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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

EVALUATION OF ELECTROCHEMICAL PROCESSES OCCURRING IN THE CATHODIC REACTION OF SOFCs

By

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Chair: Eric Wachsman
Major: Materials Science and Engineering

The need for high efficiency and low emissions power sources has created significant interest in fuel cells. Solid oxide fuel cells are desirable for their fuel versatility. The cathodic reaction is known to be one of the major causes of power losses in SOFCs, but the exact manner in which the cathodic reaction occurs is not well understood. The cathodic reaction was investigated using primarily lanthanum strontium manganite (LSM) cathode / yttria-stabilized zirconia (YSZ) electrolyte symmetric cells, as LSM is one of the most studied solid oxide cathodes and the symmetry of the sample simplifies the study. An in-depth investigation of the cathodic properties of lanthanum strontium cobalt iron oxide (LSCF) was also performed.

The areas of interest are identification of the individual processes occurring in the cathodic reaction and understanding how the reaction is influenced by experimental conditions such as temperature and pO₂. Elementary steps of the cathodic reaction can be analyzed individually using AC electrochemical impedance spectroscopy (EIS). This characterization technique gives overall polarization impedance as a function of applied frequency. The output spectra were analyzed giving information about each of the significant steps of the cathodic reaction.

The effect of microstructural and interfacial changes on the cathodic reaction was also investigated. These changes were produced by sintering at various temperatures and times. The microstructural changes were analyzed both qualitatively and quantitatively.
Ultimately, a direct relationship was established experimentally between the cathode microstructure and electrochemical performance. This relationship was modeled based on theory involving reaction kinetics.
CHAPTER 1
INTRODUCTION

The turn of the twentieth century marked the beginning of a technological explosion that has changed our world forever. From the invention of the electric light bulb to the automobile to the aeroplane, many scientific advances were made which have vastly improved the efficiency and convenience of life in an industrialized nation. These advances have not come without cost. Electrical and mechanical devices are required by Newton’s Law of Conservation of Energy to derive their power from some external source. To date, that source has primarily been fossil fuels for many industries. As technology has increased, so has our demand for fuel; unfortunately, the amount of usable fossil fuels available is finite and if we do not increase our efficiency of consumption and develop an infrastructure capable of utilizing alternative, renewable sources of fuel, fossil fuel sources will eventually simply run out. One of the most promising technological advances with the potential to enhance the efficiency and versatility with which fossil fuels are consumed is the fuel cell. In a fuel cell, chemicals, which are continually pumped in, participate in an oxidation-reduction reaction resulting in the efficient production of electricity (38 % now and 60 % by 2020 [1]).

The solid oxide fuel cell (SOFC) holds particular promise. The SOFC has been shown to be able to produce high quality power from a variety of fuel sources including but not limited to hydrogen, hydrocarbons and carbon monoxide with only heat, water and CO₂ as byproducts [2]. Researchers at Los Alamos National Laboratory have even proposed techniques for zero emission coal power plants based on SOFC technology [3]. High-efficiency power generation is not enough, however, and the primary focus of SOFC research is in decreasing the system cost of SOFCs from around 800 to 400 $/kW by 2010 [1]. The research community has adopted a two-pronged approach towards reduction of this value. First is the development of lower cost materials for SOFC stack construction. Among these materials are metal interconnects which are made feasible by lower operating temperatures. Additionally, as operational temperature is reduced, less energy is required.
to start up the SOFC; therefore, reducing the operational temperature will significantly reduce the system cost of the device.

The electrochemical efficiency of SOFCs is often limited by polarization losses which accompany the oxidation-reduction reaction. Many of these polarization mechanisms have negative activation energies; thus, losses tend to be greater at lower temperatures, placing lower limits on useful operational temperature. It is accepted that polarization losses can be divided into ohmic, concentration, and activation losses. Collective understanding beyond this simple detail is unsatisfactory. A powerful tool for investigating polarization losses associated with the cathodic reaction is electrochemical impedance spectroscopy (EIS). Impedance spectroscopy is a characterization technique which allows for the separation of contributions to overall impedance into a frequency distribution. Each discrete loss mechanism is active in a different frequency regime. An improved understanding of the polarization losses occurring during the cathodic reaction will allow future researchers to direct their efforts as they work to develop higher kW/$ SOFCs. Improvement of the fundamental understanding of the cathodic reaction using impedance spectroscopy is the focus of this dissertation.
CHAPTER 2
BACKGROUND

2.1 Solid Oxide Fuel Cell Basics

The fuel cell stack is a device which takes advantage of an oxidation/reduction reaction to generate usable electricity. The two half-reactions are separated with reduction of an oxidant and oxidation of a fuel occurring on the cathode and anode, respectively. For oxygen as the oxidant and hydrogen as the fuel, the oxidation and reduction reactions proceed according to the following respective equations.

\[
H_2 + O^{\times}_o \rightleftharpoons 2e' + H_2O + V^{\bullet\bullet}_o \quad (2-1)
\]

\[
2e' + \frac{1}{2} O_2 + V^{\bullet\bullet}_o \rightleftharpoons O^{\times}_o \quad (2-2)
\]

The fuel cell stack, consisting of the cathode, anode, electrolyte, and interconnect, is constructed in various designs including, but not limited to planar, monolithic, or tubular [4]. The anode and cathode are connected by an electrolyte which allows only the flow of ions and an interconnect which allows only the flow of electrons. The cathode must be electronically conducting to allow generated electrons to reach the load and porous to allow gas to flow to the reduction sites. The cathode must also have sufficient catalytic activity for the reduction of oxidant at operating temperatures. The anode must also be porous and electronically conductive. The anode must also possess sufficient catalytic activity for the electrochemical oxidation of the fuel, thus minimizing polarization. Since the purpose of the electrolyte is to transfer ions produced at the cathode to the anode and force electrons through the load, any electrons flowing through the electrolyte will result in voltage loss and decrease efficiency. For this reason, the electrolyte must possess minimal electronic conductivity while maintaining maximum ionic conductivity. Further, an electrolyte must be impermeable to the reacting gases. As mentioned above, the interconnect provides a path to the external load. It also joins adjacent fuel cells to one another and provides a pathway for the reacting gases to reach the electrodes, while
preventing mixing of the fuel and oxidant gases. In addition to these requirements, all components must have matching coefficients of thermal expansion, must be stable in operating conditions, and must be non-reactive with one another.

2.2 Materials of Interest

2.2.1 Yttria Stabilized Zirconia as an Electrolyte

In an SOFC, a solid oxide such as yttria stabilized zirconia (YSZ) is used as the electrolyte [2]. Pure zirconia ($ZrO_2$) is chemically stable in oxidizing and reducing environments. Pure zirconia, however, exhibits a phase transition from monoclinic to tetragonal at 1170 °C and a change from tetragonal to cubic fluorite at 2370 °C [5]. These phase transitions occur in the fabrication temperature range for fuel cell devices and are accompanied by volume changes, which are undesirable. In addition to this drawback, the ionic conductivity of pure zirconia is too low for this material to be valuable as an electrolyte. Both of these problems can be addressed by doping with various oxides ($CaO, Y_2O_3, MgO, Sc_2O_3$). Of these oxides, yttria ($Y_2O_3$) is most commonly used because of stability, conductivity, and cost [2]. Yttria doping can stabilize the cubic fluorite structure from above fabrication and operating temperatures to room temperature while increasing the oxygen vacancy concentration. During doping, the $Y^{3+}$ ions substitute on $Zr^{4+}$ cation sites according to the following reaction written in Kroger-Vink notation which is described in [6]. In this notation, the charge of a substituting species with respect to the species for which it substitutes (given in the subscript) is indicated by a prime if it is negative or a bullet if it is positive. If the species is neutral with respect to the typical species for a particular lattice site, the superscript is an “x”.

$$Y_2O_3 \xrightarrow{ZrO_2} 2Y'_Z + V^\bullet^\bullet + 3O^{\times}_o$$

This increased oxygen vacancy concentration translates into an increased ionic conductivity. Ionic conductivity in zirconia is due primarily to the presence of oxygen ion vacancies in the fluorite structure. Undoped zirconia has a relatively low concentration of these defects.
As yttria (or other dopants) is added, the concentration of oxygen vacancies increases [7]. It is shown that the maximum conductivity is obtained at around 8 mol % which is the minimum dopant concentration required to fully stabilize the fluorite structure of zirconia [8]. The decrease in conductivity at higher dopant concentration is due to defect ordering or vacancy clustering, effectively reducing the total number of active defects. At 1000 °C YSZ with 8 mol % yttria has a conductivity of 0.1 S cm\(^{-1}\). The properties of YSZ are reviewed in [9]. The ionic conductivity of YSZ, being directly proportional to the concentration and mobility of ions, is a thermally activated process. \((E_a \approx 1.0\) eV [10]). For this reason, SOFCs are limited to high operating temperatures, approaching 1000 °C for YSZ. Other types of solid oxide electrolytes such as Gadollinia \((Gd_2O_3)\) doped ceria \((CeO_2)\) or GDC and yttria stabilized bismuth oxide (YSB) have shown higher conductivities at lower temperatures and are of interest for intermediate temperature (500 - 700 °C) SOFCs. Unfortunately, these electrolytes are less stable, have some electronic conductivity or are simply newer and are therefore less understood than YSZ. The presence of yttria, which increases the oxygen vacancy concentration, extends the acceptable oxygen partial pressure range down to \(10^{-30}\) atm, which includes typical operating conditions [2].

One of the most common methods for YSZ preparation for SOFCs is tape casting. In tape casting, very fine, uniform particles of yttria and zirconia particles of the desired composition are measured out. The powder is then mixed and dispersed in a solution containing solvents, binders, and plasticisers. The slurry is then extruded in tapes which are cut to the desired size. These substrates must be sintered to maximize densification. The total conductivity of YSZ is shown to be dependent on microstructure and on the characteristics of grain boundaries in particular. The presence of grain boundaries decrease the total conductivity of YSZ. Several works have used impedance spectroscopy, to study bulk and grain boundary contributions to the conductivity of YSZ [11–14].
2.2.2 Lanthanum Strontium Manganite as a Cathode

In addition to being an excellent electronic conductor and good catalyst for reduction, the SOFC cathode must be compatible with the electrolyte of choice, limiting the possibilities for selection. An SOFC cathode material must be stable at the high temperatures required for solid oxide electrolyte operation and in an oxidizing environment. These requirements limit the possible choices for cathode materials. Fabricability, cost and thermal expansion matching further decrease the pool of materials possibilities. Strontium doped lanthanum manganite (LSM) is a popular choice as a cathode material for use with YSZ electrolytes because it is a good electronic conductor at high temperatures, has a reasonable cost, has an acceptable thermal expansion match with YSZ, and can be engineered to have high porosity [2, 15, 16]. Extensive study of LSM has resulted in a good understanding of its properties [17–19].

Lanthanum manganite (LaMnO$_3$) has a perovskite structure. The lanthanum and manganese ions both have a valency of 3+, while the oxygen ions valency is 2-. LaMnO$_3$ is orthorhombic at room temperature and shows an orthorhombic-tetrahedral crystallographic transition at about 387 °C [15, 20]. Intrinsic p-type electronic conductivity has been observed in LaMnO$_3$ due to cation vacancies. The room temperature conductivity of LaMnO$_3$ is $10^{-4}$ (S cm$^{-1}$) [21]. Substitution of strontium ions, which have a valency of 2+, for lanthanum ions causes some of the Mn ions to shift from a 3+ to a 4+ valency. This substitution can be achieved via the following reaction.

\[(1 - x)LaMnO_3 + xSrMnO_3 \xrightarrow{LaMnO_3} (1 - x)La_{La}^{x} + xSr_{Sr}^{4} + (1 - x)Mn_{Mn}^{x} + xMn_{Mn}^{4+} + 3O_{o}^{x}\] (2–4)

The presence of Mn$^{4+}$ ions enhances electronic conductivity via a polaron conduction mechanism. As predicted by the mechanism, LSM conductivity exhibits an Arrhenius dependence on temperature [15]. At 20 mol % Sr, LSM possesses an activation energy of 0.10 eV [18]. The conduction of LSM increases with temperature and Sr content up to 1000 °C and about 20 mol %, respectively [18]. At temperatures greater than
1000 °C, conductivity levels off, suggesting a semiconducting to metallic transition [18]. (Metallic conduction behavior is characterized by a negative temperature dependence in contrast to semiconductor conductivity which increases with temperature.) The Sr concentration also affects the thermal expansion coefficient of LSM. It is possible to tailor the thermal expansion of LSM to suitably match that of YSZ by modifying the Sr concentration [22].

At 1000 °C the electronic conductivity of LSM shows little dependence on oxygen partial pressure at higher oxygen partial pressures [15]. A critical oxygen partial pressure exists, below which the conductivity decreases as a function of the fourth root of oxygen partial pressure. The abrupt decrease in conductivity at the critical oxygen partial pressure is believed to be due to the decomposition of the $LaMnO_3$ phase. This critical oxygen partial pressure shifts to higher values when the temperature and/or the strontium content are increased [2].

A variety of routes are used for LSM fabrication, including, but not limited to solid state reaction [23, 24], sol-gel synthesis [24], laser ablation of dense LSM [25], spray pyrolysis, auto-ignition [26–28] and co-precipitation [29]. In solid state processing, powders containing acetates or oxides of the desired cations are mixed in the stoichiometric ratio. The powders are then mixed and subsequently milled in a solvent (acetone) solution. The slurry is then calcined to obtain the desired crystal structure. Sol-gel synthesis differs from solid state processing in that a gelling agent is added to the aqueous solution before calcination. In spray pyrolysis, aqueous solutions of nitrates with the desired cations are mixed in the stoichiometric ratio. A fuel additive is then introduced to complete combustion into metal oxides. The solution is then sprayed onto a surface and dried. Calcination is performed to produce a powder with the desired chemical structure.

Cathode deposition techniques include screen printing, plasma spraying [30], slurry coating [31] and other techniques [32–34]. After deposition, a subsequent anneal is necessary to ensure proper adhesion of the cathode to the electrolyte.
2.2.3 Lanthanum Strontium Cobalt Iron Oxide as a Cathode

As mentioned previously, the operation temperature of YSZ based SOFCs has been limited to above 800 °C. To address this issue, thin electrolyte geometries and higher conductivity electrolytes have been developed reducing the practical operation temperature. As a result, the performance of LSM has now become the primary issue. Thus, other cathodes must be developed to take advantage of intermediate temperature electrolytes. One such cathode is LSCF($La_{1-x}Sr_xCo_{1-y}Fe_yO_3$).

Like LSM, LSCF owes its electronic conducting properties to its perovskite structure. When lanthanum cobalt oxide ($LaCoO_3$) is doped with strontium oxide (SrO), the Sr atoms substitute on a La site, creating a hole to compensate as shown.

\[ SrO \xrightarrow{LaCoO_3} Sr'_La + h^+ + O_2^- \] (2–5)

In LSM, the B site ion, Mn, changes valency from 3+ to 4+ to accommodate the charge difference created on the A site. The 4+ oxidation state is unlikely for both Co and Fe (2+ and 3+ are favorable); therefore, most of the negative charge created by substitution of the dopant atoms is compensated by vacancy formation.

\[ SrO \xrightarrow{LaCoO_3} Sr'_La + \frac{1}{2}O_2 + \frac{1}{2}V_o^{2\cdot} \] (2–6)

These two reactions are related by the electroneutrality condition in LSCF, described in Equation 2–7.

\[ n + [Sr'_{La}] = 2[V_o^{2\cdot}] + p \] (2–7)

Valency changes among the Fe and Co ions account for \( n = [M'_M] \) and \( p = [M^{\ast}_M] \), while \([Sr'_{La}]\) is equal to the Sr dopant concentration. The excess holes contribute to electronic conductivity allowing the LSCF to achieve an electronic conductivity similar to that of LSM, between 200 and 300 S cm\(^{-1}\) at 900 °C. The maximum conductivity of LSCF; however is reached at significantly lower temperatures depending on the concentration of the cations \([35, 36]\). The ionic conductivity of LSCF, on the other hand, is several
orders of magnitude higher than that of LSM at the same temperature, ($0.2$ versus $10^{-7}$ S cm$^{-1}$) [37–40]. The relatively large ionic conductivity of LSCF is due to the additional vacancies which increase the oxygen ion mobility. The oxygen ion diffusion coefficient is significantly larger in LSCF as compared to LSM (about $10^{-7}$ at 800 °C versus $10^{-12}$ cm$^2$/s at 900 °C) [41]. At $pO_2$s less than around 0.01 atm, the oxygen ion diffusion coefficient begins to decrease as a function of oxygen partial pressure (possibly due to defect association) at 800 °C [42]. As a result, the ionic conductivity has a maximum at around 0.01 atmospheres despite the increase in oxygen vacancies at low $pO_2$s [43].

2.3 The Cathodic Reaction

The mechanism of oxygen reduction at the cathode/electrolyte interface is quite complex and has been the study of a multitude of works [22, 25, 34, 44–47]. The overall cathodic reaction is made up of various individual steps. The process begins as oxygen flows through the atmosphere to the interconnects. Next, oxygen diffuses past the interconnects to the surface of the porous cathode. From this point on, depending on the system, including materials, microstructure, atmosphere, and other experimental conditions, multiple pathways are possible. Before an oxygen molecule can be transformed into an ion in the electrolyte, oxygen gas must somehow pass through the cathode. This can be accomplished if individual gas molecules diffuse through voids in the porous cathode to the triple phase boundary (TPB), the location where the gas phase, cathode, and electrolyte converge. It should be pointed out that depending on the openness of the cathode (pore size, porosity and tortuosity) a convective flow in which gas molecules flow as groups, Fickian diffusion in which molecules diffuse by randomly bouncing up against one another, or Knudsen diffusion in which a wall of the cathode is most likely to cause a change in direction of propagation can occur. So, at least three distinct possibilities exist for the way in which gas can diffuse through a porous cathode to the TPB, the area where the porous cathode, gas, and electrolyte meet.
The situation is further complicated by considering that adsorption may occur at some point on the cathode surface not in the immediate vicinity of the TPB. In this scenario, the diffusion of the gas molecule through the open pore must be followed by surface diffusion of the adsorbed species toward the TPB. If surface diffusion is rather slow compared to molecular adsorption, then only oxygen molecules adsorbed in the vicinity of the TPB will become ions in the electrolyte. If surface diffusion is extremely fast, however, molecules adsorbed over the entire surface of the cathode will participate in the cathodic reaction. For intermediate surface diffusivities, surface diffusion itself may in fact limit the rate of the cathodic reaction.

Once the adsorbed oxygen species has reached the TPB, a charge transfer reaction can occur in which the adsorbed species on the cathode are converted into charge carrying ions in the electrolyte. In order for this reaction to occur, electrons (or holes) which are transferred through the electronically conducting cathode and oxygen vacancies (or ions) which have traveled through the electrolyte must reach the reaction site, i.e. the TPB. Various works have attempted to summarize the possibilities (see Figure 2-1) [48, 49]. The situation is further complicated by considering that various possibilities exist for the structure and charge of the adsorbed species.

This discussion has thus far considered only purely electronic conducting cathodes. In mixed ionic electronic conducting cathodes (MIECs) a bulk pathway exists in addition to the possible pathways mentioned above. The oxygen molecule can adsorb and participate in a charge transfer reaction at any point on the surface of the cathode. The formed ion or vacancy will then diffuse through the bulk of the cathode to the MIEC/electrolyte interface. At this point, the adsorbed ion/vacancy can be incorporated directly into the electrolyte depending on any MIEC/electrolyte interfacial resistance. If the electronic conductivity of the MIEC is much greater than the ionic conductivity (as it is in LSCF) and plenty of molecular oxygen is available at the TPB, reaction pathways involving transport of ions through the MIEC may be of higher resistance than
Figure 2-1. Possible reaction pathways for a platinum cathode on electrolyte system, illustrated by Nowotny et al. in reference [49]. Permission to reproduce was obtained from Maney Publishing, publisher of the original figure.
the competing pathway localized at the TPB. As the reaction proceeds and molecular oxygen becomes depleted in the vicinity of the TPB, ionic conduction through the MIEC become increasingly significant despite the lower ionic conductivity in the MIEC. Further complicating the system, the individual pathways must be considered to operate in parallel; depending on the relative resistance of each path, multiple pathways may operate simultaneously.

The mechanism reported depends on the type of conductivity observed (electronic versus mixed), the density of the electrode, and other materials parameters. Although LSM is generally accepted as an electronic conductor, as recently as 2003 conflicting reports were published concerning whether ionic conductivity plays a significant role in conduction in LSM. Fleig reports that for dense patterned LSM microelectrodes transport of oxide ions in the cathode is the rate determining step \[50\]. As proposed by S. Adler, even a very small ionic conductivity such as that in LSM may create an active reaction layer near the cathode/electrolyte interface in which ionic behavior is significant \[51\]. The thickness of the cathode examined may significantly influence whether the cathode is perceived as a purely electronic conductor or not.

An efficient cathode should be a porous electronic conductor or MIEC. The primary method of studying reaction mechanism is to examine the effects of changes in polarization, oxygen partial pressure, and temperature on the occurring electrochemical processes. In another work by Adler, the author concludes that for LSCF at 700 °C oxygen reduction at the gas/MIEC interface and solid state diffusion in the MIEC are the major contributing processes \[52\]. A couple of works propose an oxygen reduction mechanism that consists of three rate limiting steps for an LSM cathode. The high frequency step is attributed to charge transfer of oxygen ions from the cathode/electrolyte interface to oxygen ion vacancies in the electrolyte. The intermediate step is attributed to the dissociation of adsorbed oxygen molecules into adsorbed oxygen atoms. The low frequency step is attributed to the diffusion of oxide ions to the interface \[46, 53\]. In
another study, S. P. Jiang examined the polarization mechanism of the cathodic reaction on both LSM and LSCF cathodes [54]. The author observed that for LSM cathodes, surface dissociative adsorption and diffusion, charge transfer, and oxygen ion migration into the electrolyte were the significant reaction steps with dissociative adsorption being the rate limiting step at low temperatures and oxygen ion migration limiting at high temperatures. Further, the author found that for $\text{La}_{x}\text{Sr}_{1-x}\text{CoO}_3$, dissociative adsorption and bulk diffusion (or surface diffusion) processes are significant in cathodic reaction with LSCF cathodes. Increased performance with LSCF is also observed and is attributed to its higher oxygen ion conductivity and catalytic activity.

For purely electronic conducting electrodes, the electrochemical reaction driving fuel cell operation is restricted to the TPB [55]. Because much of the power loss in SOFCs is due to polarization loss at the cathode-electrolyte interface, degradation of this interface has a deleterious effect on the performance of the cell [55]. Increasing the TPB area, on the other hand, results in a more efficient SOFC [56] and modern SOFC structures are engineered to maximize this area. M. Ostergard was one of the first to propose and develop composite LSM/YSZ cathodes with the specific intention of increasing the TPB and therefore device performance [57]. Increasing the TPB has even been shown to increase electrochemical performance for the MIEC LSCF [58]. A quality TPB requires high porosity in the electrode and good adhesion between the electrode and electrolyte. Breakdown of this interface is a primary cause of device deterioration. Delamination of the cathode is one source of degradation of this interface degradation [59]. The reaction between electrode and electrolyte is another source of interface degradation and is the focus of one of our studies.

2.4 Impedance Spectroscopy

2.4.1 Measurement Details

Impedance at a given frequency, $Z(\omega)$, is a complex number defined by Ohm’s law as the voltage, $V(\omega)$, divided by the current, $I(\omega)$. AC electrochemical impedance
spectroscopy (EIS) is a characterization technique that measures voltage (or current) as an alternating current (or voltage) is applied to the test sample over a range of frequencies. The output is the real and imaginary components of the impedance (or equivalently a magnitude and phase angle) at each frequency measured. The data is typically displayed in a Nyquist or Bode plot. The Nyquist plot has real impedance ($Z_r$) and negative imaginary impedance ($-Z_j$) as the x and y coordinates, respectively. The sign convention used in the imaginary axis is a result of the fact that capacitive behavior often dominates the processes examined in the literature. With this choice of sign convention, the majority of phenomena of interest for SOFC applications will lie in the first quadrant. The Bode plot puts the impedance magnitude and phase angle on the y-axis and the log of frequency in the x-axis. Trouble can arise if data is fitted only to a Nyquist plot in that any two RC elements with identical resistance values, but different capacitance values will appear identical on the plot. Simultaneous use of both the Nyquist and Bode representation of the data eliminates this ambiguity. The frequency range examined is usually in the range of $0.001 - 1 \times 10^7$ Hz. The upper limit on test frequency is constrained by limitations due to the measurement device, while the lower frequency is usually limited by the time it takes for data acquisition. These limitations are often not a concern because many of the phenomena studied have a characteristic frequency lying in the measurable frequency range.

The value of impedance spectroscopy as a characterization technique is that it produces evidence of the total polarization loss at each frequency measured. For a given polarization process, loss only occurs if the perturbation occurs at a lower frequency than that processes relaxation frequency. If the perturbation occurs at a higher frequency than the relaxation frequency, the system won’t have time to dissipate any power via that mechanism. Conveniently, we can look at the entire impedance spectrum and see the individual processes contributing and their respective significant frequency ranges.
Coupling this information with other experimental data and theory allows us to identify the significant individual processes.

Each of the individual processes occurring has its own real and imaginary impedances, and characteristic frequency associated with it. The capacitive impedance, $Z_C$, the inductive impedance, $Z_L$, and the ohmic resistance, $Z_R$, as a function of frequency are given by the following relations, respectively.

$$Z_C = 1/(j\omega C)$$  \hspace{1cm} (2–8)

$$Z_L = j\omega L$$  \hspace{1cm} (2–9)

$$Z_R = R$$  \hspace{1cm} (2–10)

A single electrochemical process will trace a semicircle in the Nyquist plot with the semicircle’s diameter lying on the positive x-axis. This behavior can be modeled by a series resistance connected to a resistor and capacitor in parallel (Voigt element). The distance from the origin to the beginning of the semicircle will have a magnitude of $R_S$ (the resistance of the series resistor). This contribution to impedance is due to either ohmic resistances or any process that occurs at a frequency range much higher than the measured range. The diameter of the semicircle will have a magnitude equal to the parallel resistance ($R_{\text{parallel}}$). The peak of the semicircle will occur at the characteristic frequency, $\omega_0$. The magnitude of the height of the circle is equal to $Z_C$, which is related to the parallel capacitance ($C_P$) by the equation above. These constants are additionally related via the R-C time constant, $\tau$.

$$\tau = R_P \times C_P.$$  \hspace{1cm} (2–11)

The time constant and the characteristic frequency ($\omega$) are inversely related.

$$\tau = 2\pi/\omega.$$  \hspace{1cm} (2–12)

The time constant provides information on the kinetics of the reaction.
2.4.2 Data Analysis

Each of the processes occurring has its own resistance and capacitance and therefore, a distinct characteristic frequency associated with it. The manifestation of each discrete process is a semicircle in the complex plane. As mentioned previously, any processes with a characteristic frequency much higher than the measurement range will behave like an ohmic resistance. An actual impedance measurement usually reveals a superposition of individual semicircles, which are caused by the individual polarization processes. If two of the processes occurring have characteristic frequencies in close proximity, their individual semicircles will overlap. In order to extract information about the individual processes occurring, we must be able to separate the contributions of the various phenomena acting from one another. Ideally, all of the processes occurring can be identified in terms of their individual resistances, capacitances, characteristic frequencies, and time constants. This process is, however, non-trivial and has received considerable attention and been the subject of a multitude of works.

Impedance data is often analyzed by fitting the spectra to a model, which is based on a priori knowledge of the system. This type of model is represented by an equivalent circuit [60]. For SOFC applications, authors [11, 12] have proposed a model based on the brick layer model [61] which separates the contributions of the electrolyte bulk (intragranular), electrolyte grain boundary (intergranular), and electrode effects (charge transfer). Gas diffusion and ion migration are included among other phenomena that may contribute to the unresolved spectra. Jamnik and Maier derived a general circuit for a cell with a MIEC [62]. When applied to the special case of a SOFC, their model results in an equivalent circuit nearly identical to one used by several authors which is composed of a double layer capacitance in parallel with a series connection of a resistor and a Voigt element [63]. This equivalent circuit is the most commonly used of the nested circuits.

An inherent limitation with this method is that the fit attained is dependent on knowledge of the processes contributing to the spectrum. Two important consequences
result from this fact. The first is that black box type study is not feasible, i.e. a sample of unknown composure cannot be analyzed in this manner. The second is that the degree of certainty in model parameters attainable is limited by our confidence in the assumptions made based on a priori information. In short, even if two authors agree that a model must be developed from theory, they may derive two different models and therefore yield incomparable data. Unfortunately, not even a perfect fit of the data is proof of the correctness of the chosen model because multiple equivalent circuits differing in structure can produce the same impedance curve [64].

A second commonly used technique minimizes ambiguity at the expense of confidence in the model. This technique matches all semicircles present in the Nyquist plot with individual Voigt elements (resistor and capacitor placed in parallel) connected in series. The major advantage of this type of analysis is that comparison of data among different research groups with different assumptions about the mechanism of reaction is facilitated. The primary flaw of this technique is that assignment of parameters based on the model is difficult since the model was not constructed with specific parameters in mind. In order to assign parameters to the model, the EIS measurement must be repeated as measurement conditions and/or sample characteristics are varied. The resulting impedance spectra are then modeled and changes in the attained model parameters are then compared with theory, leading to assignment of identities of the individual parameters.

Another method sometimes called system identification [65] is based on the reasonable assumption that the input/output behavior is dependent only on the cell to be tested [66]. In system identification, instead of modeling from physical laws, a mathematical model is built based solely on the experimental data. System identification consists of three steps: pre-identification, model estimation, and model validation. In pre-identification the data is manipulated into a format suiting the chosen model. Model estimation involves determination of the various parameters of the model and model validation tests the suitability of the model [65]. The output impedance spectrum is analyzed while input,
such as experimental conditions, is varied. A model is produced, the parameters of which are subsequently related to understood physical processes. This type of analysis may utilize mathematical techniques to increase frequency resolution. The strength of this type of analysis is that black box type investigation is possible.

Mathematical techniques have been developed to aid in data analysis, and in particular to increase the resolution of the measured data [67]. For very simple systems with clear separation of electro-chemical processes, model parameters may be obtained without great difficulty. For as few as two conjoined semicircles, mathematical tools have been developed which aid in attainment of model parameters [68]. Several methods of data analysis based on Fourier analysis of the raw data have been presented [67, 69]. These methods increase the frequency range of the data, facilitating separation of the individual acting processes that show similar relaxation frequencies. In this manner, processes can be resolved which are not resolvable using conventional methods [70]. The advantages of using this type of technique include the following: 1) time constants may be obtained with little knowledge about the system, 2) separation of distributions that are not readily separable in conventional impedance data is possible, 3) a reduced sensitivity to random experimental error is gained [69]. The Kramers-Kronig relations are also used to reduce error associated with the data analysis. According to the Kramers-Kronig relations, the same information is contained in the real and imaginary components of the impedance profile; therefore, in data analysis, only one of the components needs to be considered [71]. The Kramers-Kronig relations have also been used to identify and/or reduce error in the acquired data [72]. This type of analysis is the focus of one chapter in this work.
CHAPTER 3
ERROR ANALYSIS

3.1 Introduction

As mentioned previously, it is well understood that cathodic polarization provides the largest contribution to losses suffered by the traditional SOFC system under operating conditions [73]. Unfortunately, considerable disagreement concerning the number and identity of the elementary electrochemical processes steps occurring in the cathodic reaction still exists [74]. This disagreement is due to three main factors: the method of reduction is dependent on the materials system, variations in sample preparation and measurement conditions affect the output, and subjectivity in analysis of impedance data leads to inconsistency.

Cathodic reduction has been studied on several materials systems, each producing its own results. Some of the earliest work in the area has been on platinum electrode SOFC systems [49]. Because platinum is a purely electronic conductor, the corresponding cathodic reaction is strongly dependent on the surface properties of the platinum. More recently, mixed ionic electronic conductors (MIECs) have been considered as cathodes. For these systems, the cathodic reduction reaction would involve some ionic transport through the bulk of the electrode [54]. In short, the reduction reaction pathway depends on the materials system chosen.

The next factor leading to confusion is variation in sample preparation and measurement conditions. Even for a given materials system and a single laboratory it is impossible to produce identical samples for testing from batch to batch. Slight variations in cathode thickness, cathode sintering conditions, and solid electrolyte properties may be unavoidable. Obviously, when comparing results from laboratory to laboratory, these variations increase. The bias history of the sample may also have some effect on its measured properties [75]. The measurement conditions also include the type of measurement done, i.e. 2, 3, and 4 point probe impedance measurement, each producing a different output for a single materials system.
Third, the process of impedance spectra deconvolution is shaky at best. It has been shown that multiple RC-based models can produce a given impedance spectrum [64]. Additionally, some significant processes may be enveloped by other processes and depending on the chosen method of displaying the data and sensitivity of the equipment these hidden process may be overlooked. The evaluation is further complicated by artifacts introduced in the measurement by the measurement system. These artifacts are typically accounted for by “nulling” (explained in greater detail below) or simply truncating the data to limit the imaginary impedance to negative values. Little understanding exists concerning the validity of the data points immediately after the spectrum crosses the real impedance axis.

The goal of this chapter is to analyze the quality of impedance data, particularly at high frequencies. This is accomplished by determining how the data deviates from a Kramers-Kronig consistent model. Ultimately, a method is proposed which improves the consistency of the high-frequency data. This method was used in chapters 6 and 7 of this dissertation.

3.2 Experimental

Symmetrical cathode/electrolyte/cathode test samples were produced for the work. The cathode used was LSM ((La_{0.8}Sr_{0.2})_{0.98}MnO_{3-δ}) ink supplied by Nextech Materials, Ltd. and YSZ was used as the electrolyte in this work, prepared by tapecasting (Marketech International, Inc.) The YSZ contained 8 mol % yttria and had dimensions of 10.0 × 20.0 × 0.1 mm. The cathode was screen printed on both sides of the electrolyte in two layers with a square area of 64 mm², resulting in the symmetric sample shown in Figure 3-1. A drying step was performed after the screen-printing of each layer in a Fisher Isotemp drying oven at 120 °C for one hour. After drying, sintering at 1100 °C and 1 hour was performed in a Lindberg/Blue high temperature box furnace. The resulting symmetrical samples had a cathode thickness of about 20 microns.
The samples were mounted in a quartz tube inside a Barnstead/Thermolyne furnace to control measurement temperature. The quartz tube consisted of an inlet and outlet for gas flow, gold leads running through alumina rods coated with platinum for shielding, and a pressure contact sample holder. The gold leads were connected by platinum wires to a platinum mesh, which was used as the current collector. The pressure contact holder was designed in a way that exposes the platinum mesh and adjacent cathode to the ambient gas. Air was flowed over the samples at 40 sccm. A Solartron 1260 impedance gain analyzer was used to measure the frequency response of the prepared samples.

Electrochemical impedance spectroscopy (EIS) using a Solartron 1260 impedance gain analyzer was performed in order to measure the frequency response of the prepared samples. A 50 mV AC voltage was applied and the induced current was measured to produce the impedance spectra. Measurement was made via a 2-point connection to the Solartron. Auto-integration was used under “I, long” measurement conditions with an integration time of 60 seconds. I, long is a Zplot option in which the current is measured for noise and an attempt is made to get consistency in the measurements with a maximum standard deviation of 1 % when possible. The active frequency range was
Figure 3-2. Raw impedance of lanthanum strontium manganite (LSM) measured at 900 °C in air. a) Complex plane plot. b) Imaginary impedance vs. frequency plot.

1.0 × 10^{-2} – 3.2 × 10^{7} Hz. SMART, Zplot and Zview were used to acquire and display the impedance data.

3.3 Results and Discussion

3.3.1 High-frequency Artifacts in Impedance Data

1100 °C sintered LSM on YSZ was tested by AC-impedance spectroscopy under a typical operating condition of 900 °C in air. The measurement was repeated six times to give six replicates of the data. Complex plane and \( Z_j \) versus frequency log-log plots of the first replicate are shown in Figure 3-2. The traditional complex plane plot shows a single large arc under these testing conditions. The \( Z_j \) versus frequency plot shown in Figure 3-2(b) is broken into two regions. In the figure, \(-Z_j\) is plotted for the capacitive portion of the data (lower frequencies) and \(+Z_j\) is plotted for the inductive region (higher frequencies). Displaying the data in this format directly indicates the peak frequency and therefore the time constant of the capacitive arc shown in Figure 3-2(a). The slope of Figure 3-2(b) in the low-frequency regime is constant and close to 1, indicating that only one process is dominant in this region and that a constant phase element may not be necessary for modeling in this region. As frequency increases, a high-frequency artifact becomes more and more significant. The slope change in the higher frequencies of the
capacitive arc (10³ to 10⁴ Hz) may be indicative of multiple cathodic processes; however, the contribution of the inductive artifact makes a determination difficult. We can see that around 10⁴ Hz the high-frequency artifact competes with the capacitive data leading to uncertainty in the validity of the data. This impedance profile and its 5 replicates were analyzed using the measurement model technique developed by Orazem [76].

The measurement model uses several RC Voigt elements connected in series to produce a Kramers-Kronig (KK) consistent model for the data. The KK relations are valid for systems that satisfy conditions of causality, linearity, and stability. The KK relations assert that if these conditions are valid, the real and imaginary components of impedance data contain identical information, and in fact, the real part of the data can be generated from the imaginary part, and vice-versa. The KK relations are expressed in Equations 3–1 and 3–2 for a function \( f(x) = u(x) + iv(x). \)

\[
\begin{align*}
  u(x_o) &= \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{v(x)}{x - x_o} \, dx \quad (3–1) \\
  v(x_o) &= -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{u(x)}{x - x_o} \, dx \quad (3–2)
\end{align*}
\]

Fletcher applies the KK relations to an RC circuit in [77]. An inductive artifact is an effect of the imperfect measurement technique and is not specific to the properties of the sample to be tested, i.e. it is non-causal. If the magnitude of this artifact becomes significant then the imaginary part of the data will no longer be linked to the real part and the data is no longer KK consistent. For this reason, a series of Voigt elements will not produce the arc shown in Figure 3-2(a).

When dealing with impedance data, the presence of a high-frequency artifact in the raw data is not unusual. There are three common ways to deal with this phenomena. The first is ignoring the high-frequency portion of the data, understanding that it is not useful. The second is truncating the data at the intersection with the real axis. The third is the use of “nulling”, a technique in which an impedance run is made under open and short circuit conditions and the results are subtracted from the raw impedance data. If
the first option is chosen, we must abandon any hope of recovering useful high-frequency data. Truncating the data, which is typically done at the $Z_r$ axis, gives the impression that the data kept are valid. Below, we show that truncation of the data at the $Z_r$ axis leaves corrupted data in the data set. Application of nulling files often over corrects for the inductive behavior resulting in a false semicircle in the high-frequency portion of the impedance profile.

The measurement model concept [78–80] was developed for the identification of the error-structure of frequency-domain measurements. Orazem et al. extended the model to generalized identification of distributions of time constants and ultimately, a systematic approach was developed for analysis of error structure in impedance data [72, 76]. One of the primary reasons for the development of the model was in the identification of the frequency range that was unaffected by instrumental artifacts of non-stationary behavior. In this work, the measurement model is used to determine the extent of the corruption of the raw data by the commonly observed high-frequency artifact displayed in Figure 3-2(b). Because the measurement model technique relies on a complex nonlinear least-squares (CNLS) technique for the regression of impedance profiles, (the regression is based on both the real and imaginary parts of the data, simultaneously) the solutions attained must be consistent with the Kramers-Kronig relations. In short, the actual data is fit to the following relationship and the parameters $K$, $R_o$, $R_k$, and $\tau_k$ are returned along with corresponding standard deviations.

$$Z = R_o + \sum_{k=1}^{K} \frac{R_k}{1 + j\omega\tau_k}$$  \hspace{1cm} (3–3)

Where $R_o$ describes the ohmic resistance and $K$ indicates the number of Voigt elements in the model while $R_k$ and $\tau_k$ are the polarization resistance and time constant of the $k_{th}$ Voigt element, respectively. If the data is totally inconsistent with the KK relations, the model will fail to converge to a solution and some data points may have to be removed. Because of the non-causal artifact shown in Figure 3-2(b), the high-frequency portion of
the data was not KK consistent, the measurement model would not converge to a solution if the entire data set was used. To alleviate this problem, we applied the commonly used technique of truncating the data at the $Z_r$ axis and an attempt was made to fit the remaining data using the series Voigt element model. A convergent solution; however, was not reached indicating that the data points that were kept still had significant contribution from the artifact. After removing more high-frequency data points, a solution was reached, but the model showed significant deviation from the actual data at the highest frequencies kept, leading to increased error in the model. After more high-frequency data points were removed, the high-frequency deviation between model and data disappeared and a quality fit was attained. The solution had six elements with the constants given in Table 3-1.

Figure 3-3 shows $Z_r$ and $Z_j$ vs frequency plots for the fitting. The figure shows the data with the used points as solid circles located between the vertical bars, truncated points as hollow circles outside the vertical bars, the model as a solid line and the 95% confidence intervals as dashed lines. The asymmetry shown in Figure 3-3(b) is due to the inductive artifact displayed in Figure 3-2(b). The inset figure in Figure 3-2 shows the extent to which data had to be removed to produce a quality, KK consistent solution. Data near the $Z_r$ axis is therefore unreliable.
Table 3-1. R and τ values with their respective errors (standard deviation, σ) for raw data measured at 1100 °C.

<table>
<thead>
<tr>
<th>Process #</th>
<th>R (Ω)</th>
<th>σ_R (Ω)</th>
<th>τ (ms)</th>
<th>σ_τ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element 1</td>
<td>0.883</td>
<td>0.040</td>
<td>0.064</td>
<td>0.002</td>
</tr>
<tr>
<td>Element 2</td>
<td>2.02</td>
<td>0.19</td>
<td>0.24</td>
<td>0.01</td>
</tr>
<tr>
<td>Element 3</td>
<td>5.15</td>
<td>0.11</td>
<td>0.59</td>
<td>0.02</td>
</tr>
<tr>
<td>Element 4</td>
<td>1.01</td>
<td>0.15</td>
<td>1.52</td>
<td>0.11</td>
</tr>
<tr>
<td>Element 5</td>
<td>0.111</td>
<td>0.012</td>
<td>8.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Element 6</td>
<td>0.040</td>
<td>0.004</td>
<td>70</td>
<td>11</td>
</tr>
</tbody>
</table>

Constants such as those shown in Table 3-1 were obtained for each of the 6 repeats of the impedance spectroscopy measurement. The constants obtained were compared and the real and imaginary standard deviation (σ_r,j) in the model was calculated and is displayed in Figure 3-4(a). Figure 3-4(a) shows that σ_r,j has a magnitude on the order of 10^{-3} Ω. Additionally, a consistent trend in both the real and the imaginary standard deviation values is observed; the standard deviations have their largest magnitude values in the low-frequency regime and drop off as frequency is increased. The fact that the error has a frequency dependence but still some randomness indicates that there are both stochastic and non-stochastic errors present in the data. The frequency dependent non-stochastic errors are either related to systematic experimental errors or due to imperfections in the model.

As mentioned previously, cutting off the high-frequency data at the Z_r axis is a common way of dealing with high-frequency artifacts. We used the Measurement Model to show that simply choosing Z_r axis for a cutoff point is insufficient for avoiding the problems caused by the common high-frequency artifact. To effectively avoid contributions from the high-frequency artifact, data must be cut off well above the Z_r axis to ensure reliable data.

3.3.2 Correction of High-frequency Artifacts in Impedance Data

As an alternative to eliminating high-frequency data points which may contain information (overshadowed by an artifact) the following technique is proposed. The
Figure 3-4. Standard deviation ($\sigma_{r,j}$) versus frequency determined from six replicates of data. There is no significant increase in the error of the high-frequency data, despite its being increased an order of magnitude versus the raw data. a) Raw and b) High-frequency corrected data.
Figure 3-5. Raw and high-frequency corrected data for LSM on yttria stabilized zirconia (YSZ) measured at 900 °C in air. a) Nyquist plot. b) Imaginary impedance versus frequency plot.

The highest frequency portion of the imaginary impedance data is first fit to the relationship

\[ Z_j = j \cdot 2\pi f^\beta L_{\text{exp}}, \]

where \( f \) is the frequency of the measurement, and \( L_{\text{exp}} \) and \( \beta \) are constants to be determined from the fitting. If \( \beta \) is equal to one, the expression reduces to \( Z_j = j\omega L_{\text{exp}} \), an expression for the impedance of an ideal inductor. If \( \beta \) is not equal to one, then the high-frequency artifact is not a pure inductance. This fit is valid in the high-frequency regime because as frequency gets large, the capacitive impedance, which is characteristic of the sample, approaches zero and the modeled artifact impedance approaches a large value. The high-frequency portion (3 × 10^5 to 3 × 10^6 Hz) of the raw data from Figure 3-2(b) was fitted to \( Z_j = 2\pi f^\beta L_{\text{exp}} \) and it was found that \( \beta = 1.037 \) and that \( L_{\text{exp}} = 1.46 \times 10^{-6} \). The frequency range is chosen to minimize the influence of capacitive behavior at the lower frequencies and avoid the errors in the data that are present at the highest frequencies. This fitting is subtracted from the raw data with the results shown in Figure 3-5. The high-frequency tail visible in Figure 3-2(a) is diminished and the symmetry of the imaginary impedance data displayed in Figure 3-5(b) is increased dramatically. An analysis of the Kramers-Kronig (KK) consistency of the data provides an objective method of assessing an improvement in the data.
Figure 3-6. Real fit generated from imaginary impedance data and KK relations for LSM on YSZ measured at 900 °C in air. a) Raw data. b) High-frequency corrected data.

Figure 3-6 shows the fit produced by the Measurement Model Toolbox in an impedance versus frequency format. The parameters for the fit are displayed in Table 3-2. Despite the high-frequency data manipulation, there is still some unusable data in the high-frequency regime (approaching 10^6 Hz) as shown in Figure 3-5(b). To get the measurement model to converge, we had to throw out some of the highest-frequency data; however, as shown in Figure 3-6 the usable data extends from 0.63 Hz to 50 kHz while the usable raw data extended to only 3.9 kHz as shown in Figure 3-3. By 10^5 Hz in the raw data, the high-frequency inductance has caused the imaginary resistance value to increase to a positive value of 2 Ω, making the data completely unusable. This frequency range may be crucial when trying to deconvolute impedance spectra as some cathodic processes are expected to have their peak frequency in this regime [81]. As with the raw data, six replicates were used to determine the standard deviation as a function of frequency for the high-frequency manipulated data models. Figure 3-4(b) shows the standard deviation as a function of frequency for the high-frequency manipulated data. It should be noted that the error shows the same general trend as the error from the raw data and is of the same order of magnitude. The usable data was extended an order of magnitude without compromising the quality of the data.
Table 3-2. R and τ values with their respective errors (σ_{R,τ}) for high-frequency corrected data measured at 900 °C.

<table>
<thead>
<tr>
<th>Process #</th>
<th>R (Ω)</th>
<th>σ_{R} (Ω)</th>
<th>τ (ms)</th>
<th>σ_{τ} (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element 1</td>
<td>0.402</td>
<td>0.038</td>
<td>0.023</td>
<td>0.0016</td>
</tr>
<tr>
<td>Element 2</td>
<td>1.120</td>
<td>0.081</td>
<td>0.100</td>
<td>0.0083</td>
</tr>
<tr>
<td>Element 3</td>
<td>3.97</td>
<td>0.42</td>
<td>0.378</td>
<td>0.027</td>
</tr>
<tr>
<td>Element 4</td>
<td>3.54</td>
<td>0.45</td>
<td>0.831</td>
<td>0.058</td>
</tr>
<tr>
<td>Element 5</td>
<td>0.303</td>
<td>0.062</td>
<td>3.41</td>
<td>0.53</td>
</tr>
<tr>
<td>Element 6</td>
<td>0.065</td>
<td>0.008</td>
<td>33.85</td>
<td>6.47</td>
</tr>
</tbody>
</table>

Figure 3-7 shows the real variance divided by the imaginary variance as a function of frequency for both the raw and high-frequency corrected data. For the vast majority of the data, σ_{r}^2/σ_{j}^2 is desirably between 10^{-3} and 10^{-1}. Below 10^3 Hz, there is no significant difference in between the two cases. For both data sets, the ratio σ_{r}^2/σ_{j}^2 decreases as a function of frequency to some minimum value then increases at the highest frequencies. The reason for the decrease of σ_{r}^2/σ_{j}^2 as a function of frequency is that the real part of the data and thus σ has its largest magnitude at low frequencies, while the imaginary part of the data has its largest magnitude at about 10^3 Hz. The increase in σ_{r}^2/σ_{j}^2 can be explained in that the imaginary impedance approaches zero at the highest frequencies used, therefore, σ_{j} is small compared to σ_{r} at the highest frequencies.

In the previous analysis, we used Voigt elements connected in series to fit the data and analyze the error structure. The Voigt elements used were each composed of a resistor connected in parallel to a capacitor. For some systems, a fit composed of resistors and constant phase elements (CPEs) in parallel is more useful. The constant phase element is a mathematical tool used to model a distributed time constant. A resistor in parallel with a CPE produces a depressed semicircle in the complex resistance plane described by the following equation.

$$Z = \frac{R}{1 + RQ(j\omega)^{\alpha}}$$  \hspace{1cm} (3–4)

Z is the complex impedance, R is the parallel resistor, and Q and α are the parameters of the constant phase element describing the frequency dependence and the depression.
Figure 3-7. Real Variance / Imaginary Variance ($\sigma_r^2/\sigma_j^2$) for raw and high-frequency corrected data.

of the arc, respectively. For a single CPE based Voigt element, the slope in an $Z_j$ versus frequency log-log plot at low and high frequencies tends toward $+\alpha$ and $-\alpha$, respectively. If $\alpha = 1$, the constant phase element becomes an ideal capacitor. By examining the high and low-frequency slope of Figure 3-2(b), we can determine if there is constant phase element behavior. In the linear portion of the low-frequency range of Figure 3-2(b), a slope of 0.878 was calculated. This value indicates that we have CPE behavior. Because multiple capacitor based Voigt elements are required to model a single CPE based Voigt element, we can not infer that there are six independent electrochemical processes corresponding to the six capacitor based Voigt elements used in the model. It should be pointed out however, that the value of the regression analysis is in determination of the quality and validity of the data and the focus of this work is not in identifying the number of actual physical processes contributing to the cathodic reaction.

Using 0.878 for $\alpha$, the effective capacitance ($Q_{eff}$) can be calculated as a function of frequency as follows in Equation 3–5 [82].

$$Q_{eff} = \sin\left(\frac{\alpha \pi}{2}\right) \frac{-1}{Z_j(f)(2\pi f)^\alpha}.$$  \hspace{1cm} (3–5)
In the equation, $Z_j(f)$ is the imaginary impedance as a function of frequency. Figure 3-8 shows the effective capacitance as a function of frequency calculated for LSM sintered at 1100 °C. The effective capacitance for the LSM sample stabilizes at around 1000 Hz indicating a double layer capacitance of around 100 $\mu$F.

To further illustrate the significance of data correction, we have evaluated actual parameters for the electrochemical processes occurring in the cathodic reaction of LSM on YSZ in air at high temperatures. We used a series resistance and two R-CPE Voigt elements connected in series to model the individual processes occurring in the cathodic reaction. For each of the two Voigt elements, the returned parameters were R, Q, and $\alpha$. These parameters can be used to calculate the time constant for each of the R-CPE Voigt elements according to Equation 3–6.

$$\tau = (R \times Q)^{1/\alpha}$$

Our previous work [83] has shown that this model is acceptable and that the high-frequency process can be attributed to charge transfer while the intermediate frequency process is related to adsorption of molecular oxygen. Because of the high-frequency artifact, the initial fitting for the charge transfer process in the raw data returned a Q value greater
Table 3-3. Change in polarization resistance, $R_P$, constant phase element coefficients $Q$ and $\alpha$, and time constant, $\tau$, from deconvolution of raw and corrected data for adsorption (1) and charge transfer (2) processes.

<table>
<thead>
<tr>
<th>units</th>
<th>$R_{P1}$ ($\Omega$)</th>
<th>$Q_1$ (mF)</th>
<th>$\alpha_1$</th>
<th>$\tau_1$ (ms)</th>
<th>$R_{P2}$ ($\Omega$)</th>
<th>$Q_2$ (mF)</th>
<th>$\alpha_2$</th>
<th>$\tau_2$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>8.58</td>
<td>0.120</td>
<td>0.913</td>
<td>0.531</td>
<td>0.779</td>
<td>0.0908</td>
<td>1</td>
<td>0.0707</td>
</tr>
<tr>
<td>Corrected</td>
<td>8.59</td>
<td>0.120</td>
<td>0.912</td>
<td>0.531</td>
<td>0.849</td>
<td>0.0677</td>
<td>1</td>
<td>0.0575</td>
</tr>
<tr>
<td>% change</td>
<td>$\approx 0$</td>
<td>$\approx 0$</td>
<td>$\approx 0$</td>
<td>$\approx 0$</td>
<td>8.24</td>
<td>34.0</td>
<td>n/a</td>
<td>23.0</td>
</tr>
</tbody>
</table>

than one, so we fixed this value at one, effectively modeling the charge transfer process with an RC Voigt element. Table 3-3 gives the parameters returned from the model and Figure 3-9 displays the raw and corrected data along with corresponding individual processes from the model. Both the table and figure show that the low-frequency, higher impedance process (adsorption, labeled “1” in the table) is practically unchanged by the performance of the high-frequency correction process; however, evaluation of the high-frequency process (charge transfer, labeled “2”) is significantly altered by the correction. As seen in Table 3-3 the determined value for the charge transfer polarization resistance and time constant change by 8.3 and 23 %, respectively. It is clear that the high-frequency inductive feature can significantly distort determined electrochemical parameters for high-frequency, low impedance magnitude processes. In other words, inclusion of Kramers-Kronig inconsistent data in the evaluation can lead to significant deviation of determined parameters from their actual values. Because the inductive feature has large values at very high frequencies, performance of data correction is of particular importance for those who have optimized their system to minimize impedance and improve rate of reaction.

3.3.3 Repeatability of Measurements

A repeatability study was performed using samples sintered at 1100 °C for one hour and measured at 800 °C. The first sample, sample 1, was measured three times on three consecutive days. Between measurements, the sample was cooled to room temperature, removed from the experimental set-up, then put back in and re-measured. Two more
Figure 3-9. Modeled electrochemical process occurring in LSM on YSZ measured at 900 °C in air.
samples were prepared and sintered at the same time as sample 1. The impedance data for samples 1, 2, and 3 is displayed in Figure 3-10. The figure shows that for sample 1, the total resistance increased from the first measurement to the third. It is unclear whether the instability observed indicates that the process of impedance measurement alters the sample, or whether the sample is unchanged and the resistance difference is due to variations in sample orientation. The profiles of samples 2 and 3 also show variation in total resistance. Changes of this magnitude are greater than any errors associated with the modeling of the data or any correctable error associated with high-frequency artifacts.

The series (ohmic) resistance and total cathodic resistance of the measurements shown in Figure 3-10 are displayed in Figure 3-11. The y-axis used in Figure 3-11 is the time constant of the peak, measured as the inverse of the angular frequency of the peak of the profiles in Figure 3-10. As seen in Figure 3-11(a), the series resistance of sample 1 decreases from almost 6 to about 5.2 Ω from the first to the third run. Samples 2 and 3 had series resistances of 5.1 and 5.7 Ω, respectively giving a mean series resistance of 5.6 Ω and a standard deviation of 0.45 Ω. This variation is either due to the microstructural

Figure 3-10. Repetitions of an impedance measurement taken at 800 °C in air.
Figure 3-11. Resistance values for repetitions of an impedance measurement taken at 800 °C in air. a) Series resistance. b) Cathodic total resistance.

variations in the samples (despite the fact that they come from the same batch and were sintered together) or differences in the quality of the pressure contacts. Figure 3-11(b) displays the total cathodic resistance measured for each sample. This value increases from 84 to about 112 Ω from the first to the third measurement of sample 1. Samples 2 and 3 had cathodic resistance values of 96 and 86 Ω, respectively. Samples 1, 2, and 3 had a mean cathodic resistance of 88.5 Ω and a standard deviation of 6.8 Ω. Since $\tau = RC$, the slope of the data is equal to the capacitance which was calculated to be 14.3 μF. The series resistance did not have a constant capacitance.

3.4 Conclusion

We were able to successfully apply a measurement model technique to EIS data from an LSM on YSZ sample. A Kramers-Kronig consistent model was used to fit the data and analyze the error. The model used consisted of a series resistance and six Voigt elements connected in series. As with most impedance data, a high-frequency artifact corrupted the high frequency data, limiting the frequency range of useful data. The models attained produced a good fit visually and the data values lied primarily within calculated 95% confidence intervals. It was found that the commonly used practice of truncating the data at the $Z_r$ axis left KK inconsistent data in the data set. To avoid inconsistent data, several data points at frequencies lower than the $Z_r$-axis had to be removed. The
consistency of the data was improved by fitting the high-frequency portion of the data (which was shown to be inductive in nature) to $Z_j = j\omega L$ and subtracting the result from the raw data over the entire frequency range. Performing this operation increased the amount of usable data in the high-frequency regime by an order of magnitude allowing analysis of fast occurring electrochemical processes in our other work [83]. Additionally, we have shown that the data exhibits CPE behavior and a model intended to describe the physical mechanisms of the cathodic reaction should therefore be based on R-CPE type Voigt elements. When modeling the data for the purpose of determining electrochemical parameters, high-frequency, low impedance electrochemical process are particularly vulnerable to the inductive artifact. A limiting double-layer capacitance of around 100 $\mu F$ was found at high frequencies. A repeatability study was performed and it was found that both series resistance and total cathodic resistance had standard deviations of around 8 %, which is larger than errors associated with the modeling which are generally less than 1 %.
CHAPTER 4
ELECTROCHEMICAL PROCESS IDENTIFICATION

4.1 Introduction

The cathodic reduction reaction for LSM on YSZ fuel cells was discussed in detail in section 2.3. As mentioned, the overall cathodic reaction is composed of many individual steps. For an electronic conducting cathode, such as LSM, the general sequence of steps defining the cathodic reaction is fairly well agreed on; however, the significance of each of the individual steps is still discussed. The sequence begins with the arrival of $O_2$ molecules that have diffused through the porous cathode to the vicinity of the electrolyte. At some point after this diffusion, the molecules are adsorbed (dissociatively or as complete molecules) on the surface of the LSM. These adsorbed species now diffuse on the surface of the electrode towards the triple phase boundary, the area where the cathode, electrolyte and gas phase meet. At the same time, electrons (or holes) travel through the cathode, while oxygen vacancies travel through the electrolyte. For a purely electronic conducting cathode, the oxygen species are restricted from the bulk of the electrode, the oxygen vacancies are limited to the electrolyte, and the electronic species (electrons and holes) are limited to the cathode. For the complete cathodic reaction to occur, all of these species must come together; therefore, the cathodic reaction is limited to the TPB.

Modeling of the cathodic reaction is often performed using an electrical circuit design containing inductors, capacitors and resistors. A single electrochemical step with an associated capacitance and a resistance can be modeled by a Voigt element (a single resistor and capacitor in parallel) [84, 85]. An assumption that the various electrochemical steps of the cathodic reaction occur sequentially leads to a model consisting of a series connection of Voigt elements. This is a reasonable assumption for a purely electronic conducting cathode in which only one reaction pathway is likely. Another possibility is that one or more of the steps are mutually dependent. In this scenario, a simple series connection of Voigt elements may not be suitable.
In this section impedance spectroscopy is used to examine the contribution of each of the significant electrochemical processes to the overall cathodic reaction in symmetric LSM on YSZ. A series Voigt element model (with constant phase elements in place of capacitors) is used to examine the pO$_2$ dependence, activation energies, relative polarization resistance magnitudes, and time constants the individual reactions. The activation energies and pO$_2$ dependences were compared with the values determined from other authors to aid in identification of the individual electrochemical processes.

### 4.2 Experimental

The samples were prepared and impedance tested in the same manner described in section 3.2. In this chapter, pO$_2$ was one of the variables examined. Oxygen, air, and argon gases were used to produce the desired atmospheric conditions. For pO$_2$s at or above 0.01 atm, mass flow controllers were used to regulate the flow of argon and air onto the sample, producing gas flows of known composition at 40 cc/min. For pO$_2$s of 0.001 atm and less, a ZIROX SGM5-EL electrolysis device was used to generate the desired concentration at a flow rate of 100 cc/min.
Figure 4-2. Deconvolution of an imaginary impedance versus frequency profile into various individual contributing processes.

4.3 Results and Discussion

Figure 4-1(a) and (b) are Nyquist and \(-Z''\) vs. frequency plots of symmetric LSM samples sintered at 1100 °C for 1 h at various measurement temperatures in air. The peaks and changes in slope of the \(-Z''\) vs. frequency plot indicate the characteristic frequencies of the significant steps of the cathodic reaction. The 900 °C arc in Figure 4-1(a) is basically semicircular, but not quite symmetrical. This geometry indicates that there is one large resistance process enveloping another smaller resistance high frequency process. At the lower temperatures displayed in 4-1(b), two other processes are apparent which are attributed to oxygen vacancy diffusion through the bulk and grain boundaries of the electrolyte [10]. These processes are smaller in magnitude than the cathode processes, but at lower temperatures, the cathode processes are not seen in the profile. At higher temperatures, the electrolyte processes have very small resistance and are overwhelmed by the cathodic processes and inductive artifacts.

Each of the impedance profiles included in 4-1 was separated by a subtraction technique into the various contributions. Because the primary focus of this work is identification of the individual reaction steps separated by their respective time constants, use of constant phase elements in the place of the capacitors in the Voigt elements of the
model is appropriate. Modeling with pure capacitors is limited in that multiple Voigt elements may be required to model a single process step if the behavior is inhomogeneous; otherwise, compromises may have to be made to match only a selected portion of the curve. Also, if the homogeneity changes over the range of temperatures measured, the depression angle of the arc may change, resulting in a non-Arrhenius dependence of resistance and time constant on temperature. Figure 4-2 illustrates the separation of the 500 °C measurement of symmetric LSM on YSZ cells sintered at 1100 °C into three contributing electrochemical processes. Each of the indicated electrochemical processes is modeled by a single R - CPE Voigt element. This separation was repeated at all measurement temperatures for the sample.

Figure 4-3(a) and (b) display the Arrhenius dependence of polarization resistance and time constant for the LSM 1100 °C 1 h sample. The time constant (τ) is calculated as described in Equation 4-1.

\[ \tau = (R \times Q)(1/\alpha) \]  

Equation 4-1

In Equation 4-1 R is the polarization resistance, Q and α are the non-exponential and exponential terms of the constant phase element, respectively. The activation energy (E_a) for the polarization resistances of the individual reactions can be calculated as follows.

\[ R = R_0 \exp \left( \frac{E_a}{kT} \right) \]  

Equation 4-2

In Equation 4-2, R is the polarization resistance, R_0 is a constant, k is the Boltzman constant, and T is the temperature.

Examination of Figure 4-3(a) reveals that there is some change in slope in the high temperature region of process 4. This is an indication that the changes in slope in the high temperature regime were due to either changes in the homogeneity of the dominant electrochemical process step, or a contribution from a different electrochemical process with a different activation energy. Figure 4-3(b) indicates a somewhat smoother profile in the same region for the same process. This supports the former of the two possibilities.
Figure 4-3. Temperature dependence of the separated contributions in LSM on YSZ sintered at 1100 °C for 1 h in air. The numbers indicate the process step number given in Table 4-1. a) Polarization resistance. b) Time constant.

Table 4-1. Select elementary steps of the cathodic reaction in samples sintered at 1100 °C.

<table>
<thead>
<tr>
<th>Process #</th>
<th>Process Identity</th>
<th>x in Equation 4-3</th>
<th>$E_a$ (eV)</th>
<th>$\tau$ (s) at 800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ionic diffusion (bulk)</td>
<td>0.0</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Ionic diffusion (grain boundary)</td>
<td>0.0</td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Charge transfer</td>
<td>0.0</td>
<td>0.97</td>
<td>$8.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>Dissociation and surf. diff.</td>
<td>-0.15</td>
<td>1.17</td>
<td>$1.8 \times 10^{-1}$</td>
</tr>
<tr>
<td>5</td>
<td>Gas diffusion through cathode</td>
<td>-1.1</td>
<td>0.0</td>
<td>$6.0 \times 10^{0}$</td>
</tr>
</tbody>
</table>

as the effect of varying depression angles on the resistance or time constant would be minimized in the time constant calculation. Knowledge of the Arrhenius dependence of the polarization resistance and time constant of the individual electrochemical process steps is all the information needed to generate the impedance profile as a function of only temperature. The polarization resistance and time constant activation energies are presented in Table 4-1.

Figures 4-4(a) and (b) display the influence of $pO_2$ on the various electrochemical processes occurring at 900 °C. $pO_2$s ranging from 0.21 to $1 \times 10^{-6}$ atm were created by mixing air with argon. The Figure indicates that a second process in the low frequency regime gains significant magnitude at low $pO_2$ values. The process is first resolvable at 0.001 atm and grows as $pO_2$ is further reduced. The dependence of polarization resistance on $pO_2$ is displayed in Figure 4-5. The high frequency section of Figure 4-4(b) shows an
increase in imaginary impedance for the lower partial pressure measurements. We believe that the increase in imaginary impedance above $10^5$ Hz is an experimental artifact due to induction and not the result of some new high frequency process that is not present at the higher $pO_2$s. Comparison of Figures 4-5(a) and (b) shows that the low frequency process has a significantly stronger dependence on $pO_2$ than the other processes. The dependence of polarization resistance can be expressed as a function of $pO_2$ according to the following expression.

$$R \propto (pO_2)^x \quad (4-3)$$

The exponential value, $x$, is equal to the slope of the line in Figure 4-5 and its values are indicated in 4-1. The strong dependence of this process on $pO_2$ indicates that it is very closely related to oxygen diffusion. Because impedance spectroscopy is an electrochemical measurement technique, the diffusion of gas molecules can not be registered until they are converted into a species that can participate in the electrochemical reaction [74]. A rapidly adsorbing surface, which permits an oxygen flux equal to the flow of gas through the open pores, would produce such an effect. The lowest frequency arc (process 5) in the lowest partial pressure regime is due to a process limited by the bulk diffusion of
oxygen molecules to the adsorbing surface. The two processes (process 1 and 2) which are present in the high frequency regime and at low temperatures, become hidden at higher temperatures. These processes are likely due to the electrolyte bulk and grain boundary, a conclusion supported by their determined activation energies. This leaves two as yet unidentified processes, which can be attributed to the cathode. One of these processes has much smaller impedance and is located in the high frequency regime, and the other is located in the lower frequency regime and has much larger impedance, greatly influencing the overall shape of the Nyquist plot at high temperatures. A charge transfer located at the TPB, would be rather fast process with weak dependence on $pO_2$. Figure 4-5(a) indicates that process 3 is nearly independent of $pO_2$, while process 4 is has an exponential dependence of -0.15. Charge transfer is two steps removed from molecular oxygen, while adsorption directly involves molecular oxygen; therefore, process 3 is likely due to charge transfer. Adsorption, dissociation, and surface diffusion are all possibilities for the identity of process 4, which has a stronger dependence on temperature and $pO_2$ than the charge transfer reaction. The identities of the contributing processes are summarized in Table 4-1.
4.4 Conclusion

The impedance data in this chapter was fitted using a series R-CPE Voigt element model to separate the individual processes contributing to the cathodic reaction. Three cathodic processes were identified, two of which were present under all partial pressures of oxygen. These three processes are measurement temperature dependent and are indicated in Figure 4-6. In the figure, processes 1 and 2 are due to ionic transfer through the bulk and grain boundary of the electrolyte, respectively. (The process indicated by 0 is an artifact related to overcorrection from inductance in the system.) Numbers 3 and 4 indicate cathodic process which are related to charge transfer and dissociative adsorption, respectively. Process 3 is of much smaller magnitude than 4 and close in relaxation frequency and is therefore enveloped in the figure. Process 5 is only resolvable at low \( pO_2 \)s and is related to bulk diffusion of oxygen gas to the reaction site. Polarization

![Impedance data measured at various temperatures for an 1100 °C, 1 h sintered sample at 0.002 % O_2. The numbers indicate the process identity from Table 4-1.](image)

Figure 4-6.
resistance activation energies and time constants are generated from the model parameters and given in Table 4-1. Since the process indicated by a 0 is not a result of any physical phenomena associated with the cathodic reduction reaction, it is not included in the table. It was found that charge transfer and dissociative adsorption processes were not strongly dependent on pO$_2$, whereas the bulk diffusion related process was strongly dependent on pO$_2$. 
CHAPTER 5
TERTIARY PHASE FORMATION

5.1 Introduction

For pure electronic conducting electrodes, the electrochemical reaction driving fuel cell operation is restricted to the triple phase boundary (TPB), the area where the cathode, electrolyte, and oxidant meet [55]. Authors have used composite cathodes to increase the triple phase boundary length and shown that increasing the TPB area results in reduced electrode resistance for LSM/YSZ systems [56, 57]. In dealing with single-phase cathodes, triple phase boundary length can be maximized by ensuring high porosity in the electrode and good adhesion between the electrode and electrolyte. Despite being useful for high-temperature SOFCs, the performance stability of LSM on YSZ fuel cells is an issue [2, 73, 86]. Much of the power loss in SOFCs is due to polarization loss at the cathode/electrolyte interface, one source of which is degradation of this interface. This degradation can be microstructural, such as severe coarsening and delamination, or compositional as with the formation of tertiary phases. Tertiary phases, which may form during fabrication or long term high temperature operation, are often insulating and therefore detrimental to SOFC performance [87]. These and other effects can be induced in a timely fashion through the use of high temperature anneals. The impact of microstructural and interfacial changes caused by harsh anneals on the overall cathodic reaction is studied in this chapter.

5.2 Tertiary Phase Formation

During high temperature operation, the diffusivity of the elements of the electrode and electrolyte materials is increased. Consequently, La, Mn, and Sr diffuse from the LSM electrode into the YSZ electrolyte. Of these diffusing species, Mn has been shown to be the fastest diffuser [68, 88, 89]. At 1000 °C, diffusion of Mn into YSZ is negligible, but from 1200-1400 °C Mn diffusion becomes considerable [90]. A consequence of this fact is that regions form near the interface that are deficient in Mn and therefore, high in La, Sr, Zr, and O. If concentration of these elements becomes sufficiently high, formation
of lanthanum-zirconate (LZ, La$_2$Zr$_2$O$_7$) and strontium-zirconate (SZ, SrZrO$_3$) may become favorable. Formation of secondary phases can be predicted from chemical potential diagrams [91]. Of these two phases, the one that materializes is determined by the Sr dopant concentration in the LSM and the temperature of anneal [2, 89, 92, 93]. Both of these phases have higher resistivities than YSZ so their presence is deleterious to device performance [94–97]. Chiodelli and Scaglioni have measured the conductivity of the La$_2$Zr$_2$O$_7$ layer via impedance spectroscopy [98]. The authors efficiently formed an LZ layer by solid state reaction of lanthanum oxide and a single crystal YSZ substrate. The work reports conductivities of $2 \times 10^{-4}$ and $8.6 \times 10^{-2}$ S cm$^{-1}$ for LZ and 9.5 mol % yttria YSZ, respectively at 1000 °C. Additionally, it is reported that the conductivity difference increases as temperatures are lowered. Y and Zr will also diffuse from YSZ into the LSM, however, this diffusion occurs to a lesser extent as shown by Yang et al. [86]. The presence of Sr in the LSM has been shown to suppress the diffusion of Mn into the YSZ [99]. This leads to a phase composition and reaction layer thickness that is dependent on Sr content [68]. Kenjo and van Roosmalen have independently reported that LZ formation can be suppressed by using non-stoichiometric LSM [92, 96].

Taimatsu et al. found that there is a limited temperature range, in which secondary phases form from solid state reactions, suitable for study. The work found that above 1450 °C, liquid phases were always formed at LaMnO$_3$/YSZ interfaces and near 1300 °C, reactions were too slow for their processes to be examined within a few weeks. Below 1425 °C reactions proceeded in the solid state, and morphologies of reaction zones resembled one another. Therefore, annealing near 1400 °C was used to examine the reactivity of LaMnO$_3$ with YSZ by the authors [100]. Other works have also used 1400 °C anneals to produce reaction layers [86, 88]. Yang et al. formed 3-4 micron thick reaction layers consisting of SZ and LZ with a 1400 °C 48 hr firing of a screen printed LSM (0.3 Sr) on YSZ interface.
In addition to being dependent on temperature and time, the formation of secondary phases is also dependent on the interfacial area and type. It has been shown by Kleveland et al. that secondary phases which form after 70 hr anneal at 1200 °C at a powder mixture with large interface area won’t form after 120 hr at a diffusion couple type interface (which is similar to a single-phase electrode/electrolyte interface) and that a harsher anneal is necessary to produce secondary phases at the diffusion couple interface [68].

5.3 Experimental

The samples used in this chapter were prepared and impedance tested in the same manner described in section 3.2. In this chapter; however, LSM powder provided by Nextech was used. The powder was mixed with bonders, plasticizers, and solvents to produce an ink of the desired viscosity. The LSM powder was stoichiometric with a 1:4 Sr to La ratio. After sintering at 1100 °C, samples were subjected to high-temperature post-anneals intended to simulate the possible effects of long-term operation in a timely fashion.

A JEOL 1400 SEM (scanning electron microscope) equipped with energy-dispersive X-ray spectroscopy (EDS) was used for sample imaging. X-ray diffraction (XRD) was performed on a Philips APD 3720 XRD. TEM analysis was performed using a JEOL 200CX TEM (tunneling electron microscope) by Mark Clark and is included in Appendix A. All microstructural characterization was performed at the Major Analytical Instrument Center (MAIC) at the University of Florida.

5.4 Results and Discussion

5.4.1 Electrochemical and Microstructural Characterization

An 1100 °C, 1 h sintered sample was impedance tested and then subjected to a 1400 °C 48 h anneal and retested. The effect of the 1400 °C 48 h anneal on the electrochemical behavior of the symmetric sample is displayed in Figure 5-1. In this figure a 600 °C measurement temperature was used in the frequency response analysis.
Figure 5-1. Complex plane plots measured at 600 °C of symmetrical LSM on YSZ samples as sintered and after a 1400 °C, 48 h anneal.

Upon comparison of the profile before and after the 1400 °C anneal, it is apparent that one process with a characteristic frequency of 3.2 Hz is present in both spectra. Examining the low-frequency regime reveals drastic change as the system exhibits linear behavior with an angle close to 45°. Such behavior has been reported in [64] and is described as a Warburg impedance caused by a diffusion limitation. In the high-frequency regime, a process appears in the post-annealed sample that was not apparent in the as sintered sample. The causes and significance of these changes are discussed below.

Figures 5-2 and 5-3 display EIS profiles for the sample before and after the application of a subsequent 1250 °C 48 h anneal, respectively. The EIS data was taken at low measurement temperatures where the high-frequency behavior is emphasized. Comparison of Figure 5-3(a) to 5-2(a) and 5-3(c) to 5-2(c) reveals little change in the high and intermediate-frequency processes (electrolyte bulk and grain-boundary polarization resistance, respectively) after the 1250 °C anneal. In the low-frequency regime the 1250 °C anneal seems to have a clear effect. The low-frequency process (related to molecular adsorption), which is semicircular in Figure 5-2, is replaced by Warburg behavior in Figure 5-3 (especially apparent at 500 °C). As explained by Macdonald in reference [64], Warburg
Figure 5-2. Impedance spectra for as sintered (1100 °C) sample at various measurement temperatures. a) Complex plane plot. b) High-frequency view of the complex plane plot. c) Imaginary impedance vs. frequency plot.
Figure 5-3. Impedance spectra for sample after a subsequent 1250 °C, 12 h anneal measured at various measurement temperatures. a) Complex plane plot. (b) High frequency view of the complex plane plot. c) Imaginary impedance vs. frequency log-log plot.
behavior is generally a consequence of a diffusion limitation, thus the 1250 °C 12 h anneal likely hinders the diffusion of ambient oxygen to the reaction site, significantly impeding the cathodic reaction. This is due to coarsening of the porous LSM to such an extent that the diffusion of oxygen through the cathode is reduced or eliminated. Additionally, coarsening of the LSM could greatly reduce or destroy the TPB, which will also inhibit the cathodic reaction.

Figures 5-4 through 5-6 display the microstructure of the symmetric samples at the LSM/YSZ interface. Figure 5-4 shows the as sintered microstructure after an 1100 °C 1h anneal, while Figure 5-5(a) shows the microstructure after a 1250 °C 12 h anneal. Comparison of the figures illustrates the coarsening of the LSM microstructure that occurs with an anneal of this severity. This microstructural change forecasted by the changes in the impedance profile with the harsh anneal is verified by the SEM images.

Figure 5-5(a) shows coarsening of the LSM microstructure after a 1250 °C anneal of 12 h. After 48 h the coarsening becomes more pronounced (Figure 5-5(b)). The coarsening of the LSM after 1400 °C anneal is more complete (Figure 5-6). In fact, the coarsening after only 1 hr at 1400 °C occurs to a greater degree than after 48 h at 1250 °C. Focusing on the LSM/YSZ interface, it is noticed that for the 1400 °C annealed
Figure 5-5. Scanning electron microscopy images of the LSM/YSZ interface for samples sintered at 1250 °C. a) Sintered for 12 h. b) Sintered for 48 h.

Figure 5-6. Scanning electron microscopy images of the cathode/electrolyte interface for samples sintered at 1400 °C. a) Sintered for 1 h. b) Sintered for 12 h.
samples, a coalescence of vacancies into extended interfacial pores occurs that is not present in the 1250 °C annealed samples. The effect of this microstructural change is inhibition of the cathodic reaction, by blocking electrons from reaching the TPB.

The low temperature frequency response of a test sample subjected to a 1400 °C 12 h anneal is displayed in Figure 5-7(a-c). Comparing Figure 5-7 with Figure 5-3 illuminates the differences between anneal at 1250 and 1400 °C on the impedance spectra. The electrolyte bulk and grain-boundary processes present in Figure 5-3(a) are replaced by one high-frequency process in Figure 5-7(a). The impedance magnitude of the high-frequency process visible in Figure 5-7(a) is more than an order magnitude
greater that the high-frequency process of Figure 5-3(a). This increase is due to the microstructural and interfacial changes that occur with the 1400 °C anneal including the formation of insulating tertiary phases, eradication of the TPB, and the formation of extended interfacial pores. Significant coarsening occurs at 1250 °C as displayed in Figure 5-5; however it is clear from the impedance profiles that 1400 °C sintered sample is significantly more degraded. Focusing on Figures 5-3(c) and 5-7(c), we see that the low-frequency behavior of both systems is similar with the exception of the 500 °C measurement, yet different from Figure 5-2(c). Although the 500 °C impedance profile in Figure 5-6(c) appears to begin to close off at low-frequencies, it is likely that were the low-frequency limit of the EIS decreased, a diffusion limitation tail would appear. This is an expected result of the coarsening of the LSM microstructure, which prevents free flow of molecular oxygen to the electrolyte.

Figure 5-8. High-frequency arc resistance versus anneal temperature for various anneal (temperature, time) pairs measured at 400 °C.

Figure 5-8 illustrates the dependence of the high-frequency EIS contribution on anneal temperature and time. The figure displays a gradual increase of high-frequency arc resistance with anneal at temperatures below 1400 °C. In this temperature range there is no clear dependence on anneal time. At 1400 °C, however, the impedance
increases dramatically and a positive dependence on time appears. This change occurs despite Figure 5-6 which shows that by 1 h the microstructure has become nearly dense, leaving little possibility of increased coarsening with longer time anneals. Factors other than microstructure must be considered when explaining the observed increase in high-frequency impedance.

5.4.2 Compositional Characterization

Figure 5-9 shows EDS linescans of the manganese Kα intensity at the LSM/YSZ interface of as sintered samples with and without a 1400 °C 48 h anneal. Despite the fact that Mn is known to be a fast diffuser at high temperatures [88, 90], the profile is more abrupt in the harshly annealed sample. This apparent contradiction can be explained by
considering the interfacial effects that occur in the harshly annealed sample. Extended pores at the cathode/electrolyte interface will physically hinder or prevent diffusion of Mn from the cathode to the electrolyte, effectively creating an abrupt interface. Alternatively, the formation of a Mn free phase such as lanthanum or strontium zirconate would also produce a more abrupt profile due to the expulsion of Mn from the region of formation during growth. Additionally, as Mn diffusion into the zirconate is blocked, a buildup of Mn at the edges of the zirconates is likely, resulting in a more abrupt Mn profile.

The 1250 °C, 1325 °C, and 1400 °C, 12 h annealed samples were examined by XRD as displayed in Figures 5-10(a)-(c), respectively. In all samples, energy peaks characteristic of LSM and YSZ were observed. In addition to these peaks, there is evidence of a tertiary phase present at the interface of the 1325 °C and 1400 °C annealed samples. The proximity of some of the tertiary phase peaks to the peaks of LSM hinder the analysis. To reduce the complexity of the XRD spectra, the samples were bathed in highly concentrated hydrochloric acid to remove the LSM layer. XRD of the LSM stripped samples clearly show a set of peaks corresponding to YSZ and another set of peaks for the 1325 °C and 1400 °C annealed samples. The second set of peaks matches those belonging to a known lanthanum zirconate \( \text{La}_2\text{Zr}_2\text{O}_7 \) sample. Additional compositional analysis using tunneling electron microscopy was performed by Dr. Mark Clark and is included in Appendix A. These results show that a 0.2 micron thick transitional region rich in lanthanum and zirconium forms at the LSM/YSZ interface after annealing at 1400 for 48 hours. The interfacial region was shown to have a similar crystal structure as YSZ, indicating that manganese diffuses into the electrolyte as the tertiary phase forms.

5.5 Conclusion

Electrochemical and compositional analysis has been used in this chapter to investigate the effects of harsh anneals on the electrochemical processes contributing to the cathodic reaction occurring at the LSM/YSZ interface. The electrochemical evaluation focused on low measurement temperatures to emphasize high-frequency
Figure 5-10. X-ray diffraction of samples subjected to post-anneal sintering. No LZ peaks are observed for the 1250 °C sintered sample. a) Sintered at 1250 °C. (b) Sintered at 1325 °C. c) Sintered at 1400 °C.
processes. We have seen three arcs which are related to the electrolyte bulk, electrolyte grain-boundary, and an adsorption process in the previous chapter. Application of a harsh anneal of 1250 to 1400 °C increases the impedance of the electrode dependent arc. This increase is attributed to changes in the microstructure of the LSM, which are observed via SEM and formation of the tertiary phase, lanthanum zirconate. Application of a 1400 °C anneal destroys the TPB leading to a high-frequency arc in the EIS spectra indicating that the cathodic reaction is hindered. This arc is an order of magnitude greater in impedance magnitude than the high-frequency processes present in samples annealed at lesser temperatures. Through EIS, it is found that the impedance of this arc increases with time annealed at 1400 °C. It is found that sintering above 1325 °C produces compositional changes that are consistent with the formation of lanthanum zirconate at the cathode/electrolyte interface.
6.1 Introduction

During fabrication or longterm high-temperature operation, microstructural changes occur which affect performance of LSM on YSZ devices [81]. Because high temperatures are required for fabrication, to some extent these changes can not be avoided. The overall result is that the cathodic reaction, which is dependent on oxygen gas flowing through the pores, diffusing towards the reacting site, and being transferred to the electrolyte is affected by the altered microstructure. The impact of microstructural and interfacial changes on the electrochemical steps contributing to the overall cathodic reaction is investigated in this chapter.

In a previous chapter, the impact of very high-temperature anneals on the cathodic reaction was examined. Both dramatic changes in microstructure were produced and tertiary phases were formed at the cathode/electrolyte interface, altering the cathodic reaction. In this chapter, microstructural changes are produced by sintering at lower temperatures in an attempt to decouple microstructural changes and tertiary phase formation. Additionally, non-stoichiometric LSM \((La_{0.8}Sr_{0.2})_{0.98}MnO_{3-\delta}\) was used which has been shown to decrease formation of tertiary phases [92, 96]. Establishing a direct relationship between cathode microstructure and electrochemical performance will clarify the cathodic reduction reaction pathway and aid in identification of the rate-limiting step, which is not known conclusively [73, 74].

Several works have been performed with the goal of establishing a relationship between \(L_{TPB}\) and electrochemical properties. Typically, the DC resistance, or the entire cathodic resistance determined from impedance spectroscopy are related to electrochemical performance. One of the most frequently cited works in the area was performed by Mizusaki et al. who found that total cathode conductivity, measured by impedance spectroscopy at 1000 °C, is essentially proportional to \((L_{TPB})^{-1}\) for drip
pyrolysis prepared $La_{0.6}Ca_{0.4}MnO_3$, LCM/YSZ/platinum cells sintered between 1100 and 1200 °C [101]. The results from this work are somewhat questionable since only two data points are plotted to give the observed dependence. Additionally, when a different fabrication technique was used, a non-linear power dependence of total cathodic polarization resistance on $L_{TPB}$ was reported.

Another frequently cited work was performed by Kuznecov et al. [102], who derived a relationship successfully explaining the linear dependence reported by Mizusaki i.e. $R_{cathode} \propto (L_{TPB})^{-1}$. In the model, the author assumes that surface diffusion of adsorbed species towards the TPB dominates $R_P$ and that the DC resistance can be modeled by considering this flow of adsorbed species to the TPB. The model basically relates the cathodic resistance to the flux of adsorbed species on the surface of the cathode. As reported by Macdonald et al. a surface diffusion limitation is often manifested by Warburg behavior in the impedance profile [110]; however, we did not see Warburg behavior at high-frequencies and so the development described in the work may not be appropriate for our data.

In a later work by Kuznecov et al. it is reported that for kinetics controlled by bulk diffusion through the cathode, $R_{cathode} \propto (\text{MIEC/YSZ contact area} \times L_{TPB})^{-0.5}$ [103] This development is based on the work of Adler et al. [52]. The model of Adler et al. was intended to describe cathodes with significant ionic conductivity and is reported by Adler et al. to be inconsistent with LSM behavior. This model considers flow of ionic species through the cathode bulk to be the limiting factor and calculates the conductivity from this flow. From the data of Kuznecov et al., a power dependence of -0.39 can be calculated (from only two data points) when relating total $R_{cathode}$ to $L_{TPB}$ for LSM measured at 950 °C [103].

In another work, Fleig showed that for well defined, dense patterned LSM microelectrodes of circular geometry, the total cathodic resistance is proportional to electrode diameter (D) to the -2.1 power when measured at 800 °C. In this geometry, $L_{TPB}$ is equal to the
circumference (C) where $C = \pi \times D$ and therefore, $R_P \propto (L_{TPB})^{-2.1}$. Additionally, Fleig reported that the resistance scales almost linearly with thickness and that application of a bias can change the exponent of that relationship [50, 104]. Fleig concluded that since total cathodic resistance scales inversely with electrode contact area (area = $0.25 \pi \times D^2$) and linearly with thickness, a bulk path through the electrode determines the oxygen reduction rate, with transport of oxide ions in LSM being the rate-determining step. It should be pointed out that the dense circular electrodes used by Fleig had thicknesses of only 0.1 to 0.25 $\mu$m and diameter on the order of 60 $\mu$m, so ionic transport through the electrode could be appreciable. In contrast, in the present work we used porous electrodes with thickness on the order of 20 $\mu$m and individual particle sizes of around 1 $\mu$m. Therefore, different reaction pathways are likely. For example, if an oxygen molecule is adsorbed at the center of the top of one of the circular disks, the adsorbed species must travel over 30 $\mu$m to reach the electrolyte via a surface path, but only 0.1 $\mu$m to reach the electrolyte through the cathode bulk. On the other hand, for relatively spherical particles, the path to the electrolyte via the surface will be around the same distance for both surface and bulk diffusion. Obviously, both the shape of the cathode and the relative ease of transport through the bulk versus on the surface will determine which path is favorable for an adsorbed species. Additionally, surface area (not volume normalized surface area) also scales linearly with cathode thickness and so additional evidence is needed to support the bulk transport conclusion.

One of the first authors to utilize knowledge of a relationship between polarization resistance and $L_{TPB}$ was Ostergard et. al. who decreased polarization resistance by forming composite cathodes which have increased $L_{TPB}$ [57]. It has been reported that the dependence of polarization resistance on composite cathodes thickness depends on the measurement temperature and that as composite cathode thickness increases, polarization resistance decreases until gas diffusion effects become important. [105, 106]
Because the electrolyte is sintered to a dense state at temperatures higher than the operation temperature or any other fabrication steps, its microstructure is generally considered to be stable. However, the porous microstructure required for the cathode is sensitive to the sintering of the cathode and possibly operating conditions as well. A great deal of microstructural analysis has been performed, however most of the previous work is either a surface technique such as BET (Brunauer, Emmett, Teller adsorption technique), which is usually used for powder samples or a two-dimensional microscopy technique such as conventional SEM [75]. In contrast, this work makes use of a dual beam FIB/SEM (Focused ion beam/scanning electron microscope) for microstructural characterization that allows 3-D reconstruction. Of the microstructural parameters commonly studied, four are considered to be the most critical to electrochemical efficiency. These include pore surface area, triple phase boundary length ($L_{TPB}$), porosity, and tortuosity.

An oxygen molecule, which has diffused through the gas phase to the cathode, must first be adsorbed before it can participate in the reduction reaction. This adsorption can occur very close to the TPB or further away, depending on the diffusivity of the adsorbed species. It has been proposed in fact, that oxygen reduction in an electronic conductor can be co-limited by both adsorption and surface diffusion [107]. Both adsorption and surface diffusion are dependent on the pore surface area; therefore, pore surface area is one of the key microstructural parameters for our investigation.

As coarsening occurs, small cathode particles at the interface coalesce into larger ones, thus reducing the total TPB length per surface area. Other authors have shown that increasing $L_{TPB}$ results in reduced electrode resistance for LSM/YSZ systems [57, 108]. This reduction is a direct consequence of the fact that in pure electronic conducting electrodes, the electrochemical reaction driving fuel cell operation is restricted to the TPB [55] due to the exclusion of ions from the bulk of the electronically conducting cathode and of electrons from the bulk of the electrolyte. We therefore can anticipate an increase in charge transfer resistance as sintering temperature is increased.
Porosity is the ratio of the void space in the microstructure to total volume. Before the cathodic reaction can occur in an electronic conducting cathode such as LSM, oxygen molecules must first diffuse through open pores to the vicinity of the TPB, the area where the cathode, electrolyte, and oxidant meet. An ideal microstructure has ample void space for molecular gas diffusion, while a partially dense microstructure impedes the flow of molecules to the TPB, thus inhibiting the cathodic reaction.

Tortuosity is a property that quantifies the complexity of the path through which a diffusing particle must travel in order to reach a desired destination. In terms of SOFCs, tortuosity is a unitless parameter defined as the distance traveled by a molecule exiting an impinging gas flow as it travels through the porous cathode to reach the solid electrolyte, divided by the straight-line distance. A large tortuosity corresponds to a convoluted path for a given gas molecule to traverse in order to go from the gas stream to the TPB. Because data in three dimensions is necessary for a true tortuosity analysis, very little work is published for actual systems. The dual beam FIB gives us the three-dimensional data necessary for the mathematical evaluation. We expect that cathode microstructures with a large tortuosity will show an increase in gas diffusion polarization resistance and related electrochemical properties.

6.2 Experimental

The samples were prepared and impedance tested in the same manner described in section 3.2. In this chapter, samples were sintered at temperatures ranging from 950 to 1325 °C for one hour. The sintering temperature range was chosen to produce microstructural changes which could be quantified and compared to changes in the electrochemical behavior of the samples. Microstructural images were attained using a dual beam focused ion beam / scanning electron microscope (FIB/SEM, FEI Strata DB 235) by Aijie Chen. The FIB/SEM setup is described in Appendix B.
6.3 Results and Discussion

6.3.1 Effect of Sintering on Microstructure

Figures 6-1(a) - 6-1(c) show interfacial cross sections of LSM on YSZ sintered at 1100, 1200, and 1300 °C, respectively. It is easy to see that by 1300 °C, the microstructure changes drastically. Comparison of figures 6-1(a) and (b) reveals more subtle differences. The 1100 °C annealed sample appears to be slightly more porous than the 1200 °C annealed sample. This apparent difference is so slight that to conclusively say there is any change in porosity requires quantitative calculations. High-frequency artifacts in the data were accounted for as described in section 3.3.2.

Visually, the most noticeable difference between the 1100 and 1200 °C sintered samples is in the connectivity. The 1100 °C sintered sample shows many round shaped
particles with near point-to-point inter-particular unions. The individual nature of many of the particles is maintained at 1100 °C. By 1200 °C, the individual nature of the particles is compromised. The inter-particular unions have become primarily of the face-to-face variety with face diameter almost equal to particle diameter; the connectivity has increased. By 1300 °C, the coarsening has progressed to the point that individual particles no longer exist; the material is now very connected. As the particles coalesce into large particles, the number of pores decrease and only a smaller number of large pores are left, effectively doubling the average pore diameter between 1200 and 1300 °C.

Because the TPB is of particular importance to the cathodic reaction, we closely examined the cathode/electrolyte interface. On initial inspection, it appears that the cathode to electrolyte contact surface is larger for the 1200 °C sintered sample than the 1100 °C sintered sample. Several of the particles close to the electrolyte for the 1100 °C sintered sample do not appear to contact the electrolyte. In contrast, for the 1200 °C sintered sample face-to-face contacts have been formed between the cathode and the electrolyte. The nature of interfacial voids also changes significantly between 1200 and 1300 °C. Figure 6-1(c) shows the formation of large interfacial voids at the cathode/electrolyte interface. These large interfacial voids form as smaller voids coalesce while being restricted from the dense electrolyte. Formation of these interfacial voids will greatly reduce the measurable TPB length.

FIB/SEM was performed on samples sintered at the various temperatures and microstructural features were quantified as described in Appendix B. Porosity (p), volume normalized pore surface area ($S_V$), and TPB length values were calculated at each temperature, while tortuosity ($\tau$) values were calculated from the 3-D data attained at selected temperatures. Porosity was calculated from the pore area/total area in each SEM image. The calculation was repeated for all slices in the sample and an average porosity was attained. These results are plotted in Figures 6-2 and 6-3.
Figure 6-2. Pore surface area and $L_{TPB}$ as a function of sintering temperature. a) Pore surface area. b) $L_{TPB}$.

From Figure 6-1, we can see that as the sintering temperature increases from 1100 to 1300 °C, the microstructure changes from one with small pores to a microstructure with large pores. From elementary geometry, we would expect a microstructure with many small pores to have a larger surface area than one with large pores. Figure 6-2(a) confirms this finding and shows that the volume normalized pore surface area decreases as sintering temperature increases from 1150 to 1325 °C.

Figure 6-2(b), shows that $L_{TPB}$ decreases linearly as sintering temperature is increased in the temperature range displayed. There are outliers at 1225 and 1250 °C. These deviations could be caused by localized interfacial voids, an unusually fine interfacial microstructure, or a lower than anticipated sinter. A determination as to whether the cause of the outlying points is a local anomaly or a characteristic of the bulk sample can be made by studying the electrochemical behavior of the samples in question, which is performed later.

Figure 6-3(a) shows that the porosity (calculated by Aijie Chen) starts at about 30% for a 950 °C sintered sample and increases slightly with increasing sintering temperature to 1200 °C and then begins to drop off. By 1400 °C (not shown), the porosity has dropped to less than 5% indicating an almost dense cathode layer. This trend is supported by our
Figure 6-3. Porosity and tortuosity as a function of sintering temperature. a) Porosity. b) Tortuosity. (Both parameters courtesy of Aijie Chen.)

The tortuosity was calculated (calculated by Aijie Chen) for select temperatures. Tortuosity values of 3.23, 2.18, and 4.27 were calculated for the 1100, 1200, and 1300 °C annealed samples, respectively. The minimum tortuosity occurs at about 1200 °C indicating that the gas molecules have the most direct path to the interface. Opposing trends accounts for the minimum that is observed. At low sintering temperatures, particle size remains small, and gas molecules are redirected many times as they traverse the path to the LSM/YSZ interface. At higher sintering temperatures the pores are large; however, some of the paths may become closed off, limiting the number of available pathways.

6.3.2 Effect of Sintering on Impedance

Figures 6-4 and 6-5 show 800 °C impedance measurements of LSM on YSZ sintered at various temperatures in air. Figures 6-4(a) and (b) are Nyquist plots covering the entire frequency range and high-frequencies only, respectively. The profiles shown in Figure 6-4(a) are generally asymmetrical in the high-frequency regime. The effect is more pronounced in Figure 6-4(b), which only shows the highest frequency portion of the data. The cause of this asymmetry is the presence of multiple processes occurring
Figure 6-4. Nyquist plots measured at 800 °C for LSM sintered at various temperatures in air. a) All frequencies included. b) High frequencies only.
over the frequency range examined. As sintering temperature is increased, the presence of the high-frequency process becomes more pronounced as seen in Figure 6-4(b). Figure 6-5 displays the frequency dependence of the imaginary impedance. Displaying the data in this format makes apparent the decrease in peak frequency of the overall reaction as sintering temperature is increased. The 1325 °C sintered sample shows a change in slope at about 1 kHz. An inflection is only observed when two or more electrochemical processes are significant.

Impedance Spectroscopy of LSM cathodes on YSZ substrates has been the subject of a multitude of works [53, 109]. Most authors agree that two noticeable processes occur in optimally sintered LSM on YSZ at high measurement temperatures in oxygen rich atmospheres. At low oxygen partial pressures a third process related to the diffusion of oxygen gas molecules through the open pores of the cathode to the active region is observed.

Unfortunately, agreement on the isolation and identification of the high and intermediate-frequency processes has not been as complete. Reasons for disagreement include 1) the mechanism of reaction is dependent on measurement conditions, 2) the mechanism of reaction is dependent on the sample preparation and sample history,
and 3) no consensus is reached for evaluation of impedance data. To overcome the first two problems it is important for authors to specify as completely as possible all experimental details, particularly when microstructure is not analyzed. In this work, we have characterized the microstructure and will relate electrochemical properties directly to the microstructure of each sample. The third problem is not easily solved.

Typically, impedance data is analyzed by fitting the data to an equivalent circuit. One school of thought proposes developing a model which is based on a priori knowledge of the system. Several authors have analyzed LSM on YSZ using this method. The most often used circuit contains a double layer capacitance in parallel with a series connection of a charge transfer resistance and a mass transfer related element. For electronic conductors, the mass transfer interpretation is replaced by adsorption and/or surface diffusion. The mass transfer related element is either a Voigt element, a finite-length Warburg element, or some general diffusion element that is not easily defined in terms of circuit elements. Additionally, all capacitors may be replaced by constant phase elements to account for inhomogeneities in the system. This type of circuit with slight variations has been used by several authors and is depicted in Figure 6-6 [46, 48, 63, 112, 113]. The major drawback of this model is that each author typically has their own variation of the model making comparison of parameters attained between groups difficult. The commonly used nested circuit shown in Figure 6-6 (with capacitors instead of constant phase elements) was produced from a more general model in a work by Jamnik and

![Nested element equivalent circuit used for fitting.](image)

Figure 6-6. Nested element equivalent circuit used for fitting. $Z_{hf}$ represents features occurring at too high a frequency to be analyzed. CPE1 is associated with the double layer capacitance, R1 is the charge transfer resistance, and R2 and CPE2 are related to adsorption.
Figure 6-7. Series Voigt element equivalent circuit used for fitting. $Z_{hf}$ represents features occurring at too high a frequency to be analyzed. Each Voigt element is composed of a resistor and a constant phase element.

Meyer [62]. In the model, CPE1 represents the double layer capacitance, R1 represents the charge transfer resistance, and R2 and CPE2 represent a mass transfer phenomenon. Henceforth, we will treat LSM as an electronic conductor and therefore replace the mass transfer process by adsorption and/or surface diffusion. Macdonald explains that when surface diffusion is significant the Randles equivalent circuit is expected; however, if no significantly diffusing intermediates are present the diffusional impedance is replaced by a resistor and capacitor in parallel [110]. In this work, a Warburg type slope was not seen at high-frequencies; therefore, it is likely that adsorption is more significant than surface diffusion.

An alternative equivalent circuit based on a series connection of Voigt elements is also used by many authors and displayed in Figure 6-7 [54, 84, 114, 115]. In this type of model, assignment of identities to the individual processes is accomplished by identification of activation energies, pO$_2$ dependences, bias voltage dependences, and other circumstantial evidence. The major advantage of modeling in this fashion is that comparison of efforts between different groups is facilitated; however, because the model is not derived specifically for the system, confidence is diminished. Jiang et al. has used error structure analysis to show that both of these models can accurately produce the desired response [116]. In our previous work, we examined activation energies, pO$_2$ dependences and other evidence and concluded in agreement with others that charge transfer was the high and dissociative adsorption was the intermediate frequency processes [111]. In both models, $Z_{hf}$ represents the total impedance of all processes occurring at
too high a frequency to be represented in the frequency response. These processes include electrolyte resistance, residual inductive artifacts and any ohmic resistances.

Looking back at Figures 6-4 and 6-5 we see that the intermediate frequency process has a larger polarization resistance magnitude but that the high frequency process increases in relative magnitude as sintering temperature is increased. It should be pointed out that a larger magnitude means a larger power consumption due to that mechanism, but does not necessarily mean that that mechanism is the rate-limiting step. An increase in charge transfer resistance is evidence of a decrease in the quality of the cathode/electrolyte interface, where charge transfer occurs. Charge transfer polarization resistance becomes more significant at higher sintering temperatures due to the deterioration of the triple phase boundary. As sintering temperature is decreased, this high-frequency process becomes less pronounced and inductive artifacts become significant in the high-frequency portion of the data.

Both equivalent circuit models were used to fit impedance profiles such as the ones shown in Figure 6-4. Figure 6-8 is included as an example illustrating the deconvolution of the data. The impedance profile shown is for the 1200°C sintered sample measured at 800 °C air. Figure 6-8(a) shows the data and the fitting obtained using the nested model, while Figure 6-8(b) shows the data along with the fitting (solid line) from the series model. Additionally, Figure 6-8(b) shows the inidividual components which are summed to produce the series model fitting. Because both models accurately fit the data, more analysis is necessary to determine which of the two is more appropriate.

Since the measurement was done in air, the polarization resistance due to bulk gas diffusion is negligible and only two Voigt elements are necessary in the series fitting, one for adsorption (dashed line) and one for charge transfer (dotted line). As can be seen in Figure 6-8(b), a single process with relatively large magnitude (adsorption) provides the major contribution to the profile. Above $10^4$ Hz, charge transfer becomes significant and causes the overall profile to deviate from the symmetric contribution due to adsorption.
Figure 6-8. Deconvolution of impedance profile from 1200 °C sintered sample, measured at 800 °C in air, using both equivalent circuit models. a) Nested model. b) Series model.
From each of the Voigt elements used, polarization resistance \( R_P \) values and constant phase element parameters were attained for charge transfer and adsorption. From the fitting using the nested equivalent circuit, double-layer capacitance, charge transfer resistance, and parameters associated with adsorption were attained.

The process was repeated at various sintering temperatures ranging between 1150 and 1325 °C. The sintering temperature range was chosen to begin above temperatures where sintering is incomplete and end below the melting temperature of LSM on YSZ, which is around 1450 °C \([100]\). Previous research shows that by 1400 °C, the charge transfer resistance has increased dramatically because the LSM layer is fully dense, effectively destroying any triple phase boundaries \([81]\). The impedance was performed at 800 °C in air. In future work, we will examine the cathodic reaction in low oxygen partial pressure regime and relate the bulk gas diffusion polarization resistance to porosity and tortuosity.

Figure 6-9(a) shows the sintering temperature dependence of charge transfer \( R_P \) determined from both models. For both models, the charge transfer polarization resistance increases exponentially as sintering temperature is increased. The individual nature of the Voigt elements in the series model may contribute to the improved fit for the series model as compared to the nested model for charge transfer resistance. The relatively large scatter in the charge transfer data for the nested model is related to the fact that charge transfer \( R_P \) is an order of magnitude smaller than the adsorption \( R_P \), and the two processes are solved for simultaneously. In contrast, a subtraction technique which removed processes individually was used in the deconvolution for the series model. Figure 6-9(b) shows the dependence of adsorption \( R_P \) on sintering temperature.

6.3.3 Effect of Microstructure on Impedance

6.3.3.1 Series model evaluation

Figure 6-10 relates the change in electrochemical performance caused by varying sintering temperature to the corresponding microstructural changes by showing the influence of TPB length on charge transfer \( R_P \) and the influence of pore surface area
Figure 6-9. Temperature dependence of polarization resistance \( (R_P) \) in air determined using both series and nested equivalent circuits measured at 800 °C. a) Charge transfer \( R_P \). b) Adsorption \( R_P \).
on adsorption $R_P$ with electrochemical parameters determined from the series Voigt element model. Focusing first on charge transfer, we see that the charge transfer resistance increases as triple phase boundary length decreases. In the $L_{TPB}$ vs. sintering temperature plot shown in Figure 6-2(b), we noted that there were two outlier points located at 1225 and 1250 °C and proposed reasons for their presence. When relating charge transfer $R_P$ to the actual microstructure, $L_{TPB}$, we observe only one outlier located at 1225 °C. The cause of the outlier at 1250 °C must be a bulk characteristic because the rise in $L_{TPB}$ was accompanied by a corresponding drop in charge transfer $R_P$.

Turning our attention to the data point for the 1225 °C sintered sample, we see that the lowered $L_{TPB}$ value is not accompanied by a corresponding increase in charge transfer $R_P$. In fact, the charge transfer $R_P$ for the 1225 °C sintered sample is similar in magnitude to the 1200 and 1250 °C sintered samples. Since the low $L_{TPB}$ value seen at 1225 °C is not accompanied by an increase in charge transfer $R_P$, we can conclude that the low $L_{TPB}$ value is caused by a localized phenomena such as an interfacial gap and is
not due to a characteristic of the extended microstructure. It should also be pointed out that despite this interfacial gap, the 1225 °C point fits the model when considering the error bars.

Curve fitting of the data indicates that there is a power-law dependence of charge transfer $R_P$ on $L_{TPB}$ at an 800 °C measurement temperature given by Equation 6–1.

$$R_P = 2.93(L_{TPB})^{-3.5} \quad (6-1)$$

Other authors have shown a dependence of overall polarization resistance on the inverse of $L_{TPB}$ at a measurement temperature of 1000 °C. Mizusaki et al. assumed that charge transfer in not the rate-determining reaction in the development of their model [34]. Kuznecov et al. developed a model which assumes that oxygen reduction takes place everywhere on the LSM surface, i.e. charge transfer is not limited to the triple phase boundary [102, 103]. In this scenario, polarization resistance is predicted to be proportional to $(L_{TPB})^{-1}$. This dependence was explained using models which were based on surface diffusion limitation. At lower operating temperatures, reaction kinetics associated with the charge transfer reaction may become the rate limiting step. A power law dependence can also be predicted if we consider the reaction kinetics associated with the charge transfer reaction. For a given chemical reaction, the rate of the reaction, $v$, is dependent on the concentration of the reacting species $c_A^a$ and $c_B^b$.

$$v = k(c_A)^a(c_B)^b \quad (6-2)$$

After adsorption of gas molecules on the surface of the cathode, a charge transfer reaction occurs at the cathode/electrolyte interface. J. Nowotny et al. outlined the various possible adsorption-charge transfer reaction combinations in reference [49] (see Figure 2-1). Let us assume, for now, that adsorption and charge transfer occur according to the following, respective, reactions.

$$O_2 + s \rightleftharpoons O_{2,ads} \quad (6-3)$$
\[ 2e' + \frac{1}{2} O_{2,ads} + V_{o••} \rightleftharpoons O_o^x + s \]  \hspace{1cm} (6-4)

In Equation 6–4, \( s \) is a surface site. The previous equations describe the molecular adsorption of oxygen followed by a separate charge transfer step. The rate of the charge transfer reaction indicates how quickly charged species are being transferred across the cathode/electrolyte interface. This exchange of charged species determines the exchange current, \( I_o \). It is convenient to consider the exchange current density \( (i_o) \), which is the exchange current per unit area and is given by the following relationship.

\[ I_o = i_o \times A_{int} \]  \hspace{1cm} (6–5)

In Equation 6–5, \( A_{int} \) is the planar area of the cathode/electrolyte interface, i.e. 64 mm\(^2\) in this work.

If the individual species of the charge transfer reaction are treated as reactants and products, then the exchange current density can be expressed in Equation 6–6.

\[ i_o = Q \left( k_f (c_{e'})^m (c_{O_{2,ads}})^n (c_{V_{o••}})^p - k_r (c_{O_o^x})^q (c_s)^r \right) \]  \hspace{1cm} (6–6)

In Equation 6–6, the forward and reverse rate constants are given by \( k_f \) and \( k_r \), and \( Q \) accounts for balance of units. In Equation 6–6 \( c_{e'} \), \( c_{O_{2,ads}} \), \( c_{V_{o••}} \), and \( c_s \) are the concentration of electrons, adsorbed oxygen, oxygen vacancies, and surface sites on the cathode able to participate in the cathodic reaction, respectively. The second term on the right side of the equation describes the rate of the reverse reaction. Because the electrochemical measurement was performed in an oxygen rich atmosphere we will assume this term can be neglected for simplicity.

The interfacial reaction is impeded by a charge transfer resistance, \( R_{ct} \), which under equilibrium conditions has been shown to be inversely proportional to \( I_o \).

\[ R_{ct} = \left( \frac{RT}{nF} \right) \left( \frac{1}{I_o} \right) \]  \hspace{1cm} (6–7)

In Equation 6–7, \( R \) is the gas constant, \( T \), \( n \), and \( F \) have their usual meaning.
Substituting Equation 6–5 into the charge transfer equation, Equation 6–7, gives the following expression for $R_{ct}$.

$$R_{ct} = \frac{1}{A_{int}} \left( \frac{RT}{nF} \right) \left( \frac{1}{i_o} \right) \quad (6–8)$$

Using $i_o$ from Equation 6–6, we can express $R_{CT}$ as described in Equation 6–9.

$$R_{ct} = \frac{1}{Q'k_f} (c_{e'})_{TPB}^{m} (c_{O2,ads})^{-n}_{TPB} (c_{V••})^{-p}_{TPB} \quad (6–9)$$

In Equation 6–9, $Q' = Q A_{int} nF/RT$.

The amount of species \textit{"i"} available to react per unit area ($c_i$) is limited by $L_{TPB}$ per unit area. In order to relate the number of species in the vicinity of the TPB to the bulk concentration of species in their respective phases, we need to multiply the concentration of species by the TPB volume of each respective phase.

$$c_i = (c_i)_{TPB} = (c_i)(L_{TPB})A_{TPB,i} \quad (6–10)$$

In Equation 6–10, $A_{TPB,i}$ is the cross-sectional area of the TPB for each of the respective \textit{"i"} phases. Substituting the effective concentrations of active species $[i]_{TPB}$ into Equation 6–9 gives the following expression for the dependence of $R_{ct}$ on $L_{TPB}$.

$$R_{ct} = \frac{1}{Q' nF k_f} \left[ (c_{e'})_{TPB}^{m} (c_{O2,ads})^{-n}_{TPB} (c_{V••})^{-p}_{TPB} \right]$$

$$\times (L_{TPB})^{-(n+m+p)} \quad (6–11)$$

The exponential quantity $(n+m+p)$ gives the reaction order dependence on $L_{TPB}$.

In chemical reactions the reaction order can be given by the coefficients in the balanced chemical equation. If we assume that the charge transfer reaction is of the form of Equation (6–4) and that the exponential terms, m, n, and p are given by the coefficients in Equation 6–4, then a reaction order of -3.5 is predicted and $R_{ct} \propto (L_{TPB})^{-3.5}$ which is exactly what was observed.

Thus far in this work, we have referred to the intermediate frequency process as adsorption rather than “dissociative adsorption” as often reported in the field. The
exponential dependence of 3.5 can only be predicted if complete adsorbed oxygen species participate in the charge transfer reaction; therefore, in this work, we refer to the large magnitude, intermediate frequency process as adsorption. A relationship between adsorption $R_P$ and volume normalized pore surface area is also established as shown in Figure 6-10. The data was fit to a power-law relationship resulting in Equation 6–12.

$$R_p = 1025(S_V)^{-1.76}$$  \textit{(6–12)}

Because impedance spectroscopy is an electrochemical technique, it can not detect the presence of adsorbed species unless they participate in the electrochemical reaction. If we assume that the charge transfer reaction, Equation 6–4, is the rate limiting step then the species generated in the adsorption can only be detected after the charge transfer reaction occurs, i.e. the rate we detect generation of adsorbed species is limited by the rate of the charge transfer reaction. Every time adsorption (Equation 6–3) occurs, an $O_{2,ads}$ is generated. For each $O_{2,ads}$ generated, however, the charge transfer reaction (Equation 6–4) can occur twice. We can conclude that if the reaction is charge transfer limited, and adsorption does not occur dissociatively, the rate of the adsorption reaction is one half that of the charge transfer reaction. We expect the reaction order dependence of adsorption $R_p$ on $L_{TPB}$ to be smaller than -3.5 and in fact we find it to be -1.76. It should be pointed out that the process we are referring to as adsorption is difficult to distinguish from arrival of adsorbed molecular oxygen to the triple phase boundary by other means. If surface diffusion is significant at this measurement temperature, oxygen molecules can not only arrive at the reaction site by adsorption, but also by surface diffusion after adsorption elsewhere on the cathode surface, coupling adsorption and surface diffusion. Other authors have reported a dependence of overall polarization resistance on $(L_{TPB})^{-1}$ when charge transfer is not the rate limiting step. Our dependence of 1.76 indicates that the reaction of adsorbed molecules is reduced when charge transfer is rate limiting. Our findings are not inconsistent with others in that our measurements were carried out at 800 °C.
while much of the previous work has been carried out at near 1000 °C. At the lower measurement temperature, the additional polarization components become larger aiding in deconvolution and the charge transfer reaction may be slowed, effectively changing the rate limiting step. Varying oxygen partial pressure and temperature will have an effect of changing the rate limiting step and future work will investigate the influence of oxygen partial pressure and temperature on the determined reaction order.

6.3.3.2 Nested model evaluation

Figure 6-11 shows the dependence of R1 (charge transfer) and R2 (adsorption related) from Figure 6-6 on $L_{TPB}$. Curve fitting of the data revealed power dependencies.

\[
R_1 = 7.43(L_{TPB})^{-1.6} \tag{6–13}
\]

\[
R_2 = 86.1(L_{TPB})^{-2.1} \tag{6–14}
\]
The power dependence of \( R_{CT} \) on \( L_{TPB} \) from the nested model, -1.6, is significantly different from that determined from the series model, -3.5. The power dependence of \( R_2 \) on \( L_{TPB} \) (-2.1) is consistent with the value reported by Fleig [50] for the dependence of total resistance at 800 °C. This result is not unexpected since \( R_2 \) has the larger magnitude of the two processes and makes up the majority of the cathodic impedance.

Previously, we assumed that molecular adsorption led to a chargeless adsorbed species participating in the charge transfer reaction occurring at the TPB. We now consider the possibility that oxygen adsorption leads to a negatively charged intermediate which is one of the many possible reactions proposed by Nowotny et al. [49]. The corresponding adsorption and charge transfer reactions are expressed in Equations 6–15 and 6–16, respectively.

\[
O_2, g + s + e' \rightleftharpoons O'_{2,ads} \quad (6–15)
\]

\[
\frac{1}{2}O'_{2,ads} + V_{o••} + e' \rightleftharpoons O_o'^x + s \quad (6–16)
\]

In these reactions, the adsorbed species possesses a negative charge. Because of this (and any lattice distortions associated with adsorption), the individual adsorbed species are repelled from one another. For this reason, the amount of low energy sites available may be reduced as compared to an uncharged adsorbed species. The concentration of adsorption sites may directly influence the rate of the reaction. In a work by Mizusaki et al. sites (s) were used in a model which relates the rate of the dissociative adsorption reaction to the current density of the electrode [117]. In the work, the authors were interested in the total conductivity. In this work, both charge transfer and adsorption are of interest and so we must consider the individual reactions corresponding to charge transfer and adsorption independently.

In the previous section, an expression for exchange current density was derived by assuming that the rate of reaction is directly related to the concentration of all of the individual species involved in the reaction, including \( e' \) and \( h^• \). An alternative approach is used in electrochemistry to link the exchange current to the rate of production of
electronic carriers by the oxidation and reduction reactions. For example, as described in Equation 6–16, if an $O'_{ads}$ and a $V_{o}^{**}$ combine to produce an $O^x_{o}$, an $e'$ is consumed (or alternatively, a $h^*$ is produced). This approach is based on the Butler-Volmer Equation (Equation 6–17) which depends on both the forward and reverse reactions.

$$i_n = i_o \left[ e^{\frac{\alpha_a F \eta_s}{RT}} - e^{\frac{-\alpha_c F \eta_s}{RT}} \right]$$  \hspace{1cm} (6–17)

In Equation 6–17, $R$, $T$, and $F$ have their usual meaning, $\eta_s$ describes the surface overpotential, and $\alpha_a$ and $\alpha_c$ are the anodic and cathodic apparent transfer coefficients, respectively. The Butler-Volmer equation describes the dependence of the the current density ($i_n$) on an applied potential. In EIS, small AC potentials are applied at various frequencies. In this work, the applied potential oscillates around 0 V and at 0 V, $i_n$ approaches $i_o$, the exchange current density. For this reason, it is most appropriate to consider $i_o$ in the modeling of the system. The following approach is typically used in aqueous electrochemistry where oxygen ions are $O^{2-}$ instead of $O^x_{o}$ and vacancies and reaction sites are not usually considered. In the following development, we will use this formulism, but will try and incorporate the significance of vacancies and reactions sites, which are important in solid state systems.

An expression for the exchange current density ($i_o$), using the formalism of Newman, can be expressed by the following relation after rearranging terms [118].

$$i_o = nF \left[ k_a^\beta \prod_i (c_{i,anodic})^{\beta p_i} \right] \left[ k_c^{1-\beta} \prod_i (c_{i,cathodic})^{(1-\beta)q_i} \right]$$  \hspace{1cm} (6–18)

In Equation 6–18, $n$ represents the number of charges transferred in the step, $F$ is Faraday’s constant, $k_c$ and $k_a$ are cathodic and anodic rate constants, $c_{i,anodic}$ and $c_{i,cathodic}$ are the concentrations of the anodic and cathodic species, respectively and $p_i$ and $q_i$ are the coefficients of the anodic and cathodic species in the charge transfer reaction (Equation 6–16), respectively. Whether an electron is consumed in the forward reaction (hole is produced), or an electron is produced in the reverse reaction, net charge is flowing.
in the same direction. For this reason, the forward and reverse reactions both add to the net exchange current.

There is an activation energy associated with this reaction and a different activation energy is associated with the reverse reaction, i.e. the production of $O_{2,ads}'$ and $V_o^{••}$ from the dissolution of an $O_o^x$. Even with no applied potential, these reactions may occur due to the internal energy of the system. If a potential is applied; however, it will affect the two activation energies in different manners, depending on the direction of the bias and the particulars of the system. For instance, in $(La_{0.8}Sr_{0.2})_{0.98}MnO_{3−δ}$, there are about four times as many $Mn_{3Mn}$ as there are $Mn_{•Mn}$. Because of the availability of $Mn_{3Mn}$ to change valencies, a bias which favors the production of holes will more efficiently create current than the reverse. Such an influence can be accounted for by the utilization of the symmetry factor, $β$. Upon examination of Equation 6–18, we see that if $β = 0$, then the anodic reactants are disregarded in the calculation of the exchange current density.

This situation corresponds to Equation 6–16 proceeding only in the forward direction. A $β$ value of 0.5 represents both the forward and reverse reactions occurring in unison, an equilibrium condition.

And so, from Equations 6–18 and 6–16 we have the following relations.

$$i_o = nFk_c[(c_{O_{2,ads}}')^{0.5}c_{V_o^{••}}]$$

$$β = 0.5 : \quad i_o = nFk_c^{0.5}k_a^{0.5}[(c_{O_{2,ads}}')^{0.25}(c_{V_o^{••}})^{0.5}(c_{O_o^x})^{0.5}(c_s)^{0.5}]$$

Combining equation 6–19 and equation 6–8, we have expressions for $R_{ct}$.

$$R_{ct} = \frac{1}{A_{int}} \left( \frac{RT}{nF^2} \right) \frac{1}{k_c}[(c_{O_{2,ads}}')^{-0.5}[(c_{V_o^{••}})]^{-1}]$$

$$β = 0.5 : \quad R_{ct} = \frac{1}{A_{int}} \left( \frac{RT}{nF^2} \right) \left( \frac{1}{k_c k_a} \right)^{0.5}[(c_{O_{2,ads}}')^{-0.25}(c_{V_o^{••}})^{-0.5}(c_{O_o^x})^{-0.5}(c_s)^{-0.5}]$$

The quantity $c_i$ describes the concentration of the $i^{th}$ species which is available to participate in the interfacial reaction. The concentration of the $i^{th}$ species per unit area
available to participate in the interfacial reaction is limited by the amount of $L_{TPB}$ in that unit area and is described in Equation 6–10.

Application of Equation 6–10 to Equation 6–20 gives a direct relationship between $R_{CT}$ and $L_{TPB}$. So we have: if $\beta = 0$,

$$R_{ct} = \frac{1}{A_{int}} \left( \frac{RT}{nF} \right)^{1} \left( \frac{1}{k_c} \right)^{1} \left( \frac{c_{O_{2,ads}} (A_{TPB, O_{2,ads}})}{[c_{V_0^{\bullet\bullet},(A_{TPB,V_0^{\bullet\bullet}})]^{-0.5} [c_{O_{2,ads}} (A_{TPB, O_{2,ads}})]^{-0.5} [c_s (A_{TPB,s})]^{-0.5}} \right) \times (L_{TPB})^{-1.5} \quad (6–21)$$

if $\beta = 0.5$,

$$R_{ct} = \frac{1}{A_{int}} \left( \frac{RT}{nF} \right)^{0.5} \left( \frac{1}{k_c k_a} \right)^{0.5} \times \left( \frac{c_{O_{2,ads}} (A_{TPB, O_{2,ads}})}{[c_{V_0^{\bullet\bullet},(A_{TPB,V_0^{\bullet\bullet}})]^{-0.25} [c_{V_0^{\bullet\bullet},(A_{TPB,V_0^{\bullet\bullet}})]^{-0.5} [c_{O_{2,ads}} (A_{TPB, O_{2,ads}})]^{-0.5} [c_s (A_{TPB,s})]^{-0.5}} \right) \times (L_{TPB})^{-1.75} \quad (6–22)$$

Thus, depending on how far reaction 6–16 is displaced from equilibrium, the exponential dependence of $R_{CT}$ on $L_{TPB}$ will be between -1.75 and -1.5. This is consistent with the observed trend of the nested data, $R_{CT} \propto (L_{TPB})^{-1.6}$.

The adsorption reaction which produces the intermediate species $O_{2,ads}^{\prime}$, is expressed in Equation 6–15. Application of the exchange current equation (Equation 6–18) to the adsorption reaction gives the following relations.

If $\beta = 0$:

$$i_o = n F k_c [(c_{O_{2,g}})(c_s)]$$

$\beta = 0.5$:

$$i_o = n F (k_c k_a)^{0.5} [(c_{O_{2,g}})^{0.5} (c_s)^{0.5} (c_{O_{2,ads}}^{\prime})^{0.5}]$$

Applying these exchange current densities and the concentration equation (Equation 6–10) to the charge transfer equation (Equation 6–8) gives the following relationships between $R_p$ and $L_{TPB}$ for the adsorption reaction given in Equation 6–15.
If $\beta = 0$,

$$R_{\text{ads}} = \frac{1}{A_{\text{int}}} \left( \frac{RT}{(nF)^2} \right) \frac{1}{k_c} \times \left( \left[ c_{O_2,g}(A_{TPB,O_2,g}) \right]^{-1} \left[ c_s(A_{TPB,s}) \right]^{-1} \right) \times (L_{TPB})^{-2} \quad (6-24)$$

if $\beta = 0.5$,

$$R_{\text{ads}} = \frac{1}{A_{\text{int}}} \left( \frac{RT}{(nF)^2} \right) \left( \frac{1}{k_c k_a} \right)^{0.5} \times \left( \left[ c_{O_2,g}(A_{TPB,O_2,g}) \right]^{-0.5} \left[ c_s(A_{TPB,s}) \right]^{-0.5} \left[ c_{O_2,ads,O_{2,ads}}(A_{TPB,O_{2,ads}}') \right]^{-0.5} \right) \times (L_{TPB})^{-1.5} \quad (6-25)$$

From data deconvolution using the nested equivalent circuit, a power dependence of adsorption polarization resistance on $L_{TPB}^{-2.1}$ was observed. This dependence was identical to the power dependence reported by Fleig for total cathodic resistance [50]. The observed power dependence, -2.1, most closely matches the $\beta = 0$ case which predicts a power dependence of -2. For many chemical reactions, $\beta$ has a value close to 0.5. For this $\beta$, a power dependence of -1.5 is predicted for the adsorption related process. If $\beta = 0$, the dissociative adsorption reaction described in Equation 6–15 is not in equilibrium, which is consistent with the idea that dissociative adsorption is the rate limiting step as reported by others [119].

6.3.3.3 Nested relation to pore surface area

As described previously by Fleig, total cathodic polarization resistance (and thus the resistance of the adsorption related process) scales inversely with cathode/electrolyte contact area and linearly with cathode thickness [50]. This tendency was explained by Fleig by considering bulk transport of ionic species through the cathode. For this bulk transport to occur, adsorption must occur on either the entire pore surface area or an active region of the pore surface area which is within some critical distance, $\delta$ of the cathode/electrolyte interface. In either case, the area on which adsorption can occur is directly proportional to the volume normalized pore surface area, $S_V$. Alternatively, if
surface diffusion rather than bulk diffusion dominates, adsorption may still occur either over the entire surface area or some portion of this area within a distance, \( \delta \), of the cathode/electrolyte interface. In each of these scenarios, the area on which adsorption can occur will be limited by the surface area per unit volume \( S_V \).

For simplicity, we will treat only one of the possibilities listed in the previous paragraph here; however, adsorption for each of the scenarios should be limited by \( S_V \). For the moment, assume adsorption occurs according to Equation 6–15 over the entire surface area of the cathode. In addition, assume that surface diffusion of adsorbed intermediates is not a limiting factor. This assumption is reasonable, as Warburg behavior was not seen in the various impedance profiles. An exchange current exists based on the generation of the charged intermediates \( O'_{2,ads} \), which will participate in the charge transfer reaction at the TPB after diffusing to an active location. There is a resistance to this electrochemical reaction which can be expressed as \( R_{ads} \). The exchange current density \( (i_{o,ads}) \) is not directly dependent on \( L_{TPB} \) since adsorption is not limited to the TPB, like charge transfer, but may occur over the entire surface area. The total exchange current, however, is limited to the total pore surface area per unit volume. The resistance to the adsorption reaction described in Equation 6–15, can be expressed according to Equation 6–8. Previously, for charge transfer, \( A_{int} \) was the planar geometric area of the cathode. For adsorption, \( A_{int} \) must be replaced by \( A_{int,pore} \), which represents the pore/cathode interfacial area as described in Equation 6–26.

\[
A_{int,pore} = S_V \times A_{int} \times t_{cathode} \quad (6–26)
\]

In Equation 6–26, \( S_V \) represents the surface area per unit volume, \( A_{int} \) is equal to 64 mm\(^2\), and the cathode thickness (\( t_{cathode} \)) is equal to about 20 \( \mu \)m. Substitution of Equation 6–26 into Equation 6–8 gives the following relation.

\[
R_{ads} = \frac{1}{S_V A_{int} t_{cathode}} \left( \frac{RT}{nF} \right) \left( \frac{1}{i_{o,ads}} \right) \quad (6–27)
\]
Figure 6-12. Relation of adsorption polarization resistance determined from a nested model to surface area per unit volume (measured in air at 800 °C). Red line represents the actual fit and dashed line represent a power dependence of -1.

The exchange current density, $i_{o,ads}$ now represents the formation of the charged intermediate, $O_{2,ads}'$ as adsorption occurs. Figure 6-12 displays the dependence of $R_{ads}$ on $S_V$. The fitting in the figure reveals $R_{ads} \propto (S_V)^{-1.3}$, which is close to a power dependence of -1, as illustrated by the dashed line in the figure.

Observation of the trend lines in Figure 6-12 reveals that all of the data points except two lie along the dashed line. If the dependence of adsorption polarization resistance does indeed show a dependence on pore surface area to the -1 power, then the same process would show a dependence on $L_{TPB}$ to the -2 power, if the surface area is proportional to the triple phase boundary length squared. This is a reasonable assumption if the particles are relatively uniform in size and spherical in shape. The power dependence observed in Equation 6–14 and Figure 6-11 can be explained using both models. Further research is required to determine which is valid.
6.4 Conclusion

We have evaluated the effects of sintering temperature on both the electrochemical and microstructural characteristics of LSM on YSZ symmetric cells. A FIB/SEM system was used to analyze the microstructure. 3-D images were used to determine the tortuosity at select sintering temperatures, while evenly spaced 2-D images were used for the evaluation of triple phase boundary length, volume normalized pore surface area, and porosity. Impedance data from LSM on YSZ symmetric samples measured at 800 °C was fitted to two commonly used models, generating different results.

Use of a series Voigt element model led to a power dependence of -3.5 for charge transfer resistance on $L_{TPB}$ and a dependence of -1.75 for adsorption polarization resistance on volume normalized surface area. The exponential dependence of -3.5 was predicted by application of principles of reaction kinetics to a charge transfer step involving uncharged adsorbed molecular oxygen ($O_{2,ads}$). In this model, we assumed that the coefficients of the species in the charge transfer reaction determines the power dependence of the respective species in the current exchange reaction, the concentration of the species able to participate in the cathodic reaction are linearly dependent on the amount of triple phase boundary length per unit area, and that the reverse reactions are negligible.

Comparison of electrochemical parameters from the nested model to the microstructural data revealed a dependence of -1.6 and -2.1 for charge transfer and adsorption on $L_{TPB}$, respectively. For these processes, power dependences of -1.5 and -2, respectively, were predicted by assuming that the adsorbed intermediate is of the form $O'_{2,ads}$, the exchange current can be expressed by Equation 6–18, the concentration of the species able to participate in the cathodic reaction are linearly dependent on the amount of triple phase boundary length per unit area, and that the value of $\beta$ is equal to zero.

Since adsorption polarization resistance makes up the majority of the total cathodic resistance, this individual process can be compared to the results of others who reported
only total cathodic resistance or conductivity. Our results were consistent with those of Fleig [50] whose analysis was performed on the same material at the same measurement temperature. Fleig concluded that since total cathodic resistance is proportional to $(L_{TPB})^{-2}$, and scales linearly with cathode thickness, bulk conductivity through the LSM is significant. We have proposed an alternate explanation for LSM which does not depend on bulk ionic diffusion through LSM which has a low ionic conductivity at 800 °C. Other authors have used higher measurement temperatures and produced results inconsistent with ours; however, few data points were used to demonstrate a relationship between resistance and $L_{TPB}$. Additionally, it is reported that a change from Warburg behavior to non-Warburg behavior occurs at around 800 °C indicating that the rate limiting step may undergo a transition in this temperature regime [113] The works of Kuznecov et al. (LSM, 950 °C) and Mizusaki et al. (LCM, 1000 °C) were performed at higher temperatures were faster reaction kinetics at the TPB and higher ionic conductivity in LSM are expected [103].

Polarization resistance of the adsorption related process was observed to have a power dependence of -1.3 on volume normalized pore surface area. A dependence of -1 is predicted by both models, assuming uniform geometry of particles as previously discussed. It was demonstrated that both interpretations of the adsorption data from the nested model will predict the observed dependence of $R_P$ on $L_{TPB}$. For this reason, future work is necessary to determine the correct model.


7.1 Introduction

Thus far, this work has focused on the cathodic reaction of LSM on YSZ. The cathode LSM is a purely electronic conductor and has an operating temperature from 800 to 1000 °C. Because high operating temperatures increase the $/kW system cost of SOFCs, interest has shifted to other cathodes. Composite cathodes and mixed ionic electronic conductors (MIECs) have shown promise for the intermediate temperature range. The cathode LSCF ($La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ}$) is one of the most studied MIECs and projects an operating temperature significantly less than 800 °C.

Although the ionic conductivity of LSCF is less than its electronic conductivity (0.03 vs 2.9 S cm$^{-1}$ at 800 °C) the ionic conductivity is significantly higher than that of LSM ($10^{-7}$ S cm$^{-1}$) [38–40]. The active region for cathodic reduction is no longer restricted to the TPB. In effect, the cathodic reaction can occur at the cathode/gas/electrolyte TPB, the cathode/gas interface, or the current collector/gas/cathode interface. The preferred site of the cathodic reaction depends not only on the ionic and electronic conductivity of the cathode, but also on the catalytic nature of the MIEC and the current collector, the thickness of the cathode, the resistance of species transferred across the various interfaces, and the local oxygen concentration at the prospective reaction site [48]. These reaction pathways act in parallel and therefore, the reaction will proceed in whatever manner minimizes total resistance. Because the electronic conductivity of LSCF is significantly greater than the ionic conductivity, the preferred reaction pathway is with charge transfer occurring at or near the cathode/gas/electrolyte TPB where plenty of oxygen (enough oxygen to efficiently convert the electronic current in the cathode to ionic current in the electrolyte) is present. If the required ionic current is greater than that which the supply of oxygen allows (concentration polarization), then the ionic conducting properties of LSCF become significant. The active reaction area will expand up the surface of the
MIEC to regions where more oxygen is available. As subsequent oxygen molecules are taken further from the TPB an oxygen gradient is created [51].

For this reason, in oxygen rich atmospheres an impedance profile similar to the case of our electronic conducting cathode (LSM) is anticipated. Our previous results showed that for LSM, two electronic processes (charge transfer and adsorption) dominate the cathodic reaction in air. In low partial pressures of oxygen a third electrochemical process, related to the bulk diffusion of gaseous oxygen appears at very low frequencies. For LSCF, in addition to these three processes, an additional arc should be present due to ionic transport through the MIEC whenever the third arc, associated with concentration polarization is present.

7.2 Experimental

The samples were prepared and impedance tested in the same manner described in section 3.2. In this chapter, however, the LSM was replaced with LSCF supplied by Nextech Materials, Ltd. Sintering was performed for one hour at temperatures ranging from 800 to 1150 °C. Sintering at temperatures above and below 1000 °C was performed in Lindberg/Blue high and low temperature box furnaces, respectively. Argon and air were combined to produce a flow rate of 100 sccm for \( pO_2 \) less than 0.21 %. For \( pO_2 \) greater than 0.21 %, oxygen mixed with argon was used rather than air. High-frequency artifacts in the data were accounted for as described in section 3.3.2

7.3 Results and Discussion

Figures 7-1(a) and (b) show Nyquist plots measured in air at 700 °C for symmetric LSCF on YSZ samples sintered at high and low temperatures, respectively. The corresponding imaginary impedance vs. frequency plot is shown in Figure 7-2. For sintering temperatures above 900 °C the magnitude of the impedance profile increases as sintering temperature is increased, as shown in Figure 7-1(a). For temperatures below 900 °C, the polarization resistance magnitude does not decrease significantly as sintering temperature is reduced. As sintering temperature is reduced, the form
Figure 7-1. Impedance response of lanthanum strontium cobalt iron oxide (LSCF) on YSZ in air at various sintering temperatures. a) High sintering temperatures. b) Low sintering temperatures.

Figure 7-2. Imaginary impedance versus frequency for LSCF measured at 700 °C in air at various sintering temperatures.
Figure 7-3. Application of a series Voigt element based equivalent circuit to LSCF sample sintered at 1000 °C and measured at 700 °C in air.

of the profile degrades and the shape becomes more depressed as shown in Figure 7-1(b). This depression is typically viewed as a distribution of time constants among the significant electrochemical processes occurring. At the lowest sintering temperature, 800 °C, the impedance profile may not be stable due to the proximity of sintering and testing temperatures. The first well-defined arc occurs at 950 °C and above 950 °C the polarization resistance magnitude increases rapidly with temperature. This provides an indication that 950 °C is the optimum sintering temperature for LSCF on YSZ. From Figure 7-2, it is clear that the 1000 °C sample has two frequency peaks, one at around 30 Hz, and one at around 10^4 Hz. This trend continues as sintering temperature is increased as indicated by the asymmetric nature of the profiles. By 1150 °C both processes are similar in magnitude and frequency and thus difficult to distinguish.

A series Voigt element model was used to fit the impedance data of the 1000 °C sintered sample. Figure 7-3 displays the polarization contributions which make up the impedance profile of the 1000 °C sintered sample, measured at 700 °C in air. Like in LSM, there is a small magnitude high-frequency process and a larger magnitude
intermediate-frequency process. A similar fitting was performed for each of the profiles shown in Figure 7-2. At the lowest sintering temperatures, the fitting was complicated by the depressed nature of the profile, while at the highest sintering temperatures deconvolution was difficult due to the low relaxation frequencies of some of the processes. The shape of the profiles and the quality of the fitting, leads us to assume that two processes contribute to the overall impedance profile when measured in air at 700 °C, particularly at intermediate sintering temperatures such as 1000 °C.

Figure 7-4 shows the polarization resistances obtained from fitting each of the impedance profiles shown in Figure 7-2 with a series Voigt element model. The figure shows a minimum in charge transfer polarization resistance at 900 °C and a minimum in adsorption polarization resistance at 850 °C. At sintering temperatures above 900 °C, adsorption polarization resistance becomes larger in magnitude than charge transfer, while below 900 °C the trend is less pronounced. It is likely that by 950 °C good inter particular adhesion between the individual LSCF particles and adhesion between the LSCF and the YSZ has been achieved. Sintering above 950 °C only degrades the cathode as evidenced
by the increased polarization resistance. It is anticipated that this increased polarization resistance is accompanied by microstructural and possibly phase changes which will be verified by FIB/SEM in the future.

The 950 °C sintered sample was impedance tested in a variety of pO\textsubscript{2}s at 700 °C. Figures 7-5(a) and (b) display the results of the impedance testing broken down into high and lower pO\textsubscript{2} regimes, respectively. From Figure 7-5(a), we see that there is little change in the imaginary impedance vs. frequency plot from 58 to 10 % oxygen. Evidently, the mechanism of the cathodic reaction is unchanged by variations in pO\textsubscript{2} concentration if oxygen is still quite abundant. There is a slight increase in polarization resistance as pO\textsubscript{2} is dropped from the high value of 58 to 10 % oxygen. At 3 % oxygen, we begin to see a deviation from the simple two process profile occurring at higher pO\textsubscript{2}s. By 0.67 % oxygen, we can clearly see the formation of two low frequency process which are not present above 10 %. Deconvolution of the sample measured at 0.09 % O\textsubscript{2} is shown in Figure 7-6. In the figure, four cathodic processes are apparent. For LSM, we saw one new process at low partial pressures of oxygen attributed to concentration polarization and related to bulk gas diffusion to the reaction site. For LSCF, two low frequency processes appear simultaneously. It is likely that one process is due to concentration polarization created by the lack of oxygen molecules available at the reaction zone and the second process is related to LSCF compensating for this inavailability of oxygen molecules. The two high-frequency cathodic processes do not appear to be significantly affected by the change in oxygen concentration from 3 % to 0.32 %. Below 0.32 %, the low-frequency processes continues to become more pronounced, particularly the lowest frequency one which displays a sharp dependence on pO\textsubscript{2}. Surprisingly, in this regime, the overall magnitude of the highest-frequency polarization resistance (charge transfer) decreases as pO\textsubscript{2} decreases. This trend is opposite the effect seen when oxygen is abundant. As concentration polarization becomes more prominent, the reaction mechanism shifts in such
Figure 7-5. Impedance response at various oxygen partial pressures of 950 °C sintered LSCF on YSZ measured at 700 °C. a) High oxygen partial pressures. b) Low oxygen partial pressures.
a way that minimizes the contribution of the original charge transfer reaction, possibly due to $V_{o^{**}}$ formation.

The impedance profiles of Figures 7-5(a) and (b) were fitted using a four Voigt element based series model with the results displayed in Table 7-1 and Figures 7-7 through 7-9. As mentioned previously, the bulk diffusion process is not apparent at higher pO$_2$s and therefore model parameters for the bulk diffusion process begin at lower pO$_2$s. Figure 7-7 shows the series resistance contribution. Unlike LSM, LSCF shows an increasing ohmic resistance ($R_s$) as pO$_2$ is decreased. Fitting the data points to Equation 4-3 gives a dependence of ohmic resistance on pO$_2$ to the 0.054 power. As mentioned in the background section, the electronic conductivity of LSCF is created by formation of holes when Sr is incorporated on a La site in the lattice. As pO$_2$ is reduced, an increasing number of vacancies are formed reducing the concentration of holes; therefore, the ionic conductivity goes up while the electronic conductivity goes down. This decrease in electric conductivity of the MIEC causes the trend seen in Figure 7-7.
Table 7-1. Polarization resistance values in Ωs for various elementary steps of the cathodic reaction in lanthanum strontium cobalt iron oxide samples sintered at 950 °C and measured at 700 °C at various oxygen partial pressures.

<table>
<thead>
<tr>
<th>pO₂ (%)</th>
<th>Rs</th>
<th>Rct</th>
<th>Rads</th>
<th>Rion</th>
<th>RBD</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.0</td>
<td>9.16</td>
<td>1.87</td>
<td>5.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>41.0</td>
<td>9.50</td>
<td>1.86</td>
<td>5.80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>21.0</td>
<td>9.76</td>
<td>1.83</td>
<td>6.27</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12.5</td>
<td>10.03</td>
<td>2.06</td>
<td>6.85</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3.0</td>
<td>10.74</td>
<td>1.97</td>
<td>7.71</td>
<td>0.71</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>10.73</td>
<td>1.06</td>
<td>7.87</td>
<td>1.51</td>
<td>0.53</td>
</tr>
<tr>
<td>0.67</td>
<td>11.88</td>
<td>2.12</td>
<td>8.49</td>
<td>2.07</td>
<td>0.73</td>
</tr>
<tr>
<td>0.09</td>
<td>12.02</td>
<td>0.92</td>
<td>7.75</td>
<td>2.44</td>
<td>6.24</td>
</tr>
<tr>
<td>0.003</td>
<td>11.95</td>
<td>0.66</td>
<td>5.62</td>
<td>3.67</td>
<td>69.69</td>
</tr>
</tbody>
</table>

Figure 7-7. Ohmic series polarization resistance from model fitting for LSCF sintered at 950 °C and measured at 700 °C as a function of pO₂.
Wang et al reported that for LSCF \((La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ})\) the hole is the major carrier for \(pO_2\)s above 0.03 % oxygen at 800 °C \([43]\). The electroneutrality condition in LSCF is given in Equation 7–1.

\[
n + [Sr'_{La}] = 2[V_o^{••}] + p
\]  

(7–1)

Valency changes among the Fe and Co ions account for \(n = [M'_{M}]\) and \(p = [M^{••}_{M}]\), while \([Sr'_{La}]\) is equal to 0.2. Also in \([43]\), a plot of conductivity (measured by 4 point probe) on \(pO_2\) reveals a dependence of about 0.094 in the high partial pressure regime at 800 °C. From the data of Bucher et al. reported a conductivity power dependence of 0.097 at 700 °C can be calculated \([120]\). Because the hole is the major carrier, the power dependence of \(h^{•}\) on \(pO_2\) should also be about 0.097. The power dependence observed, 0.054, close to this value.

For charge transfer, the power dependence observed, 0.077, is also close to the power dependence of ionic conductivity of LSCF reported by Wang. This value has greater error due to the very low \(R\) value reported. A charge transfer resistance independent of \(pO_2\) would indicate that this process occurs in a similar fashion as for purely electronically conducting LSM. However, \(V_o^{••}\) formation would reduce \(R_{ct}\) as is observed. The decrease in \(R_{ct}\) at low \(pO_2\)s also may indicate that this process becomes increasingly insignificant as the ionic pathway through the MIEC bulk becomes favorable.

The intermediate-frequency arc was previously attributed to an adsorption related process. For LSCF, this process shows two distinct regimes. At partial pressures above 0.32 %, intermediate-frequency polarization resistance decreases as \(pO_2\) increases, while below 0.32 % (approaching concentration polarization), the polarization resistance decreases as \(pO_2\) decreases. The corresponding power dependencies are -0.086 and 0.099 for the high and low \(pO_2\) regimes, respectively. For high \(pO_2\), the reactions is likely confined to the vicinity of the TPB and therefore, we observe a negative \(pO_2\) power dependence like that observed in LSM (-0.15 for adsorption/surface diffusion). In the
Figure 7-8. High-frequency polarization resistances as a function of $pO_2$ for LSCF on YSZ sintered at 950 °C and measured at 700 °C. a) Charge transfer $R_P$. b) Adsorption $R_P$. 
low pO2 regime, a positive dependence or $R_P$ on pO2 is observed. At low pO2s, the bulk path in the MIEC becomes active; therefore, less surface diffusion of adsorbed species is required. The positive dependence observed may be a direct indication that adsorption and surface diffusion are coupled in this system.

Figure 7-9(a) shows the partial pressure dependence of the ionic process. This process was not seen in LSM at low pO2s, and so this process must be directly related to the ionic conductivity of the MIEC. There are three regimes, two of which are visible in Figure 7-9: 1) pO2 > 3 % oxygen, 2) 3 % oxygen > pO2 > 0.67 % oxygen, and 3) pO2 < 0.67 % oxygen. In the first regime, any resistance associated with this process is two small to analyze (therefore no data points above 3 % oxygen). In this regime activation polarization dominates and the cathodic reaction is confined to the TPB, like in LSM. In regimes two and three, the vacancy concentration in the MIEC has increased enough to make ionic conductivity through the MIEC bulk a competitive pathway. As mentioned near the end of Section 2.2.3, ionic conductivity in LSCF displays a maximum at around $10^{-2}$ atm [42]. Below this concentration, a sharp drop off in ionic conductivity exists as reported by Wang et al. [43]. In regime 2, the ionic conductivity in the MIEC is at a maximum and so bulk processes in the MIEC are favorable. In regime 3, the ionic conductivity in the MIEC decreases significantly, possibly due to defect association. In addition, the vacancy concentration at the MIEC/gas interface is high, so reaction can occur as soon as the holes arrive at a possible reaction site. This process is limited by the flow of $h^*$ through the MIEC. Since the hole is the primary carrier in LSCF, the conductivity dependence of LSCF on pO2 should match the polarization resistance of this process. The observed dependency of $R_P$ on pO2, 0.095, is in very close agreement with the findings of Wang et al. and Bucheret al. from whose data power dependencies of conductivity on pO2 of 0.094, and 0.097 can be measured, respectively.

In regime two, a very strong dependence on pO2 is observed. This is explained by considering that this process step effectively competes with the bulk gas diffusion
Figure 7-9. Low-frequency polarization resistance as a function of pO\textsubscript{2} for LSCF on YSZ sintered at 950 °C and measured at 700 °C. a) MIEC specific process $R_p$. b) oxygen gas diffusion $R_p$. 
related process (Figure 7-9(b)). At all pO$_2$s, the resistance of this process is less than the polarization resistance associated with bulk gas diffusion as seen in Figures 7-9(a) and (b). At low pO$_2$s, a concentration gradient is formed in the vicinity of the TPB and to compensate, the bulk path through the MIEC becomes active, reducing the total resistance. As pO$_2$ increases, less of a concentration gradient is formed and the bulk gas diffusion resistance decreases; reaction via the TPB becomes favorable. If no concentration gradient exists, the reaction should take place completely in the vicinity of the TPB and since the electronic conductivity is much higher than ionic conductivity in LSCF and the alternate reaction pathway (through the bulk of the MIEC) is not favorable. The measured value of -0.86 for the dependence of bulk gas polarization resistance on pO$_2$ is close to the value of unity seen for the bulk diffusion process in the electronic conducting cathode. The reason for the diminished value could be related to the fact that true concentration polarization may not be achieved because oxygen molecules are not strictly provided from regions in the immediate TPB vicinity due to the contribution of the ionic process.

The dependences of the various processes on measurement temperature and oxygen partial pressure is summarized in Table 7-2. Trending of the total resistance measured by impedance was reported by Murray et al. and is included in the table [58]. The trend of the total resistance follows the that of the largest $R_P$ of the individual processes. At low pO$_2$s, Murray reported a discontinuity in total resistance dependence on pO$_2$ and speculated that different mechanisms limit the cathode performance in different pO$_2$ regimes. Our results support that hypothesis.

Figure 7-10 displays the effects of sintering temperature on the electrochemical processes occurring at 700 °C and 0.09 % oxygen. This partial pressure was chosen to put the cathodic reduction reaction in the concentration polarization regime (less than 0.67 % oxygen) discussed above. Like in Figure 7-4 there is a high and a low sintering temperature regime and they separate at around 950 °C. Focusing first on sintering
Table 7-2. Properties of the various cathodic processes in lanthanum strontium cobalt iron oxide. The results of Murray et al. [58] for total resistance are included. The small $pO_2$ dependencies observed are close to the $pO_2$ dependency of the hole concentration in LSCF (0.094) reported by Wang et al. [43] and the ionic conductivity of LSCF at higher $pO_2$s (0.097) reported by Bucher et al. [120].

<table>
<thead>
<tr>
<th>Process</th>
<th>$R_p$ ($pO_2 &gt; 0.01$ atm)</th>
<th>$R_p$ ($pO_2 &lt; 0.001$ atm)</th>
<th>$E_a$ (air)</th>
<th>$E_a$ (0.09 % O$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic</td>
<td>-0.054</td>
<td>-0.054</td>
<td>-0.40</td>
<td>-0.38</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>0.077</td>
<td>0.077</td>
<td>-1.72</td>
<td>-1.63</td>
</tr>
<tr>
<td>Adsorption</td>
<td>-0.086</td>
<td>0.098</td>
<td>-1.41</td>
<td>-1.56</td>
</tr>
<tr>
<td>MIEC process</td>
<td>-0.71</td>
<td>-0.095</td>
<td>n/a</td>
<td>-1.50</td>
</tr>
<tr>
<td>Bulk gas diffusion</td>
<td>-0.85</td>
<td>n/a</td>
<td>n/a</td>
<td>0.50</td>
</tr>
<tr>
<td>Total $R_p$ - Murray</td>
<td>-0.91</td>
<td>-0.038</td>
<td>-1.63</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 7-10. Parameters from model fitting for LSCF at 0.09 % oxygen, measured at 700 °C as a function of sintering temperature.
temperatures above 950 °C, we see that there are only two significant electrochemical processes. It should be pointed out that gas diffusion and ionic conductivity through the MIEC bulk may still occur, but the magnitude of charge transfer and adsorption overshadow the other two processes. Charge transfer and adsorption increase with sintering temperature at low oxygen concentrations in a manner similar to that seen at high oxygen concentrations. In the low partial pressure regime, four processes are apparent. The gas diffusion related process is independent of sintering temperature up to 1000 °C. This may indicate that the microstructure is relatively stable at the sintering temperatures for which this process could be observed. Formation of tertiary phases may significantly alter the charge transfer resistance while not significantly affecting bulk gas diffusion. The MIEC specific process is nearly independent up to 950 °C, but drops at 1000 °C. The formation of a tertiary phase at the cathode electrolyte interface could effectively block transfer of ionic species from the MIEC to electrolyte, effectively reducing efficiency of ionic transport in the cathode and making other reaction pathways more favorable. Alternatively, if connectivity increases with sintering, the path for diffusion of ionic species may become more direct, thus reducing the resistance of this process. Clearly, microstructural and compositional analysis is necessary for a more complete analysis. Both charge transfer and adsorption seem to be relatively constant below 1000 °C, with charge transfer showing a minimum at 950 °C and adsorption showing a minimum at 900 °C.

Minima for charge transfer and adsorption occur at the same sintering temperatures at higher pO₂s as shown in Figure 7-4.

Figures 7-11(a) and (b) show the activation energies determined by varying the measurement temperature of the 950 °C sintered sample measured in air and at 0.09 % oxygen, respectively. The activation energy for charge transfer is -1.72 and -1.63 eV in air and at 0.09 % oxygen, respectively, while the activation energy for adsorption is -1.56 and -1.41 eV in air and at 0.09 % oxygen, respectively. Activation energies for the MIEC specific (-1.50 eV) and bulk diffusion (0.50 eV) were also determined for the low
Figure 7-11. Activation energies of various electrochemical processes for 950 °C sintered LSCF on YSZ. a) Measured in air. b) Measured at 0.09 % oxygen.
oxygen concentration measurement. Activation energy values for charge transfer and adsorption are higher than those measured for LSM (-0.97 and -1.2 for charge transfer and adsorption, respectively as reported in Section 4.3. The positive correlation with measurement temperature seen for bulk gas diffusion in Figure 7-11(b) may be caused by an increasing oxygen gradient formed in the vicinity of the TPB since the other processes occur more efficiently at higher temperatures.

7.4 Conclusion

LSCF behaves similarly to LSM in high \( pO_2 \) s. At \( pO_2 \) s greater than 3.0 % oxygen the cathodic reaction is confined to the TPB where charge transfer and adsorption and/or surface diffusion are the only significant electrochemical processes. In air, the activation energy of the charge transfer and adsorption related process are -1.72 and -1.56 eV, respectively. Charge transfer shows a weak dependence on \( pO_2 \) at high oxygen concentrations while adsorption has a \( pO_2 \) power dependence of -0.086.

As \( pO_2 \) is reduced, an alternate reaction pathway involving ionic transport through the bulk of the MIEC becomes more significant. This change is manifested by the formation of two additional low-frequency arcs in the impedance profile. LSM, on the other hand, presents only one new arc, related to the bulk gas diffusion of oxygen, in the concentration polarization regime. The second arc is a most likely a result of a surface exchange process at the gas LSCF interface which leads to a pathway for ionic conductivity through the MIEC bulk. At low \( pO_2 \) s, this pathway becomes more favorable because 1) a concentration gradient forms depleting the region near the TPB of molecular oxygen and 2) an increased number of oxygen vacancies (leading to higher ionic conductivity) form in the MIEC due to the low \( pO_2 \) of the ambient gas. At low \( pO_2 \) s, the activation energies of charge transfer and adsorption are -1.63 and -1.56 eV, respectively, while for the process specific to the MIEC and bulk gas diffusion, the activation energies are -1.50 and 0.50 eV, respectively.
As for pO$_2$ dependences under concentration polarization, charge transfer polarization resistance appears to decrease slightly as partial pressure is decreased, although significant scatter in the data leads to uncertainty in the trending. A decrease in polarization resistance due to charge transfer could be explained by the simple fact that a smaller percentage of the ionic current through the electrolyte is supplied by oxygen ions that have passed through the TPB compared to the cathodic reaction at higher pO$_2$s. For this reason, there is less total power loss due to charge transfer polarization resistance and the reduction in polarization resistance is anticipated. The power dependence of adsorption polarization resistance on pO$_2$, 0.099, can similarly be explained by a decreasing percentage of the electrolyte current being supplied by adsorbed oxygen molecules which pass through the TPB. At low pO$_2$s, polarization resistance of the process associated with surface exchange of oxygen molecules leading to bulk ionic transport through the MIEC increases as pO$_2$ decreases. Two regimes are observed, possibly indicating the point at which ionic conductivity in the LSCF no longer limits the supply of oxygen ions to the MIEC/electrolyte interface from the bulk of the cathode. As for bulk diffusion, a power dependence of -0.85 is reported for low pO$_2$s.
CHAPTER 8
CONCLUSIONS

The electrochemical properties of the cathodic reaction were investigated by impedance spectroscopy and other characterization techniques with a goal of identifying the significant individual processes. In order to accomplish this task, high-frequency impedance data had to be analyzed. Unfortunately, the quality of this data was diminished by high-frequency inductive artifacts. The influence of these artifacts on impedance data was analyzed and it was found that several data points at frequencies lower than the \( Z_r \)-axis had to be removed from the raw data if the raw data was to be used. The quality of the data was improved by fitting the high-frequency portion of the data (which was shown to be inductive in nature) to \( Z_j = j\omega L \) and subtracting the result from the raw data over the entire frequency range. Performing this operation increased the amount of usable data in the high-frequency regime by an order of magnitude allowing analysis of fast occurring electrochemical processes.

It was found that the in air at high temperatures two processes are most significant, charge transfer and adsorption. The dependencies of these two processes on measurement temperature and oxygen partial pressure were investigated in chapter three. It was found that the charge transfer resistance is smaller in magnitude than the adsorption related process. In addition to these two processes, a bulk diffusion related process becomes significant at low partial pressures of oxygen. Polarization resistance activation energies and time constants are generated from the model parameters and given in Table 4-1.

The cathodic reaction was found to be dramatically influenced by the sinter applied. In addition to altering the microstructure, over-sintering can also cause the formation of tertiary phases. The electrochemical reaction was drastically inhibited at the highest sintering temperatures. At these sintering temperatures, it was shown that lanthanum zirconate, an insulating layer had formed at the cathode/electrolyte interface.

To separate the effects of microstructure from tertiary phase formation, sintering at lower (but still high) temperature of non-stoichiometric LSM was performed. SEM/FIB
was used to quantitatively analyze the microstructural changes occurring. By relating the microstructural parameters to the electrochemical changes, direct relationships were developed which were predicted by theory.

The study was extended to LSCF in the final chapter. It was found that the cathodic reaction on LSCF behaves similarly to LSM at high partial pressures of oxygen. In comparison to LSM, LSCF had larger magnitude activation energies for charge transfer and the adsorption related process. At lower partial pressures of oxygen, the ionic reaction pathway becomes significant and an arc in the impedance profile not seen in LSM appears. LSCF samples were sintered at various temperatures and corresponding evolution of the impedance profile was examined. The data taken in this chapter is to be compared to microstructural information from the samples which is yet to be extracted.
Figure A-1. Tunnelling electron microscopy image of LSM on YSZ interface, with Energy dispersive spectrometry (EDS) profiles inset. For EDS profiles, Blue = Zirconium, Red = Manganese, Green = Yttrium, Purple = Lanthanum, Yellow = Strontium. (Courtesy of Mark Clark)

The interface of an LSM/YSZ sample sintered at 1400 °C for 48 hours was analyzed using energy dispersive spectroscopy (EDS) and tunneling electron microscopy (TEM) by Dr. Mark Clark. A TEM image with superimposed EDS linescans of the LSM/YSZ interface is displayed in Figure A-1. The linescans indicate that the amount of diffusion is element specific; interfacial pores is not likely the cause of the abrupt profile seen in Figure 5-9(b). The abruptness of the manganese profile compared to the lanthanum profile indicating that lanthanum, but not manganese from the electrode is diffusing into the YSZ. Like the lanthanum profile, the concentration profile of zirconium also exhibits a gradual decrease, though this time the concentration gradient is decreasing.
from the electrolyte towards the electrode. The yttrium and strontium EDS intensities are lower than the other elements and don’t provide any conclusive support, although their concentration dropoff in the transition region appears to be more abrupt like manganese than gradual like lanthanum and zirconium. These diffusion characteristics are evidence of a 0.2 micron thick transitional region, which is rich in both lanthanum and zirconium, but lacking in manganese and the other measured elements. TEM was used to investigate the crystal structure of the electrolyte, electrode and transitional regions.

Selected-area diffraction patterns (SADPs) of the electrode, Figure A-2(a), and electrolyte, Figure A-2(b) were attained using a 200 kV accelerating voltage, a camera length of 20 cm. Comparison of the figures allows a clear distinction between these regions. The electrolyte displayed a diffraction pattern indicative of an fcc crystal with a beam direction along the [112] zone axis. The pattern of the electrode was not as trivial due to the electrode’s complex crystal structure. The pattern of the transition region, Figure A-2(c), was identical to that of the electrolyte, suggesting that the transitional region is formed by the diffusion of lanthanum from the LSM region into the YSZ region, preserving the crystal structure of the YSZ. Another possibility is that the transition region exhibited a phase change, but the new phase was also of cubic body structure with a similar lattice constant.
Figure A-2. Selected-area diffraction patterns for LSM, YSZ, and the transitional region. Patterns attained for the [112] beam direction with a 200 kV accelerating voltage. a) Diffraction pattern for LSM. b) Diffraction pattern for YSZ. c) Diffraction pattern of the transitional region.
A dual beam FIB/SEM (FEI Strata DB 235) was used to create a three-dimensional image of the microstructure of the symmetric samples as described below. The symmetric samples were mounted on a 45° aluminum mount, which was tilted another 7° so that the face of the symmetric cathode was parallel to the ion beam as shown in Figure B-1.

Before exposure of the sample to the ion and electron beams, the symmetric samples were sputter coated with platinum to minimize charging and protect the sample. The dual beam FIB/SEM was used to ablate successive layers of specified thickness with SEM imaging after each ablation. These uniformly spaced 2-D images were then aligned, producing a 3-D image. Serial milling in the z-direction was conducted with steps of about 50 nm per slice using a Ga⁺ ion beam. About 30 images were taken per sample. After each FIB slice, SEM imaging was performed at a magnification of 12,000X. This mill-image-mill procedure was repeated from the platinum protective surface coating, through the cathode and down to the dense YSZ electrolyte. The SEM images were taken at 38° with respect to the sample face normal resulting in elongation of the raw images in
the x direction with $x_{\text{actual}} = x_{\text{raw}} \cdot \cos(38^\circ)$. The images had to be edited using Adobe Photoshop in order to adjust for the projection effects of the images. In this manner, a three dimensional map of the microstructure was created and later used to quantify the microstructural parameters of interest.

Porosity ($p$), volume normalized pore surface area ($S_V$), and TPB length values were calculated at each temperature, while tortuosity ($\tau$) values were calculated from the 3-D data attained at selected temperatures. Porosity was calculated from the pore area/total area in each SEM image. The calculation was repeated for all slices in the sample and an average porosity was attained. These results are plotted in Figures 6-2 and 6-3.

The pore surface area reported is normalized per unit volume. From [121, 122], the pore surface area ($S_V$) per unit volume can be calculated according to Equation B–1.

$$S_V = \iiint_{S} \frac{dS}{L^3} = 2P_L$$

In Equation B–1, $dS$ is the surface area element, $L^3$ is the unit volume, and $P_L$ is the number of phase changes (gas to solid) per unit length and was counted manually from each of the SEM images through the bulk of the cathode.

The triple phase boundary length ($L_{TPB}$) was calculated by application of the following equation [121, 122].

$$L_{TPB} = (\pi/2)P_L$$

For $L_{TPB}$, $P_L$ was counted from the pore/LSM phase changes per unit length in the SEM images at the LSM/YSZ interface. The units for the calculation of $L_{TPB}$ and $S_V$ are $\mu m^{-1}$, which is dimensionally accurate for a length normalized per unit surface area and an area normalized per unit volume.

The tortuosity was the only microstructural parameter that was not attained for each SEM and averaged making use of the uniformly spaced FIB slices. Tortuosity was calculated by estimating the length a gas particle must travel as it departs the impinging gas flow and travels to the electrolyte divided by the straight-line thickness. The method
used for the tortuosity calculation was based on the definition of tortuosity. The length traveled by a gas particle was calculated by first determining x, y, and z coordinates of the center of pores in adjacent slices and then tracking the changes in pore center location from slice to slice. Equation B–3 can be used to estimate the total distance traveled by a particle \( L_\tau \) using the Pythagorean Theorem.

\[
L_\tau = \sum_{i=1}^{N} \sqrt{(x_{n+1} - x_n)^2 + (y_{n+1} - y_n)^2 + (z_{n+1} - z_n)^2}
\]  

(B–3)

In Equation B–3 \((x_n, y_n, z_n)\) are the coordinates of the nth point used and there are N total points determined. Once attained, \( L_\tau \) can be divided by the straight-line distance to give the tortuosity.

The volume normalized pore surface area was calculated as described in Equation B–1 using three SEM images for each sintering temperature. For each image a line was taken in three directions for a total of nine measurements per sintering temperature. The temperature dependence of the average pore surface area and corresponding standard deviation as a function of temperature is plotted in Figure 6-2(a). For the area normalized triple phase boundary length, a single line near the interface was taken from each of three SEM images per sintering temperature. The results were averaged and plotted in Figure 6-2(b).
REFERENCES


BIOGRAPHICAL SKETCH

Jeremiah Robinson Smith was born at an early age in Long Beach, California to Paul and Peggy Smith. At the age of three, Jeremiah, his sister Dionne, and his brother Paul Jr. moved along with Mr. and Mrs. Smith to San Antonio Texas. When he was eight, the Smiths moved to Maryland. It wasn’t long before Jeremiah made new friends in Maryland, but still longed for Texas. Mrs. Powell’s fourth grade class was one of the toughest academic years of Jeremiah’s life. (If his mother had not decided to do some of Jeremiah’s endless homework Jeremiah would never have made it past the fourth grade.)

As the years went by, Jeremiah began to identify with Maryland and eventually no longer considered himself a Texan although his loyalty to the Dallas Cowboys never waivered.

While taking classes at Glenallan Elementary School (Go Gators!), Jeremiah discovered that he was a good student. Receiving $2 for an A and $1 for a B was all the extra motivation Jeremiah needed to become a consistent member of the honor roll. As Jeremiah matured, he realized that a big part of his academic success was that he grew up with two bright older siblings who exposed him to new ideas and were always happy to help him with his homework. Jeremiah was happy to attend John F. Kennedy, the same high school attended by his brother and sister. As Jeremiah’s high school years began to come to an end, Jeremiah was sad to see his brother and sister spend less and less time at home and eventually move out of the house. Jeremiah decided that he too would move out and placed a premium on scholarship offers that included room and board. This was one of the key factors that led him to choose University of Maryland, Baltimore County (UMBC) for schooling over Howard University, where his brother and sister attended college.

Room and board wasn’t the only reason Jeremiah attended UMBC. One of Jeremiah’s regrets from high school was that very few of his high school friends were black, despite the fact that his high school was extremely diverse. Jeremiah was recruited to UMBC to join the Meyerhoff Scholarship program, a program devoted to developing black Ph.
D.s in the fields of science and engineering. Although Jeremiah didn’t understand what a Ph. D. was at the time, he related to the other recruited students and decided to become a Meyerhoff Scholar. To this day, some of Jeremiah’s best friends are other Meyerhoff Scholars. At UMBC, Jeremiah majored in physics partly because he had always had an intrinsic curiosity about the world and partly because physics was viewed as the toughest major. As graduation approached, the coursework became more and more abstract and therefore less and less interesting to Jeremiah and he realized he didn’t want to pursue graduate studies in physics. Jeremiah discovered the field of materials science and engineering by chance and elected to attend graduate school at the University of Florida.

Upon arrival at the University of Florida, Jeremiah joined the research group of Dr. Kevin Jones. Jeremiah was happy to join Dr. Jones’ group because the focus of the research was on silicon technology, an area that had direct industrial importance, unlike many of the fields in graduate level physics. After about three years of study, Dr. Jones was promoted to chair of the Department of Materials Science and Engineering and was forced to cut back on his research. Jeremiah was saddened to learn that the project with which he was involved was not being renewed. Jeremiah was invited to join the research group of Dr. Eric Wachsman. He was grateful and excited to accept the invitation as he would be involved in a project focusing on fuel cell research. This research was appealing to Jeremiah because not only did it have immediate technological significance (unlike the abstract physics which bored him), but also had environmental impact. Jeremiah was undeterred by those who informed him that his project was extremely difficult and questioned if it was even possible. At several points, Jeremiah became discouraged including when he realized his goal of graduating in two additional years was unrealistic. Fortunately, many people encouraged and prayed for Jeremiah during these times and he never quit trying. Jeremiah graduated with his Ph. D. in 2007.