. 2-13 may be approximated by

\[
\eta_{\text{act}} \approx \frac{RT}{n F i_0} i = R_{\text{ct}} i 
\]

(2-14)

Where \(R_{\text{ct}} = \frac{RT}{n F i_0}\) is an intrinsic charge transfer resistance which is restricted to the electrolyte/electrocatalyst interface. Note that this resistance term (or any resistance term) is
often normalized into an area specific resistance (ASR). This is accomplished simply by multiplying the resistance by an area term (such as electrode area).

Virkar et al.\textsuperscript{13} have developed an expression showing the profound effect of adding an ionically conducting phase (such as YSZ) to a conventional electronically conducting cathode (such as LSM). In composite electrodes, the reaction zone, or region over which the process of charge transfer occurs, is spread out from the electrocatlayst/electrolyte interface into the electrode and as a result the activation overpotential may be lower than the intrinsic one given in Eq. 2-14. Thus an effective charge transfer resistance, $R_{ct}^{\text{eff}}$, is defined and used in its place; i.e. \[ \eta_{act} = R_{ct}^{\text{eff}} i. \] The expression for $R_{ct}^{\text{eff}}$ is rather lengthy and won’t be reproduced here. However, assuming the electrode is sufficiently thick, $R_{ct}^{\text{eff}}$ can be approximated by \[ R_{ct}^{\text{eff}} \approx \frac{BR_{ct}}{\sqrt{\sigma_i(1-V_v)}} \] (2-15)

where B is the grain size of the electrolyte (or ionically conducting phase) in the composite electrode, $V_v$ is the fractional porosity, and $\sigma_i$ is the ionic conductivity of the electrode (or that of the ionically conducting phase in the composite electrode). Using as an illustration, typical values for the parameters—$R_{ct}=1.2$ $\Omega$cm$^2$, $\sigma_i=0.02$ S/cm, B=2 $\mu$m, $V_v=0.35$—give an effective charge transfer resistance for a porous dual-phase composite cathode, $R_{ct}^{\text{eff}}=0.14$ $\Omega$cm$^2$. This is nearly an order of magnitude reduction in the intrinsic charge transfer resistance value of 1.2 $\Omega$cm$^2$ (or equivalently an order of magnitude increase in the effective exchange current density value) obtained for the porous single-phase electronic conducting cathode where the reaction is limited to the cathode/electrolyte interface.
It should be noted that the non-simplified model for $R_{\text{ct}}^{\text{eff}}$ takes into account the effect of cathode thickness (Figure 2-12). In general, if $\sigma_i$ is sufficiently high, the value of $R_{\text{ct}}^{\text{eff}}$ will decrease with thickness down to an asymptotic value (the plots where $R_{\text{ct}}^{\text{eff}}$ increase with thickness simply illustrate the deleterious effect if $\sigma_i$ is low enough and explains the peculiar behavior of certain composite electrodes reported in the literature).\(^{43}\) This effect of improved performance by increased thickness is validated by a series of current-voltage plots in Figure 2-13.

The decrease in performance for the 85 $\mu$m thick sample is presumably due to concentration polarization effects. A value for $R_{\text{ct}}^{\text{eff}}$ can be extracted from these plots by measuring the cell resistances from the near-linear regions and subtracting the electrolyte ASR (which can be obtained using independent impedance spectroscopy measurements, see Appendix A). These results agree well with the theoretical model (Figure 2-14). Mogensen and Skaarup\(^{32}\) observed the same behavior of lowered polarization resistance with increasing thickness of LSM-YSZ composite cathodes (Figure 2-15). These authors also report that the addition of 50 weight% YSZ to La$_{0.85}$Sr$_{0.15}$MnO$_3$ decreased the polarization resistance from 0.77 $\Omega$cm$^2$ to 0.16 $\Omega$cm$^2$ at 900ºC.

Based on Eq. 2-15, increasing the ionic conductivity of the ion-conducting phase will improve cathode performance, everything else being constant. This effect has been explained in that higher ionic conductivities allow ions produced deeper within the electrode to reach the electrolyte, thus effectively increasing the width of the reaction zone.\(^{38}\) Murray and Barnett inspected this effect by substituting the YSZ phase with a material that is known (Figure 2-16) to have higher ionic conductivity—gadolinium-doped ceria (GDC)—and compared the behavior of LSM/YSZ and LSM/GDC composite cathodes, as well as that of pure LSM (Figure 2-16).\(^{38}\)
The results show that replacing the YSZ phase with GDC significantly lowers (by approximately 50%) the polarization resistance at each temperature observed. Note also the large improvement in behavior of both composite cathodes over pure LSM. A comparison is also made to show how the type of electrolyte onto which an electrode is applied can influence performance—the polarization resistance of pure LSM on GDC is 1/3 that of pure LSM on YSZ. This result indicates that the kinetics of LSM electrochemical reactions are faster on GDC electrolyte surfaces than on YSZ surfaces. The effect of electrolyte is much smaller in LSM/GDC composites, but the slight reduction in polarization resistance observed on GDC electrolytes likely results from replacement of the LSM/YSZ 3PB at the cathode/electrolyte interface with LSM/GDC 3PB. However, the LSM/GDC 3PB already present in this composite cathode dominate the electrode performance, hence the small effect of the electrolyte on performance.

A model incorporating the effects of concentration polarization and activation polarization at higher current densities (using a Tafel approximation to the Butler-Volmer equation,

\[ \eta_{\text{act}} \approx a + b \ln(i) \]  

where a and b are parameters influenced by electrode microstructure and thickness) also predicts an effective exchange current density which is over an order of magnitude higher for LSM/YSZ composite cathodes compared to single-phase LSM cathodes at 800°C.\(^\text{13}\)

Wu and Liu\(^7\) reported the performance of dual phase yttrium-doped bismuth oxide (YSB)-silver (YSB/Ag) composite cathodes on BaCe\(_{0.8}\)Gd\(_{0.2}\)O\(_3\) electrolytes (Figure 2-17). It is seen in Figure 2-17a that Ag/YSB shows a much reduced overpotential than Ag—at 40mA/cm\(^2\), the overpotential of YSB/Ag is only 52% that of pure Ag. It is worth mentioning that there are two inherent problems that limit the performance of pure Ag cathodes. One is its relatively high
thermal coefficient of expansion, yielding poor adhesion to electrolyte surfaces. The other is that it readily densifies at low temperatures (850-900°C), and results in dense electrodes and hence poor performance. The addition of a ceramic phase to Ag, in addition to increasing the TBP length, can prevent electrode densification and improve thermal compatibility and adhesion to electrolyte surfaces. Figure 2-17b shows the effect of the volume fraction of Ag in the composite on cathode performance. A rapid drop (indicative of percolation behavior) is realized around 55 vol% Ag. If porosity (20 vol%) is taken into account, the vol% Ag and YSB at which minimum resistance is reached are 44% and 36%, respectively. This agrees well with the EMPT, but is inconsistent with ambipolar diffusion theory, which is discussed below.

For a specific electrode, a number of conductivities may be defined such as electronic, ionic and total. It is the simultaneous transport of electronic and ionic species that is crucial in electrodes that have mixed conduction. This is measured as ambipolar conductivity. Note that since electron mobilities are much larger than that of ions, ambipolar diffusion predicts that for these dual-phase composites, higher ambipolar conductivities are expected if the volume fraction of the ion-conducting phase is higher than that of the electron-conducting phase (Figure 2-18), which is in contrast to the results in Figure 2-17b where the electron-conducting phase volume fraction is larger. Yet in Figure 2-19, a minimum resistance is reached at higher GDC content in LSM/GDC dual phase composites. The apparent contrast in behavior can be explained by the simple fact that the overall performance of a porous electrode is not solely determined by mixed ionic-electronic transport properties in the solid phase of the electrode, but also by the inherent catalytic property of the 3PB, as well as by gas transport to or away from the 3PB. One might conclude, therefore, that the inherent catalytic activity of Ag is higher than that of LSM.
Maguire et al.\textsuperscript{41} examined the performance of Co-rich (x=0.3) and Fe-rich (x=0.7) La\(_{0.84}\)Sr\(_{0.16}\)Co\(_{1-x}\)Fe\(_x\)O\(_3\) (LSCFe3 and LSCFe7, respectively) as well as Pt cathodes on GDC electrolytes. Figure 2-20a shows the results of DC electrical conductivity measurements (Appendix A) for LSCFe3 and LSCFe7 versus temperature. As expected, the Co-rich composition shows a higher conductivity than the Fe-rich composition—at 800°C, the conductivities are 643 S/cm and 115 S/cm for LSCFe3 and LSCFe7, respectively. Figure 2-20b shows the results from steady-state cathodic polarization measurements (Appendix A) for the two LSCF compositions as well as for Pt. For simplicity the cathodic overpotential and current densities are expressed as positive quantities. For a given overpotential, LSCFe3 will pass a higher current than LSCFe7, and as expected both LSCF compositions will pass higher currents than Pt electrodes, since LSCF is an MIEC.

An ion exchange depth profiling (IEDP) comparison between manganates and cobalt-ferrites\textsuperscript{44} (Figure 2-21) shows that oxygen exchange coefficient, k (cm\(^{-1}\)) (the rate constant associated with transfer of oxygen species across a solid/gas interface), and the oxygen self-diffusion coefficients, D\(^*\) (cm\(^2\)/s), are orders of magnitude higher in the cobalt-ferrites, indicating the relative ease with which such chemical processes proceed in these materials (Appendix A). These results give credence to the supposition that mixed conducting cathodes extend the reaction zone beyond the 3PB.

Ishihara et al.\textsuperscript{31} studied the effect of the A-site dopant in Ln\(_{0.6}\)Sr\(_{0.4}\)MnO\(_3\) (Ln=La,Pr,Nd,Sm,Gd,Yb, and Y) perovskite cathodes on YSZ electrolytes. Figure 2-22 shows the results of electrical conductivity, cathodic polarization, and fuel cell power density (Appendix A) measurements.
In all cases, the Pr substitution exhibits the highest performance. Note that the cathodic overpotential of PrSM is only 25% that of LaSM at the current density and temperature used for this measurement. At 1000°C, the maximum power density is nearly the same for PrSM and LaSM, indicating that the electrolyte is the main contributor to the voltage losses. At lower temperatures, the difference becomes more pronounced, illustrating the importance of the activity for the cathodic reaction. The voltage drop due to cathodic overpotential was smaller in the PrSM cell, allowing it to exhibit the same power density at 700°C as LaSM at 800°C. Microstructural effects were negligible since BET surface area measurements and particle sizes (Appendix A) were determined to be nearly the same in both these cases. Chemical effects were thus predominant. This has been explained in that Pr oxides exhibit a large nonstoichiometry in air since the stable valence number of Pr ions is intermediate between 3 and 4. In addition, Steele et al. reported that the activity for the dissociation of oxygen molecules to oxygen ions can be expressed by the exchange current density, and this strongly influences cathodic overpotential. The slope of cathodic overpotential-current density plots provides a measure of the exchange current densities (Appendix A). The exchange current density of PrSM was shown to be nearly three times greater than that of LaSM.

Kharton et al. tested a number of different cathode materials on bismuth oxide-based electrolytes. Bismuth oxide was detected on the Ln$_{1-x}$Sr$_x$CoO$_3$ cathode surface after sintering. Other solid solution phases involving the diffusion of lanthanum and strontium ion diffusion were also detected. The interaction of cobaltites with YSZ electrolytes occurs much more slowly than with bismuth oxide-based electrolytes, even though YSZ electrolytes are sintered 200°C higher than bismuth oxide, as evidenced by electrode resistances which are 2-4 times larger on yttrium stabilized bismuth oxide (YSB) electrolytes than on YSZ electrolytes.
In a landmark paper, Shao and Haile\textsuperscript{46} reported on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) as a new cathode material for IT-SOFCs. Unlike typical MIEC cathodes, the A-site cation of BSCF is an alkaline-earth element as opposed to a rare-earth element. Utilizing BSCF on a thin-film samarium-doped ceria (SDC) electrolyte, high power densities (1010 mW/cm\textsuperscript{2} and 402 mW/cm\textsuperscript{2} at 600 °C and 500 °C, respectively) were obtained when operated with humidified hydrogen as the fuel and air as the cathode gas. The cathode ASR, as determined symmetrical cell testing, was $0.055–0.071$ Ω\textsuperscript{-}cm\textsuperscript{2} at 600 °C, and $0.51–0.60$ Ω\textsuperscript{-}cm\textsuperscript{2} at 500 °C. The excellent performance of this material is reportedly due to its exceptionally high oxygen diffusivity, especially at lower temperatures, allowing for high rates of oxygen electro-oxidation.

### 2.5 Strategies for Improving Cathodic Performance

In order to attack the problem of improving cathode performance, one must not only understand the various mechanistic steps involved in the oxygen reduction reaction but must also be able to identify the slowest (rate-determining) step. In addition, one must have a viable strategy toward accelerating this step. These strategies may be broken down into two categories—morphological improvements, which involve changes to cathode geometry or microstructure and electrocatalytic improvements, which encompass all other improvement methods. There are many approaches to these problems; a few examples are discussed below.

Tsai and Barnett\textsuperscript{9} illustrated several methods for identifying mass-transport limitations in cathode materials. A voltage/power density versus current density plot is conducted first in air, then in pure $\text{O}_2$. If the slope of the voltage-current density plot, i.e. the resistance, is larger in air than it is in pure $\text{O}_2$, mass-transport limitation can be assumed. Note that in the case of MIECs the ionic conductivity of the cathode may be $\text{pO}_2$-dependent, hence this behavior may not necessarily be indicative of mass-transport limitation. Mass-transport limitations can arise due to
surface diffusion, gas diffusion, dissociative adsorption\textsuperscript{9} or bulk transport.\textsuperscript{38} Both dissociative adsorption and surface-diffusion are thermally activated processes that should have strong temperature dependences, while gas diffusion will not. Thus, if any limiting current that is present increases as temperature is increased, one of the first two steps may be the limiting factor. Gas diffusion will depend on factors such as porosity and pore size. Thus, if any limiting current that is present increases as porosity and pore size increase, gas diffusion may be the limiting factor. These morphological factors can thus be utilized to accelerate the gas diffusion process. Also, if a change in test apparatus flow rates changes the polarization properties of the test cell, gas diffusion may be the limiting factor.\textsuperscript{20} For dual phase composite cathodes, if high frequency arcs are observed in the impedance spectrum whose behavior is independent of pO\textsubscript{2}, bulk ionic conduction in the ionic conducting phase may be the limiting factor. This can be confirmed by a comparison of the activation energy (Appendix A) of the resistance of this high frequency arc in the composite cathode to that for ionic conduction in the pure ceramic phase. If these values are similar, bulk diffusion can be considered the limiting factor.\textsuperscript{38}

Godickemeier et al.\textsuperscript{33} discussed how overpotential-current density relationships (Appendix A) may behave under a pure diffusion-limited process, a pure charge-transfer controlled process and combination of charge-transfer control at low current densities and diffusion control at high current densities (Figure 2-23). It is seen that there is a Butler-Volmer-type behavior for pure charge-transfer control, and a limiting current for pure diffusion control.

For dual phase mixed conducting cathodes, one morphological approach to enhance the charge transfer rate is to reduce the particle size of the ionic conductor while keeping the electronic conductor particles relatively large. The smaller particles form more contact points with the larger particles, creating a greater density of reaction sites within the cathode compared
to the case when all particles are approximately the same size. This effect is illustrated in Figure 2-24 where a particle broken into four equal pieces will have twice the 3PB length per unit area (8L) as the unbroken particle (4L).

For single phase mixed conductors, a wide particle size distribution is desired. Small particles are advantageous since they tend to create large grain boundary areas. These grain boundaries are high-energy sites, where the charge transfer reaction preferably occurs. However, small particles have the disadvantage of creating large tortuosity (harmful to gas phase diffusion) and poor connectivity. One electrocatalytic approach to improving charge transfer kinetics is to dope the electrode with redox cations such as Tb⁺⁴/Tb⁺³ or Pr⁺⁴/Pr⁺³.

Arrhenius plots of log(R) versus 1/T, where R is the cathode resistance of interest, yield straight lines with slopes that depend primarily on the activation energy of the rate limiting process. A change in slope over the investigated temperature range thus indicates a change in the rate controlling process. An investigation of La₁₋ₓSrₓCoO₃₋δ cathodes (x=0.2, 0.3, and 0.4) on La₁₋ₓSrₓGa₁₋ₓMgₓO₃₋δ (LSGM) electrolytes utilizes Arrhenius plots of the logarithm of interface conductivity (defined as the reciprocal of area-specific polarization resistance) as a function of temperature for different applied cathodic voltage (E) conditions (experimental details are discussed in Appendix A) to help elucidate that the rate limiting step in these cells was due to bulk diffusion of oxygen ions in the LSC cathode as opposed to surface diffusion of adsorbed oxygen on the LSC surface. The general procedure and results are discussed, briefly, below.

Figure 2-25 shows the Arrhenius behavior at E=0V. Since the activation energies for all samples are similar, it can be assumed that similar reaction mechanisms and the same rate-limiting step are at play. Figure 2-25b shows the Arrhenius behavior (for x=0.2 and x=0.4) for
applied cathodic voltage conditions. It is seen that the activation energies for the lower Sr content sample are more sensitive to changes in applied voltage. As described in Section 2.3.3, under cathodic polarization conditions, the pO$_2$ at the cathode/electrolyte interface is lowered and the oxygen vacancy concentration in the cathode increases due to defect equilibrium requirements. The driving force for surface diffusion depends on the oxygen partial pressure between the surface of the cathode grains and the reaction sites at the electrolyte surface. Since this gradient is generated by the applied cathodic overpotential, it should be similar for all samples (x=0.2, x=0.3, and x=0.4) at a given value of cathodic voltage. Thus, if this step were rate limiting, one would expect to see the similar activation energies for x=0.2 and x=0.4 as at each voltage. This behavior was not observed, thus surface diffusion is determined not to be the rate-limiting step.

Bulk diffusion depends on oxygen vacancy concentration. As mentioned above, applied cathodic voltages tend to increase the concentration of vacancies in the bulk of the cathode. Changes in vacancy concentrations (on a percentage basis) for LSC cathodes with lower concentrations of A-site dopants may be more sensitive to changes in applied voltage than for those with high A-site dopant concentrations. As a result, the activation energies will be more sensitive to changes in voltage as well. Since this is the experimentally observed behavior, this is assumed to be the limiting step.

The surface oxygen exchange rate, k, determined by ion exchange depth profiling (IEDP) can be used to evaluate the surface activity of a cathode (Appendix A). A comparison of the activation energy of the k values with the activation energy of interface conductivity values at E=0V (described above) can clarify whether or not oxygen adsorption/desorption on the cathode surface with charge transfer and oxygen incorporation at the cathode surface is rate-limiting. If
these activation energies are similar, this step may be considered as rate-limiting. Oxygen surface exchange rates can be increased by increasing oxygen vacancy concentrations, or by doping the cathode with a noble metal since noble metals are known to be good catalysts for the oxygen reduction reaction.

The exchange current density (which can be determined experimentally as described in Appendix A) is related to \( p_{O_2} \) at a given temperature by

\[
\gamma
\]

where \( k \) is a constant which is independent of \( p_{O_2} \) and \( \gamma \) is an exponent that depends on the reaction mechanism and rate-limiting step. A plot of \( \log(i_o) \) versus \( \log(p_{O_2}) \) should thus give insight into the rate-controlling mechanism at a given temperature of interest.

**2.6 Summary**

The above discussion detailed background information on the basic principles of SOFCs, highlighted the importance of the cathode for reduced SOFC operating temperatures, and presented the three basic classes of SOFC cathodes—single phase electronic conductors, dual phase composite cathodes, and single phase MIEC conductors. In addition, conventional and state-of-the-art cathodes were presented, as were several methods by which the dominant mechanism for observed cathodic losses can be identified. Not all methods and materials described above were used in the following studies, but a general awareness of these facts provides an essential framework from which the studies could be built.
Figure 2-1. Schematic representation of a typical SOFC button cell.

Figure 2-2. Theoretical values of oxygen partial pressure on the anode (calculated from Eq. 2-8) and cell potential (calculated from Eq. 2-4) as a function of temperature. Fuel is hydrogen bubbled through water at room temperatures.
Figure 2-3. Schematic representation of an SOFC stack.

Figure 2-4. Illustrative representation of typical current-voltage profile for an SOFC illustrating different types of electrochemical losses that arise when current is drawn from the cell.
Figure 2-5. Cubic fluorite (AO$_2$) crystal structure with A-site cations occupying the cube corners and face centers, and oxygen anions occupying the tetrahedral interstitial sites.

Figure 2-6. Reported ionic conductivity values for common SOFC electrolyte materials. [Figure adapted from Solid State Ionics Vol. 75, B.C.H. Steele, Interfacial reactions associated with ceramic transport membranes, 157-165 (1995) with permission from Elsevier.]

\[
\frac{L}{\sigma} = 0.15 \, \Omega \text{cm}^2
\]

Figure 2-8. Schematic representation of three phase boundary lines between electronic conducting particles, the ion conducting electrolyte and the gas phase for single-phase electronic conducting cathodes.
Figure 2-9. Schematic representation of three phase boundary lines between electronic conducting particles, ion conducting electrolyte as well as ion conducting particles, and the gas phase for two-phase composite cathodes.

Figure 2-10. ABO₃ cubic perovskite crystal structure. (a) A-site cations at cube center, B-site cations at corners, and oxygen anions at face centers. (b) Black spheres—A-site cations, grey tetrahedra—oxygen anions at corners, B-site cations at center.
Figure 2-11. Schematic representation of various reaction pathways for the oxygen reduction reaction in a MIEC.

Figure 2-12. Effect of cathode thickness on $R_{\text{ct}}^{\text{eff}}$. [Reprinted from Solid State Ionics, Vol. 131, A.V. Virkar, J. Chen, C. W. Tanner, J. W. Kim, The role of electrode microstructure on activation and concentration polarizations in solid oxide fuel cells, 189-198 (2000) with permission from Elsevier.]

Figure 2-14. Agreement between model (Eq. 2-15) and experiment for LSM-YSZ composite cathodes. [Reprinted from Solid State Ionics, Vol. 131, A.V. Virkar, J. Chen, C. W. Tanner, J. W. Kim, The role of electrode microstructure on activation and concentration polarizations in solid oxide fuel cells, 189-198 (2000) with permission from Elsevier.]
Figure 2-15. Effect of cathode thickness on polarization resistance for LSM-YSZ composite cathodes. [Reprinted from Solid State Ionics, Vol. 86-88, M. Mogensen and S. Skaarup, Kinetic and geometric aspects of solid oxide fuel cell electrodes, 1151-1160 (1996) with permission from Elsevier.]

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Ionic Conductivity (Ωcm⁻¹)</th>
</tr>
</thead>
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<tr>
<td>YSZ</td>
<td>600</td>
<td>3.2x10⁻³</td>
</tr>
<tr>
<td>GDC</td>
<td>600</td>
<td>3.1x10⁻²</td>
</tr>
<tr>
<td>YSZ</td>
<td>750</td>
<td>1.8x10⁻²</td>
</tr>
<tr>
<td>GDC</td>
<td>750</td>
<td>7.9x10⁻²</td>
</tr>
</tbody>
</table>

Figure 2-16. Effect of electrolyte phase composition on polarization resistance of various conventional SOFC cathode materials. [Reprinted from Solid State Ionics, Vol. 143, E. Perry Murray, S.A. Barnett, (La,Sr)MnO₃-(Ce,Gd)O₂ₓ composite cathodes for solid oxide fuel cells, 265-273 (2001) with permission from Elsevier.]
Figure 2-17. Effect composition on (a) cathode overpotential, and (b) interfacial resistance for Ag-YSB composite cathodes. [Reprinted from Journal of the American Ceramic Society, Vol. 81, Z. Wu, M. Liu, Ag-Bi$_{1.5}$Y$_{0.5}$O$_3$ composite cathode materials for BaCe$_{0.8}$Gd$_{0.2}$O$_3$-based solid oxide fuel cells, 1215-1220 (1998) with permission from Blackwell Publishing.]

Figure 2-19. Effect of composition on interfacial resistance of GDC-LSM composite cathodes. [Reprinted from Solid State Ionics, Vol. 143, E. Perry Murray, S.A. Barnett, (La,Sr)MnO$_3$-(Ce,Gd)O$_{2-x}$ composite cathodes for solid oxide fuel cells, 265-273 (2001) with permission from Elsevier.]
Figure 2-20. (a) Arrhenius conductivity plot of selected Fe loadings in LSCF, and (b) cathode polarization performance comparison. [Reprinted from Solid State Ionics, Vol. 127, E. Maguire, B. Gharbage, F.M.B. Marques, J.A. Labrincha, Cathode materials for intermediate temperature SOFCs, 329-335 (2000) with permission from Elsevier.]
Figure 2-21. IEDP for (a) LSM and (b) LCCF. [Reprinted from Journal of Power Sources, Vol. 49, B.C.H. Steele, Oxygen transport and exchange in oxide ceramics, 1-14 (1994) with permission from Elsevier.]
Figure 2-22. Effect of A-site dopant on (a) electrical conductivity, (b) cathodic polarization, and (c) fuel cell power density for various Ln$_{0.6}$Sr$_{0.4}$MnO$_3$ (Ln=La,Pr,Nd,Sm,Gd,Yb, and Y) perovskite cathodes on YSZ electrolytes. [Reprinted from Journal of the Electrochemical Society, Vol. 142, T. Ishihara, T. Kudo, H. Matsuda, Y. Takita, Doped PrMnO$_3$ perovskite oxide as a new cathode of solid oxide fuel cells for low temperature operation, 1519-1524 (1995) with permission from ECS.]
Figure 2-23. Overpotential-current density curves for (a) diffusion, (b) charge transfer, and (c) mixed control. [Reprinted from Solid State Ionics Vols. 86-88, M. Gödickemeier, K. Sasaki, L. J. Gauckler and I. Riess, Perovskite cathodes for solid oxide fuel cells based on ceria electrolytes, 691-701 (1996) with permission from Elsevier.]

Figure 2-24. Effect of electron-conducting particle size on 3PB length.
Figure 2-25. Arrhenius behavior of interface conductivity for LSC cathodes (a) varying Sr content at E=0V, and varying voltage for (b) La$_{0.8}$Sr$_{0.2}$CoO$_3$-$\delta$ and (c) La$_{0.6}$Sr$_{0.4}$CoO$_3$-$\delta$. [Reprinted from Electrochimica Acta, Vol. 46, T. Horita, K. Yamaji, N. Sakai, H. Yokokawa, A. Weber and E. Ivers-Tiffée, Oxygen reduction mechanism at porous La$_{1-x}$Sr$_x$CoO$_3$-d cathodes/La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.8}$ electrolyte interface for solid oxide fuel cells, 1837-1845 (2001) with permission from Elsevier.]
CHAPTER 3
STABILITY OF SILVER-BISMUTH OXIDE CATHODES

3.1. Introduction

The primary function of SOFC cathodes is to aid in the oxygen reduction reaction, Eq. 2-1. It is evident from this equation that oxygen reduction must occur where the gas phase, the cathode, and the electrolyte are in intimate contact. These boundaries form one-dimensional lines called three phase boundary (3PB) lines. As shown in Fig. 2-8, the reaction zone is restricted to a narrow region at the electrolyte/cathode interface. The reaction zone can be extended to a three-dimensional volume above this interface by introducing a second, ion-conducting phase, Fig. 2-9. The performance of these dual phase cathodes is significantly improved due to the increase in available sites for oxygen reduction.

A well-behaved cathode must be a good catalyst for oxygen reduction, highly conductive, and chemically and thermally compatible with the electrolyte. In addition, for mobile applications, the cathode must be stable at operating temperature for over 40000 hours.52

As described in Section 2.4 (Eq 2.15), increasing the ionic conductivity of the ion-conducting phase should improve cathode performance, since higher ionic conductivities allow ions produced deeper within the electrode to reach the electrolyte, thus effectively increasing the width of the reaction zone. Due to the high concentration of oxygen defects present in its crystal structure, stabilized bismuth oxide exhibits excellent ionic conductivity, ranking among the highest of all fast-ion conductors at 600 °C.22 Thus, dual phase composite cathodes utilizing some metal, Me, as the electronically conducting phase and a bismuth oxide-based material as the ionically conducting phase are expected the exhibit low resistance compared to similar dual phase cathodes containing the same metal Me and some other ceramic phase with lower ionic conductivity.
conductivity. It should be noted that below 600 °C, stabilized bismuth oxide undergoes defect ordering, where the conductivity rapidly decreases with time.53 The exact transition temperature has not yet been fully resolved.

Silver is known to be an excellent catalyst for the oxygen reduction reaction, has high electronic conductivity, and is relatively inexpensive. Composites of silver and YSB exhibit some of the lowest area-specific resistance (ASR) values known to date for YSZ electrolyte substrates, over the temperature range of interest.39 However, the long-term stability of these materials remains unchecked.

In this study, the long-term stability of Ag-YSB and Ag-ESB composites were examined. Ag-YSB composites were chosen to directly study the long-term stability of the system reported in the literature.39 Ag-ESB composites were studied for verification purposes and to improve performance (due to the higher ionic conductivity of ESB compared to YSB).54 YSB (for Ag-YSB composites) and ESB (for Ag-ESB composites) were chosen as the electrolyte substrates, since these should be chemically and thermally compatible with their respective composite cathodes, and to help identify possible ordering phenomena or phase transformation of the stabilized bismuth oxide phase. For comparative purposes, the composition used in this study was based on that used by Xia et. al.39 The isothermal annealing temperature was chosen to be 650 °C to avoid defect ordering in the bismuth oxide phase. It should be noted that at this temperature, YSB undergoes a cubic to rhombohedral phase transformation,55,56 but its onset is somewhat sluggish and can be monitored by impedance measurements.

3.2. Experimental

YSB (Bi$_{0.75}$Y$_{0.25}$O$_{1.5}$) and ESB (Bi$_{0.8}$Er$_{0.2}$O$_{1.5}$) powders were prepared by conventional solid-state synthesis. Stoichiometric amounts of bismuth oxide (Alfa Stock #10658) and yttrium oxide (Alfa Stock #11181) or erbium oxide (Alfa Stock #11309) were ball-milled in ethanol for
24 h. The solutions were then dried at 90 °C for 4 h, calcined at 800 °C for 15 h, crushed and sieved (325 mesh size). These powders were uniaxially pressed at ~70 MPa using a cylindrical ½” die, isostatically pressed at 250 MPa, and sintered at 890 °C for 15 h to form electrolyte support pellets. All pellets measured ~1.1 cm in diameter. ESB and YSB pellets measured ~3.1 mm and ~3.6 mm in thickness, respectively. The relative porosities of the ESB and YSB pellets were 90% and 85% of theoretical, respectively, as measured using ImageJ software (1.37v, Wayne Rasband).

Composite Ag-bismuth oxide cathode inks were prepared by adding Ag (Alfa Stock #41598) to the sieved oxide powders (volume ratio of Ag:bismuth oxide = 60:40). Ethanol and organic vehicles (α-terpineol as the solvent, di-n-butyl phthalate as the plasticizer, and polyvinylbuteral as the binder) were added (generally in a 3:1:2 volume ratio) until a viscosity appropriate for brushing was achieved. A similar recipe was followed for preparing the pure silver electrode ink. Symmetric cells were prepared by paint brushing the cathode slurry to each side of the bismuth oxide pellets, drying at 120 °C for 1 h, and firing at 750 °C for 1 h.

Electrochemical impedance analysis was performed using a Solartron 1260 Impedance/Gain-Phase Analyzer. Silver mesh current collectors and leads were pressed against the samples in a quartz reactor by the use of a ceramic screw-and-bolt assembly. Cell temperature was maintained at 650 °C for 100 h and monitored by a thermocouple flanking the sample. Cell response was measured over a frequency range of 32 MHz to 0.1 Hz, with an AC voltage amplitude of 100 mV. Cell responses were not corrected for porosity effects.

Electron probe microanalysis (EPMA, JEOL Superprobe 733) was performed on a sample with pure silver electrodes to determine if any diffusion of silver into the electrolyte had occurred during testing. A sample was annealed at 750 °C for 48 h, encased in epoxy resin and
set for 24 h. The sample was then polished down to 1 μm, and a linescan was performed across the electrolyte/cathode interface—the atomic percentage of each element present recorded at each position in the scan.

Cathode morphology was characterized by the use of a JEOL model JSM-6335F field-emission scanning electron microscopy (FESEM). Samples which had undergone long-term stability testing were compared against virgin samples to detect any visible microstructural changes that might have occurred during testing.

X-ray diffraction (XRD Philips model APD 3720) using Cu Kα1 (λ = 1.54056 Å) was employed to determine inter-phase reactivity between silver and ESB. The diffraction patterns of mixed raw powders were compared against mixed powders which were annealed at 750 °C for 48 h.

3.3 Results and Discussion

3.3.1. Compositional Optimization

The first goal of this study was to produce silver-bismuth oxide cathodes with ASR values comparable to those reported by Xia et al.39 Figure 3-1 shows the impedance spectra and corresponding trend in cathode ASR over a range of composition for the Ag-ESB system at 600 °C. A minimum value observed at 50 vol% ESB. This result is reasonable since, for a two-phase composite whose particle sizes are roughly the same, and assuming the solid phases and pores are randomly distributed and the porosity is open and sufficiently large, the 3PB length should reach a maximum if the two solid phases are present in equal fractions of the overall electrode volume. As discussed previously, 3PB length is important in two-phase composite cathode systems since the oxygen reduction reaction that is occurring can only proceed at sites where all three reactants are present—as the cathode 3PB length increases, so do the number of reaction sites, and hence cathode activation polarization decreases.
Electrode area specific resistance (ASR) was calculated from

\[
\text{ASR} = \frac{R_p A}{2}
\]

(3-1)

where \(R_p\) is the electrode polarization discussed above, \(A\) is the electrode area, and the factor ‘2’ is used to account for the fact that each cell contains two (approximately identical) electrodes. Note that electrode area does not account for electrolyte surface variations due to surface porosity.

Figure 3-2 shows the comparison of the ASR obtained in this study for Ag-ESB cathodes (on an ESB electrolyte) with the results adapted from Xia et al.\textsuperscript{39} for Ag-YSB (on YSZ honeycomb electrolytes) and other reported cathodes. The Ag-ESB composite cathode has an ASR of 0.18 \(\Omega\text{cm}^2\) at 600 °C, making it one of the lowest-resistance electrode systems reported to date and a significant improvement over that produced by Xia et al.\textsuperscript{39} who obtained an ASR of 0.3 \(\Omega\text{cm}^2\) at 600 °C for their Ag-YSB composite. Note that two samples of the Ag-ESB optimized composition were tested to confirm reproducibility. The second sample had a slightly higher value of ASR (0.20 \(\Omega\text{cm}^2\) at 600 °C), but was still significantly lower than the Ag-YSZ literature value.

3.3.2. Stability: Thermal Performance Decay due to Microstructural Evolution

Having met and exceeded the benchmark for cathode performance obtained in the literature, the long-term stability of these composites could now be assessed. Impedance spectra for the long-term testing of pure Ag, Ag-ESB and Ag-YSB systems at 650 °C are shown in Figure 3-3, with the data \(R_s\)-corrected for ease in comparison. That is, the high-frequency real-axis intercept (bulk resistance or \(R_s\)) of each spectrum has been subtracted from the real component of each data point in the spectrum. Plotted this way, the low-frequency real-axis
intercept corresponds to the electrode polarization resistance, $R_p$. It is clear from this figure that
the electrode polarization for each system increases with time.

Electrode ASR (calculated using Eq. 3-1) is plotted against time for all systems at 650 °C
in Figure 3-4. The initial zero time value of ASR for the Ag-YSB and Ag-ESB systems were
similar—0.04 $\Omega$cm$^2$ and 0.06 $\Omega$cm$^2$, respectively. Surprisingly, the Ag-YSB electrode system
exhibited lower resistance than the Ag-ESB system, despite the higher ionic conductivity of the
ESB phase. This could be due to surface porosity effects discussed above, but other
microstructural factors will be addressed below. Also, the resistance of these electrodes is
significantly lower than that reported by Xia for their Ag-YSB system at the same temperature
(greater than 0.1 $\Omega$cm$^2$), again, making it one of the lowest-resistance electrode systems reported
to date. Differences in processing routines could lead to variations in electrode porosity,
thickness, relative particle sizes, and inter-particle necking, accounting for the observed
differences in performance between the two studies and between the two electrodes Ag-YSB and
Ag-ESB. In addition, since the present electrode study was performed on electrolytes having the
same composition as the ionic conducting phase in the electrodes, the interfacial (electrode-
electrolyte) resistance may be lower than similar electrodes placed on YSZ electrolytes.

All systems experience significant increases in ASR during the 100 h stability
experiment—both the Ag-YSB and Ag-ESB electrode ASR values increased by around 70%
(from 0.04 $\Omega$cm$^2$ to 0.07 $\Omega$cm$^2$ (75%) and from 0.06 $\Omega$cm$^2$ to 0.10 $\Omega$cm$^2$ (67%) for Ag-YSB and
Ag-ESB respectively), while the pure Ag system experiences a near fourfold increase (from 0.92
$\Omega$cm$^2$ to 3.55 $\Omega$cm$^2$) during the same length of time. Linear regression of the data (based on the
first 10 h of testing) yields a degradation rate of 4.4x10$^{-4}$ $\Omega$cm$^2$/h for Ag-ESB and 1.2x10$^{-4}$
$\Omega$cm$^2$/h for Ag-YSB. The pure Ag electrode degrades at a rate more than two orders of
magnitude faster—\(8.7 \times 10^{-2} \Omega \text{cm}^2/\text{h}\). It should also be mentioned that the rate of change in ASR with time is linear for Ag-ESB electrodes, while for the Ag-YSB system deviates slightly from linearity beginning approximately 50 h after commencement of testing. For the pure Ag system, this rate of change is strongly non-linear and the non-linear trend is in the opposite direction compared to the Ag-YSB system. Various possible causes for these observations are addressed below.

Figure 3-5 plots the relative conductivity (from \(R_s\)) versus time for both bismuth oxide electrolyte systems. Relative conductivity is calculated as the ratio of the electrolyte conductivity (determined from impedance spectra high-frequency intercepts) at time, \(t\), to the initial conductivity value at \(t=0\). Both electrolytes seem to be relatively stable—both maintaining over 90% of their initial conductivities—however, YSB experiences significant decay in conductivity starting 50 h into testing, while ESB underwent a slight increase in conductivity (\(+3.0 \times 10^{-5} \text{ S cm}^{-1}/\text{h}\)). The trend for YSB is consistent with results reported by Fung and Virkar\(^5\) where YSB undergoes a cubic-rhombohedral phase transformation at this temperature. Post-mortem XRD studies confirm formation of a rhombohedral phase. Jiang and Wachsman\(^1\) showed that ESB undergoes no such phase transformation, which is consistent with the trend for ESB in Figure 3-5.

Since the resistance of bulk-related phenomena of both systems remained relatively constant during the first half of the stability test, it may be concluded that little if any defect ordering has occurred in the YSB and ESB electrolytes up to 50 h. It follows that minimal defect ordering has occurred in the bismuth oxide phase of each cathode over this period. Further, during this initial 50 h regime, the trend in electrolyte conductivity is slightly upward for ESB, and slightly downward for YSB. This trend is opposite to that observed for cathode ASR values,
where the cathode containing YSB decayed at a slower rate than that containing ESB, suggesting the impact of the bismuth oxide phase on cathode degradation is minor at this temperature. In addition, the ASR of the pure Ag electrode rises at a much faster rate than either composite system. Thus, it is suspected that the silver phase is the major source of the observed increase in electrode polarization. However, the more dramatic decay in YSB conductivity at longer times may cause the observed non-linear increase in ASR with time for the Ag-YSB system (Fig. 3-4), as the same phenomenon observed for the electrolyte conductivity may be occurring in the YSB phase inside the composite electrode.

EPMA, XRD, and FESEM analysis were performed on several samples to elucidate the compositional and microstructural changes that might transpire during testing. For EPMA measurements, Y$_2$O$_3$ and Bi$_2$O$_3$ standards were prepared by pressing and sintering pellets of the commercial powders. Figure 3-6 shows the results of EPMA testing on a YSB sample prepared with pure silver electrodes and annealed at 750 °C for 48 h. The atomic percent of all elements is consistent with what is expected on both sides of the interface. Thus, it is concluded that no silver has diffused across the interface into the electrolyte.

X-ray diffraction patterns of mixed silver and erbium-stabilized bismuth oxide powders (ESB) before and after heat treatment at 750 °C for 48 h are shown in Figure 3-7. The patterns reveal no evidence of inter-phase reactivity after heat treatment. Since silver neither diffused into nor reacted with the electrolyte phase at 750 °C, it is reasonable to assume the same is true for all samples tested at 650 °C.

Microstructural comparisons of the three different electrode systems before firing, after firing, and after testing at 650 °C for 100 h are shown in Figures 3-8 through 3-10. Energy dispersive spectroscopy (EDS) confirmed that for backscattered SEM images, the lighter phase
was ESB and the darker phase was Ag. All three systems exhibit a dramatic growth of the silver phase after firing at 750 °C for 1 h. However, the silver phase in the composite electrodes show significantly less growth and coalescence compared to the pure Ag system, as the ceramic phase helps restrict the migration and ultimate agglomeration of the silver phase. After 100 h of testing at 650 °C, the pure Ag electrode appears fully dense. The porosity of the Ag-ESB electrode decreased significantly after testing. Domains of coalesced silver are evident, and ESB particles between these domains have been forced closer together, further reducing porosity and 3PBs. Growth and coalescence of the silver phase is also evident in the Ag-YSB electrode though to a lesser extent. It is believed that the smaller starting size of the YSB particles (as evidenced in the unfired electrode micrographs) helped to lower the mobility of the silver phase by providing the electrode with a higher surface area through which the silver phase must migrate.

Although the primary function of the silver phase to conduct electrons toward the 3PBs is unaffected by these microstructural changes, increased grain size correlates with reduced 3PB lengths, and hence a smaller reaction zone for oxygen reduction. Further, increased density can lead to concentration polarization effects, where the reaction species (oxygen admolecules) are being supplied to the reaction sites more slowly than they are being consumed. The trends in electrode ASR shown in Figure 3-4 can be rationalized in terms of these microstructural observations. Pure Ag undergoes the most dramatic densification during testing, and also exhibits the most dramatic rise in ASR with time. It is reasonable to expect that as the densification process of Ag nears completion, changes in porosity and 3PB lines will slow, and hence the electrode ASR will level off at longer times, as was observed. The composite electrodes experience a much less severe change in microstructure after firing and during testing, particularly the Ag-YSB system. This is reflected in the two-order slower rate of ASR increase.
for these composite systems, and the slightly slower rate for Ag-YSB compared with Ag-ESB. The finer silver phase microstructure of the fired, untested Ag-YSB electrode relative to the untested Ag-ESB electrode may also explain why the electrode containing YSB exhibited the lower initial zero time ASR value despite the higher ionic conductivity of ESB.

Transgranular platelet structures similar to those observed by Fung\textsuperscript{55,56} were found in the YSB phase of the electrode and in the electrolyte near the electrode interface (not shown), consistent with the assertion that a cubic-rhombohedral phase transformation occurred during testing. This phase transformation likely led to the observed drop in electrolyte conductivity and rise in electrode ASR at longer times, both of which seem to begin around 50 h.

From the above observations, it is concluded that the main source of instability of the composite Ag-bismuth oxide electrodes is the migration of the silver phase, rather than reactivity or defect ordering of the stabilized bismuth oxide phase. Moreover, silver migration was demonstrated to be even more severe when operating under an applied bias\textsuperscript{57,58}. This issue as well as microstructural approaches toward improving the stability of these electrodes is discussed Chapter 4 of this dissertation.

3.4 Conclusions

Silver-bismuth oxide composite cathodes have been prepared which perform as well as (and even better than) similar composites presented in the literature. The long-term isothermal stability of pure silver, Ag-ESB, and Ag-YSB electrodes was examined. Each system exhibited significant increases in electrode area specific resistance during 100 h of testing at 650 °C under open-circuit conditions. On the basis of electrochemical impedance as well as chemical and microstructural analysis, it is concluded that Ag-bismuth oxide composites have inadequate microstructural stability for long-term, IT-SOFC cathode applications. Microstructural evolution of the silver phase is deemed to be responsible for degradation in performance over time due to
grain growth and electrode densification. However, since the microstructural evolution of the composite electrodes was not as severe as that of pure silver, and since the Ag-YSB composite, at least initially, was more stable than the Ag-ESB composite, it is likely that further improvements in stability for the composite system will result from replacing the relatively large bismuth oxide particles with smaller particles, or by infusing inert nano-sized oxide particles into the microstructure. This concept will be explored in Chapter 4 of this dissertation.
Figure 3-1. (a) Impedance spectra and (b) electrode ASR vs silver content of Ag-ESB showing compositional optimization at 600 °C, between 40-70 vol% Ag using 5 vol% composition steps.
Figure 3-2. Arrhenius plot, adapted from Xia et. al.,\textsuperscript{39} comparing the ASR of Ag-ESB (this work) with the best cathodes reported in the literature at the start of this study. [Adapted from Applied Physics Letters, Vol.82, C. Xia, Y. Zhang and M. Liu, Composite cathode based on yttria stabilized bismuth oxide for low-temperature solid oxide fuel cells, 901-903 (2003) with permission from American Institute of Physics.]
Figure 3-3. Impedance spectra obtained from a symmetrical Ag-ESB/ESB/Ag-ESB (a), Ag-YSB/YSB/Ag-YSB (b), and Ag/ESB/Ag (c) cells tested at 650 °C over a period of 100 h. The data are Rs-corrected. Arrows indicate direction of increasing time.
Figure 3-4. Electrode ASR vs. time for Ag-ESB, Ag-YSB, and pure Ag at 650 °C. Linear regression based on first 10 h of testing for each electrode system.
Figure 3-5. Change in electrolyte relative conductivity vs. time for ESB and YSB at 650 °C.
Figure 3-6. EPMA cross-section linescan of a sample having pure silver electrodes, annealed at 750 °C for 48 h.
Figure 3-7. XRD spectra of Ag-ESB powder mixtures before and after co-firing at 750 °C for 48 h. “F” markers identify cubic fluorite peaks of the ESB phase, “Ag” markers identify silver peaks.
Figure 3-8. SEM micrographs comparing the morphology of Ag-ESB electrodes before (a) and after (b) firing at 750 °C for 1 h and (c) after testing at 650 °C for 100 h.
Figure 3-9. SEM micrographs comparing the morphology of Ag-YSB electrodes before (a) and after (b) firing at 750 °C for 1 h and (c) after testing at 650 °C for 100 h.
Figure 3-10. SEM micrographs comparing the morphology of pure Ag electrodes before (a) and after (b) firing at 750 °C for 1 h and (c) after testing at 650 °C for 100 h. Delamination caused by fracturing for SEM analysis.
CHAPTER 4
IMPROVING THE STABILITY OF SILVER-BISMUTH OXIDE CATHODES THROUGH MICROSTRUCTURAL CONTROL

4.1 Introduction

Recent literature results demonstrate that a composite cathode consisting of a silver phase as the electronic conductor and a stabilized bismuth oxide phase (in this case yttrium stabilized bismuth oxide, YSB) as the ionic conductor exhibits outstanding performance, compared with other frequently studied systems (Fig 3.1). In Chapter 3, the stability of this system was assessed and determined to be a problem due to the high mobility of the silver phase. It was incidentally shown that composite electrodes which contained an oxide phase in addition to a silver phase exhibited better stability compared to pure silver electrodes. This effect has also been demonstrated in the literature. Furthermore, microstructural evolution and cathode ASR degradation was less severe when the oxide phase was composed of finer particles.

In addition, it was shown that operation under an applied DC bias causes an electromigration type effect on the silver phase, resulting in a build-up of silver phase at the electrode-electrolyte interface at one side of a symmetrical cell, and a migration of silver to the surface of the other side. Stable SOFC components should deliver relatively constant, non-changing performance for thousands of hours of operation. The goal of this study was to improve the stability of this electrode system under open-circuit conditions as well as under an applied DC bias through microstructural means.

4.2 Experimental

In this work, silver-ESB20 composite electrodes were studied because of the high ionic conductivity of ESB20. Also, based on the results presented in Chapter 3, ESB20 shows no phase transformation or defect ordering at the temperature of interest. Erbium oxide and bismuth
oxide powders were weighed in proper amounts to yield Er₀.4Bi₁.₆O₃. The powders were ball milled in ethanol for 24 h using YSZ grinding media, dried on a hot plate with stirring, then calcined at 800 °C for 10 h. The calcined powder was then crushed by mortar and pestle and sieved (325 mesh). Green ESB20 pellets were prepared by uniaxial pressing (approximately 70 MPa) followed by isostatic pressing (250 MPa). These green bodies were then fired at 890 °C for 15 h. The sintered pellets had densities 94% ±2% of theoretical, were 1.12 cm ±0.02 cm in diameter and 0.29 cm ±0.01 cm in thickness.

For the electrode slurry, the crushed and sieved ESB20 powders were either used as-prepared or a vibratory mill was used to reduce particle size. For vibratory milling, 10 g of powder plus 300 g of cylindrical zirconia grinding media and 200 ml isopropyl alcohol were placed into 250 ml Nalgene bottles. These bottles were covered with duct tape and placed into a Sweco model M18-5 vibratory mill for seven days using appropriate counter weights. Inks were prepared by combining organic vehicles with mixtures of metallic (silver) and ceramic (ESB20 alone or ESB20 and Tosoh 8YSZ) powders. Once an appropriate viscosity was reached (consistency of honey), the inks were applied to both sides of the electrolyte substrates by screen printing (AMI model HC-53 screen printer) to give symmetrically-electroded cells. The hole size of the screen printing mask was large enough to prevent preferential screening of larger particles. The electrodes had thicknesses of ~30 μm and geometric surface areas of ~0.79 cm². These cells were dried at room temperature for 1 h, followed by drying at 120 °C for 1 h. This process was repeated for a second coat. The doubly-coated cells were then fired at 750 °C for 1 h.

Electrochemical performance of the electrodes was assessed using impedance spectroscopy. Silver mesh current collectors and platinum lead wires were pressed against the
samples in a quartz reactor by the use of a ceramic screw-and-bolt assembly. The quartz reactor was placed into a temperature-controlled furnace, and air was fed through the reactor at 50 cc/min using a BOC mass flow controller. A Solartron 1260 frequency response analyzer was used in standalone mode for unbiased testing using a frequency range of 32 MHz to 0.01 Hz and an AC voltage amplitude of 100 mV. A Solartron 1287 interface was added for testing under an applied bias of 250 mV.

X-ray diffraction (XRD) patterns of various powders were recorded with a Philips APD 3720 diffractometer using Cu Kα1 (λ = 1.54056 Å). Step scans were taken over a range of 2θ angles from 20° to 100° with 0.04° steps.

Number-average particle size distributions were determined using a Brookhaven ZetaPlus instrument using a light scattering technique dilute suspensions of powder in an ethanol medium.

Scanning electron microscopy (SEM) was used to analyze electrode microstructures. Both JEOL JSM 6400 scanning electron microscope and JEOL JSM 6335F field emission scanning electron microscopes were used in this study for generating secondary and backscattered microstructural images.

4.3. Results and Discussion

4.3.1 Nano YSZ Additions

The addition of bismuth oxide grains acts to inhibit silver phase grain growth in silver-YSB composites. Further, a common method used to avoid grain growth in commercial alloys is to add a dispersion of fine particles, which restricts grain size according to

\[ R_L = \frac{r}{6f} \]  

(4-1)

where \( R_L \) is the limiting grain radius, \( r \) is the particle radius, and \( f \) is the volume fraction of particles—thus grain size is reduced by decreasing the particle size radius, or increasing the
volume fraction of particles (both of which increase the surface area of the particles).\textsuperscript{60} It is proposed that increasing the surface area of the ceramic phase in silver-containing cermets will further inhibit silver phase mobility. The first attempt to improve the stability of this electrode system involved the use of nano-sized ceramic particles. Nano-sized 8 mol\% YSZ powder was used in this study as it is readily available, relatively inexpensive (~$100 per kilogram, or 10\% the cost of GDC nano-sized particles), and non-reactive toward silver and ESB20 at the temperature range of interest (Fig. 4-2). Various YSZ/ESB compositions were tested, keeping the silver volume fraction constant. That is, cathodes with composition $\text{Ag}_x(\text{YSZ}_y-\text{ESB}_{1-y})_{1-x}$ were prepared, where $x = 0.5$, and $y = 0, 0.05, 0.10$, and 0.15 represent fractions of the total cathode solids volume.

Impedance spectra and electrode ASR (calculated from Eq. 3-1) versus time under no applied bias are shown in Figures 4-2 and 4-3, respectively. Two arcs are present in the spectra for all electrodes suggesting the impedance is governed by two competing processes, however it is not known at this time which electrochemical processes correspond to each arc. The arcs are more distinct for electrodes containing nano-sized YSZ, and it is clear that all samples containing the YSZ powder additions were significantly more stable compared to the YSZ-free sample. The electrode ASR degraded at a rate of $4.1 \times 10^{-4} \Omega \text{cm}^2/\text{h}$, $1.3 \times 10^{-5} \Omega \text{cm}^2/\text{h}$, $2.5 \times 10^{-5} \Omega \text{cm}^2/\text{h}$ and $3.1 \times 10^{-5} \Omega \text{cm}^2/\text{h}$ for 0\%, 5\%, 10\%, and 15\% YSZ, respectively. The largest stability improvement (a 97\% reduction in ASR vs. time slope) was achieved at the lowest YSZ loading, 5\%. In addition, the initial zero-time ASR value of this composition was 31\% less than that of the YSZ-free composition (0.043 $\Omega \text{cm}^2$ and 0.062 $\Omega \text{cm}^2$ for 5\% and 0\% YSZ, respectively), despite the substitution of 5 vol\% YSZ for the high conductivity ESB20 phase. Samples with higher concentrations of YSZ exhibited higher initial ASR values, as expected—$0.057 \Omega \text{cm}^2$ and
0.077 \Omega \text{cm}^2 for 10\% and 15\%, respectively—but showed electrode stability improvement over the non-YSZ composite. However, the ASR vs. time slopes increased as YSZ content increased.

A backscatter electron microscopy comparison between tested samples (Fig. 4-4) shows how the silver particles have been restrained from coalescence, allowing porosity to remain open and three phase boundaries to remain high, compared to the case with no YSZ additions. Further, the size of the silver grains decreases with increased YSZ content. Figure 4-5 is a secondary electron image comparing the 15\% YSZ sample before and after testing. Grain size and porosity appear to be comparable before and after testing. However, the edges of the silver particles in the as-fired sample are smooth, while in the tested sample, the edges are rough, due to envelopment of YSZ into the silver particles. It is possible that this effect further reduces the 3PB length between metallic, gaseous, and ESB20 phases, contributing to the observed increase in ASR with time for these electrodes. This could also explain the observed increased ASR vs. time slopes with increasing YSZ content.

4.3.2. ESB20 Particle Size Reduction

The second attempt to improve electrode stability involved reduction of initial particle size of the ESB20 powder. This strategy is similar to the addition of nano-YSZ particles—more energy is required for the silver phase to migrate over a given distance in the electrode. However, the overall ionic conductivity of the cathode as well as the reactive 3PB lines should not be compromised, unlike YSZ additions. This is also a more cost-effective approach than strategies involving alloying silver with precious metals to reduce Ag mobility, as suggested by Jaiswal et. al.\textsuperscript{57}

Figure 4-6 shows the reduction in particle size that was obtained from the use of vibratory milling. Number average particle size was reduced from \sim 1 \mu m to \sim 300 nm. Note that the size
distributions may be skewed to lower particle sizes since larger particles settle out of suspension quickly, and consequently may be omitted from the measurement count. All ESB powders were ground with YSZ ball media—both ball milled and vibratory milled powders. In addition, the hardness of ESB20 is much lower than that of YSZ. Further, the mass of the ball media used before and after ball milling and vibratory milling was nearly unchanged (< 0.01 wt%). Hence YSZ contamination from milling should be minimal and is expected to have little influence on the results.

The long term, unbiased impedance study comparing composites prepared with (ESB<sub>VM</sub>) and without (ESB<sub>S</sub>) vibratory milling of the ESB20 phase, shown in Figures 4-7 and 4-8, reveal the vast improvement in stability the reduction in ESB20 particle size imparts on this system. As in Chapter 3, linear trends in ASR with time are observed, and the degradation rate of silver-ESB20 composites at 650 °C was reduced from 4.10x10<sup>-4</sup> Ω cm<sup>2</sup>/h to 1.91x10<sup>-5</sup> Ω cm<sup>2</sup>/h—a 95% drop with the reduced ESB20 particle size.

As can be seen in Figure 4-8, the initial, zero time ASR value was also lowered by 25%, from an already-low 0.062 Ω cm<sup>2</sup> for the Ag-ESB<sub>S</sub> composite to 0.048 Ω cm<sup>2</sup> for the Ag-ESB<sub>VM</sub> composite—this is most likely due enhanced 3PB and may be attributed to suppression of silver migration during electrode sintering, leaving both porosity and 3PB length high.

This experiment was repeated with an external 250 mV DC bias applied across the cells to simulate operating conditions, and the results are shown in Figures 4-9 and 4-10. The improvement in performance and stability is evident, though not as pronounced as the unbiased case. After about 15 hours of testing, the ASR exhibits a linear increase with time. The ASR vs. time slope under 250 mV bias at 650 °C is reduced by 50% (from 1.6x10<sup>-3</sup> Ω cm<sup>2</sup>/h to 8.0x10<sup>-4</sup> Ω cm<sup>2</sup>/h) when smaller ESB20 particles are used to prepare the composite electrodes.
Both macroscopic and microscopic changes in the electrodes prepared with larger ESB20 particles before and after bias testing are immediately recognized (Fig. 4-11). Optically, after testing, the electrode surface of the working electrode was silver in color. The counter electrode of the tested cell appeared red in color, and a ring of silver color could be seen along its edge. The microstructural changes are also dramatic. A cross-sectional view of the counter electrode shows silver dendrite-like structures at the electrolyte interface, and nearly pure ESB20 at the electrode surface. The silver phase clearly migrates in one direction—towards the electrode/electrolyte interface in the counter electrode and towards the surface of the working electrode. Oxygen is reported to have high solubility and mobility in silver.\textsuperscript{51,52} It is possible that the application of a bias across the cell leads to an electro-migration effect where the silver phase is dragged along in the direction of oxygen flux, as observed by Jaiswal et. al.\textsuperscript{57}

In contrast, the microstructure of the counter and working electrodes prepared with vibratory milled ESB20 particles after bias testing are quite comparable and no segregation of silver phase at the counter electrode/electrolyte interface is detected (Fig. 4-12), indicating silver phase migration was significantly suppressed by the smaller particle size. So, not only did the small ESB20 particles reduce initial ASR, and enhance microstructural stability with no bias, but also improved microstructural stability under bias testing.

4.4. Conclusions and Future Work

Addition of 5 vol\% 8YSZ nano powders significantly improved unbiased electrode stability by 97 %, and reduced the initial, zero time ASR value by 31 %. Similar results were obtained when YSZ-free electrodes were prepared from ESB20 powders composed of particles hundreds of nanometers in size as opposed to electrodes prepared from ESB20 powders composed of micron-sized particles—the zero time ASR value was reduced by 25 %, and ASR vs. time slope during unbiased testing of the silver-ESB20 system at 650 \textdegree C was reduced by 95
Finally, ASR vs. time slopes during testing under a 250 mV external applied bias were lowered by 50% using the smaller ESB20 particles due to suppression silver phase electromigration. The stability of composite silver-ESB20 electrodes under an applied bias still needs some improvement. Improvements are likely with further reduction in ESB20 particle size down to several tens of nanometers. Also, as the operating temperature of SOFCs is reduced, the migration of the silver phase will be suppressed even further. These electrodes perform well even in the 500-550 °C range, but defect ordering in the bismuth oxide phase becomes an issue at these temperatures. Currently research is being done to overcome this issue as well.61
Figure 4-1. XRD spectra of Ag-ESB-YSZ powder mixtures before and after co-firing at 750 °C for 10 h.

Figure 4-2. Nyquist plots for silver-ESB20 composite electrodes containing 0 vol% (a), 5 vol% (b), 10 vol% (c), and 15 vol% (d) 8YSZ nanoparticles. Samples were tested at 650 °C in air for 100 h under no applied bias. Note that the electrolyte resistance has been subtracted from all Nyquist plots.
Figure 4-3. Effect of time on ASR of silver-ESB20 composite electrodes containing various volumetric amounts of 8 mol% YSZ nanoparticles. Measurements taken at 650 °C in air under no applied bias.
Figure 4-4. Backscatter electron microstructural images of tested [650 °C, 100 h in air under no applied bias] silver-ESB20 electrodes containing 0 vol% (a), 5 vol% (b), 10 vol% (c), and 15 vol% (d) 8YSZ nanoparticles.
Figure 4-5. Secondary electron microstructural images of an untested (a) and tested (b) silver-ESB20 electrodes containing 15 vol% 8YSZ nanoparticles.

Figure 4-6. Results of particle size analysis (number average) for the sieved and vibratory-milled ESB20 powders.
Figure 4-7. Nyquist plots (a) and imaginary part of impedance plotted as a function of log-scale frequency (b) for 50-50 vol% silver-ESB20 composite electrodes, where the ESB20 phase was prepared from sieved (larger curves) and vibratory milled (smaller curves) powders. Samples were tested at 650 °C in air for 100 h under no applied bias. Note that the Nyquist plots have been shifted so that the high frequency intercept with the real axis crosses at 0 Ω.
Figure 4-8. Electrode ASR vs. time for 50-50 vol% silver-ESB20 composite electrodes, where the ESB20 phase was prepared from sieved (triangles) and vibratory milled (circles) powders. Samples were tested at 650 °C in air for 100 h under no applied bias.
Figure 4-9. Nyquist plots (a) and imaginary part of impedance plotted as a function of log-scale frequency (b) for 50-50 vol% silver-ESB20 composite electrodes, where the ESB20 phase was prepared from sieved (larger curves) and vibratory milled (smaller curves) powders. Samples were tested at 650 °C in air for 40 h under a 250 mV bias. Note that the electrolyte resistance has been subtracted from all Nyquist plots.
Figure 4-10. Electrode ASR vs. time for 50-50 vol% silver-ESB20 composite electrodes, where the ESB20 phase was prepared from sieved (triangles) and vibratory milled (circles) powders. Samples were tested at 650 °C in air for 40 h under a 250 mV bias.
Figure 4-11. Microstructural images of silver-ESB20 composite electrodes, where the ESB20 phase was prepared from sieved powders—surface before testing (a) and cross-section of the counter electrode (b), working electrode surface (c), and counter electrode surface (d) of a cell after 48 h of testing at 650 °C under a 250 mV applied bias.
Figure 4-12. Cross-sectional microstructural images of silver-ESB20 composite electrodes, where the ESB20 phase was prepared from vibratory milled powders, after 48 h of testing at 650 °C under a 250 mV applied bias—working electrode (a) with close-up view of the working electrode/electrolyte interface (b) and counter electrode (c) with close-up view of the counter electrode/electrolyte interface (d).
CHAPTER 5
HIGH PERFORMANCE COMPOSITE Bi$_2$Ru$_2$O$_{7-\delta}$-Bi$_{1.6}$Er$_{0.4}$O$_3$ CATHODES FOR IT-SOFCs

5.1 Introduction

The critical role microstructure plays in the electrochemical performance of composite cathode systems has been demonstrated. In Chapter 3 the isothermal instability of a composite cathode consisting of Ag as the electronic conducting phase and ESB20 as the ionic conducting phase was demonstrated.\textsuperscript{59} The study showed a 70% rise in ASR for Ag-ESB20 from 0.06 $\Omega \text{cm}^2$ to 0.10 $\Omega \text{cm}^2$, after 100 h at 650 $^\circ$C. Microstructural evidence revealed a correlation between agglomeration of the constituent phases (arising from migration of the silver phase) and the increased resistance. Chapter 4 showed that this microstructural evolution could be inhibited using nano-sized ceramic particles, resulting in a 95% reduction in the ASR degradation rate, as well as a 25% reduction in the initial ASR.\textsuperscript{62} From these studies, it is clear that relative particle sizes, agglomeration, and phase segregation can have dramatic impact on 3PB lengths and the surface area of catalytic active sites, and thus electrode resistance. In addition, the electrode thickness and the addition of current collection layers can influence performance by altering in-plane electronic conduction, as well as mass transport.\textsuperscript{13,39} In this chapter, these microstructural considerations will be used in order to improve the performance of a new class of SOFC cathodes—ruthenate oxide – ESB20 composites.

Ruthenium oxides are known to be catalytically active for oxygen reduction.\textsuperscript{63,64} By selection of a sufficiently large A-site dopant cation in ($A_2$Ru$_2$O$_7$), such as Pb or Bi, its band structure is altered in such a way so as to render its behavior metallic, with conductivity increasing as temperature decreases.\textsuperscript{65} These properties make metallically-conductive ruthenate oxides good candidates for SOFC composite cathodes.
It was recently demonstrated that composite cathodes consisting of Bi$_2$Ru$_2$O$_7$ (BRO7) as the electronic conducting phase and ESB20 as the ionic conducting phase on GDC electrolytes exhibit outstanding performance compared with other frequently studied systems. The low resistance ($3.47 \, \Omega \text{cm}^2$ and $0.08 \, \Omega \text{cm}^2$ at 500 °C and 700 °C, respectively) of this composite may be attributable in part to the high ionic conductivity of the ESB20 phase in combination with the catalytic activity of the ruthenate phase. Note that bismuth was chosen as the A-site dopant, as it is the same as the host cation of the ESB20 phase, and should improve chemical compatibility. Additionally, bismuth ruthenates have been reported to have better stability than lead ruthenates above 600 °C.\textsuperscript{67,68}

The goal of this study is to reduce the ASR of the BRO7-ESB20 electrode system on ESB20 electrolytes by microstructural optimization.

5.2. Experimental

5.2.1. Electrolyte and Electrode Preparation

A conventional solid-state synthesis route was used to prepare ESB20 and BRO7 powders. Er$_2$O$_3$ (99.99 %, Alfa Aesar) and Bi$_2$O$_3$ (99.999 %, Alfa Aesar) powders were weighed in proper proportions to yield Er$_{0.4}$Bi$_{1.6}$O$_3$. The same raw Bi$_2$O$_3$ powder and RuO$_2$·XH$_2$O (99.99 %, Alfa Aesar, where the moles of hydration, X, varies with batch used, normall X≈2.8) were weighed in stoichiometric amounts to yield Bi$_2$Ru$_2$O$_7$. The respective powders were ball milled in ethanol for 24 h using YSZ grinding media, dried on a hot plate with stirring, then calcined at 800 °C for 15 h (for ESB20) or at 900 °C for 10 h (for BRO7). The calcined BRO7 powder was leached in HNO$_3$ to remove an impurity sellinite phase as described by Jaiswall.\textsuperscript{66} The ESB20 and BRO7 powders were separately crushed by mortar and pestle and sieved (325 mesh).

Green ESB20 pellets for use as electrolyte supports were prepared by uniaxial pressing (approximately 70 MPa) followed by isostatic pressing (250 MPa). These green bodies were
then fired at 890 °C for 15 h. The sintered pellets had densities 94% ±2% of theoretical, were 1.12 cm ±0.02 cm in diameter and 0.29 cm ±0.01 cm in thickness.

For the electrode slurry, the crushed and sieved ESB20 powders were either used as-prepared or a vibratory mill was used to reduce particle size. For vibratory milling, 10 g of powder plus 300 g of cylindrical zirconia grinding media and 200 ml isopropyl alcohol were placed into 250 ml Nalgene bottles. These bottles were covered with duct tape and placed into a Sweco model M18-5 vibratory mill for seven days using appropriate counter weights.

Sedimentation was performed to further reduce particle size and size distribution. Powders were mixed in a medium (1 g / 50 ml ratio) in Nalgene bottles, ultra-sonicated for 30 min to break up soft agglomerates, and allowed to settle for ~24 - 48 h. The supernatant was carefully collected with pipettes and dried to 80 °C. Note that isopropanol was used as the sedimentation medium in preference to de-ionized water to avoid the formation of Bi(OH)₃ platelettes which convert to α-Bi₂O₃ upon firing. The subscript designation and volume mean diameter, dᵥ, for each starting powder is given in Table 5-1.

BRO7 and ESB20 powders were then weighed in appropriate ratios. For studies involving the use of sonication and sedimentation, BRO7-ESB20 powders were combined in isopropanol and ultra-sonicated to achieve more intimate mixing. Inks were prepared by combining organic vehicles with these mixtures of BRO7 and ESB20 powders or pure BRO7 for the current collector. Once an appropriate viscosity was reached, the inks were applied to both sides of the electrolyte substrates by paint brushing to give symmetrically-electroded cells. These cells were dried at room temperature for 1 h, followed by drying at 120 °C for 1 h, and firing at 800 °C for 2 h. Note that in order to vary electrode thickness, or for the addition of the current collector, successive layers were added after the drying stage, but before the firing stage. This was done to
reduce densification and grain growth within the cathode, as well as minimize ruthenium loss in the volatile BRO7 phase, both of which that may occur when firing each coat separately. Two was the standard number of coats applied to each cell.

For testing under SOFC operating conditions, dense YSZ pellets with reference electrode bores were prepared. YSZ pellets with 99% theoretical density were prepared by slip casting into a porous mold. The slip suspension was prepared using 30 vol% 8YSZ powder (Tosoh) in de-ionized water and an appropriate amount of citric acid pre-dissolved (~0.3 wt% citric acid to YSZ). Ammonium hydroxide was added dropwise to the mixture, with vigorous shaking, until a water-like consistence was reached. The slip was allowed to dry in the mold for 1 day and polished into flat disks of ~2 mm thickness. Holes were carefully drilled halfway into the green pellets with a 1/16 inch bit. The pellets were then fired at 1400 °C for 4 h. NiO-YSZ (50-50 wt%) pasts were applied to the hole-free side of the YSZ pellets, dried, and fired at 1300 °C for 1 h. Pt wire was beaded on one end using a torch, dipped into Pt paste, carefully inserted into the hole, and fired at 1100 °C for 2 h, along with a Pt current collector on the anode side of each cell. The cathodes (LSM-YSZ, LSCF-GDC, and BRO7-ESB) were then applied and fired at appropriate temperatures and times. LSM20 powders were obtained from Nextech Corporation, 8YSZ from Tosoh, LSCF from Praxair, and GDC10 from Rhodia, Inc. BRO7 and ESB powders were prepared in-house as described above. Pt current collectors were applied to LSM-YSZ and LSCF-GDC cathodes. A pure BRO7 current collector was applied to the BRO7-ESB cathode. Current collectors were co-fired with each cathode. In order to improve the mechanical strength of the reference electrode, the hole was backfilled with YSZ slip and fired at 700 °C.

Anode-supported cells were prepared by co-pressing ~0.35 g GDC powder onto a NiO-GDC substrate (~4 g) in a 1 1/8” cylindrical die. The NiO-GDC substrate was first pressed at
~14 MPa. Next, GDC was carefully and uniformly spread across the surface, and pressed at ~42 MPa. The pellets were then pressed isostatically at 250 MPa, and fired at 1450 °C for 4 h using a 3 °C/min heating rate and a 400 °C, 1 h binder burnout step. The cells were then electroded in the usual fashion.

5.2.2. Characterization

Electrochemical performance of the electrodes was assessed using impedance spectroscopy. Silver mesh current collectors and platinum lead wires were pressed against the samples in a quartz reactor by the use of a ceramic screw-and-bolt assembly. The quartz reactor was placed into a temperature-controlled furnace, and air was fed through the reactor at a rate of 50 cc/min using a BOC mass flow controller. A Solartron 1260 frequency response analyzer was used in standalone mode for unbiased testing using a frequency range of 32 MHz to 0.01 Hz and an AC voltage amplitude of 100 mV.

X-ray diffraction (XRD) patterns of various powders were recorded with a Philips APD 3720 diffractometer using $\lambda_{K\alpha(Cu)} = 1.5406 \text{ Å}$. Step scans were taken over a range of 20 angles from 20° to 100° with 0.04° steps.

A JEOL JSM 6400 scanning electron microscope (SEM) was used in this study for microstructural characterization. In addition, a JEOL TEM 200CX transmission electron microscope (TEM) was also used in this study for particle size characterization. Average particle sizes and electrode porosities were characterized statistically from SEM and TEM micrographs using ImageJ software.

For each powder, the volume mean diameter, $d_v$, was calculated from Eqn. (5-1)
\[ d_v = \sqrt[3]{\frac{\sum_{i=1}^{n} d_i^3}{n}} \]

where \(d_i\) is the equivalent sphere diameter of each particle and \(n\) is the total number of particles analyzed by the ImageJ software. Note that particle sizes are reported in terms of a volume-average as opposed to a number-average as this choice is more consistent with other commonly-reported microstructural properties such as porosity and composition.

Statistical stereology on epoxy-resin embedded, polished samples revealed that all electrodes had \(\sim\)40 vol\% porosity.

For current-voltage measurements, cells were sealed (anode side) to an alumina tube using ceramabond (Aremco). The setup was then placed into a furnace, cured, and taken up to testing temperature. Air and \(\text{H}_2/\text{H}_2\text{O}\) gas mixtures were used as the oxidant and fuel gases, respectively. Flow rates were maintained at 30 ccm using mass flow controllers. Cell OCP was monitored using a Solartron 1287 potentiostat until a stable value was reached, and current-voltage measurements were taken with the same instrument. A Solartron 1260 frequency response analyzer was used for impedance measurements.

5.3. Results and Discussion

5.3.1. Chemical Compatibility

Chemical stability testing results between BRO7 and ESB20 are shown in Fig. 5-1. XRD patterns of BRO7 and ESB20 powder mixtures before and after heat treatment at 800 °C for 10 h are comparable, and reveal no evidence of inter-phase reactivity, suggesting these materials are chemically compatible at this temperature.
5.3.2. Reproducibility/Compositional Optimization

Before any microstructural optimization was conducted, BRO7-ESB20 composites were first compositionally optimized on ESB20 electrolytes using readily available powders—ESB20 prepared from conventional solid-state synthesis and solid-state BRO7 powders which underwent an additional vibratory milling step (ESB20_s-BRO7_VM). Optimization in composition was constrained between 25 and 75 wt% ESB with steps of 12.5 wt% ESB (and 6.25 wt% ESB at critical intermediate compositions). ESB Figure 5-2 shows typical impedance and Bode spectra obtained at 625 ºC in air under no applied bias. Note that as in previous chapters, these and all future impedance plots have been Rs-corrected for ease in comparison. That is, the high-frequency real-axis intercept, Rs, of each spectrum, which is composed of the bulk electrolyte resistance and possibly electrode sheet resistance and lead contact resistance, has been subtracted from the real component of each data point in the spectrum. At 625 ºC, each impedance plot appears to be composed of a single arc (Fig. 5-2a), and the characteristic frequency increases with ESB20 content (Fig. 5-2b). It is interesting to note that the width of the imaginary impedance vs. log frequency spectrum is narrower toward the extremes of the concentration range than at intermediate compositions, suggesting a mechanistic overlap at these intermediate compositions, and in fact, a minimum value is observed at 56 wt% ESB20 over the range of temperatures tested.

Figure 5-3 shows the trend in cathode ASR (calculated from Eq. 3-1) vs. composition for the ESB20_s-BRO7_VM system over a range of temperatures. Since the densities of BRO7 and ESB20 are approximately the same (~8.9 g/cm³), the observation of an ASR minima near 50 wt% of each phase is consistent with the effective medium percolation theory and 3PB maximization. For a two-phase composite whose particle sizes are roughly the same, and assuming the solid phases and pores are randomly distributed and the porosity is open and
sufficiently large, the 3PB length should reach a maximum if the two solid phases are present in equal fractions of the overall electrode volume. In the ESB20s-BRO7_{VM} study, BRO7 particles are a factor of ~2 smaller than ESB20 particles hence percolation and 3PB length maximization can occur at non-equal volume fractions of the two phases. As discussed above, 3PB length is important in two-phase cathode systems since the oxygen reduction reaction that is occurring can only proceed at sites where all three reactants are present—as the cathode 3PB length increases, so do the number of reaction sites, and hence cathode activation polarization decreases.

Note that this result differs from earlier results,^66 where a minimum was observed between 31-43 wt% ESB. One possible explanation may be differences in powder synthesis techniques between the two studies. ESB20 was obtained through conventional solid state synthesis in this study (micron-sized particles), as opposed to a wet chemical route (yielding nano-sized particles) used by Jaiswall, et al.~^66 Further, in the present study the BRO7 powders were vibratory milled for seven days versus three days (Jaiswall, et al.);~^66 hence, yielding, on average, smaller BRO7 particles in the present study. Consequently, the ESB20-to-BRO7 particle size ratio in the present study should be appreciably larger. As the ESB20-to-BRO7 particle size ratio decreases, percolation of the ESB20 phase—and hence compositional optimization of the cermet cathode—becomes feasible at smaller ESB20 volume fractions.

Note that there also appears to be a difference in activation energies between the electrodes obtained in this study (1.02 eV) compared with Jaiswall, et al. (~1.3 eV).~^66 The electrode ASR at 500 °C are comparable (3.11 Ωcm² for the present study compared to 3.37 Ωcm²), but are quite different at 700 °C (0.17 Ωcm² for the present study compared to 0.08 Ωcm²). It is not clear at this juncture what mechanism leads to this lower activation energy. It has frequently been reported that the surface of bismuth oxide-based electrolytes is active for the adsorption of
oxygen species. It is believed that bismuth strongly enhances the surface oxygen exchange rate.\textsuperscript{69-71} This is evidenced by the factor of 10\textsuperscript{3} larger surface oxygen exchange rate for bismuth oxide based solids compared to YSZ solids. In addition, bismuth-based electrolytes have been reported to be catalytically active towards oxygen dissociation and charge transfer.\textsuperscript{72,73} It is thus possible that the use of ESB20 (rather than GDC) as the electrolyte support, which results in additional ESB20 sites at the cathode/electrolyte, may result in the observed drop in activation energy.

### 5.3.3. Optimization by Particle Size Ratio

Having shown an acceptable level of reproducibility in performance, microstructural optimization was next carried out. Given the difference in optimum concentration between the two compositional studies discussed above, careful consideration was given with respect to the choice of concentration to use for the microstructural study. It was decided to fix the BRO7-ESB20 composition at 50-50 wt\% (approximately 50-50 vol\%) so as to minimize any possible bias that might arise from skewing the composition toward either end of the spectrum.

Electrode microstructure was first optimized according to starting particle size ratio, constrained to the particle sizes obtained from crushing and sieving as well as vibratory milling. Particle sizes of the constituent phases were altered using vibratory milling as well as a combination of sonication and sedimentation, as explained in the experimental section. Figures 5-4 and 5-5 show representative samples of each particle system used in the present study. Figure 5-4 compares BRO7 and ESB20 powders as prepared from solid state synthesis, and directly after vibratory milling. Particle size analysis (from imaging software) reveals that the volume mean diameter was reduced by a factor of approximately two after seven days of vibratory milling—from \(\sim 1.31 \mu m\) to \(\sim 0.73 \mu m\) for BRO7 and from \(\sim 1.31 \mu m\) to \(\sim 0.81 \mu m\) for
ESB20. Note however that each set of vibro-milled powders still contains a small number fraction (but significant volume fraction) of large, unbroken particles. Figure 5-5 shows the further reduction in particle size and agglomeration that can be obtained by sonication and sedimentation.

Four different electrode structures were first examined using only “as-prepared” powders (BRO7$_S$-ESB20$_S$, BRO7$_S$-ESB20$_{VM}$, BRO7$_{VM}$-ESB20$_S$, and BRO7$_{VM}$-ESB20$_{VM}$), each containing a 1:1 volume ratio of the constituent phases. An SEM image of the four fully-fired electrodes is shown in Figure 5-6.

Figure 5-7 shows typical impedance spectra and Bode plots obtained at 625 ºC for these electrodes in air under no applied bias. Plots of ASR vs. reciprocal temperature are given in Figure 5-8. These results show that the composites exhibiting the lowest resistance are those composed of both large and small particles. All composites containing at least one vibro-milled phase have significantly lower resistance than the composite composed entirely of large particles, as expected, due to the increased 3PBs. The activation energies for all electrodes are similar (1.03eV ± 0.03eV), as are their characteristic frequencies (Figure 5-7b), suggesting a common rate-determining mechanism for the different electrodes. It is not known at this time which mechanism is dominant; more work is needed to clarify this issue via testing under different oxygen partial pressures. However, it is evident that the magnitude of the impedance of this mechanism has been markedly affected by these microstructural considerations.

Comparing the two systems where the different phases have more similar grain size (BRO7$_{VM}$-ESB20$_{VM}$ and BRO7$_S$-ESB20$_S$), the electrode composed of vibro-milled particles exhibits the lower ASR, as expected. The systems composed of dissimilarly-sized particles (BRO7$_{VM}$-ESB20$_S$ and BRO7$_S$-ESB20$_{VM}$) exhibit nearly the same performance, with the
BRO7_{VM}-ESB20_{S} electrode having the lowest ASR of 0.43 Ωcm^2 at 625 °C. Interestingly, the electrodes containing dissimilar grain sizes exhibit lower ASR values than the electrodes containing more similar grain sizes, despite being shifted towards non-optimal composition ratios, as discussed above. Recall that, although the optimal composition of BRO7_{VM}-ESB20_{VM} was 56 wt% ESB20, for the microstructural study a 1:1 ratio was used. One possible explanation for this observation could be the formation of soft agglomerates of fine particles during synthesis, as can be seen for the as-prepared ESB20_{VM} and BRO7_{VM} powder in Figure 5-5.

Another possibility, as discussed in Section 2.5, is that smaller particles create a larger degree of microstructural tortuosity, which can restrict gas phase diffusion.\(^{13}\)

Note also that initially, samples used in this study were prepared with a single coat of cathode paste. However a large drop in the ASR of the BRO7_{S}-ESB_{VM} was observed when a sample of greater thickness was tested, hence a two-coat standard for thickness was adopted. The effects of cathode thickness on performance is discussed in Section 5.3.5.

### 5.3.4 Sonication and Sedimentation

As mentioned in Section 5.3.3, as-prepared vibratory-milled powders contain a significant volume fraction of unbroken, micron-sized particles. Focused ion beam (FIB) analysis and reconstruction (a video file which can not be reproduced here) also reveals a degree of phase segregation in the fired electrodes. The next stage in the microstructural development involved the use of sedimentation for further reductions in particle size and a narrower particle size distribution. Also, ultra-sonication was used to break up soft agglomerates and improve phase distribution in the cathode.

The results are shown in Figures 5-9 and 5-10. Impedance results show a large reduction in resistance for all systems where the raw vibro milled phase was replaced with the supernatant phase. It is clear from Figure 5-9b that the impedance spectrum of the fully-supernatant
composite is composed of two arcs. Comparing the spectrum of this electrode with the other electrodes, it appears that the low frequency process is the most affected by these microstructural changes, and its resistance has been lowered to the point where the low and high frequency processes are in competition with each other.

Figure 5-10 overlays the Arrhenius behavior of composites which underwent sonication and sedimentation with those composed of as-prepared powders. Both composites consisting of a mixture of large and small particles underwent comparable ASR reductions. However, the ASR reduction was the most dramatic for the composite comprised entirely of small particles. Clearly this composite benefits the most from the combination of reduced particle size and the more intimate sonicated mixing. Not only were the soft agglomerates of each phase broken up, but also the reduced particle size distribution translates into a larger number fraction of sub-micron sized particles in each vibratory milled phase. This in turn translates into a larger 3PB length. As discussed in Section 5.3.3 reduction in particle size gives rise to increased tortuosity which can inhibit gas phase diffusion. However, as mentioned above, the spectra presented in Figure 5-9 indicate that a reduction in particle size, size distribution, and phase agglomeration provided by sonication and sedimentation primarily reduces the impedance of a single low-frequency process. Since a higher-frequency process is only discernable once the impedance of the low-frequency process is dramatically reduced, it is reasonable to conclude that the improvements provided by increased 3PB lengths vastly outweigh any degradation resulting from increased tortuosity. The minimum ASR observed was 0.10 $\Omega \text{cm}^2$ at 625 °C for the ESB20\textit{SUP}-BRO7\textit{SUP} system.
5.3.5. Effect of thickness and current collection

The effect of thickness on ASR for the different composite microstructures is illustrated in Figure 5-11. In each case, ASR is reduced as thickness is increased, over the range of thicknesses studied. The ESB20\textsubscript{SUP}-BRO7\textsubscript{S} system exhibited a one order of magnitude drop in ASR between the first and second coating. This observation was confirmed to be reproducible (from repeated testing on once-coated samples), and is believed to be due to a current collection issue where the electrode thickness is insufficient for BRO7 phase percolation. That the ESB20\textsubscript{S}-BRO7\textsubscript{S} system did not show as significant an ASR reduction as the ESB20\textsubscript{SUP}-BRO7\textsubscript{S} system can be attributed to a reduction in BRO7 phase connectivity caused by the fine ESB20\textsubscript{SUP} particles percolating between adjacent BRO7\textsubscript{S} grains. The volume percent porosity (open symbols) of each composite tested is overlaid on Figure 5-11, and is relatively constant (40±7 vol%). There is no apparent trend between thickness and porosity over this narrow range, and hence the porosity variation between electrodes tested is expected to have minimal influence on the thickness vs. ASR results. It is also interesting to note that electrode ASR continues to drop, even at thicknesses beyond 100-200 μm. As stated in Section 2.4, in general, if the conductivity of the ionically conducting phase in a composite electrode is sufficiently high, the effective charge transfer resistance will decrease with thickness down to an asymptotic value. This indeed appears to be the case in Figure 5-11, and the exceedingly high ionic conductivity of the ESB20 phase may explain why dominant concentration polarization effects do not show up at these electrode thickness values.

In order to improve connectivity of the electronic conducting phase, a new batch of twice-coated samples was prepared, this time using a pure BRO7\textsubscript{S} current collector layer. This layer did not adhere well to the two electrode systems which utilized fine particles of ESB20.
However, for the other systems, there is a dramatic drop in the resistance of the low-frequency process, as shown in Figure 5-12. For the BRO7SUP-ESB20s system, the high-frequency process now seems to dominate the performance. As shown in Figure 5-13, the ASR of these systems was reduced significantly—by factor of four (from 0.58 $\Omega \text{cm}^2$ to 0.15 $\Omega \text{cm}^2$) in the ESB20s-BRO7s system, and by a factor of three (from 0.22 $\Omega \text{cm}^2$ to 0.076 $\Omega \text{cm}^2$) in the ESB20s-BRO7SUP system. The former system composed of large BRO7 grains exhibited a larger overall ASR reduction than the system composed of fine BRO7 grains, as expected from enhanced current collection. That is, percolation and phase connectivity is more easily achieved when the phase is comprised of small particles and more difficult when the phase is comprised of large particles. Thus, it is expected that the ESB20s-BRO7SUP system will have inherently better electronic phase connectivity than the ESB20s-BRO7s system, hence introduction of a current collecting layer should have less of an influence in the former system. The ESB20s-BRO7SUP system exhibited the lowest ASR of all systems studied (0.73 $\Omega \text{cm}^2$ and 0.03 $\Omega \text{cm}^2$ at 500 ºC and 700 ºC, respectively). This is a marked improvement over earlier results (3.47 $\Omega \text{cm}^2$ and 0.08 $\Omega \text{cm}^2$ at 500 ºC and 700 ºC, respectively) and is comparable to landmark results reported by Zhao and Haile$^{46}$ for Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF), especially at lower temperatures due to the lower activation energy of BRO7-ESB20 compared with BSCF.

Further improvements are expected by improving the adhesion of the current collection layer to the system composed entirely of fine particles since this exhibited the best performance of all systems without a current collector. In addition, further compositional optimization may be performed on each specific system studied in this work. As mentioned previously, bismuth ruthenate is known to be volatile, and bismuth oxides are known to undergo an ordering
phenomenon at temperatures below ~600 °C. Thus, the stability of this system above 600 °C should be examined.

5.3.6. Direct comparison with conventional cathode systems

Rather than simply comparing results with literature data, in-house LSM-YSZ and LSCF-GDC composites were synthesized. The similarity in processing routines of the different composite systems provides a more direct comparison with conventional cathode systems. The four different materials (LSM from Nextech, YSZ from Tosoh Corporation, LSCF from Praxair, and GDC from Rhodia) were obtained and have very fine initial particle sizes. The conventional composites were first optimized according to composition (using 5 vol% steps between 40-60 vol% of each phase using 5 vol% composition steps), firing temperature (using 50 °C steps between 1000 °C and 1300 °C), and firing time (using 1 h intervals between 1-4 h).

All three sets of composites (LSM-YSZ, LSCF-GDC, and BRO7_{VM}-ESB_{S}) were applied to dense YSZ pellets with Ni-YSZ anodes. Using the same electrolyte substrate for each system minimizes the effect the electrode/electrolyte interface has on cathode performance. YSZ was selected as the substrate since it is more easily sintered than GDC, and unlike ESB, can withstand the firing temperatures used for LSM-YSZ and LSCF-GDC composites (1100 °C and 1150 °C, respectively). Further, testing was done under actual SOFC operating conditions using a solid state adaptation of the Luggin probe configuration (Figure 5-14). The embedded reference electrode in this configuration more accurately samples a well-defined equipotential surface, allowing for more accurate measurement of electrolyte and electrode impedances, compared with other ‘surface-configured’ reference electrodes which sample a more averaged effective potential, leading to greater likelihood of inaccurate electrolyte measurements and distorted electrode arcs\textsuperscript{74}. Further, 3-point testing under SOFC operating conditions allows
direct assessment of cathode polarization as a function of current density, giving insight into real-world behavior of these cathode systems.

Cathodic polarization can be calculated using Eq. 5-2

\[ \eta_{\text{cathode}} = E_m - E_{\text{YSZ,ref} \parallel \text{cat}} \]  

(5-2)

where \( E_m \) is the potential measured between the cathode and the embedded reference electrode, and \( E_{\text{YSZ,ref} \parallel \text{cat}} \) is the potential drop due to the YSZ electrolyte between the reference electrode and the cathode. This potential drop can easily be measured in-situ using impedance spectroscopy between the cathode and reference electrode. The high-frequency intercept of the impedance spectrum with the real axis (\( Z'_{hf, pt \parallel \text{cat}} \)) allows calculation of the ASR of the YSZ electrolyte between the reference electrode and the cathode (Eq. 5-3)

\[ \text{ASR}_{\text{YSZ,ref} \parallel \text{cat}} = Z'_{hf, pt \parallel \text{cat}} \times A \]  

(5-3)

where \( A \) is the active area of the cell (the cathode area).

The voltage drop due to the YSZ electrolyte between the reference electrode and the cathode is then simply the ASR value obtained from Eq. 5-3 multiplied by the cell current density. Since the electrolyte resistance is ohmic, its resistance is independent of current density, a single, open-circuit impedance measurement of \( Z'_{hf, pt \parallel \text{cat}} \) can be used to determine the cathode overpotential at all current densities \( i \) measured (Eq. 5-4).

\[ \eta_{\text{cathode}}(i) = E_m(i) - i \times Z'_{hf, pt \parallel \text{cat}} \times A \]  

(5-4)

A similar 3-point impedance measurement between the reference electrode and anode provides the ohmic resistance between the anode and the reference electrode \( Z'_{hf, pt \parallel \text{an}} \), as well as the polarization resistance of the anode.

As one accuracy check, the embedded reference electrode effectively partitions the ohmic contribution of the electrolyte and allows separation electrode polarization. Thus, summing up
the partitioned ohmic contributions from the 3-point impedance measurement \( (Z'_{\text{hf, pt || an}} \text{ and } Z'_{\text{hf, pt || cat}}) \) should give the same value of ohmic resistance as a simple 2-point measurement between the anode and cathode (Eq. 5-5).

\[
Z'_{\text{hf, 2-point}} = Z'_{\text{hf, pt || an}} \text{ and } Z'_{\text{hf, pt || cat}} \quad (5-5)
\]

Further, the sum of the real and imaginary parts of the cathodic and anodic impedances measured using the 3-point configuration should be the same as the real and imaginary parts of the total electrode impedance measured using the 2-point configuration (Eqs. 5.6).

\[
Z'_{\text{tot, 2-point}} = Z'_{\text{cat, 3-point}} + Z'_{\text{an, 3-point}} \quad (5-6a)
\]

\[
Z''_{\text{tot, 2-point}} = Z''_{\text{cat, 3-point}} + Z''_{\text{an, 3-point}} \quad (5-6b)
\]

Such an analysis is shown in Figure 5-15 for the LSM-YSZ system measured at 650 °C. There is a slight (~2 %) deviation between the electrolyte resistance measured from 2-point and 3-point measurements. The agreement between the total electrode resistance measured from both configurations is better (deviation ~1 %). The deviations arise most likely from human error involved in fabrication of the Luggin probe cell, but overall, the agreement is acceptable. The high value of total cell ASR (44.5 Ωcm\(^2\)) arises mainly from the fact that testing is done on thick (~2 mm) YSZ pellets. The cathode ASR measured (6.6 Ωcm\(^2\)) agrees reasonably well with data for LSM-YSZ reported in the literature (Figure 3-2).

Current-voltage data for the same cell under the same conditions is shown in Figure 5-16. The slope of the line near open-circuit conditions gives a measure of the total cell ASR, which under these conditions is 45.5 Ωcm\(^2\). This shows good agreement with the total ASR determined from impedance measurement discussed above. Cathodic polarization at 650 °C as a function of current density for the 3 systems studied is shown in Figure 5-17. As expected, the polarization drop across the BRO7\(_{\text{VM}}\)-ESBS composite cathode was significantly lower than that of
conventional materials. The ASR of BRO7_{VM}-ESB, calculated from the slope of the cathodic overpotential-current density plot, is 0.9 Ωcm\(^2\). This value is significantly higher than that obtained earlier for this system at 650 °C (~0.5 Ωcm\(^2\)). The discrepancy is most likely due to the fact that in the current study, testing was done on a YSZ electrolyte while previous testing was done on ESB electrolytes. YSZ not only has orders of magnitude lower ionic conductivity than ESB at this temperature, but also does not have the catalytic activity of ESB, as discussed in Section 5.3.2.

5.3.7. Performance under operation

To gauge the viability of using BRO7-ESB composites, good performance should be demonstrated. In order to demonstrate good performance, three samples were prepared using Ni-GDC anode-supported electrolytes with relatively thin (~50 μm) GDC electrolytes. To evaluate performance of this cathode on ESB, one sample was coated with a thin film (~25 μm) of ESB, yielding a bilayer electrolyte with GDC on the fuel side and ESB on the air side. Note that the GDC layer is necessary to protect the ESB layer, which decomposes under reducing conditions. A LSCF-GDC composite cathode with a Pt current collector was used on one of the cells as a reference standard. The optimized BRO7-ESB composite with a pure BRO7 current collector was used on the other two cells (one with an ESB/GDC bilayer, the other having a GDC single layer electrolyte).

The results of current-voltage testing at 650 °C are shown in Figure 5-18 as well as in Table 5.2. Results on the single-layer GDC show that the BRO7-ESB composite has slightly better performance than LSCF-GDC (total cell ASR is 0.81 and 0.85 for BRO7-ESB and LSCF-GDC, respectively). Since the anode supports and the electrolytes were all prepared at the same time, resistances due to the anode and electrolyte should be the same for both cells, so the slight
improvement can be attributed mainly to the cathode. Since the electrolyte is ~50 μm thick, much of the total cell resistance should be due to the electrolyte. Thus the improved cathode performance is masked to some extent due to the resistance of the electrolyte (as well as the anode).

The cell utilizing a bilayer electrolyte had significantly better performance compared with the other cells (362 mW/cm² maximum power density and 0.53 Ωcm² ASR), despite the added resistance caused by inserting an ESB layer between the GDC and the cathode. This is partly due to a degree of catalytic activity present at the surface of the ESB electrolyte, and the role the cathode/electrolyte interface plays in the cathode resistance, as discussed in Sections 5.2.3 and 5.2.6. The full picture of the improved performance is not fully understood at this point. Further, there may be some stability issues at this temperature as post-mortem SEM analysis reveals formation of an interlayer between the cathode and the ESB layer (Figure 5-19). More work is required to resolve these issues. However, it is clear that these cathodes have potential for use in lower temperature SOFCs.

5.4. Conclusions

BRO7 was shown to be chemically compatible with ESB20. Microstructural engineering by a combination of mechanical crushing, ultrasonication, and sedimentation was shown to be an effective way of lowering electrode ASR, and the results seem to be consistent with 3PB length maximization theory. Application of a pure BRO7 current collector to the electrode surfaces further improved electrode performance. The lowest value of ASR attained ranged from 0.73 Ωcm² at 500 ºC to 0.03 Ωcm² at 700 ºC is one of the lowest SOFC electrode ASR values reported to date. Direct comparison of BRO7VM-ESBS with conventional LSM-YSZ and LSCF-GDC composite cathodes were made using a solid-state adaptation of the Luggin probe
configuration to extract cathode overpotentials as a function of current density. Results show BRO7VM-ESB to have a significantly lower cathodic overpotential than these conventional composites. Current-voltage testing of the optimized composite was done on anode-supported cells. A maximum power density of 362 mW/cm² was attained at 650 °C using a ~75 mm thick ESB/GDC bilayer electrolyte. It is believed that this material would be a good candidate cathode for low temperature SOFCs.
Table 5-1. Volume mean diameter ($d_V$), as well as subscript and symbolic designations for different sets of starting powders. Hashed and white circles represent ESB particles, black and gray circles represent BRO particles.

<table>
<thead>
<tr>
<th>Phase subscript designation</th>
<th>Type of powder</th>
<th>$d_V$ ESB20 ($\mu$m)</th>
<th>$d_V$ BRO7 ($\mu$m)</th>
<th>Symbol</th>
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</thead>
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<td>1.31</td>
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</tr>
<tr>
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<td>0.73</td>
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</tr>
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<td>0.06</td>
<td><img src="gray_black" alt="Symbol" /></td>
</tr>
</tbody>
</table>

Table 5-2. Cell open circuit potentials (OCP), maximum power densities (MPD), and ASR for selected SOFCs at 650 °C from current-density measurements.

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>OCP (V)</th>
<th>MPD (mW/cm²)</th>
<th>ASR ($\Omega$cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF-GDC on GDC</td>
<td>0.91</td>
<td>250</td>
<td>0.85</td>
</tr>
<tr>
<td>BRO7-ESB on GDC</td>
<td>0.90</td>
<td>269</td>
<td>0.81</td>
</tr>
<tr>
<td>BRO7-ESB on ESB/GDC</td>
<td>0.87</td>
<td>362</td>
<td>0.53</td>
</tr>
</tbody>
</table>
Figure 5-1. XRD spectra for mixtures of BRO7-ESB20 before and after heat treatment at 800 °C for 10 h.
Figure 5-2. Nyquist (a) and Bode (b) plots at 625 °C for different compositions of BRO7\text{VM-ESB20s} electrodes tested in air.
Figure 5-3. Effect of electrode composition for the ESB20S-BRO7VM system.
Figure 5-4. SEM micrograph of as-prepared BRO7 powders before (a) and after (b) vibro-milling as well as ESB20 powders before (c) and after (d) vibro-milling.
Figure 5-5. TEM micrograph of BRO7<sub>VM</sub> powders before (a) and after sonication and sedimentation (b), as well as ESB<sub>VM</sub> powders before (c) and after (d) sonication and sedimentation. Powders were dispersed onto lacey carbon TEM grids.
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Figure 5-7. Nyquist (a) and Bode (b) plots at 625 °C for different 50-50 wt% BRO7-ESB20 electrode microstructures tested in air.
Figure 5-8. Arrhenius plot of ASR vs reciprocal temperature for the four different microstructures studied.
Figure 5-9. Nyquist (a) and Bode (b) plots at 625 °C for different 50-50 wt% BRO7-ESB20 electrode microstructures tested in air before (open symbols) and after (closed symbols) sonication and sedimentation of electrode powders.
Figure 5-10. Arrhenius plot of ASR vs reciprocal temperature—a comparison between electrodes prepared from as-prepared powders (open symbols) and powders which underwent ultrasonication and sedimentation (closed symbols). Arrows indicate ASR drop for comparable systems.
Figure 5-11. Effect of electrode thickness on ASR at 625 °C for the four different electrode microstructures prepared after ultrasonication and sedimentation of the as-prepared powders. Hollow symbols represent electrode porosity.
Figure 5-12. Nyquist (a,c) and Bode (b,d) plots at 625 °C for 50-50 wt% BRO7-ESB20 at different thicknesses without (open symbols) and with (closed symbols) pure BRO7 current collectors. Note: The BRO7SUP-ESBS system is shown at left and BRO7S-ESBS is shown at right.
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Figure 5-15. Impedance spectra for LSM-YSZ composite comparing and total cell impedance measured using 2-point configuration with that calculated from the sum of the anode and cathode impedance measured using 3-point Luggin reference probe configuration. Data has been normalized according to cathode area.
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Figure 5-17. Cathode overpotential versus current density data for selected cathode materials on Luggin probe cells at 650 °C using hydrogen bubbled through water as the fuel gas and air as the oxidant gas.
Figure 5-18. Current-voltage measurement for selected cells at 650 °C using hydrogen bubbled through water as the fuel gas and air as the oxidant gas.
Figure 5-19. SEM image of optimized BRO7-ESB composite cathode on SOFC with Ni-GDC anode support with ESB/GDC bilayer SOFC after current-voltage testing.
CHAPTER 6
CONCLUSIONS

The solid oxide fuel cell is a promising candidate for future generation power generation technologies. Since they do not rely on combustion of fuels, they are more efficient, quieter, and cleaner than conventional technologies. However, in order to be more practical and cost-effective, cell operating temperatures must be lowered to 500 °C and below. With the inception of thin-film electrolytes and electrolytes with ionic conductivities higher than conventional YSZ materials, much of the temperature reduction focus has shifted to electrode (anode and cathode) development. The oxygen reduction reaction (Eq. 2-1a and 2-1b), being more of a thermally-activated process than that of fuel oxidation (Eq. 2-2 and 2-3), becomes a severely limiting process at lower temperatures. Hence, low and intermediate-temperature SOFCs require cathodes with a high degree of catalytic activity towards oxygen reduction as well as a microstructure which maximizes the number of reaction sites (3PBs) and facilitates oxygen transport toward and incorporation into the electrolyte. It is also important that the cathode be microstructurally stable with time so that performance does not degrade over the lifetime of the cell.

In the first part of this dissertation, the isothermal stability of a low-resistance cermet cathode, silver-stabilized bismuth oxide was examined. Prior to stability testing, a preliminary study of compositional optimization (between 40 and 70 vol% Ag phase at intervals of 5 vol% Ag) was carried out on Ag-ESB20 composites in order to achieve a degree of agreement with data published in the literature. The minimum in cathode ASR (achieved at 50 vol% ESB20) was 0.18 Ωcm² at 600 °C, a significant improvement over that produced by Xia et al. who obtained an ASR of 0.3 Ωcm² at 600 °C for their Ag-YSB composite. For the stability study, pure Ag, Ag-ESB20, and Ag-YSB electrodes were isothermally tested at 650 °C for 100 h. All
systems experienced significant degradation in electrochemical performance during the test—both the Ag-YSB and Ag-ESB electrode ASR values increased by around 70% (from 0.04 Ωcm$^2$ to 0.07 Ωcm$^2$ (75%) and from 0.06 Ωcm$^2$ to 0.10 Ωcm$^2$ (67%) for Ag-YSB and Ag-ESB respectively), while the pure Ag system experienced a near fourfold increase (from 0.92 Ωcm$^2$ to 3.55 Ωcm$^2$) during the same length of time. Linear regression of the data (based on the first 10 h of testing) yielded a degradation rate of 4.4x10$^{-4}$ Ωcm$^2$/h for Ag-ESB and 1.2x10$^{-4}$ Ωcm$^2$/h for Ag-YSB. The pure Ag electrode degraded at a rate more than two orders of magnitude faster—8.7x10$^{-2}$ Ωcm$^2$/h. Electrolyte conductivities during the first 50 h of testing were relatively stable. SEM analysis revealed significant microstructural evolution during the 100 h of testing at 650°C. The pure Ag electrode appears fully dense. The porosity of the Ag-ESB20 electrode appeared lower after testing—domains of coalesced silver are evident, and ESB20 particles between these domains have been forced closer together, further reducing porosity and 3PBs. Growth and coalescence of the silver phase was also evident in the Ag-YSB electrode though to a lesser extent. It is believed that the smaller starting size of the YSB particles (as evidenced in the unfired electrode micrographs) helped to lower the mobility of the silver phase by providing the electrode with a higher surface area through which the silver phase must migrate. XRD and EPMA analysis revealed neither evidence of inter-phase reactivity between silver and stabilized bismuth oxide nor diffusion of silver into the electrolyte. In light of the electrochemical, microstructural, and chemical evidence presented, it was concluded that electrode microstructural evolution due to growth, agglomeration, and coalescence of the silver phase, rather than chemical reactivity of the bismuth oxide phase, was responsible for the observed degradation in electrochemical performance.
Next, attempts were made to reduce the microstructural evolution of the silver phase in Ag-ESB20 composites, and hence improve electrochemical performance stability. This was done by infusing the electrode with small particles (nano-size 8YSZ or vibratory-milled ESB20 particles) in order to increase electrode surface area which in turn would increase the amount of energy required for the silver phase to migrate over a given distance in the electrode. The addition of 5 vol% 8YSZ nano powders significantly improved unbiased electrode stability by 97%, and reduced the initial, zero time ASR value by 31%. Similar results were obtained when YSZ-free electrodes were prepared from ESB20 powders composed of particles hundreds of nanometers in size as opposed to electrodes prepared from ESB20 powders composed of micron-sized particles—the zero time ASR value was reduced by 25%, and ASR vs. time slope during unbiased testing of the silver-ESB20 system at 650 °C was reduced by 95%. The ASR vs. time slopes during testing under a 250 mV external applied bias were lowered by 50% using the smaller ESB20 particles due to suppression silver phase electro-migration. The stability of composite silver-ESB20 electrodes under an applied bias still needs some improvement. Improvements are likely with further reduction in ESB20 particle size down to several tens of nanometers. Also, as the operating temperature of SOFCs is reduced, the migration of the silver phase will be suppressed even further.

Finally, porous composite electrodes consisting of BRO7 and ESB20 were synthesized and characterized using impedance spectroscopy on symmetric cells. Electrode performance was first manipulated compositionally by varying the weight percent of each phase in the composite, and a minimum ASR of 0.17 Ωcm² at 700 °C was achieved at 56 wt% ESB20. Next, microstructural influences on electrode resistance were examined by varying starting particle sizes of BRO7 and ESB20 powders using combinations of as-prepared sieved powders and
vibro-milled powders. Comparing the two systems where the different phases have more similar grain size (BRO7VM-ESB20VM and BRO7S-ESB20S), the electrode comprised of vibro-milled particles exhibits the lower ASR, as expected. The systems composed of dissimilarly-sized particles (BRO7VM-ESB20S and BRO7S-ESB20VM) exhibit nearly the same performance, with the BRO7VM-ESB20S electrode having the lowest ASR of 0.43 Ωcm² at 625 ºC. Further ASR reductions were achieved using a combination of sedimentation to further reduce particle size and size distributions as well as ultrasonication to break up soft agglomerates. It is clear from Figure 5-9b that the impedance spectrum of the fully-supernatant composite is composed of two arcs. Comparing the spectrum of this electrode with the other electrodes, it is the low frequency process is the most affected by these microstructural changes, and its resistance has been lowered to the point where the low and high frequency processes are in competition with each other. Since the impedance reduction at one frequency range was conspicuous while there appeared to be no corresponding impedance rise at any other frequency range, it was concluded that the 3PB improvements provided by reduced particle size, size distribution, and phase agglomeration outweighs any possible degredation provided by increased electrode tortuosity. The minimum ASR observed was 0.10 Ωcm² at 625 ºC for the ESB20SUP-BRO7SUP system. The effect of electrode thickness was also studied by applying successive coats of the electrode inks to the electrolyte substrates. For all electrodes tested, electrode ASR dropped as thickness increased, even at thicknesses approaching 200 μm. The exceedingly high ionic conductivity of the ESB20 phase minimizes concentration polarization effects, explaining why these effects are not observed even at such high values of electrode thickness. Lastly, application of a pure BRO7 current collector was found to dramatically improve performance. Using these optimization techniques, a minimum electrode ASR of 0.73 Ωcm² and 0.03 Ωcm² was achieved at 500 ºC and
700 °C, respectively. This is a marked improvement over earlier results (3.47 Ωcm² and 0.08 Ωcm² at 500 °C and 700 °C, respectively) and is comparable to results reported BSCF, especially at lower temperatures due to the lower activation energy of BRO7-ESB20 (~1.0 eV) compared with that of BSCF (~1.2 eV), making it one of the lowest resistance cathode materials reported to date at such low temperatures. Further optimization for these composites is likely with improved current collector adhesion, since the ESB20SUP-BRO7SUP system performed better than the ESB20s-BRO7SUP system without a current collector. In addition, compositional optimization on the optimized microstructure is incomplete at this point, since only 1:1 wt% ratios were explored, thus supplemental compositional studies are likely to yield lower ASR values still.

Direct comparison of BRO7VM-ESBS with conventional LSM-YSZ and LSCF-GDC composite cathodes were made using a solid-state adaptation of the Luggin probe configuration to extract cathode overpotentials as a function of current density. Results show BRO7VM-ESBS to have a significantly lower cathodic overpotential than these conventional composites. Current-voltage testing of the optimized composite was done on anode-supported cells. A maximum power density of 362 mW/cm² was attained at 650 °C using a ~75 mm thick ESB/GDC bilayer electrolyte.

Low-temperature performance and long-term stability testing under cell operating conditions should also be conducted to finalize the feasibility of utilizing these materials as lower-temperature SOFC cathodes. Unfortunately since bismuth oxide-based materials tend to undergo defect ordering phenomena and/or phase transformations over much of the temperature range of interest (400 °C to 600 °C), care must be taken when analyzing these composite materials within this temperature range.
This section does not contain detailed information about the fundamentals of each
technique. Instead it focuses on experimental design, testing procedure, typical results, and
derivation of important parameters for SOFC systems. Some key issues will be discussed.

**A.1. Electrochemical Impedance Spectroscopy**

Electrochemical impedance spectroscopy (EIS) is a valuable tool for characterization of
electrochemical processes. A small AC potential (across a range of frequencies) is applied to the
sample, and the current response (impedance using Ohm’s Law) through the sample is measured
over a range of frequencies. This response is usually represented as a “Nyquist” or “Cole-Cole”
plot where the real part of the impedance is the abscissa and the imaginary part of the impedance
the ordinate (usually the negative and positive portions of the imaginary axis are reversed for
simplicity). The response of the cell is usually modeled in terms of equivalent circuits, i.e., a
group of electrical circuit elements (resistors, capacitors, inductors) that are connected in a way
that would give the same response as the cell.

A common cell response feature (a semi-circle), and its equivalent circuit representation (a
resistor and capacitor in parallel) are shown in Figure A-1. Such behavior could be
characteristic, for example, of a double-layer capacitance (due to charge separation between
electrode and electrolyte) in parallel with a resistance to charge transfer or a polarization
resistance. Notice that the magnitude of the impedance decreases as frequency increases. The
semi-circle is characteristic of a single “time-constant”. Typical impedance plots of
electrochemical cells contain more than one time constant (semi-circle) indicative of more than
one electrochemical process, and often only a portion of one or more of the semi-circles is seen.
Often two time constants will overlap and the semi-circles must be deconvoluted in order to
determine each individual contribution. Also it should be mentioned that many times in the study of solid samples, the center of the semi-circle may be depressed below the x-axis. The equivalent circuit is similar to that in Figure A-1, but the capacitor is replaced by a so-called constant-phase element. A capacitor can be thought of as a constant phase element whose phase angle (the phase difference between voltage and current responses) is 90°. When this phase angle is somewhat less than this, a depressed semi-circle is observed. This behavior has been explained in a number of ways. Surface roughness of the electrode is one explanation—for example, it is common for electrochemical cells with solid electrodes (which typically have rough surfaces) to display this behavior while it is not observed on mercury electrodes (which are atomically smooth).

Another common cell response feature on a Nyquist plot is a straight line with a 45° angle (Figure A-2). This feature is usually modeled by a so-called Warburg impedance and is characteristic of semi-infinite diffusion. As shown in Figure A-2, in many cases at low frequencies, the plot forms an arc. This is justified because at high frequencies, the time for a molecule to diffuse through, for example, a porous cathode, is much longer than the period of the applied AC stimulus, hence the molecule does not ‘see’ that the cathode is of finite thickness.

The response of a cell can be perfectly modeled by a number of different equivalent circuits. Knowledge of the physical processes occurring in each cell can help identify the most appropriate model. The model can be justified by altering a single aspect of the cell (grain size, for example—Figure A-3)\textsuperscript{75} and verifying that the impedance spectrum changes in such a way that is as predicted by the model.

Another typical cell response and equivalent circuit model are shown in Figure A-4. This figure will be used as an example for calculation of various cell parameters. The simplest
parameter to extract is the total ohmic resistance of the cell, given as $R_{el}$ in the figure. This is also known as the solution or electrolyte resistance. It should be noted at this point that while in this case the electrolyte response behaves as a pure resistor, in many polycrystalline electrolytes the response may exhibit some capacitive behavior due to the grains (bulk) and the grain boundaries, hence up to two semi-circles may appear in this region of the Nyquist plot (as in Figure A-3). $R_{ct}$ is the charge transfer resistance (which is controlled by the kinetics of the charge transfer reaction), and is measured as the difference between the extrapolated low frequency real axis intercept and the high frequency axis intercept. As mentioned in Chapter 2, the speed of the charge transfer reaction can be modeled by the Butler-Volmer equation. Since in IS the applied signal is small, the overpotential (the electrode potential minus the equilibrium potential for the reaction) should be small, and the Butler-Volmer equation becomes

$$R_{ct} = \frac{RT}{nFi_o}$$  \hfill (A-1)  

where R, T, n, and F have their usual meanings, and $i_o$ is the exchange current density. Thus if $R_{ct}$ is known, the exchange current density can be calculated.

Diffusion of species toward and away from the reaction sites usually gives the linear response shown at the low frequency end of the figure. Naturally this is not the only form of spectrum observed, and $R_{ct}$ is not the only non-electrolyte resistance reported. Polarization resistance, $R_p$, and the more general electrode resistance, $R_{el}$ are frequently reported. However, in most all cases, the value for the resistance is measured as the difference between low and high frequency real-axis intercepts of the arc of interest.

Since resistance is not a materials parameter, cell geometry is usually taken into account, and IS results are reported in terms of resistivities or conductivities. For a particular resistance,
where \( \rho \) is the resistivity, \( \sigma \) is the conductivity, \( A \) and \( l \) are the area and length over which a uniform current is carried, respectively. It is seen, for example, that the ohmic contribution can be identified by performing a series of experiments, holding all experimental conditions the same while changing electrolyte thickness—a plot of \( \Omega \) versus electrolyte thickness should be a straight line with intercept zero. Area specific resistance is another parameter that is commonly reported, and is simply the resistance of interest multiplied by the area of interest—for example, the electrode resistance multiplied by the electrode area gives the electrode area-specific resistance [\( \Omega \text{cm}^2 \)].

These properties will often show an Arrhenius relationship with temperature, and a log plot of these parameters versus reciprocal temperature will give a straight line, the slope of which is reported as the activation energy of the specific process. With this brief description of EIS, one can begin to imagine how this technique can be utilized to help interpret cell behavior, as well as help determine rate-controlling processes.

**A.2. Current-Voltage Measurements**

There are a number of different ways to perform current-voltage (IV) measurements. Figure A-5 shows a common fuel cell testing apparatus and typical results.

A seal is used to isolate and expose the two electrodes to different oxygen potentials (high \( pO_2^- \) on the cathode and low \( pO_2^+ \) on the anode). This sets up a Nernst potential across the fuel cell, as mentioned previously. Current is drawn from the cell, and the resulting cell voltage is recorded as a function of the magnitude of current drawn per unit of electrolyte area. Power
density is often plotted on the same graph. Two samples can be compared by changing one element of the cell, such as the cathode, while keeping all other aspects of the cell constant. The performance can be considered to improve if the slope of the current-voltage plot is decreased or if the power density maximum is increased.

To isolate the response of the electrodes, current-interruption is often used. The ohmic and non-ohmic contributions of the voltage \( \eta_c \) between the cathode and Ref C can be separated by the use of a fast electronic switch since the ohmic drop (relaxation of ionic and electronic charge carriers) is order of magnitudes faster than the non-ohmic processes (discharge of the double layer at the cathode/electrolyte interface and diffusion processes). A plot of \( \eta_c \) versus time and a deduction of the relative (between cathode and reference electrode) non-ohmic cathodic overpotential are shown in Figure A-6a. This process is repeated over a range of currents and a plot of cathodic overpotential versus current density is obtained (Figure A-6b).

Another technique to accomplish the same result, i.e., determination of cathodic overpotential is shown in Figure A-7. Here, the sample is not sealed, instead the process is driven by an applied voltage, \( E \), between the working and reference electrodes. The cathodic overpotential is estimated by

\[
\eta_c = E - IR_\Omega
\]  

where \( I \) is the current and \( R_\Omega \) is the ohmic resistance, as described earlier. Note that an impedance spectrometer (FRA in Figure A-7) is used to determine the value of \( R_\Omega \) at each value of \( E \) applied.

The same data can be obtained using a combination of a fuel cell test (Figure A-5) and EIS. A horizontal line drawn at the voltage intercept (current density equals zero) represents the theoretical open circuit cell voltage, \( E^0 \). As the current density is increased, the cell voltage
drops by an amount equal to $E^0 - E(i)$. The ohmic contribution to this drop is simply $iR_\Omega$, where $R_\Omega$ is determined, as before, by impedance spectroscopy. The electrode contribution to the voltage drop is then given by

$$\eta = E^0 - E(i) - iR_\Omega$$  \hspace{1cm} (A-5)

For clarity, a typical analysis is shown in Figure A-8. Murray and Barnett\textsuperscript{38} have also separated electrolyte in order to obtain cathode overpotentials using a simple symmetrical cell (a cell composed of the two electrodes of the same [cathode] material separated by the electrolyte). In their measurements, a voltage was applied and plotted against the current measured. Again, EIS was used to determine the electrolyte ohmic contributions, and these were subtracted from the applied voltage to yield cathode overpotential versus current results (Figure A-9). The results can be verified by comparing the cathode polarization resistance (the slope of the cathode overpotential at zero current) to the magnitude of the polarization resistance determined by EIS. The authors report good agreement.

It should be mentioned that some authors use these cathodic overpotential versus current density plots (in the range of low overpotential) as an alternate way to extract exchange current density values. Rearrangement of the low current approximation to the Butler-Volmer equation (Eq. 2-14) gives

$$i_0 = \left( \frac{RT}{nF} \right)i$$  \hspace{1cm} (A-6)

where $i/\eta$ is the low current slope of the current density-overpotential plot.

**A.3. DC Electrical Conductivity**

Figure A-10 shows the current and voltage Pt reference electrode arrangement for DC conductivity measurements. The sample, in this case, is a relatively (~90%) dense pellet of the
electrode material composition being surveyed. A constant current is passed between points a and b, and then b and c and the resulting voltage drop is measured across d and c, or a and d, respectively. Two resistance values are then estimated by the equations

\[
R_{ab,cd} = \frac{V_{dc}}{i_{ab}} \quad (A-7a)
\]

\[
R_{ad,cb} = \frac{V_{ad}}{i_{bc}} \quad (A-7b)
\]

Taking into account the flat, disc-shaped geometry, the conductivity of a sample of thickness d can be estimated by the equation

\[
\sigma = \frac{2 \ln(2)}{\pi d \left( R_{ab,cd} + R_{ad,cb} \right)} \quad (A-8)
\]

**A.4. Oxygen Exchange Measurements**

The resistance of mixed conducting cathodes is caused by several different processes such as the exchange of oxygen from the gas to the solid, the diffusion of oxygen through the electrode, gas phase diffusion through the pores, and the transfer of oxygen from the electrode into the electrolyte. Oxygen exchange measurements are a valuable tool in the determination of which process most greatly influences the cathode resistance. One such experimental technique that is gaining in popularity is the isotope exchange/depth profiling method (IEDP). In this technique, dense pellets of the electrode material composition being surveyed are placed in a secondary ion mass spectrometer (SIMS). The samples are first annealed in a high purity oxygen atmosphere at the measurement temperature. After the initial anneal, the chamber is switched (at a time labeled t=0) to an \(^{18}\)O-rich atmosphere, and the sample is again annealed. At some time, t, depth profiling is performed on the sample by the use of a 5-15 keV primary ion beam (typically Xe) at normal incidence to the sample surface, and the normalized isotopic ratio \(^{18}\)O/(\(^{16}\)O+\(^{18}\)O)]
is measured via the SIMS instrument and plotted as a function of depth below the sample surface.

The data is then fitted to the solution to Fick’s second law of diffusion. The appropriate surface boundary condition used to solve this differential equation has been described as

\[
k(C^i _g - C^i _s) = -D \left( \frac{\partial C^i _s}{\partial x} \right)
\]

where \( k \) is the surface exchange coefficient, \( D \) is the oxygen self-diffusion coefficient, \( C^i _g \), \( C^i _s \), and \( C^i _x \) are the isotopic ratios in the gas, surface, and in the solid at depth \( x \), respectively. From a fit of the data to the solution to Fick’s second law, one obtains values for the parameters \( k \) and \( D \). The magnitude of these parameters provides valuable insight into the interpretation of oxygen reduction kinetics.

A.5. Thermogravimetric Analysis (TGA)

A TGA is used to measure the change in mass of a sample as a function of temperature. These weight changes can result from a number of different processes, such as chemical reactions and decomposition. The sample is prepared and placed on a microbalance and heated in an appropriate atmosphere. TGA is sensitive enough to detect weight changes on the order of a fraction of a microgram. This technique is useful for quantitative determination of oxygen nonstoichiometry, and the experimental procedure has been described in detail. Figure A-11 shows typical results of oxygen nonstoichiometry calculations using information obtained from TGA experiments.

A.6. Microstructure

Microstructural evaluation is of critical importance in the study of cathode materials. Many models used to describe electrode performance involve microstructural parameters such as
porosity, grain size, tortuosity, etc. In addition, it is important in many cases for a material to be single phase—both before and after electrochemical testing. For example, minor impurities introduced by interdiffusion between cathode and electrolyte can lead to resistive interlayer phases. These phases can lead to an alteration of diffusion and surface exchange properties of the system.\(^{77}\)

A variety of techniques can be utilized to study microstructures. Scanning electron microscopy (SEM) is a powerful technique that can be used to help determine grain size, porosity, and tortuosity.\(^{77}\) In addition SEM can easily measure other parameters that may be of interest such as cathode thickness. X-ray diffractometry (XRD) is another commonly employed technique. It can be used by application of Bragg’s law to determine the theoretical density of a material. In addition, phase purity (both before and after electrochemical testing) can be judged based on the peak spectrum it produces. A quantitative determination of surface area is often desired, and this can be done on both powder samples and sintered, dense samples.\(^{77}\) Thermal expansion coefficients can be determined by utilizing a dilatometer.

It should be mentioned that there are many complexities involved in each technique; this is particularly true for electrochemical measurements. The possible sources of experimental error are numerous and will not be discussed here. Care should be taken in the preparation of each test in order to minimize experimental error.
Figure A-1. (a) Equivalent circuit model and (b) typical impedance spectroscopy cell response.

Figure A-2. Impedance response showing diffusion behavior at high frequencies.

Figure A-3 Impedance response for as-sintered (1500 °C, 4 h) HS3Y samples (circles), annealed at 1200 °C for 110 h in both 10% H₂ balance N₂ atmosphere (triangles), and air (diamonds) showing the effect of increasing grain size (decreasing grain boundary length). [Reprinted from Solid State Ionics, Vol. 76, S.P.S. Badwal, Grain boundary resistivity in zirconia-based materials: effect of sintering temperatures and impurities, 67-80 (1995) with permission from Elsevier.]
Figure A-4. (a) Response and (b) equivalent circuit for mixed kinetic and charge transfer control.

Figure A-5. (a) Fuel cell testing schematic and (b) illustrative representation of typical response.

Figure A-6. (a) Typical current-interruption response, and (b) calculated experimental cathodic overpotentials. [Reprinted from Solid State Ionics Vols. 86-88, M. Gödickeemeier, K. Sasaki, L. J. Gauckler and I. Riess, Perovskite cathodes for solid oxide fuel cells based on ceria electrolytes, 691-701 (1996) with permission from Elsevier.]
Figure A-7. Alternative electrochemical testing setup for cathodic overpotential.

Figure A-8. Illustrative representation of separation of electrode contribution from fuel cell test response.

Figure A-10. Electrode arrangement for DC conductivity measurements.

Figure A-11. Oxygen nonstoichiometry data for various Co and Fe B-site dopant concentrations. [Reprinted from the Ph. D. Dissertation of J.E. ten Elshof, Dense inorganic membranes: studies on transport properties, defect chemistry, and catalytic behavior, (1997) with permission from the author and The Universite of Twente.]
LIST OF REFERENCES


BIographiesketch

Matthew Camaratta was born in Lakewood, New Jersey on October 14th, 1975. He grew up in Madison, Connecticut, where he gained an appreciation for outdoor activities including ice skating, hiking, and climbing. In 1987 he moved to Huntsville, Alabama with his family, and later to Pensacola, Florida, where he attended the International Baccalaureate program at Pensacola High School. There he made several strong friendships including Chess Club friends Eric Ray and Fletcher Thomas, as well as future best man, Robert Van Hoose. In 1994, Matthew began attending the University of Florida. He was followed one year later by his friend Robert. The two quickly formed a band and dubbed themselves ‘Baker Act’ after a particular Florida law, and together with a talented horn section played over 50 live performances throughout Florida. In 1997 Matthew began dating his future wife, Tonya Bervaldi, and in 1998 they traveled the countryside. During this time, Matthew’s awareness of and sensitivity to his actions and the ramifications they have on his surroundings blossomed and led him to join Dr. Eric Wachsman’s solid oxide fuel cell research group. The wealth of knowledge, experience, and friendships he formed during these years was immeasurable. On August 24th, 2002, Matthew and Tonya were married. Five years later their bond continues to strengthen due to their many shared ideologies and love for the outdoors. In all matters, both strive to keep a sense of urgency and curiosity. He will receive his Ph. D. in materials science and engineering in December of 2007.