

NORTHWESTERN UNIVERSITY

Analysis of Electrochemical Performance and Degradation of Solid Oxide Fuel Cell Cathodes

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Field of Materials Science and Engineering

By

Hongqian Wang

EVANSTON, ILLINOIS

September 2018

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Abstract

Analysis of Electrochemical Performance and Degradation of Solid Oxide Fuel Cell Cathodes

Hongqian Wang

This dissertation presents research on solid oxide fuel cell (SOFC) cathodes. It specifically covers two main topics: the electrochemical performance of porous two-phase composite cathodes, and the degradation mechanisms of porous single-phase mixed conducting cathodes. Current-voltage measurement and electrochemical impedance spectroscopy were used extensively to evaluate the cell performance. The impact of microstructure on electrode resistance was studied by using focused ion beam-scanning electron microscopy (FIB-SEM), utilizing both two-dimensional (2D) and three-dimensional (3D) images. To investigate the mechanisms of electrode degradation during long-term operation, FIB-SEM 3D tomography was used to analyze the microstructural evolution, and a novel selective chemical etching method was developed to examine the surface compositional changes.

Densification of $\text{Y}_{0.16}\text{Zr}_{0.92}\text{O}_{2-\delta}$ (YSZ) electrolyte at a reduced temperature, 1250 °C, was achieved by utilizing Fe_2O_3 as sintering aid, allowing single-step co-firing fabrication of anode- and cathode-supported SOFCs consisting of $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$ (LSM)-YSZ cathodes, YSZ electrolytes, and Ni-YSZ anodes. The resultant LSM-YSZ cathode had higher polarization resistance than a cathode that was fired separately at an optimized temperature of 1175 °C. Analysis of FIB-SEM images showed that co-firing caused more sintering and coarsening than in the optimally-fired LSM-YSZ, reducing triple phase boundary (TPB) density. It was found that

reducing the firing time slightly decreased cathode polarization resistance and increased cell power output. To compensate for the over-sintering of LSM-YSZ during co-firing, $(\text{Sm}_{0.5}\text{Sr}_{0.5})\text{CoO}_3$ (SSC) was infiltrated into LSM-YSZ cathodes in the cathode-supported SOFCs in order to enhance the TPB density. However, coarsening of the nano-scale SSC was observed during the preliminary life tests, leading to significant cell degradation. On the other hand, cathode-supported SOFCs allowed the use of thinner anodes, and hence exhibited high fuel utilization as well as high steam utilization when operating under electrolysis mode.

The study of degradation mechanisms was conducted on single-phase mixed conducting electrodes, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF). Temperature-induced degradation was investigated on both LSCF symmetric-electrode cells and microtubular full cells consisting of LSCF cathodes. It was found by FIB-SEM 3D tomography that particle coarsening only occurred at sufficiently high temperatures, $\geq 950^\circ\text{C}$. The performance degradation observed at temperatures $< 950^\circ\text{C}$ was attributed to Sr segregation to particle surfaces, which inhibited the oxygen surface exchange process. A selective chemical etching method with inductively couple plasma-optical emission spectrometry (ICP-OES) detection was developed to quantitatively analyze the Sr surface segregation on the porous LSCF electrodes. This method was also found to be applicable to systems other than LSCF, such as quantifying Ba surface segregation in $\text{La}_{0.5-x}\text{Pr}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ (LPBC) cathodes. Additionally, degradation during reversing current operation was examined on LSCF symmetric-electrode cells. Results showed that the primary source of the degradation was also associated with Sr surface segregation, with a smaller contribution from current-induced coarsening.

Acknowledgements

Completion of my doctoral dissertation would not be possible without the help, assistance, and support from many people. I would like to express my sincere gratitude to all of them.

First and foremost, I would like to express my deepest appreciation to my advisor, Prof. Scott Barnett, for his excellent guidance over the past five years. He has supported me throughout my thesis research with his incredible patience and knowledge whilst allowing me the room to work in my own way. More importantly, his optimistic and sweet personality has always inspired me to face things positively and with courage. I could not have imagined having a better advisor for my Ph.D. pursuit.

I would also like to thank my committee members Prof. Sossina Haile, Prof. Peter Voorhees, and Dr. Brian Ingram for their valuable advice and support, as well as taking the time to read this document and hear my speak.

I am highly indebted to my mentors – Dr. David Kennouche and Dr. Zhao Liu for their supervision on 3D tomographic techniques, and Dr. Zhan Gao for teaching me all about SOFC fundamentals and fabrication methodologies. I am also grateful to all the fellow graduate students, both past and present: Dr Gareth Hughes for showing me how to assemble dual atmosphere testing rig; Dr. Beth Miller for her great advice on graduate classes and especially how to make delicious cakes; Dr. Ann Call for showing me her super cute cats; Dr. Kyle Yakal-Kremiski for his patience on answering my innumerable questions when picking up his research after he graduated; Dr. Justin Railsback for all the valuable discussions on MIEC cathodes and our collaboration on LSCF degradation study. I have greatly enjoyed working with all my present lab mates: Qinyuan Liu, the

most awesome girl I have ever met and also my best friend; Xiankai Yu, who I could always consult about Li-ion batteries; Matthew Lu, who always seemed enthusiastic and encouraged me to participate in MSSA 5K events; Travis Schmauss, who I had joyful scientific and non-scientific conversations with; Sam Miller and Maxwell Dylla, who always gave good suggestions during group meetings even though their research is on thermoelectric materials.

I greatly appreciate and acknowledge the help from the post-doctoral researchers and visiting scholars in my group, Dr. Roberto Scipioni, Dr. Beom-Kyeong Park, Dr. Tenglong Zhu, Dr. Koichi Hamamoto, and Dr. Shanlin Zhang.

I am extremely thankful to my advisees, Yifan Sun, Kuan-Hua Chiu, and Kunli Yang, for their hard and excellent work. It was a great pleasure to mentor them in the lab.

Additionally, this work could not be accomplished without my many collaborators. Special thanks to Dr. Ghislain Rupp, Prof. Andreas Limbeck and Prof. Jürgen Fleig from Vienna, Dr. Hirofumi Sumi from Japan, Dr. Diana Garcés and Dr. Liliana Moggi from Argentina, and Dr. Chal Park and Prof. Katsuyo Thornton from University of Michigan. My sincere thanks also goes to all the facility managers who have provided great assistance in conducting numerous experiments in this work, Dr. Dean Miller, Dr. Jiajun Wang, Dr. Keith MacRenaris, and Dr. Karl Hagglund.

I also want to thank my family and lifelong friends for all their support. My parents have encouraged and helped me at every stage of my life. My uncle Charlie has always been supportive, giving me valuable advice on both my personal and academic experience. Finally, I would like to thank my husband Timmy for his continued love and support ever since our sophomore year at Purdue.

List of Abbreviations

AFL	Anode Functional Layer
DRT	Distribution of Relaxation Time
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
FIB	Focused Ion Beam
GDC	Gadolinium-Doped Ceria
ICP-OES	Inductively Coupled Plasma-Optical emission Spectrometry
LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$
LSM	$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$
MIEC	Mixed Ionic-Electronic Conducting
OCV	Open Circuit Voltage
ORR	Oxygen Reduction Reaction
PSD	Particle Size Distribution
ReSOC	Reversible Solid Oxide Cell
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
SSC	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$
TPB	Triple Phase Boundary
XRD	X-ray Diffraction
YSZ	Yttria-Stabilized Zirconia

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Chapter 1

Introduction

Solid oxide fuel cells (SOFCs) are fully solid-state electrochemical devices that directly convert chemical energy in fuels to electrical energy with low pollutant emissions.¹⁻³ By combining fuel and oxygen across an ionic conducting oxide, the cells produce electricity. SOFCs have received great interest due to their potential for high efficiency, low emission, and fuel flexibility. They can be used as distributed stationary power generators, as well as energy storage devices when coupled with renewable energy sources. In order to meet the requirements for SOFC commercialization, fabrication process, performance, and stability of the devices must be clearly addressed.

For industrial application, the fabrication steps will directly influence the manufacturing cost, input energy and time. Simplification of the fabrication process while retaining the high quality/performance is highly desirable. In traditional SOFC fabrications, thick anodes are usually used to mechanically support the whole structure, and fired together with the electrolytes. Cathodes are applied and fired at lower temperatures in a second step because they generally exhibit lower melting temperatures. Co-firing of the cathode with the anode|electrolyte structure is highly favorable as it is a requirement for fabrication strategies of the entire SOFC stack. It also allows more possible geometries to be fabricated, such as cathode-supported cells. To achieve the co-firing, it is critical to reduce the densification temperature of the electrolytes, as well as maintaining the cathode electrochemical performance.

The overall performance of SOFCs is heavily dependent on electrode and electrolyte microstructures. The electrolyte densification greatly influences the open circuit voltage (OCV), and the thickness of the electrolyte directly contributes to the ohmic loss. The electrodes generally have more complex structures. They are responsible for diffusion of the reactant gases, electrochemical reactions, and transport of the ions to and from the electrolytes. Understanding the relationship between microstructure and electrochemical performance is important for optimization of the cell design and improvement of the cell performance. SOFC cathodes are of particular interest as they are typically the primary contributor to cell resistance. In this work, 3D tomographic technique utilizing FIB-SEM has been used to quantitatively analyze the cathode microstructure, and compare with its electrochemical characteristics.

In addition to cell performance, stability is another great challenge for SOFC commercialization, as the requirement of operating at high temperatures leads to significant degradation over time. Reducing the operating temperature is essential for improving the cell's long-term stability and decreasing the system's production cost. This can be achieved by infiltrating nano-scale particles into porous composite or scaffold structures, or by using the porous single-phase mixed conducting materials, where the reaction sites are expanded to the entire particle surface. Although reducing the operating temperature can effectively decrease the degradation induced by temperature, there will still be significant degradation at longer times. Additionally, the current running through the cells during operation is found to be also responsible for performance degradation. Understanding the degradation mechanisms is critical for prediction and improvement of cell stabilities. The temperature- and current-induced degradations of a common single-phase mixed conducting cathode, LSCF, have been studied in this work.

In this dissertation, performance and degradation mechanisms of SOFC cathodes, including porous composite and porous single-phase mixed conducting structures, will be discussed. The outline of the work is as follows:

Chapter 2 covers the fundamentals of SOFCs, including structures and materials for electrolytes and electrodes, thermodynamic and kinetics. It also describes the measurements used to characterize electrochemical performance, the importance of microstructure, and the possible degradation mechanisms.

Chapter 3 introduces the FIB-SEM 3D tomographic technique, which has been extensively used in this work to analyze the electrode microstructure. The sample preparation, data collection and analysis are detailed in this chapter.

The studies conducted in this thesis work starts from Chapter 4. Chapter 4 demonstrates the fabrication of anode-supported SOFCs via single-step firing at reduced temperature. The effects of firing temperature and time on the cathode microstructure and resistance, and the overall cell performance are discussed. The single-step firing also allows fabrication of SOFCs with a cathode-side as mechanical support. This geometry allows use of a thinner anode, which typically exhibits high fuel and steam utilization due to improved gas diffusion, and therefore is applicable to reversible SOCs. Chapter 5 discusses the fabrication of cathode-, more precisely in a SOC, oxygen-electrode-supported cells using single-step firing. The electrochemical performance, during both fuel cell and electrolysis operations, has been evaluated using j - V and EIS measurements. The relatively large polarization loss ascribed to thick oxygen-electrode has been reduced by infiltration of nano-scale SSC particles into LSM-YSZ electrodes.

In addition to electrochemical performance, electrode degradation is another focus in this work. Chapters 6 and 7 present the study of degradation mechanisms of LSCF cathodes at various ageing temperatures in symmetric-electrode and full microtubular cell geometries, respectively. The work on microtubular cells is a collaboration with National Institute of Advanced Industrial Science and Technology (AIST) in Nagoya, Japan. The microstructural evolution has been analyzed using 3D FIB-SEM tomographic technique. The surface cation modification, in this case Sr surface segregation, has been quantified by selective chemical etching with ICP-OES detection. The quantitative Sr measurement on porous LSCF electrodes has been developed in collaboration with Prof. Jürgen Fleig from Vienna University of Technology in Vienna, Austria. Influence of reversing current on the LSCF electrodes has been investigated jointly with Dr. Justin Railsback and shown in Chapter 8. Again, the changes in microstructure and surface cation composition have been examined.

The application of the selective chemical etching method to another system, Ba surface segregation in LPBC electrodes, is illustrated in Chapter 9. This is a collaborative work with Dr. Liliana Mogni from CONICET/CNEA in Bariloche, Argentina. The LPBC electrodes have been synthesized, characterized, and life tested. The possible degradation mechanisms – microstructural evolution and Ba surface segregation – have been studied.

Finally, Chapter 10 discussed the future work for degradation study of LSCF, mainly the coarsening of LSCF particles during long-term operation, followed by a summary of all the work presented in this thesis in Chapter 11.

Chapter 2

Background

Looking at today's energy consumption in the U.S., ~ 40% is due to electricity generation, and ~ 70% electricity generation has been rejected. The electricity generation also accounts for ~ 40% of total CO₂ emissions.⁴ Therefore, a cleaner electricity generation with improved efficiency is in demand. Fuel cells have been proposed as highly efficient and clean for multiple potential applications ranging from hand-held power generators to vehicle power sources, from large distributed power plants to energy storage solutions for renewable energy sources. While specifically for solid oxide fuel cells (SOFCs), the main applications lie on the stationary power generator and energy storage solutions, given the requirement of high temperature operation. SOFCs stand out for a number of reasons. Fully solid-state allows many different geometries to be fabricated. High operating temperatures, usually 600 – 1000 °C, lead to enhanced electrode kinetics and the ability to use lower cost, non-precious metal catalysts. The elevated temperature operation also enables internal reforming and directly operating on carbonaceous fuels. Moreover, the high-quality heat can be extracted and utilized in co-generation systems, increasing overall efficiencies up to 85%.

While the advantages of SOFCs are well-established, there are several drawbacks to this technology. Although there are many benefits of high temperature operation as mentioned above, it also causes fast material degradation such as microstructural and compositional changes, as well as issues with material compatibility, elemental interdiffusion, formation of secondary phases, and delamination of the multi-layer structure, etc. The use of hydrocarbons can lead to carbon

deposition, or coking, on the fuel electrodes, blocking the active reaction sites.⁵ In addition, contaminants such as sulfur impurities in the hydrocarbon fuel can degrade cell performance even at parts per million (ppm) levels.⁶ Cr poisoning has also been reported when using stainless steel interconnectors.⁷⁻⁹

2.1. Solid Oxide Fuel Cell Fundamentals

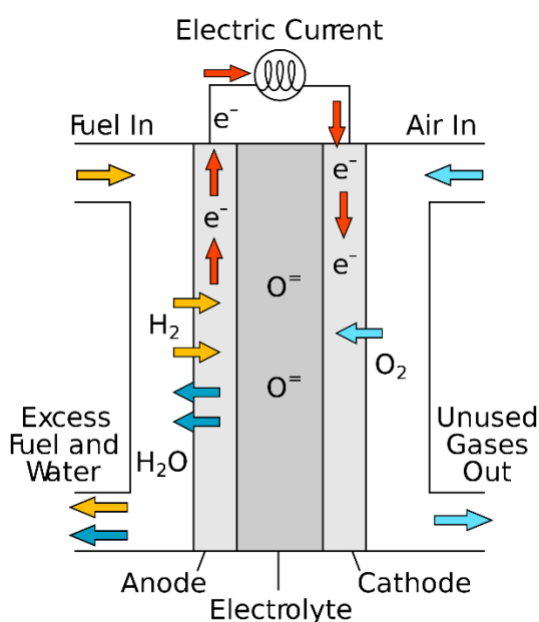
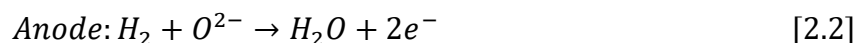


Figure 2.1. Schematic diagram of an operating SOFC.¹⁰

SOFCs are solid state devices that directly convert chemical energy into electricity. They consist of a porous anode and a porous cathode separated by a dense electrolyte, as shown in Figure 2.1. Oxidant, usually oxygen, is reduced at the cathode. Fuel, which is ideally hydrogen, is oxidized at the anode. The electrolyte allows transport of oxygen ions between the two electrodes, but it is dense enough to prevent gas flow and is an electronic insulator. Thus, in order to maintain charge

neutrality, the electrons are forced through an external circuit, producing electricity. The reactions happening at each electrode and the overall reaction are described below.¹



These reactions run towards the right during fuel cell mode, generating electricity. Conversely, if an external voltage is applied to the system, it will run in the reverse direction as an electrolysis cell, splitting water into H_2 and O_2 . In addition to H_2 , SOFCs can be operated on other fuels such as CO. Simple hydrocarbons such as methanol, propane and natural gas can also be utilized, as the high temperature operation can facilitate internal reforming reactions to generate reacted fuels.¹¹

2.1.1. Electrolyte

The electrolyte of a typical SOFC is a fully dense, ionically conducting oxide sits between anode and cathode. It serves as a barrier to separate the fuel and oxidant. Only oxygen ions are allowed to transport through while passing of electrons are prohibited. The electrolyte needs to be stable in both reducing and oxidizing environments, as well as chemically and mechanically compatible with electrode materials surrounding it.^{1, 2, 12, 13}

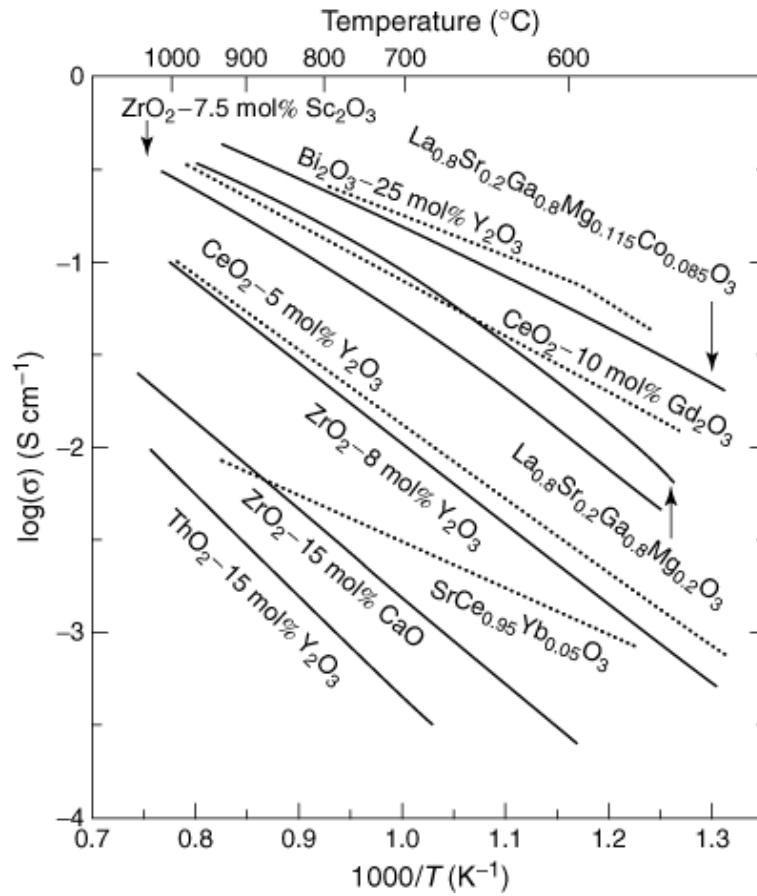


Figure 2.2. Arrhenius plot of ionic conductivity for a variety of electrolyte materials.¹⁴

The resistance of the electrolyte is critical to SOFC performance. It decreases with decreasing electrolyte thickness and increasing operating temperature. Therefore, thin electrolytes (usually $< 10 \mu\text{m}$) are used in traditional SOFC configurations. The operating temperature is usually chosen to keep the electrolyte resistance below $0.1 \Omega \cdot \text{cm}^2$. Typically, electrolyte materials for SOFCs utilize fluorite or perovskite structures, as they can have oxygen ion conductivity of up to 0.1 S/cm over the relevant range of SOFC operating temperatures.¹⁴ The temperature dependence of the ionic conductivity for some common electrolyte materials is shown in Figure 2.2.

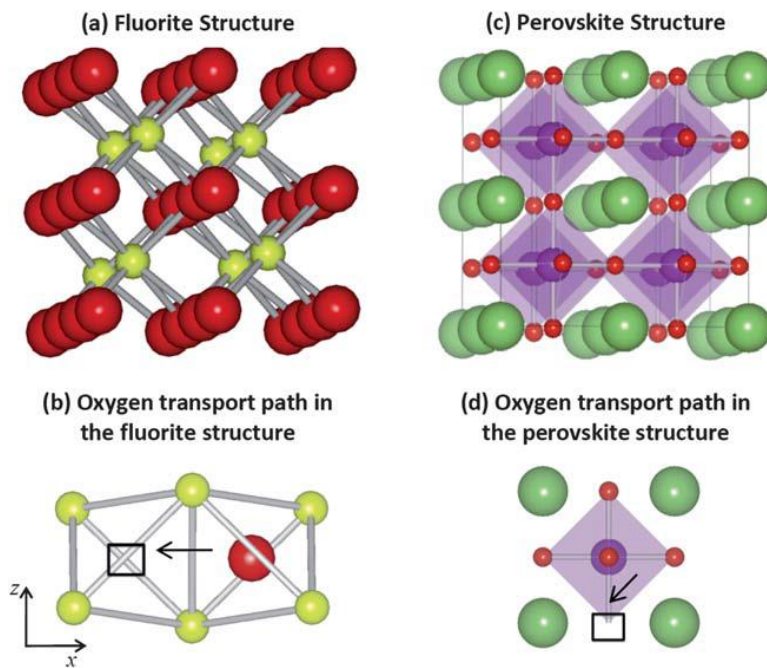


Figure 2.3. Crystal structure and oxygen migration path in fluorite (a, b) and perovskite (c, d) structures.¹⁵

The most common material is 8 mol.% yttria-stabilized zirconia (YSZ). Yttria-doping makes the cubic structure more stable and introduces additional oxygen vacancies, resulting in enhanced ionic conductivity (0.03 S/cm at 800°C ¹⁶) and reduced activation energy (0.8 eV ^{13, 17}). The good stability of YSZ over a wide oxygen partial pressure range is also a big advantage. Another widespread material used for SOFC electrolyte is gadolinia-doped ceria (GDC). It has a higher ionic conductivity (0.13 S/cm at 800°C and 0.035 S/cm at 600°C ¹⁷⁻¹⁹) and lower activation energy (0.52 eV ¹⁷) relative to YSZ, allowing it to be used at lower operating temperatures. However, GDC is less stable with variation in oxygen partial pressure and exhibits substantial electronic conductivity in the reduced atmosphere.¹⁸ Both YSZ and GDC adopt fluorite structure, shown in Figure 2.3a. The pathway by which oxygen diffuses through the structure is shown in Figure 2.3b. The lanthanum gallate perovskite materials, especially doped with strontium and

magnesium (LSGM) have also been used due to high ionic conductivity at intermediate temperatures and good stability with oxygen partial pressures, but issues occur in material reactivity and compatibility during processing.²⁰⁻²² The crystal structure and oxygen transport path in the perovskite are shown in Figures 2.3c and d, respectively.

2.1.2. Anode

The anode is responsible for oxidation of the fuel, so catalytic activity toward the fuel oxidation is desired. It is porous so that gaseous fuel can diffuse through to the active reaction sites. It also needs to be both ionically and electronically conductive to allow transport of oxygen ions to the reaction sites and conduct of electrons produced from the reaction to the external circuit. Additionally, the materials used for SOFC anode should have good stability at high temperatures and in reducing environments, as well as good chemical compatibility with the electrolyte. Having similar thermal expansion with other cell components is also very important.^{23, 24}

A typical anode in an SOFC is a cermet composite of nickel and YSZ, in which Ni provides the electronic conductivity and catalytic activity for fuel oxidation while YSZ supplies the ionic conductivity. Ni is often introduced as NiO during processing. The porosity is then created by reduction of NiO to Ni when exposing to fuel at elevated temperatures. The porosity can also be increased by addition of pore formers such as starch or graphite, etc. One of the most important characteristics of anode that directly relates to cell performance is triple phase boundary (TPB) density, defined as the density of the regions where electronically conductive, ionically conductive and pore phases are present and thus the reaction zone. For a TPB to be active, all three phases must be percolated (electronically conductive material to the current collector, ionically

conductive material to the electrolyte, and pores to the fuel inlet). The percolation is greatly affected by the fraction of each phase. Studies have shown that at least 30 vol.% Ni (~ 50 wt.% NiO) is needed to allow electronic connectivity to the external circuit,²⁵ and 60:40 wt.% NiO:YSZ yields the optimal anode performance.^{26, 27}

Anode utilizing Ni-YSZ also has some drawbacks. Coarsening and sintering of Ni particles have been observed, leading to performance degradation.²⁸ Besides, large volumetric change of Ni particle during redox cycling can stress the surrounding YSZ structure, and hence cause cracking.^{29, 30} Additionally, the sulfur existing in natural gas, which is used in most commercial systems, has been found to poison Ni even at low concentrations.^{31, 32} Coking on Ni has also been observed when operating on carbon-containing fuels.³³ To remedy these issues, electrically conductive perovskite ceramics have been studied as alternate materials^{5, 34}, although with lower performance and higher cost.³⁵

2.1.3. Cathode

The cathode is where the reduction of oxygen into oxygen ions takes place. Similar to the anode, the cathode is porous to allow diffusion of gaseous oxygen; electronically conductive for the electrons to transport to the reaction sites and ionically conductive to provide pathways for the oxygen ions from the reaction sites to the electrolyte. Stability at high temperatures and in oxidizing environment, as well as good chemical and mechanical (thermal expansion) compatibility with the electrolyte are also critical requirements for cathode materials. Additionally, it is favorable that the cathode has catalytic activity towards the reduction of oxygen to lower its activation energy.

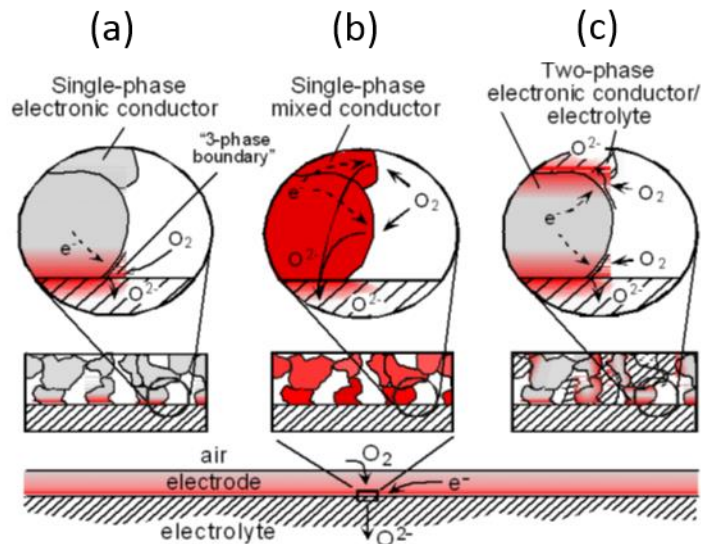


Figure 2.4. Different types of SOFC cathode structures. Porous single-phase electronically conductive oxide where reactions take place at the electrode-electrolyte interface (a), porous single-phase mixed conductor where reactions take place at the electrode surface (b) and porous two-phase composite where reactions take place at the active TPBs (c).³⁶

There are three main types of SOFC cathode structures, as illustrated in Figure 2.4.³⁶ For the single-phase electronic conducting materials (Figure 2.4a) such as $(\text{La,Sr})\text{MnO}_3$ (LSM), reduction of oxygen is confined to the electrode/electrolyte interface. The active reaction zone can be greatly enhanced by introducing an ionically conducting oxide, usually the same material as the electrolyte, to form a porous composite microstructure (Figure 2.4c). Another type is utilizing single-phase mixed ionic-electronic conducting (MIEC) materials (Figure 2.4b) such as $(\text{La,Sr})\text{CoO}_3$ (LSC) and $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ (LSCF). As the name suggests, these materials have both ionic and electronic conductivities, and hence the reduction of oxygen can take place over a significant portion of the electrode surface.³⁶ The rate-limiting steps for ORR in the single-phase MIEC electrodes are typically oxygen surface exchange and oxygen ion bulk diffusion.³⁷ The use of MIEC materials extends the active region for the ORR, thereby improving the kinetics at lower

temperatures, which makes them suitable for intermediate-temperature (IT)-SOFCs. However, the limited chemical compatibility may require the use of interfacial barrier layers.^{3, 38}

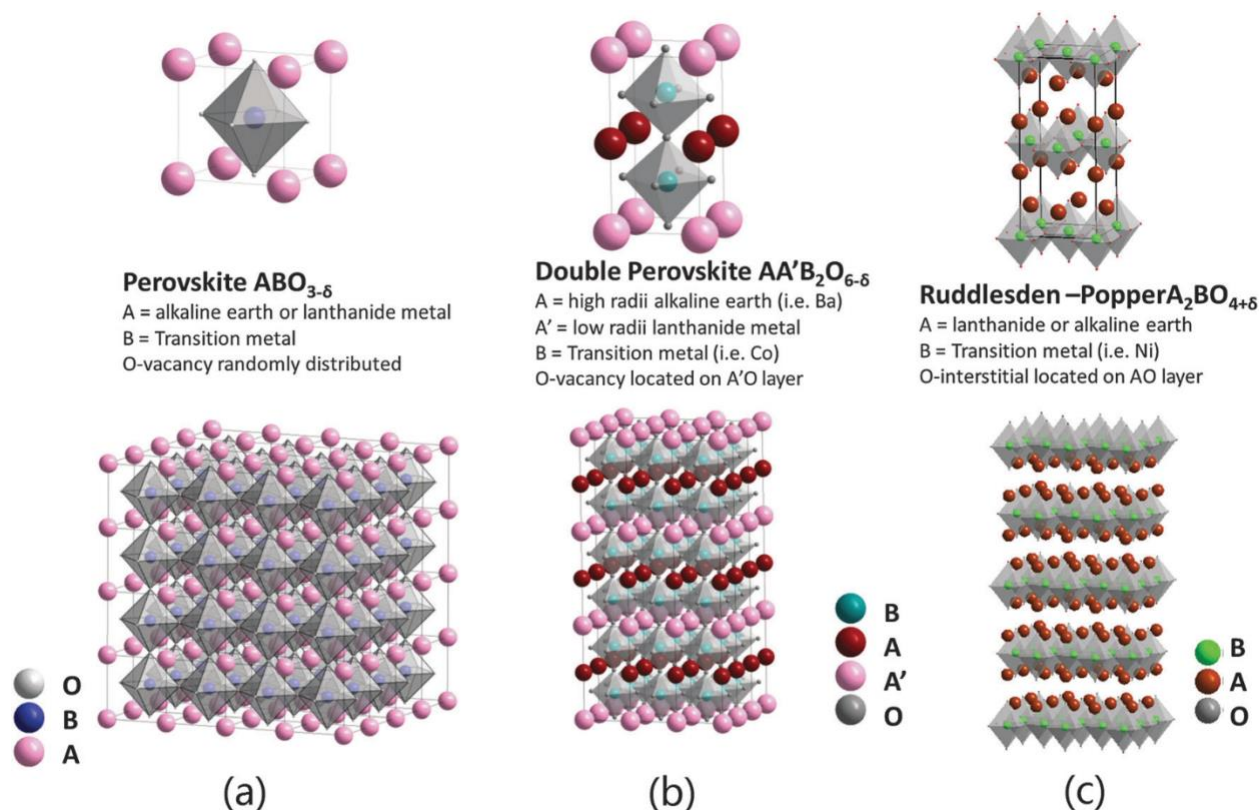


Figure 2.5. Crystal structures of three main families of MIEC cathode materials: cubic perovskite (a), layered double perovskite (b) and Ruddlesden-Popper (c).³⁹

To date, three main families of MIEC oxides have been received great interest as potential IT-SOFC cathodes: the cubic perovskites, the double perovskites and the Ruddlesden-Popper phases.³⁹ The crystal structures are shown in Figure 2.5. The cubic perovskites, including LSCF family of compounds, exhibit high electrical and ionic conductivity.⁴⁰ The material conducts electrons through the small polaron hopping mechanism. Transport of oxygen ions is through oxygen vacancy diffusion, with 8 mS/cm at 800 °C. The $\text{LnBaCo}_2\text{O}_{5+\delta}$ layered perovskites have high electrical conductivity, as well as high oxygen surface exchange and oxygen ion diffusion

rates.^{39, 41, 42} The Ruddlesden-Popper phases such as $\text{Nd}_2\text{NiO}_{4+\delta}$ are perovskite-related MIECs where the mobile oxygen species are interstitials.^{43, 44} They have alternating regions of perovskite and rock-salt layers. Ruddlesden-popper phases have relatively low electronic conductivity compared to other perovskite-related compounds, but their advantage lie in compatible thermal expansion with the commonly used electrolyte materials.

2.2. Thermodynamic and Kinetics

The Nernst potential, given in Eq. [2.4], is the theoretical open circuit voltage (OCV) of a cell. In practice, the operating voltage is reduced from the Nernst potential by three main resistances from ohmic loss, electrochemical reaction kinetics and gas diffusion limitations, as shown in Figure 2.6.¹⁴

$$E = E^\circ + \frac{RT}{zF} \ln \left(\frac{\prod_i a_{rea,i}^{b,i}}{\prod_j a_{prod,j}^{b,j}} \right) = E^\circ + \frac{RT}{zF} \ln \left(\frac{\prod_i p_{rea,i}^{b,i}}{\prod_i p_{prod,i}^{b,j}} \right) \quad [2.4]$$

where E° is the ideal potential at standard temperature and pressure, R is the gas constant, T is temperature, z is the number of electrons exchanged in the reaction, F is Faraday's constant, a and p are activity and partial pressure of the reactant or product specie, respectively.

Ohmic polarization (η_{ohm}) comes from resistance to charge transport. Since transport mobility of ions is orders of magnitude smaller than electrons, majority of the ohmic loss is observed in the electrolyte, and can be calculated by Ohm's law:

$$\eta_{ohm} = jR \quad [2.5]$$

where j is the current density and R is the sum of electronic, contact and ionic resistances.

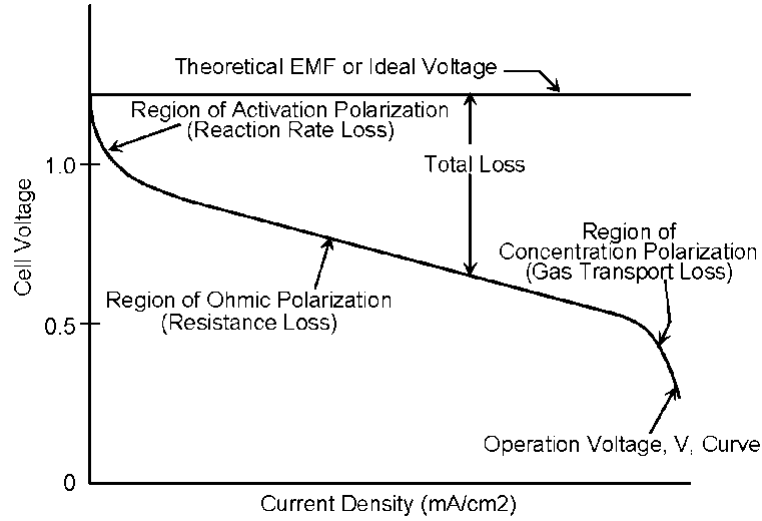


Figure 2.6. Ideal and actual current-voltage characteristics for an SOFC.¹⁴

Concentration polarization (η_{conc}) is caused by the gas transport limitation in the electrodes. Especially at high current densities, the cell output can be limited by finite gas diffusion kinetics which deplete reactant concentration near electrode reaction sites. The concentration polarization can be expressed by

$$\eta_{conc} = \frac{RT}{zF} \left(1 + \frac{1}{\alpha} \right) \ln \left(\frac{j_L}{j_L - j} \right) \quad [2.6]$$

where α is the transfer coefficient, j_L is the limiting current density, which represents the situation when the reactant concentration drops to zero near the reaction sites, and thus the cell cannot sustain a higher current density. j_L can be calculated by

$$j_L = zF D_{eff} \frac{C_R^0}{\delta} \quad [2.7]$$

where C_R^0 is the bulk concentration of reactant, δ is the electrode thickness, and D_{eff} is the effective diffusivity, which relates to electrode porosity and tortuosity.

Activation polarization (η_{act}) is attributed to the kinetic losses of the electrochemical reactions at the cathode and anode. For instance, in the cathode there will be losses due to oxygen adsorption, dissociation and diffusion, etc. The activation polarization is related to current density by the Butler-Volmer equation:

$$j = j_0 \left\{ \exp\left(\frac{\alpha z F \eta_{act}}{RT}\right) - \exp\left(-\frac{(1 - \alpha) z F \eta_{act}}{RT}\right) \right\} \quad [2.8]$$

where j_0 is the exchange current density.

2.3. Electrochemical Characterization

2.3.1. Current-voltage characteristics

The overall performance of a fuel cell can be quantitatively evaluated by its current-voltage response. A typical measurement involves stepping the voltage from OCV to 0 V and measuring the corresponding current (called “potentiostat”); or it could be a stepping current being applied and measuring the corresponding voltage (called “galvanostat”). Figure 2.7 shows a typical j - V curve. Power density can be calculated by multiplying voltage by current density, showing on the right-hand axis. To take reliable j - V measurements, it is important that the system is at steady state, meaning that the voltage and current do not change with time. Another important aspect is that the test conditions, such as temperature, reactant partial pressures and gas flow rates, should be clearly noted, as they will dramatically affect fuel cell performance.

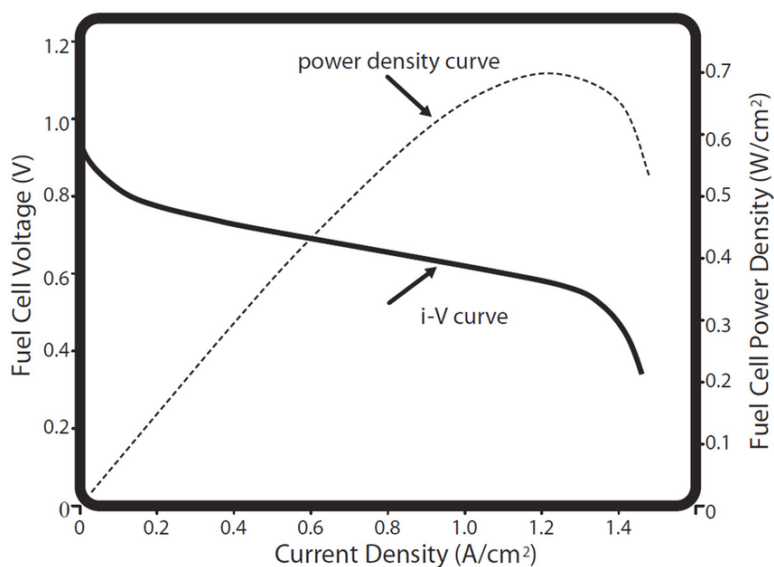


Figure 2.7. j -V and power density curves for a fuel cell.²

2.3.2. Electrochemical impedance spectroscopy

Although j -V curve can provide the overall performance of a fuel cell, and by carefully analyzing the data the activation losses can be approximated using the Tafel equation, a more sophisticated test is required to better differentiate between all the major sources of loss in a fuel cell. Electrochemical impedance spectroscopy (EIS) is the most widely used technique to do this. It is a dynamic measurement functions by applying a small sinusoidal voltage at a specific frequency and recording the amplitude and phase shift of the resulting current response, shown in Figure 2.8. The measurement is then repeated over a set range of frequencies. The recorded amplitude and phase shift can be reinterpreted as a real and an imaginary components.

The resulting data can be plotted in two ways: a Nyquist plot (Figure 2.9a) with the real portion of the impedance on the x-axis and the imaginary portion on the y-axis; a Bode plot with the frequencies on the x-axis and the imaginary impedance response on the y-axis (Figure 2.9b).

In the Nyquist plot, the left-most intercept corresponds to the ohmic resistance, usually coming from the electrolyte and electrical contacts; the right-most intercept is the total resistance; and the distance between the two intercepts is the polarization resistance. In the Bode plot, the characteristic frequencies associated with different processes in the cell are seen as peaks.

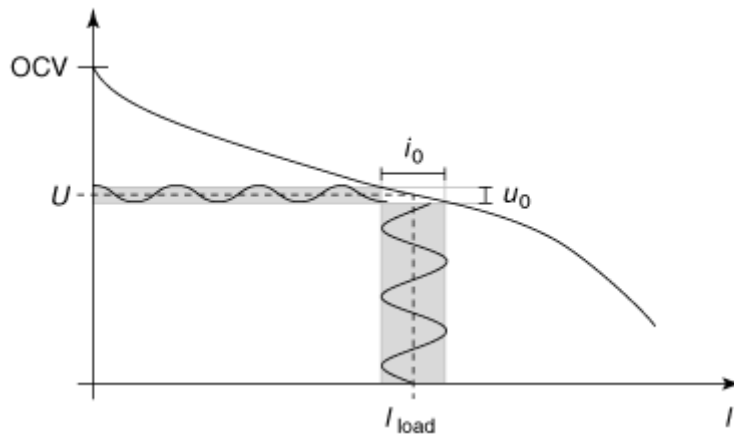


Figure 2.8. Schematic diagram of applied oscillating voltage and the resulting current with a phase shift.¹⁴

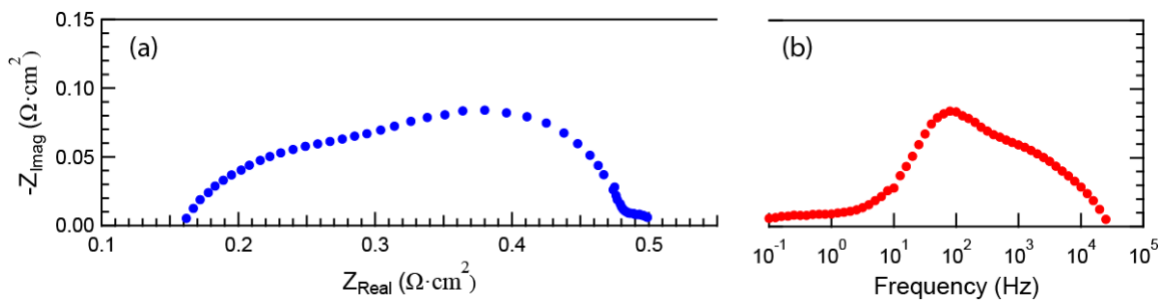


Figure 2.9. Example of Nyquist (a) and Bode (b) plots.

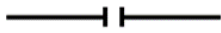
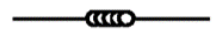
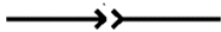
2.3.3. Equivalent circuit modeling

The EIS data can be analyzed mathematically using equivalent circuit modeling to determine the processes that occur inside a fuel cell. For example, groups of resistors and

capacitors can be assigned to describe the behavior of electrochemical reaction kinetics, ohmic conduction processes, and mass transport.²

The ohmic response of the cell is represented by a simple resistor. It is time independent, and is shown as a point on the Nyquist plot. The responses from the anode and cathode can be represented by resistors in parallel with a capacitor or a constant phase element (CPE). The Nyquist plot will appear as a perfect semi-circle when a resistor is in parallel with a capacitor (called RC element). Rather than a capacitor, a CPE is frequently used when modeling fuel cell electrodes. It is similar to a capacitor, but with an exponent modifying the equation. The resulting circuit is referred to as Cole or RQ element. Some of the most commonly used equivalent circuit elements for fuel cells are listed in Table 2.1.

Table 2.1. Equivalent circuit elements.⁴⁵

Element (Parameter / Units)	Impedance	Symbol	Characteristic Frequency
Resistor ($R / \Omega\text{cm}^2$)	$Z = R$		-
Capacitor (C / Fcm^{-2})	$Z = \frac{1}{i\omega C}$		-
Inductor (L / Hcm^2)	$Z = i\omega L$		-
Constant Phase Element ($Q / \text{Fcm}^{-2}, n$)	$Z = \frac{1}{(i\omega Q)^n}$		-
RC Element ($R / \Omega\text{cm}^2, C / \text{Fcm}^{-2}$)	$Z = \frac{R}{1 + i\omega RC}$		$f_{ch}(\text{Hz}) = \frac{1}{2\pi RC}$
Cole / RQ Element ($R / \Omega\text{cm}^2, C / \text{Fcm}^{-2}$)	$Z = \left(\frac{1}{(i\omega Q)^{-n}} + \frac{1}{R} \right)^{-1}$		$f_{ch}(\text{Hz}) = \frac{1}{2\pi QR^{(1/n)}}$

2.3.4. ALS model

For MIEC cathodes with facile internal mass transport such as LSCF (which will be studied in this work), it has been shown that the electrochemical behavior is dominated by oxygen surface exchange and solid-state oxygen diffusion.³⁷ The contributions of these processes to the overall electrode kinetics can be related quantitatively to the bulk properties of the MIEC electrodes, known as ALS model.³⁷ The impedance response is described by a Gerischer element, or sometimes a depressed Gerischer expression⁴⁶ is used to give an improved model on the low frequency region. The depressed Gerischer element is shown in Eq. [2.9], where $0 < \alpha < 1$, which has the similar form as the phenomenological Havriliak-Negami dielectric dispersion relation.⁴⁷

$$Z_G = R_G \sqrt{\frac{1}{1 + (j\omega t_G)^\alpha}} \quad [2.9]$$

where R_G and t_G are the characteristic resistance and time, respectively, related to the chemical processes of oxygen surface exchange and bulk diffusion, given by the ALS model as^{37, 48}

$$R_G = \frac{RT}{4F^2} \sqrt{\frac{\tau}{4a(1 - \varepsilon)D_\delta k_\delta c_{mc}^2 \chi_v}} (pO_2)^{-0.25} \quad [2.10]$$

$$t_G = \frac{(1 - \varepsilon)\chi_v}{4aA_0 k_\delta} (pO_2)^{-0.5} \quad [2.11]$$

where τ is the tortuosity, ε is the porosity, and a is the pore-electrode interfacial area per volume. The oxygen concentration c_{mc} , oxygen vacancy fraction χ_v , and the thermodynamic factor A_0 for a number of MIEC materials at various temperatures have been reported in literatures.⁴⁸⁻⁵¹ k_δ and D_δ

are normalized oxygen surface exchange rate and solid-state oxygen bulk diffusion coefficient, respectively. They are related to the chemical coefficients (k_{chem} and D_{chem}), measured utilizing conductivity relaxation, and the tracer coefficients (k^* and D^*), measured by isotope exchange depth profiling (IEDP) coupled to secondary ion mass spectrometry (SIMS) by the following expressions:

$$D_{\delta} = \frac{D^*}{x_v} = \frac{D_{chem}}{A_0} \quad [2.12]$$

$$k_{\delta} = \frac{k^*}{x_v} = \frac{k_{chem}}{A_0} \quad [2.13]$$

The values of chemical and tracer coefficients have been measured by a number of research groups, although mostly done on thin film samples.^{50, 52, 53} Based on the ALS model, the impedance response of the MIEC cathodes can be estimated if the electrode microstructures and the kinetic coefficients are known. This, in turn, can be used to determine the kinetic parameters k and D with known electrode impedance and microstructures.^{48, 54}

2.4. Microstructure

The performance of a SOFC depends greatly on its microstructure. In composite electrodes such as Ni-YSZ anode and LSM-YSZ cathode, the electrochemical reactions occur at the TPBs where all three phases (pore phase, electronically conducting phase, and ionically conducting phase) are present. In addition, for a TPB to be active, the electronically conducting phase need to be connected to the external circuit; the ionically conducting phase need to be connected to the electrolyte; and the pore phase need to be percolated by the gas inlet. Figure 2.10 illustrates a

schematic diagram of microstructure and reaction sites in a SOFC with composite electrodes. As mentioned earlier in Section 2.1.3, some materials with mixed conductivity such as LSCF, SSC, and NNO have been extensively studied as cathode materials. The active reaction zone is the entire surface of the electrode material that can be accessible by the gas phase. The increased reaction sites typically allow improved performance and make them suitable for intermediate-temperature operations. An alternative approach to fabricate the SOFC electrodes is to make a scaffold, usually using the same material as the electrolyte, and infiltrate with a nitrate solution of the electrode materials.⁵⁵ This method allows formation of electrodes with nano-sized particles, and thus with increased TPBs. SOFCs with infiltrated electrodes are typically used for operation at intermediate temperatures, as coarsening will easily occur at elevated temperatures for the nano-sized particles.

Cell fabrication plays a key role on the microstructure. For a functional SOFC, the electrolyte need to be dense enough to prevent gas linkage, whereas the electrodes need to be porous, as needed to facilitate the electrode reactions. Factors such as starting powder particle sizes, ramping rates during sintering, and the sintering temperatures, etc. are critical to achieve the final desired structure. Additionally, additives such as pore former and sintering aid are usually used to provide desired porosity and shrinkage, respectively. The effects of fabrication conditions (e.g. sintering temperature, addition of pore former and sintering aid, etc.) on electrode microstructure and performance have been extensively studied for both anode and cathode.^{56, 57} Cell fabrication with utilization of Fe_2O_3 as a sintering aid for YSZ electrolyte will be discussed in this work.

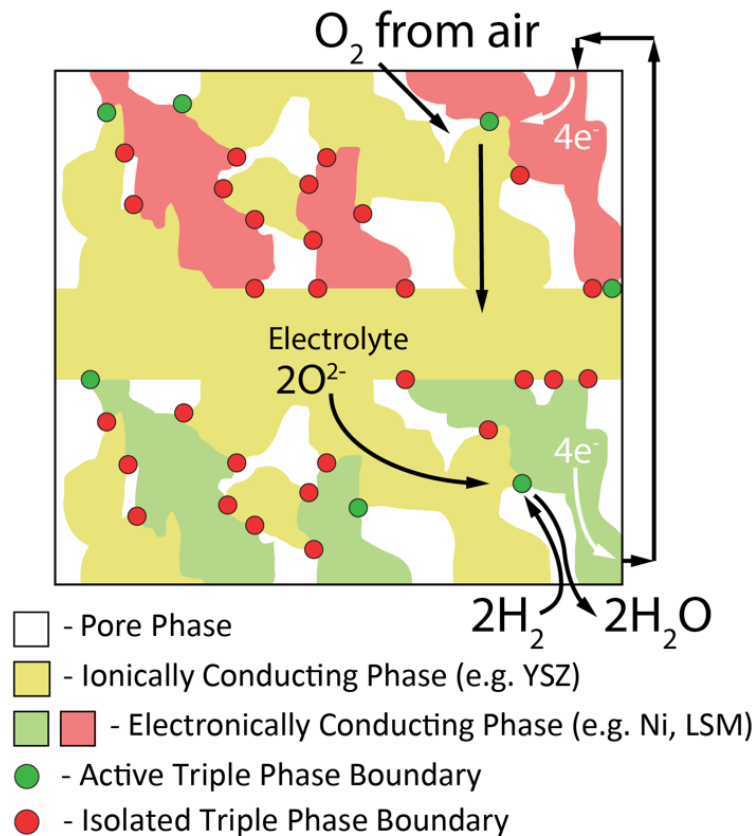


Figure 2.10. Schematic diagram of microstructure and reaction sites in a SOFC with composite electrodes. Active and isolated TPBs shown are defined in 2D.⁵⁸

2.5. Cell Degradation

Being energy devices working at high temperatures, non-uniform partial pressures and large current densities, SOFCs experience great challenges in long-term stability. The commercialization of SOFCs requires them to operate with $< 1\%$ degradation per 1,000 h for more than 40,000 h.¹⁴ Therefore, understanding the degradation mechanisms at operating conditions is important for improving the cell performance and durability. While many degradation mechanisms exist in different parts of SOFCs due to their complex structures, the degradation study in this work will only focus on cathodes, especially LSCF. LSCF cathodes

can be susceptible to degradation by mechanisms including reactions with YSZ electrolytes leading to formation of secondary phases, Cr poisoning from steel stack components, Sr surface segregation, and microstructural coarsening. Only the degradation mechanisms intrinsic to LSCF will be addressed in this work, i.e., particle coarsening and Sr surface segregation.

Particle coarsening is believed to be the most common degradation mechanism in SOFC electrodes as the operating temperatures are typically $> 60\%$ of the materials' melting temperatures, which leads to significant reduction in particle surface area, decrease in TPB density and loss of percolation. The coarsening of LSCF particles has been noted by Shah *et al.*⁵⁹ in the infiltrated LSCF cathodes during ageing at elevated temperatures, along with increased polarization resistance. It has been found that the polarization resistance versus time can be predicted reasonably well based on microstructural models. The microstructural change of LSCF under various conditions will be studied here by 3D FIB-SEM tomography.

In addition to particle coarsening, LSCF also exhibits Sr surface segregation, which depresses the surface activity and hinders the oxygen surface exchange process.^{9, 60-63} This is believed to be an important issue for the stability of advanced SOFCs utilizing LSCF cathodes, as well as other MIEC materials containing Sr. Unfortunately, the origin of Sr segregation is not well explained due to the chemical complexity of the cathode surface. A number of studies have been carried out to measure the Sr surface segregation either qualitatively or quantitatively. However, most of them were made on dense thin films, utilizing techniques such as X-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS).⁶⁴⁻⁶⁷ Recently Rupp *et al.*⁶⁸ reported a novel

technique utilizing chemical etching with on-line inductively coupled plasma optical emission spectrometry (ICP-OES) detection to successfully quantify the Sr-rich surface species on the dense $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) thin films. However, little research has been done on the measurement of Sr segregation for porous SOFC electrodes. The development of technique for measuring Sr surface segregation on porous LSCF will be discussed in this work.

Chapter 3

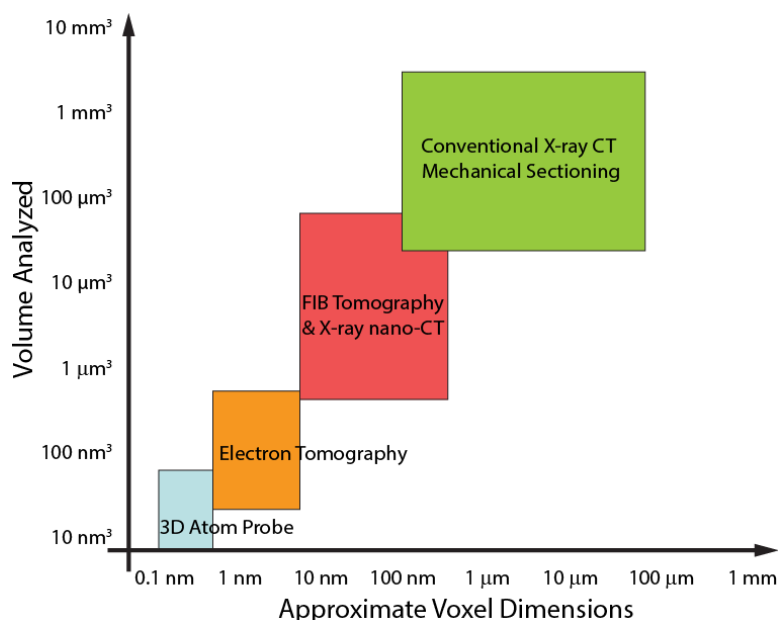
Three Dimensional Tomography

Figure 3.1. Capabilities of several 3D tomographic characterization methods.⁶⁹

The importance of electrode microstructure and its influence on cell performance have been introduced in the previous chapter. Many characterization methodologies have been used to analyze the microstructural features, such as scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), energy dispersive spectroscopy (EDS), and scanning probe microscopy and its derivatives such as atomic force microscopy. However, all of them only provide near-surface information, i.e., 2D analysis. To achieve truly quantitative materials characterization, methodologies providing 3D information are required. Specifically for SOFC, 3D characterization enables the measurement of a number of important geometric properties that cannot be obtained using 2D analysis, such as phase connectivity and tortuosity. Several 3D

tomographic techniques have been developed that are suitable for different applications and size scales, shown in Figure 3.1. Focused ion beam (FIB)-SEM and transmission X-ray microscopy (TXM) techniques are most practical for SOFCs, considering their feature sizes. FIB-SEM will be used for microstructural analysis in this work.

3.1. FIB-SEM 3D Technique

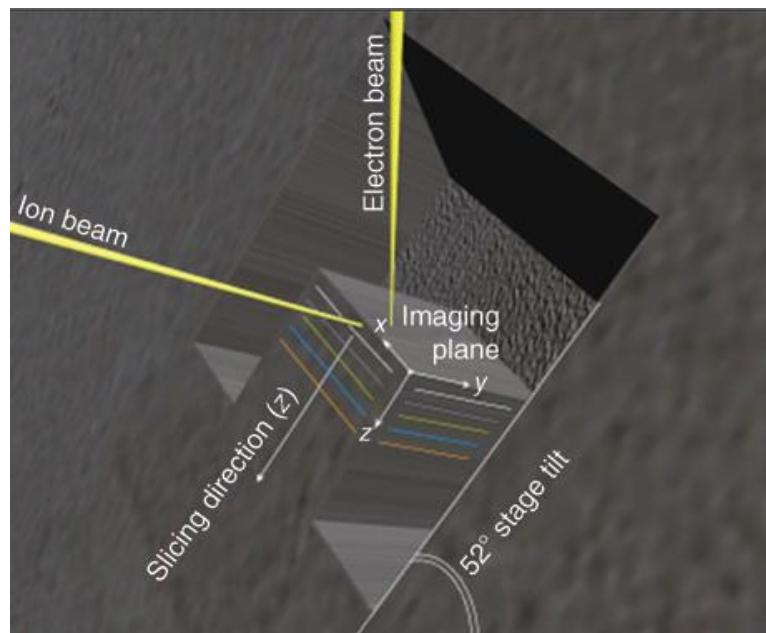


Figure 3.2. Schematic illustration showing the geometry of a FIB-SEM.⁷⁰

FIB-SEM is a dual beam instrument, where the focused ion beam, typically a source of gallium ions, is used to mill the specimen, exposing a surface that can be imaged by SEM. The two beams are usually separated by an angle as shown in Figure 3.2, in order to mill and image of the same region. By carefully controlling the energy and intensity of the ion beam, it is possible to perform nano-machining with resolutions as high as ~ 5 nm. FIB-SEM is commonly used to do

lift-out for TEM sample preparation. In situ milling and imaging also allow for tomographic data collection.

When collecting tomographic data using FIB-SEM, the FIB is used to mill thin slices of the specimen with defined thickness, usually 10 to 50 nm, and the SEM takes image of the exposed cross-sectional surface between each slicing. The process is sometimes called FIB-SEM serial sectioning. The pixel size of each image is defined by the resolution of the SEM, while the pixel size in the milling direction is the distance between each slicing. The collected images can be ordered sequentially and virtually reconstructed using 3D software such as Amira. FIB-SEM serial sectioning is a powerful 3D tomographic technique. However, it also has some downsides. First, it is a destructive technique where the same region cannot be imaged twice. Second, it is a time consuming technique that limits the reconstructed volume. Another common issue is the curtaining effect created from variation in the beam energy, usually resulted from uneven top surface.

3.2. Sample Preparation

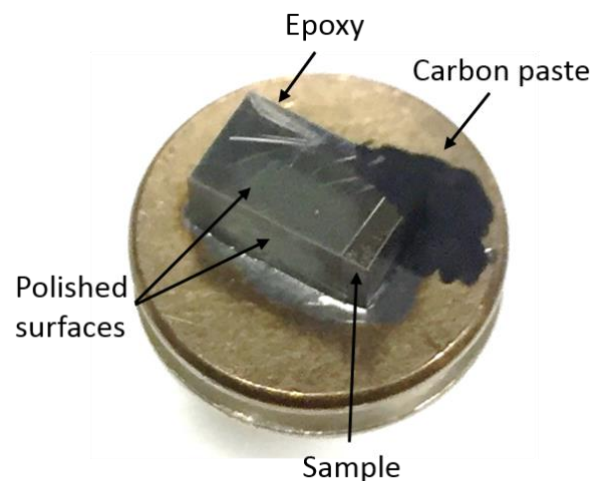


Figure 3.3. Sample mounting geometry for FIB-SEM serial sectioning.

To prepare the sample for FIB-SEM serial sectioning, the specimen is first vacuum infiltrated with low-viscosity epoxy. This allows imaging of the top-most exposed surface between ion milling steps, as the pores in the electrodes are filled with epoxy to prevent imaging the materials lie behind the surface of interest. Additionally, the epoxy has little interaction with the electron beam, providing contrast from the electrode and electrolyte materials. After infiltration, the sample is cut and polished before glued to a SEM stub. Polishing is a critical step in the sample preparation, especially the top surface. A flat and smooth top surface will significantly reduce the curtaining issue during FIB-SEM imaging. To prevent charging, a graphite colloidal suspension or a graphite tape is usually applied to connect the sample (near the region to be imaged) to the stub. And finally, ~ 30 nm of osmium is coated to the sample to enhance the electronic connection between the sample and the SEM stub.

3.3. Image Processing

Imaging data collected by FIB-SEM almost always has artifacts and characteristics that need to be correctly adjusted and segmented in order to conduct proper 3D reconstruction and calculations.

3.3.1. Alignment

The first step in image processing of data collected on FIB-SEM is alignment. Since there is an angle between the SEM beam and the imaged surface, the region of interest will shift upwards as milling proceeds. Although this shift can be slightly compensated for using the automatic electron beam shift function incorporated in the instrument, small variations between each image still exist. Manual beam shift by the operator, as well as minor changes during the data collection

such as chamber temperature, sample drift and charging, will also cause image shifts. The image alignment can be done using IMOD software.^{71, 72} An initial alignment is done manually using the Midas alignment Graphical User Interface (GUI), followed by automated minor alignment. The automated alignment is repeated until the images are adequately aligned.

3.3.2. Lighting correction

Lighting correction is sometimes needed to improve the brightness and contrast of the images. This can be simply done using ImageJ, either for each image individually or for the entire data set. The latter is preferable since the data set usually contains hundreds of images.

In addition to normal brightness and contrast adjustments, the images collected by FIB-SEM may encounter shadowing effect. As milling proceeds, a trench is slowly created into the sample. The milled materials are easily redeposited on the trench wall, shielding the electron beam and leading to certain regions on the image (usually on the left or right) appear to be darker. This artifacts created by shadowing effect can be corrected using a method developed by Dr. Scott Cronin.⁷³ The grayscale variation in an image is analyzed and fit with a polynomial equation to normalize the grayscale intensities. This method can be applied both horizontally and vertically.

3.3.3. Segmentation

The calculation of microstructural parameters requires each phase to contain only one grayscale value. Therefore, the images containing continuous grayscale values need to be segmented. It is a critical step in the image processing that directly related to the calculation accuracy. The simplest method, which is used in this work, is thresholding. It works by assigning

a single grayscale value to pixels with a defined threshold range so that each phase is represented by a unique grayscale value. For example, in a Ni-YSZ three-phase system, Ni phase will have grayscale value = 255 (appear as white), YSZ will have grayscale value = 127 (appear as gray), and pore phase will have grayscale value = 0 (appear as black). This method works well when the histogram has well defined peaks for each phase as in Figure 3.4, which can be achieved for most of the common SOFC electrodes, with proper imaging conditions used during data collection. To determine the best threshold value, several methods have been developed, such as using the minima between two peaks, or using midpoint between two peaks, etc. The ImageJ software has a number of thresholding methods built in. The image segmentation in this work was performed via the multi-level Otsu's method using ImageJ. It involves iterating through all the possible threshold values and calculating a measure of spread for the pixel levels on each side of the threshold, and to find the threshold value where the sum of both spreads is at its minimum.⁷⁴

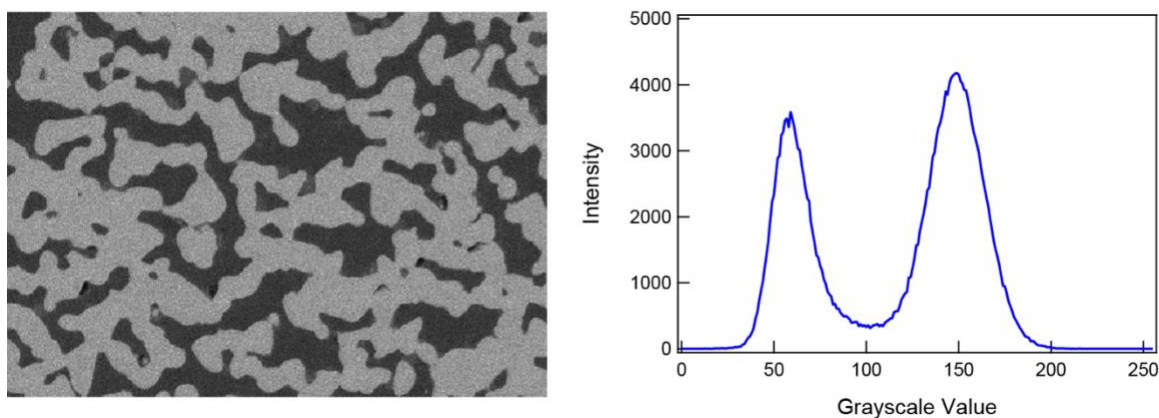


Figure 3.4. SEM image of the FIB-milled surface and its histogram.

It is important to note that thresholding is insensitive to edges and features of the micrographs besides the pixel intensity, so it is possible to have a single pixel of one phase surrounded by pixels of another phase. This is not physically possible in the SOFC system and

should be counted as artifacts. Methods such as “dust and scratch” developed by Dr. Scott Cronin,⁷³ and “remove outliers” function built in ImageJ can be used to eliminate some nonphysical pixel features.

3.4. Calculation of Microstructural Parameters

3.4.1. Phase volume fraction

The phase volume fraction is calculated by counting the number of voxels of a given phase and normalizing it to the total number of voxels (Eq. [3.1]).

$$\text{Volume fraction of given phase} = \frac{\sum \text{Voxels of given phase}}{\sum \text{Total number of voxels}} \quad [3.1]$$

3.4.2. Phase connectivity

Phase connectivity is a geometric property that cannot be determined with 2D analysis. The calculation is done by first creating a 3D mesh of the given phase, and then a connected component labeling algorithm (function “bwlabeln” in Matlab) is running through the reconstruction volume. A percolated region is defined when a phase is connected to any face of the reconstruction volume. When a phase is not connected to any other region of the same phase or any face of the reconstruction volume, it is considered to be isolated. For SOFC application, a more sophisticated method, called directional connectivity, has been used. This method requires some knowledge of the reconstruction volume related to the overall sample geometry, e.g., the face which is at the electrode/electrolyte interface. The ionically conducting phase is only considered as percolated when it is connected to the electrolyte. The electronically conducting

phase and the pore phase need to be connected to the current collector and gas flow channel, respectively, usually the same side. In this approach, there will be another phase region that can be neither defined as percolated or isolated. These regions are not percolated in the current reconstruction volume, but may be percolated outside the reconstruction volume, and therefore are defined as unknown.

3.4.3. Surface area

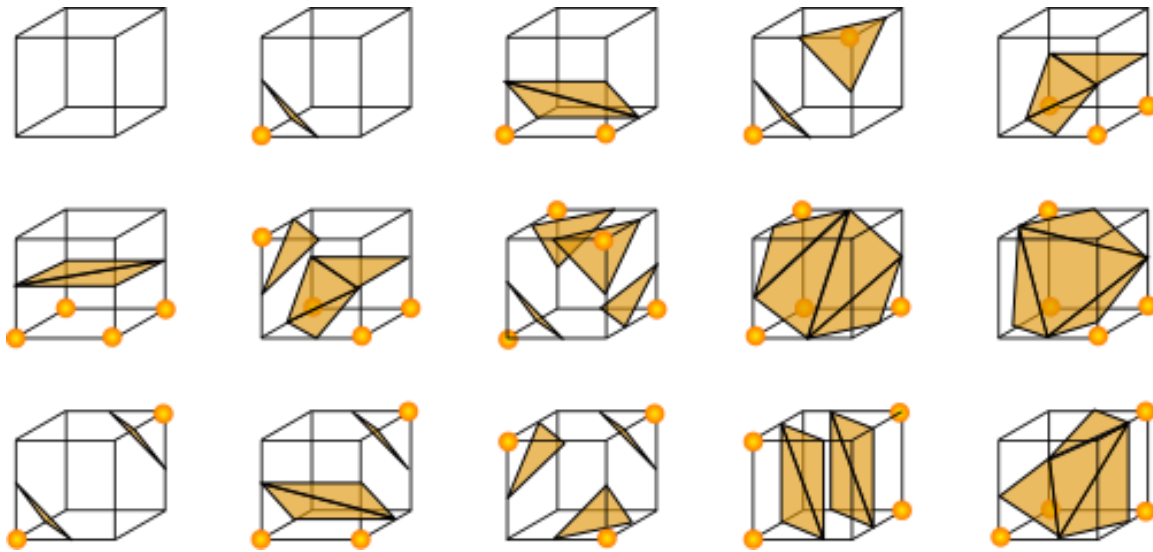


Figure 3.5. The 15 cube configurations from the marching cube algorithm.⁷⁵

Surface area is an important microstructural parameter for SOFC electrodes. In the single-phase MIEC cathodes, it is directly related to the electrochemical performance, as it is the reaction site for the ORR. Even for the two-phase composite electrodes, the surface area is related to the particle size, and can be used to track the particle coarsening. To calculate the surface area from the FIB-SEM data, a marching cube algorithm is used to create 3D surface mesh.⁷⁵ The algorithm works by constructing cubes where the vertices are assigned to values of the voxel centers. Then

the polygons needed to represent the part of the isosurface that passes through a cube can be determined. Each polygon has a defined surface area that can be easily calculated. Figure 3.5 illustrates the 15 possible configurations of surfaces for neighbors (cube vertices) from the marching cube algorithm. The polygons, however, overestimate the surface area. An iterative smoothing function has been developed to eliminate the overestimation, making use of a spring constant to allow the vertices to relax.⁷⁶

3.4.4. TPB density

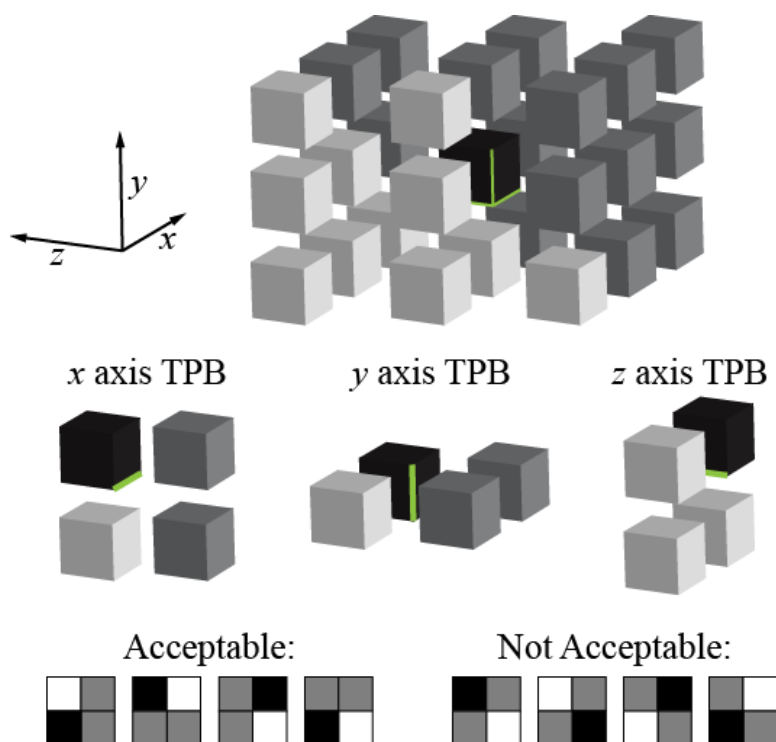


Figure 3.6. Schematic of the TPB calculation algorithm.⁷³

In two-phase composite electrodes, TPBs are where the electrochemical reactions take place, and thus directly related to the electrode resistance. It is computed by examining each voxel and determining if any side qualifies as a TPB. As shown in Figure 3.6, only three edges shared

by one vertex of a voxel are considered in order to avoid double counting. Each edge is shared by four voxels. If three are different with the similar voxels sharing a face, it is considered as a TPB. The TPB length is calculated by summing all the qualified voxel edge length. Normalizing it to the total reconstruction volume yields the TPB density.

This method overestimates the actual TPB length, as in reality, the TPBs are continuous and smooth. Several methods have been developed to correct this error. Figure 3.7 shows smoother TPBs approximated by using midpoint or centroid of the TPB segments.⁷⁷ Another approach is to apply a correction factor. A value of 1.455 was calculated by Dr. James Wilson.⁷⁶

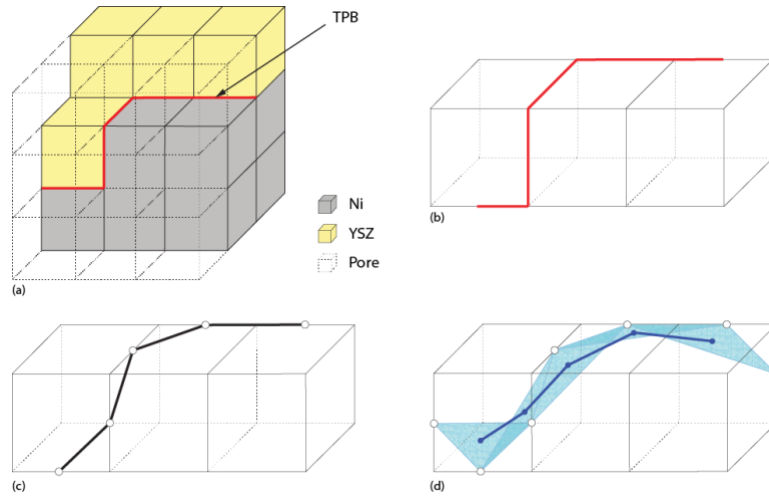


Figure 3.7. TPB length calculation methods. (a) One of the possible voxel arrangements, (b) edge segment length, (c) midpoint length, and (d) centroid length.⁷⁷

3.4.5. Particle size distribution

Particle size is difficult to define for non-discrete particles, as is the case for SOFC electrodes. A method developed by Holzer, *et al.*⁷⁸ has been used to calculate particle size distribution (PSD) in this work. Inspired by mercury intrusion porosimetry, the continuous phase

was fitted with spheres of varying radius and the volume being occupied are measured to give a cumulative PSD. A 2D schematic of the calculation algorithm is shown in Figure 3.8, but the calculation is done in 3D. An Euclidean distance of the given phase is created. The most inner point defines the largest circle that can fit within the particle, and the area covered by this circle is recorded. Next, when moving outward to a new Euclidean distance line, the largest circle that can fit within the particle is smaller, but it occupies more area of the particle. The process is repeated until the particle is fully covered. The recorded area and radius of the fitting circles are then plotted, giving the cumulative PSD, also shown in Figure 3.8. A conventional PSD can be obtained by taking the derivative of this curve.

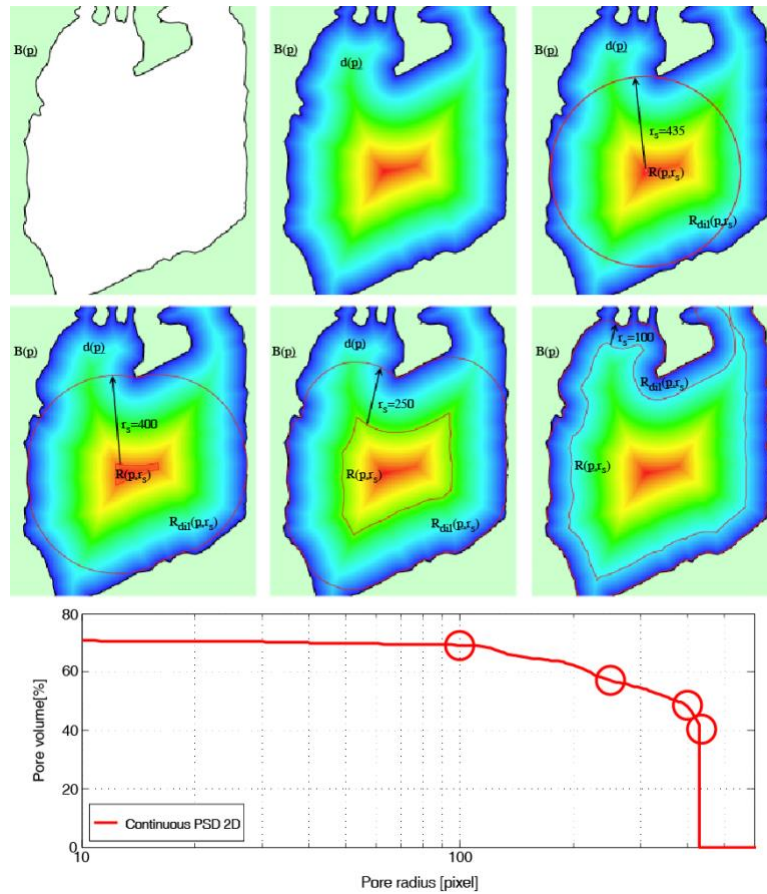


Figure 3.8. Schematic of the “continuous particle size distribution” algorithm.⁷⁸

3.4.6. Phase tortuosity

Phase tortuosity is an important parameter for characterizing transport properties. It is defined as the ratio between the actual tortuous path length of a given phase to the straight-through path length. In SOFC electrodes, tortuosity of the pore phase is related to the gas diffusion through the pores; tortuosity of the ionically conducting phase is related to the ionic diffusion of oxygen ions from the reaction sites to the electrolyte, or vice versa. Electron transport is orders of magnitude larger than gas and ionic transports, and hence is often ignored. Tortuosity can be calculated in several ways.⁷⁹⁻⁸¹ The method used in this work is a geometrical calculation where the path length is computed by distance propagation.⁸² The algorithm starts by labeling the phase of interest located in the starting plane with distance of unity. The neighboring voxels of the phase of interest are then labeled with their effective distance. Different ways to define the neighboring distance are shown in Figure 3.9. The procedure is repeated directionally through the phase network until all the voxels are labeled with a distance. The resulting distance curve can be interpreted using four different methods, shown in Figure 3.10.

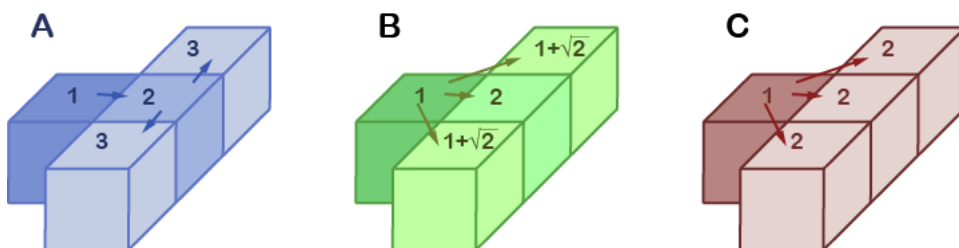


Figure 3.9. Three ways to define the neighboring distance: (A) city-block, (B) quasi-Euclidean and (C) chess-board.⁸²

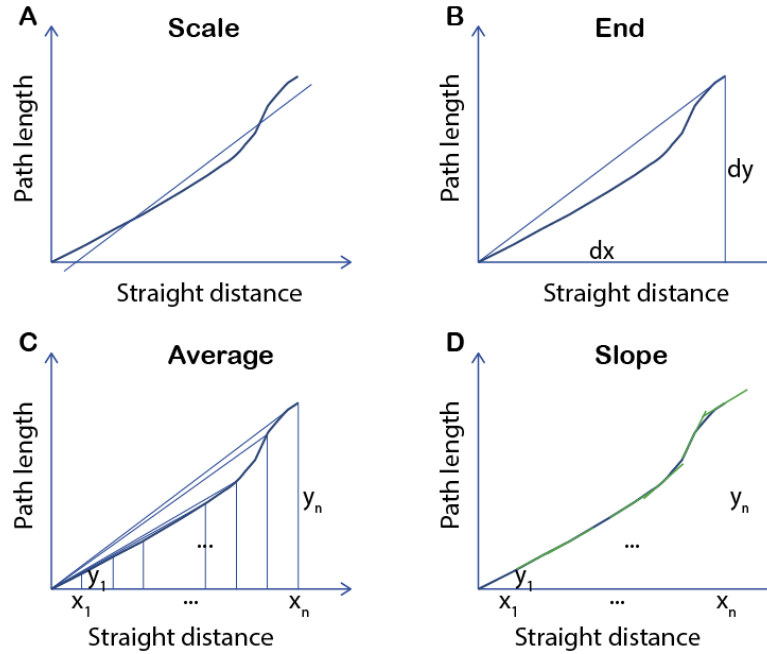


Figure 3.10. Four different methods to extract the tortuosity from the distance curve. (A) Scale: the curve is fitted with a linear regression, tortuosity is the slope. (B) End: tortuosity is the average path length at the end plane divided by the straight distance. (C) Average: tortuosity is the average tortuosity from each plane. (D) Slope: tortuosity is extracted by average of all local slopes.⁸²

3.5. Statistical Requirements and Error Analysis

Several requirements must be met to get statistically reliable microstructural results. First, voxel resolution must be high enough to resolve small features, including not only particles but also particle surface roughness and texture, in the reconstruction volume. It also needs to be sufficiently small to avoid voxelized geometric effects. Generally, the voxel size needs to be 10 – 15 times smaller than the smallest particle of interest.

In contrary to voxel size, the reconstruction volume must be large enough to be representative. A study by Dr. Scott Cronin has found that the reconstruction volume needs to be 16 times larger than the largest particle in the electrode, in order to limit the error < 3% for TPB

density.⁷³ This works counter to the voxel size requirement, as the images are usually collected with pixels of 1024×768 . That is saying, the larger reconstruction volume is compensated by lower resolution. Therefore, samples with a wide range of feature sizes, e.g. infiltrated scaffold where the scaffold is on the order of microns whereas the infiltrated particles are on the order of tens of nanometers, are difficult to image. To calculate the error induced by volume representativeness, the reconstruction volume is usually divided into sub-volumes and the convergence is analyzed.

There are also errors related to segmentation. Considering the thresholding method used in this work, segmentation is strongly dependent on the grayscale contrast of the images. Although there are many image processing methods that can be used to correct artifacts, it is important to realize that the better quality of the starting imaging data, the smaller the segmentation errors will be, and the easier it is to be confident in the representativeness of the final reconstruction. With both voxel resolution and reconstruction volume requirements being met, it is generally accepted that the 3D tomographic technique utilizing FIB-SEM has an error level of $\sim 5\%$ in analyzing SOFC electrodes.

Chapter 4

Anode-supported Solid Oxide Fuel Cells Fabricated by Single Step Reduced-Temperature Co-Firing

4.1. Introduction

Anode-supported solid oxide fuel cells (SOFCs) with $\text{Y}_{0.16}\text{Zr}_{0.92}\text{O}_{2-\delta}$ (YSZ) electrolytes are usually fabricated using at least two high-temperature firing steps: co-firing of the anode and electrolyte followed by application and firing of the cathode.^{83, 84} This is based primarily on differences in desired firing temperatures – the YSZ electrolyte is densified at $\sim 1400^\circ\text{C}$ – whereas cathode materials, typically based on $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$ (LSM), are usually fired at $\lesssim 1200^\circ\text{C}$. Also, the two-step process reduces possible reactions between cathode and electrolyte during firing. On the other hand, there are a number of reasons why single-step fired SOFCs are desirable. First, it simplifies the process, reducing the processing time and input energy, important given the general need to reduce SOFC cost in order to improve commercial viability.⁸⁵⁻⁸⁹ Second, single-step firing is a requirement for fabrication strategies where the entire stack, including cells, gas channels and interconnectors, are fired together.⁹⁰ Third, it allows the fabrication of cells with a cathode-side mechanical support instead of an anode support.

In order to achieve single-step firing, the temperature should be reduced to allow a good cathode microstructure, while still densifying the YSZ electrolyte. YSZ electrolyte densification as low as 1200°C has been demonstrated when utilizing an appropriate sintering aid, e.g. Fe_2O_3 .^{91,}

⁹² Recently, anode-supported SOFCs with YSZ/GDC bi-layer electrolytes have been produced by

co-firing with Fe_2O_3 sintering aid at 1250 °C, but with the cathode added in a second lower-temperature firing step.^{57, 93, 94} These temperatures are still above the ideal firing temperature for LSM-YSZ cathodes of ~ 1175 °C.⁹⁵ Also, the shrinkage that occurs during single-step co-firing will exacerbate cathode densification, further reducing ideal cathode firing temperature. In the prior reports on single-step firing,^{96, 97} anode-supported SOFCs were fired at 1300-1330 °C, and a $(\text{La}_{0.85}\text{Ca}_{0.15})_{0.97}\text{MnO}_3$ (LCM) cathode that is more refractory than LSM was used to avoid over-sintering and coarsening. Even so, reducing the co-firing temperature from 1330 to 1300 °C resulted in a decrease in cathode particle size from ~3.13 to ~2.32 μm , improving cell performance. Lower co-firing temperatures are desirable to reduce cathode sintering and coarsening, and to allow different cathode compositions.

In this chapter, fabrication of NiO-YSZ support|NiO-YSZ AFL|YSZ|LSM-YSZ|LSM SOFC by single-step firing at 1250 °C with a Fe_2O_3 sintering aid is described. The cells are characterized using SEM/EDS and FIB-SEM, current-voltage measurements, and impedance spectroscopy. Porous electrodes and dense electrolyte are obtained without significant element interdiffusion, and good cell performance is demonstrated.

4.2. Experimental Procedures

4.2.1. Cell fabrication

The cells consist of NiO-YSZ anode support, NiO-YSZ anode functional layer (AFL), YSZ electrolyte, LSM-YSZ cathode functional layer and LSM current collector. Figure 4.1a illustrates the schematic flow diagram for fabrication of the cells by tape casting and single-step firing. The anode supports were prepared by mixing NiO and YSZ with 1:1 weight ratio, along with Tapioca

starch (10 wt.%) as pore former, xylene and ethanol as solvent, and fish oil as dispersant. 3 mol.% Fe_2O_3 was used as sintering aid to ensure shrinkage matching with other layers during sintering. The above materials were ball milled for 24 h, followed by addition of appropriate binders and plasticizers, and a second ball milling was conducted for 24h. The AFL slurry consisting of NiO and YSZ with 1:1 weight ratio and YSZ slurry with 3 mol.% Fe_2O_3 as sintering aid were prepared using the same dispersant, solvent, binders and plasticizers. The LSM-YSZ with 1:1 weight ratio cathode functional layer slurry and the LSM cathode current collector slurry were prepared in the same way, using graphite (30 wt.%) with an average particle size of 2.2 μm as pore former. The resulting anode, electrolyte and cathode slurries were cast on the polyethylene terephthalate (PET) carrier film by tape casting at room temperature. The final structure was fabricated by laminating NiO-YSZ anode support, NiO-YSZ AFL, YSZ, LSM-YSZ, and LSM tapes at 80 °C for 30 min under a pressure of 5000 psi, with a thick graphite layer on top of the cathode to protect the cell from being damaged during lamination.⁹⁸ The laminated cells were then punched into pellets with 19 mm diameter and sintered at 1250 °C for either 4h (denoted single-step 4h) or 2h (single-step 2h).

To investigate the effect of cathode co-sintering on microstructure and electrochemical performance, a cell with a separately fired cathode was also prepared. As shown in Figure 4.1b, the NiO-YSZ anode support, NiO-YSZ AFL and YSZ electrolyte with 3 mol.% Fe_2O_3 were fabricated using the same method as the single-step co-fired cells, except that the support/AFL/YSZ structure was fired without the cathode for 4h at 1250 °C. LSM-YSZ (1:1 weight ratio) cathode functional layer ink was then screen printed on the electrolyte surface and fired at 1175 °C for 1h. Finally, a pure LSM current collector ink was screen printed and fired at

1150 °C for 1h. Note that no pore former was used in the cathode layers, unlike the single-step fired cathodes.

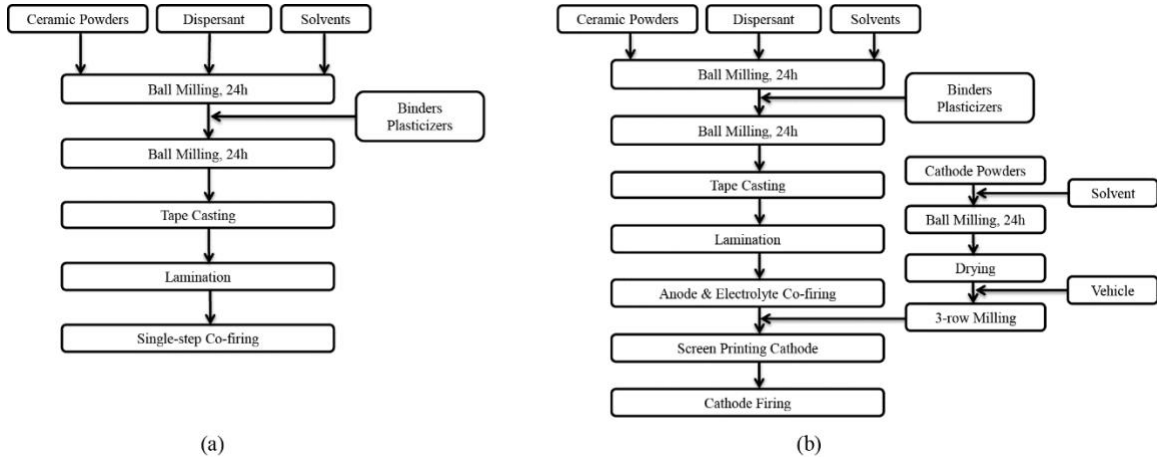


Figure 4.1. Schematic flow diagram for fabrication of anode-supported SOFCs by single-step co-firing (a) and with separate cathode firing (b). In (a), all the steps through Tape Casting were repeated for each of the five different cell component materials, which were then laminated and fired together. In (b), the anode and electrolyte materials were processed separately through the Tape Casting step, while the cathode functional layer and current collector inks were prepared, printed, and fired separately.

4.2.2. Electrochemical characterization

Cell current-voltage testing was carried out from 700-800 °C in humidified hydrogen (3 vol.% H₂O) fuel with flow rate of 100 sccm, and air oxidant at a flow rate of 200 sccm. EIS measurements were performed using a Zahner IM6 electrochemical workstation with the cells at open circuit voltage (OCV) in the frequency range from 100 mHz – 100 kHz. H₂-H₂O-Ar mixtures with various H₂ partial pressures (pH₂) and O₂-Ar with various O₂ partial pressures (pO₂) were used in the EIS measurements. The resulting spectra were modeled using an equivalent circuit, consisting of an inductor L, ohmic resistor R₀, and three resistor-constant phase element (R-QPE) units in series: LR₀(RQ)(RQ)(RQ) with $Z_{QPE} = (i\omega Q)^{-n}$. Figure 4.2 shows a typical data fit, for

example, to the EIS data taken at 800 °C for the single-step 4h cell. Other cells exhibited similar fitting quality.

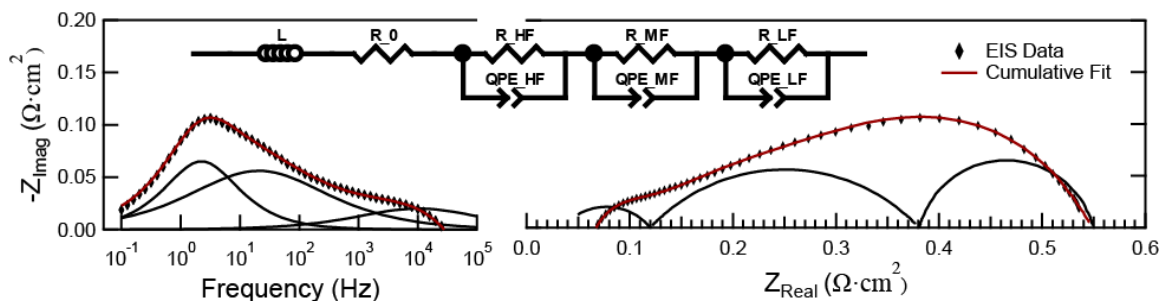


Figure 4.2. Equivalent circuit fitting of EIS data for single-step 4h cell tested at 800 °C using humidified H₂ as fuel and lab air as oxidant. The three main responses are shown separately, along with the overall fit. Note that the inductance, which arises primarily from the measurement circuit and affects the spectrum at the high frequency, is not shown separately, but is included in the cumulative fit.

4.2.3. Microstructural characterization

After testing, the cell microstructure and elemental diffusion were examined with SEM and EDS. The cell cathodes were also prepared for 2D cross-sectional imaging by epoxy infiltration and mechanical polishing.^{56, 99} The imaging was done in a FEI Helios FIB-SEM after a final FIB polishing of the cross section. The secondary electron (SE) detector with accelerating voltage of 2 kV was used for imaging because it provided the best contrast between LSM and YSZ.

4.3. Results & Discussion

4.3.1. Microstructural and chemical characterization

Figure 4.3 shows fracture cross-sectional SEM images providing an overview of (a) the separately fired and (b) the single-step 2h cells. Only 2h-firing cell is shown here since the 4h-

firing cell has similar structure. The thicknesses of the LSM current collector, LSM-YSZ cathode, YSZ electrolyte and NiO-YSZ anode functional layer are $\sim 20\ \mu\text{m}$, $\sim 20\ \mu\text{m}$, $\sim 10\ \mu\text{m}$ and $\sim 20\ \mu\text{m}$, respectively, for both cells. The SEM images show that both the cathode and anode functional layer are porous, as needed to facilitate the electrode reactions. Large pores are evident in the anode support resulting from the starch pore former. A porosity of $\sim 20\%$ develops in the anode functional layer, even without the use of pore formers, via the reduction of NiO to Ni upon exposure to fuel.¹⁰⁰ The YSZ electrolyte shows slightly larger porosity than in the traditional 1400°C -fired cell,⁹³ but with a low enough volume fraction that they are presumably isolated pores. The single-step-fired cathode showed a coarser microstructure, presumably due to the higher firing temperature.⁵⁶ The porosity evident the separately fired cathodes resulted from incomplete sintering, whereas the porosity in the single-step co-fired cathodes resulted mainly from the addition of 30 wt.% graphite pore former. Note that attempts to make single-step-fired cathode without pore formers resulted in too-high density.

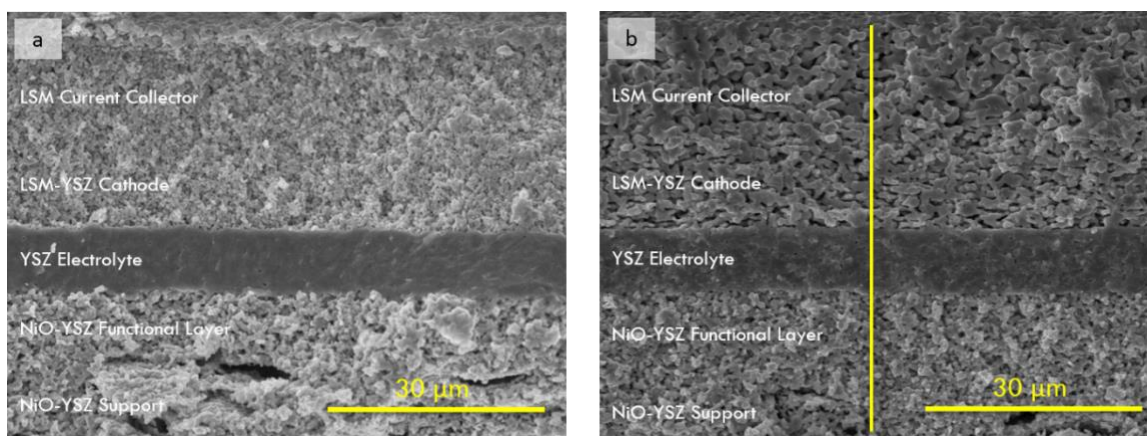


Figure 4.3. Fracture cross-sectional SEM images of the separately fired (a) and single-step 2h (b) cells, taken after electrochemical testing.

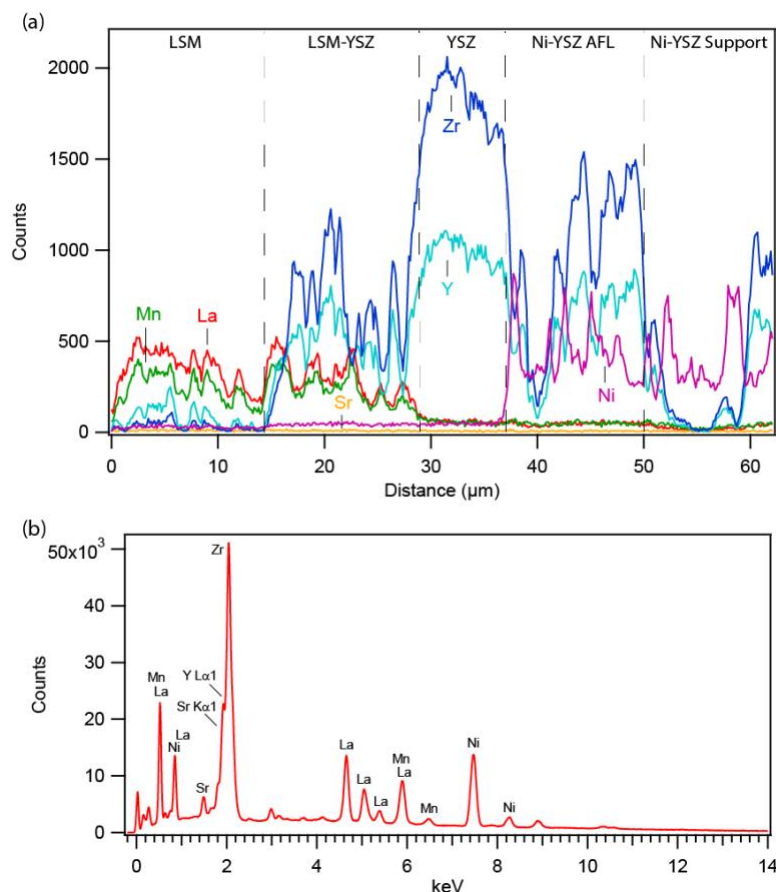


Figure 4.4. (a) EDS intensity line scans, taken along the line shown in Figure 4.3b, showing the spatial variation of the Y, Zr, Ni, La, Sr and Mn peak signals in the single-step 2h cell. (b) An EDS sum spectrum, indicating the peak energies used for each element in the line scan.

Figure 4.4a shows an example EDS line scan, taken along the yellow line in Figure 4.3b. In general, the LSM, LSM-YSZ, YSZ, and NiO-YSZ layers retain clear sharp interfaces on the scale resolvable by SEM-EDS ($\sim 1 \mu\text{m}$); thus, there is no detectable elemental interdiffusion during the co-firing process. Although there appeared to be a small amount of Y in the LSM current collector, this was an artifact due to an overlap between the Y La1 (1.923 keV) and Sr K α 1 (1.807 keV) peaks, as shown in the EDS spectrum in Figure 4.4b. Unfortunately, this peak overlap makes it difficult to determine if there is any formation of strontium zirconate at the LSM-YSZ interface.

There is no increase of the La signal at the cathode/electrolyte interface that might indicate lanthanum zirconate formation.

In order to clarify how the single-step firing process affected the cathodes in these cells, microstructural analysis was done using SEM imaging of FIB-polished cross sections. In addition, the cathode pore space was filled with epoxy, providing clear contrast between pores and solid phase. Furthermore, imaging conditions were used that provided reasonable contrast between the LSM and YSZ phases. Figure 4.5 shows the FIB-SEM images for single-step-fired (2h and 4h firing time) and separately fired cathodes. While the single-step-fired cathode structures appear similar, the separately fired cathode shows a much smaller feature size. Stereological analyses of the 2D images, shown in Table 4.1, were used to quantify these microstructural differences. The ratio of the LSM and YSZ volume fractions are within measurement error of the expected volume ratio of 0.91:1 LSM:YSZ. The pore volume fraction decreased from 36.5% to 27.6% upon increasing the firing time from 2 to 4 h, indicating increased cathode sintering. The measured specific surface areas of the three phases, along with measured TPB densities, are also displayed in Table 4.1. Increasing the firing time slightly decreased the specific surface areas and the total TPB density, indicating an increase in the average particle sizes via increased particle coarsening. The separately fired cathode had a substantially higher surface area and total TPB density than the co-fired cathodes; although the porosity was similar to the single-step-fired cathodes, this indicates reduced sintering because no pore former was used in this case. These differences can presumably be explained by the lower firing temperature and time, as well as the constraint of a non-shrinking electrolyte/anode support in the separately fired cathode case.

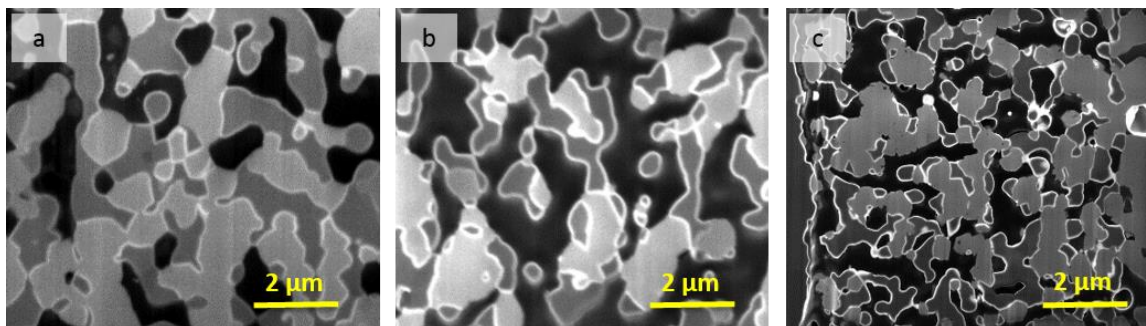


Figure 4.5. 2D cross-sectional SEM images for single-step 4h (a), single-step 2h (b) and separately fired (c) cells. The samples were epoxy infiltrated, polished and ion-milled to achieve good contrast between LSM (light gray), YSZ (dark gray) and pore (black).

Table 4.1. Values calculated from the 2D cross-sectional images of different cells.

Microstructural Parameter	Single-step 4h	Single-step 2h	Separately fired
LSM Vol.%	36.4	31.1	33.5
YSZ Vol.%	36.0	32.4	35.6
Pore Vol.%	27.6	36.5	30.8
LSM Specific Surface Area (μm^{-1})	1.70	1.88	3.02
YSZ Specific Surface Area (μm^{-1})	2.17	2.37	3.46
Pore Specific Surface Area (μm^{-1})	1.90	1.70	3.16
Total TPB Density (μm^{-2})	1.33	1.64	4.05

4.3.2. Electrochemical characterization

Figure 4.6 compares the voltage-current characteristics for the different cells, measured at 800 °C. A number of cells were tested for each fabrication method. Data shown are from the best-performing cell of each method. The separately fired cell yields a maximum power density of 1.08 W/cm² at 800 °C, higher than those of the single-step co-fired cells – 0.85 and 0.91 W/cm² for 4h- and 2h-firing cells, respectively. Similar trends were observed in measurements at lower cell operating temperatures (summarized in Table 4.2). The OCV values of the single-step-fired cells are ~ 1.055 V at 800 °C in 97%H₂-3%H₂O and air. For comparison, anode-supported cells with

pure dense YSZ electrolytes (sintered at 1400 °C) and tested in this same setup yielded about the same OCV.¹⁰¹ This suggests that there was little effect of any additional porosity in the present cells, and that any electronic conductivity caused by Fe₂O₃ is negligible. Note that these OCV values are slightly lower than the calculated Nernst potential of 1.10 V for the present fuel and oxidant compositions; this has been explained by the Ag seals used in the test setup, which appears to slight leakage.¹⁰¹ The separately fired cell has slightly lower OCV in Figure 4.6, probably due to worse leakage at the Ag seal.

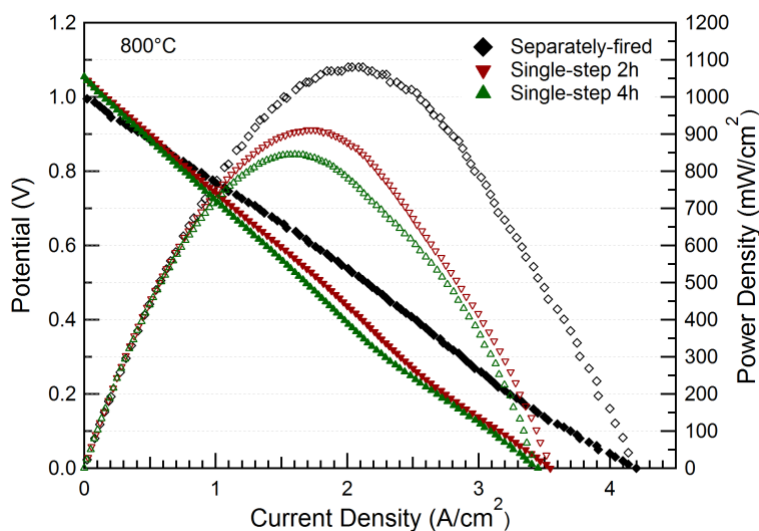


Figure 4.6. Voltage and power density versus current density for different cells operating at 800 °C.

Table 4.2. OCV and $P_{\max}$ of different cells operating at different temperatures.

	Single-step 4h		Single-step 2h		Separately fired	
	OCV (V)	$P_{\max}$ (W/cm ²)	OCV (V)	$P_{\max}$ (W/cm ²)	OCV (V)	$P_{\max}$ (W/cm ²)
800°C	1.054	0.85	1.055	0.91	0.995	1.08
750°C	1.062	0.44	1.068	0.49	1.020	0.82
700°C	1.071	0.26	1.077	0.29	1.030	0.56

Figure 4.7 presents Bode and Nyquist plots of the EIS data from the cells shown in Figure 4.6. The ohmic resistances are 0.06-0.07 $\Omega\cdot\text{cm}^2$ for all cells, as expected for a $\sim 10\ \mu\text{m}$ thick YSZ electrolyte at this temperature, indicating no measurable decrease in the ionic conductivity of YSZ due to Fe-doping. The slightly lower ohmic resistance of the separately fired cell is presumably a result of cell-to-cell variations, e.g. a slightly thinner electrolyte. The total area specific resistance values for single-step 4h, single-step 2h and separately fired cells are 0.51 $\Omega\cdot\text{cm}^2$, 0.44 $\Omega\cdot\text{cm}^2$ and 0.20 $\Omega\cdot\text{cm}^2$, respectively, in good agreement with the trend in power density shown in Figure 4.6.

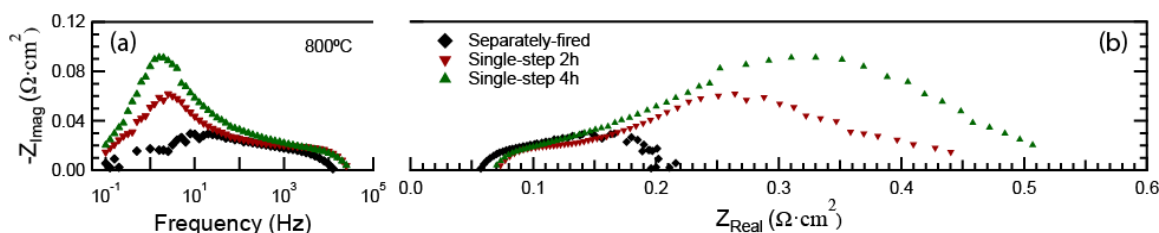


Figure 4.7. Bode (a) and Nyquist (b) plots of EIS data from different cells measured at 800 °C at OCV.

The equivalent circuit fits shown in Figure 4.2, for the single-step 4h fired cell, showed three main electrode responses: a dominant low-frequency (LF) response centered at $\sim 3\ \text{Hz}$, along with a broad response ranging up to $> 10,000\ \text{Hz}$ that was fit with a MF response centered at $\sim 60\ \text{Hz}$ and a HF response centered at $\sim 15,000\ \text{Hz}$. The EIS data for the single-step fired cells in Figure 4.7 were also fit well by the same circuit, even though the three responses are not so obvious in the spectra. The MF and HF responses do not vary significantly with cathode processing conditions. The LF response clearly increases with the increase in firing time from 2 to 4 h. For the separately fired cell, the LF response is mostly eliminated, which can be explained based on prior results on similar LSM-YSZ cathodes showing that the dominant response shifts from 100-

1000 Hz for low firing temperatures (1075-1175 °C) to 1-10 Hz for high firing temperatures (1225-1325 °C).⁵⁶ In general, it can be concluded that the LF response decreases with decreasing cathode firing temperature and time; this is readily explained by the associated increase in cathode TPB density shown in Table 4.1.

In order to more clearly associate the EIS responses with specific electrochemical mechanisms, EIS measurements were taken at varying O₂ and H₂ partial pressures and different temperatures, using single-step 4h fired cells as an example. Figure 4.8 shows the Bode and Nyquist plots of EIS data measured at 800 °C under different cathode pO₂ with 97% H₂ – 3% H₂O at the anode. The response at LF increases and shifts to slightly lower frequency as pO₂ decreases, providing additional evidence that this is a cathode response. The other responses at higher frequency do not increase significantly.

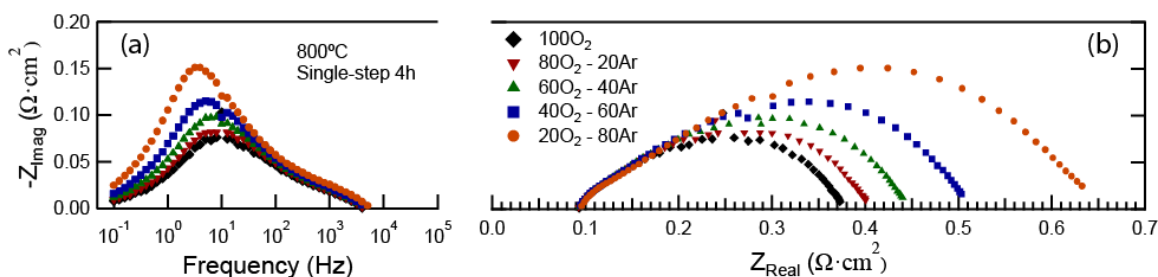


Figure 4.8. Bode (a) and Nyquist (b) plots of EIS data from single-step 4h cell measured at 800 °C under different pO₂. Humidified hydrogen is used on the anode side. Note that these measurements were done in a different test setup than the others in this paper, with synthetic air (20%O₂ – 80%Ar) instead of lab air, and with a different cell; thus, the magnitudes of the EIS responses do not agree exactly with other EIS data.

Figure 4.9 shows Bode and Nyquist plots of EIS data from the single-step 4h fired cell measured at 800 °C under different pH₂ with air on the cathode side. The LF and MF responses grow larger and shift to lower frequency with decreasing pH₂, but the HF response increases only

very slightly. These frequencies agree well with those normally observed for Ni-YSZ anodes,^{102, 103} and are correlated to anode gas conversion (~ 1 Hz), anode gas diffusion (~ 10 Hz) and charge transfer (~ 1000 Hz). Regarding Figure 4.7, it is not surprising that the MF and HF responses are very similar in the different cells, given that the anodes are identical. The anode response at LF overlaps with the main cathode response, which is responsible for the LF response changes with cathode processing.

Bode and Nyquist plots of EIS data from the single-step 4h fired cell taken at varying temperatures are shown in Figure 4.10. There is a general increase in the response magnitudes across a broad range of frequencies. Although the gas conversion and gas diffusion components of the LF response should not be strongly temperature dependent, the cathode response should be strongly temperature dependent. Similarly, the charge-transfer anode response at ~ 1000 Hz should also be temperature dependent. Finally, the response at $\sim 10,000$ Hz is probably associated with YSZ grain boundaries in the LSM-YSZ cathode,⁵⁶ which should have a strong temperature dependence with no p_{H_2} dependence. These three responses explain the temperature dependence shown in Figure 4.10.

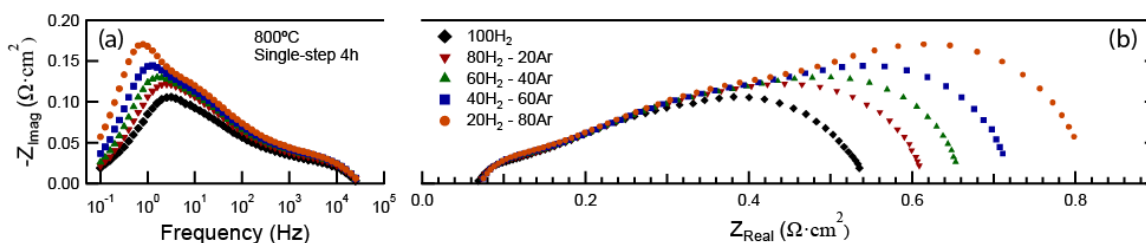


Figure 4.9. Bode (a) and Nyquist (b) plots of EIS data from single-step 4h cell measured at 800 °C under different H_2 partial pressures. The water steam partial pressure is constant at 0.03 atm. Flow air is used on the cathode side.

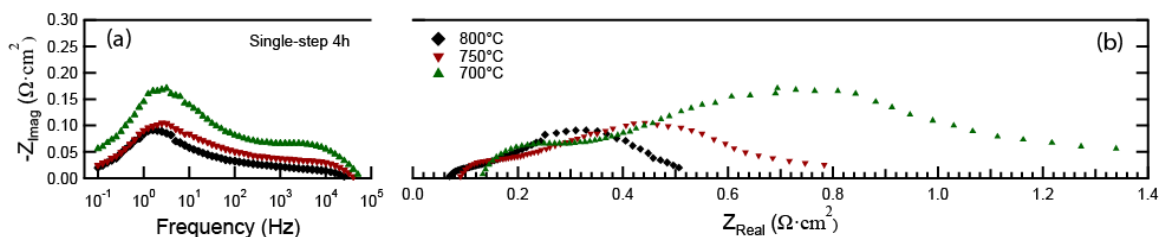


Figure 4.10. Bode (a) and Nyquist (b) plots of EIS data from single-step 4h cell measured at different temperatures.

Based on the EIS data taken at different $p\text{O}_2$, $p\text{H}_2$ and temperatures, it is clear that the increase in LF response with increasing cathode firing temperature and time is attributed to a cathode electrochemical process. There is a clear correlation between the magnitude of this LF response and the measured TPB densities (Table 4.1). Furthermore, the results show that the majority of the polarization resistance for the single-step fired cells is from the cathode.

4.4. Conclusions

Ni-YSZ anode supported SOFCs with YSZ electrolytes and LSM-YSZ cathodes have been successfully fabricated by single-step firing at 1250 °C, using Fe_2O_3 as a YSZ sintering aid. Area-specific resistance was $0.44 \Omega \cdot \text{cm}^2$ and maximum power density was 0.91 W/cm^2 for a 2 h firing time. Increasing the firing time to 4 h increased the cell resistance to $0.51 \Omega \cdot \text{cm}^2$ and decreased power density. For comparison, a conventional cell where the cathode was fired separately at a lower temperature showed much better cell performance. The changes in performance were a direct result of changes in the cathode impedance response at 1-10 Hz, and correlated well with increases in TPB density with increasing cathode firing temperature or time. That is, the requirement of co-firing the LSM-YSZ cathodes at the relatively high temperature of 1250 °C in the single-step fired cells leads to a relatively large polarization loss at 1-10 Hz. In order to achieve

higher-performance single-step co-fired cells, it will be necessary to achieve a finer-scale cathode microstructure with higher TPB density. This can be achieved either by suppressing cathode coarsening/sintering via further reductions in the co-firing temperature, or by replacing LSM with a more refractory cathode material such as (La,Ca)MnO₃.

4.5. Acknowledgements

The authors gratefully acknowledge financial support by the National Science Foundation Ceramics Division under grant number DMR-1506925, and the Institute for Sustainability and Energy at Northwestern (ISEN). The authors also acknowledge the assistance of the Electron Probe Instrumentation Center (EPIC) at the NUANCE Center-Northwestern University for microstructural analysis, which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); and the State of Illinois, through the IIN.

Chapter 5

Fabrication of Oxygen-electrode-supported Solid Oxide Cells

5.1. Introduction

Solid oxide cells (SOCs) have received increasing attention not only as electrolyzers for fuel production from renewable electricity, but also as electrical energy storage devices.¹⁰⁴⁻¹¹⁰ Much of the SOC research and development has focused on fuel-electrode-supported cells; although these were primarily developed for fuel cell applications, they have also been applied in electrolysis. However, oxygen-electrode-supported cell designs could be useful to minimize mass transport limitations during electrolysis or reversible applications. Solid oxide electrolysis produces pure oxygen, which will tend to displace air in the oxygen electrode at high current densities where mass transport current limitations become important. For a reversible SOC application, the oxygen produced during electrolysis can be stored and then used during fuel cell operation.¹⁰⁵ The presence of pure oxygen mitigates the significant gas diffusion limitations encountered with thick oxygen electrodes when working with air.¹¹¹ On the other hand, the fuel electrode can be significantly thinner than in a fuel-electrode-supported cell, alleviating gas diffusion limitations that otherwise make it difficult to achieve high steam utilization during electrolysis, and high fuel utilization in fuel cell operation.¹¹²⁻¹¹⁴

Processing issues pose a significant barrier to the realization of high-performance oxygen-electrode-supported cells. First, most oxygen-electrode materials have much lower melting temperature than electrolyte materials, making it difficult to find a processing temperature where

the electrolyte is densified while retaining sufficient electrode porosity, surface area, and TPB density. This is exacerbated by the fact that common oxygen electrodes such as LSM-YSZ require higher TPB density than Ni-YSZ fuel electrodes.⁹⁵ Second, the high co-firing temperature may enable electrode/electrolyte reactions and/or interdiffusion. Thus, it is critical to reduce the electrolyte sintering temperature to allow co-firing of the electrolyte and oxygen electrode. For example, sintering aids have been used to enable single-step firing of entire SOCs, including NiO-YSZ fuel electrode supports, YSZ electrolytes, and $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_{3-\delta}$ (LSM)-YSZ or $(\text{La}_{0.85}\text{Ca}_{0.15})_{0.97}\text{MnO}_{3-\delta}$ (LCM)-YSZ electrodes.^{96, 97, 115} These cells had electrodes with good porosity, dense electrolytes, were free of significant elemental interdiffusion, and yielded good cell performance. However, it was shown that the LSM-YSZ electrodes had a relatively low TPB density and hence higher polarization resistance compared to traditional two-step fired cells, due to the higher firing temperature and free shrinkage during co-firing.¹¹⁵ It is expected that similar processing conditions can be used for fabrication of oxygen-electrode-supported cells.

In this chapter, we demonstrate successful fabrication of oxygen-electrode-supported SOCs consisting of LSM current collector, LSM-YSZ oxygen-electrode, YSZ electrolyte, and NiO-YSZ fuel-electrode, using a reduced-temperature single-step firing process. Some of the cells also had $(\text{Sm}_{0.5}\text{Sr}_{0.5})\text{CoO}_3$ (SSC) infiltrated into the LSM-YSZ electrode in order to enhance its performance. The electrochemical characteristics were studied, using current-voltage measurements and impedance spectroscopy, with both air and pure oxygen at the oxygen electrode and with different $\text{H}_2/\text{H}_2\text{O}$ contents at the fuel electrode.

5.2. Experimental Procedures

All cells were prepared on oxygen-electrode supports containing as-received LSM (Praxair, $d_{50} = 1.1 \mu\text{m}$) and 1000 °C-8 h pre-coarsened LSM ($d_{50} \approx 1.8 \mu\text{m}$) in 1:1 ratio, along with tapioca starch (5 wt.%) and graphite (20 wt.%) as pore former, xylene and ethanol as solvent, and fish oil as dispersant. The above materials were ball milled for 24 h, followed by addition of poly(vinyl butyral) (PVB) as binder, butyl benzyl phthalate (BBP) and polyalkylene glycol (PAG) as plasticizer. The mixture was then ball milled for another 24 h. The oxygen-electrode slurry consisting of as-received LSM and YSZ with 1:1 weight ratio, tapioca starch (5 wt.%) and graphite (20 wt.%) as pore former was prepared using the same solvent, dispersant, binder and plasticizers. The YSZ with 3 mol.% Fe_2O_3 as sintering aid and NiO-YSZ with 1:1 weight ratio slurries were prepared in the same way. The resulting oxygen-electrode, electrolyte and fuel-electrode slurries were casted on PET carrier films at room temperature. After drying, the LSM oxygen-electrode support, LSM-YSZ oxygen-electrode, YSZ electrolyte and NiO-YSZ fuel-electrode tapes were laminated at 70 °C for 30 min under a pressure of 5000 psi., followed by one-step sintering at 1250 °C for 2 h.

For some cells, the oxygen-electrodes were infiltrated with a 1M solution containing Sm, Sr, and Co nitrates in a ratio of 0.5:0.5:1 mol. Cells were fired at 450 °C for 0.5 h after each infiltration. Each sample was infiltrated 2 times, resulting in a 4.0 mg $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) deposition. Oxygen-electrode calcination was done at 800 °C at the beginning of cell testing.

Current-voltage measurements were taken at various temperatures ranging from 800 °C to 650 °C from OCV to 0.3 V. Humidified hydrogen (3 vol.% H_2O) with flow rate of 100 sccm was

used as fuel. Flow air at 200 sccm or pure oxygen at 100 sccm was used as oxidant. Electrolysis testing was performed on the SSC-infiltrated cells, with oxygen-electrode being exposed to pure oxygen with flow rate of 100 sccm, while the fuel electrode was supplied with hydrogen flowed at 100 sccm through a heated H₂O-containing bubbler. The temperature of the bubbler was adjusted to produce vapor pressure ranging from 3 vol.% to 70 vol.%. EIS spectra were collected using a Zahner IM6 electrochemical workstation under OCV over a frequency range of 100 mHz – 100 kHz. During life tests, the cells were exposed to 50 vol.% H₂/50 vol.% H₂O at the fuel-electrode and pure oxygen at the oxygen-electrode. Direct current with a current density of 1 A/cm² was applied for ~ 100 h. The current was also applied in the reverse direction to perform life test under electrolysis mode. The voltage response during life tests was recorded by the LabView program. The current loading was interrupted once per day for EIS measurement, taken at OCV. The microstructure of the tested cells was examined by SEM and EDS.

5.3. Results & Discussion

5.3.1. Microstructure

Figure 5.1a shows fracture cross-sectional SEM image of the non-infiltrated cell. Only non-infiltrated cell is shown here since the SSC-infiltrated cell has similar structure. The thicknesses of the NiO-YSZ fuel-electrode, YSZ electrolyte, LSM-YSZ oxygen-electrode and LSM current collector are ~ 20 μm, ~ 15 μm, ~ 300 μm and ~ 300 μm, respectively. The SEM image shows that both the fuel- and oxygen-electrodes are porous, as needed to facilitate the electrode reactions. The fuel-electrode porosity, ~ 20%,¹⁰⁰ is developed via NiO reduction to Ni upon exposure to fuel. The oxygen-electrode porosity is provided by addition of 5 wt.% starch and 20 wt.% graphite as pore

former. The larger pores provided by starch facilitate the oxidant diffusion through the electrode, whereas the smaller pores provided by graphite maintain high TPB density for electrode reactions. The LSM current collector (not shown in the figure) is consist of LSM particles with two different sizes, in order to improve shrinkage match during single-step firing. LSM has relatively high shrinkage compare to the rest of the cell components. Pre-coarsening of the LSM particles at 1000 °C for 8 h results in an increase in D50 from 1.1 μm to 1.8 μm , measured by particle size analyzer (not shown here). Mixing the as-received and pre-coarsened LSM particles in 1:1 ratio leads to increase in the particle packing density, and thus reducing the shrinkage. The porosity in the LSM current collector is also provided by starch and graphite pore former. The YSZ electrolyte shows small pores with low enough volume fraction that they are presumably isolated pores.

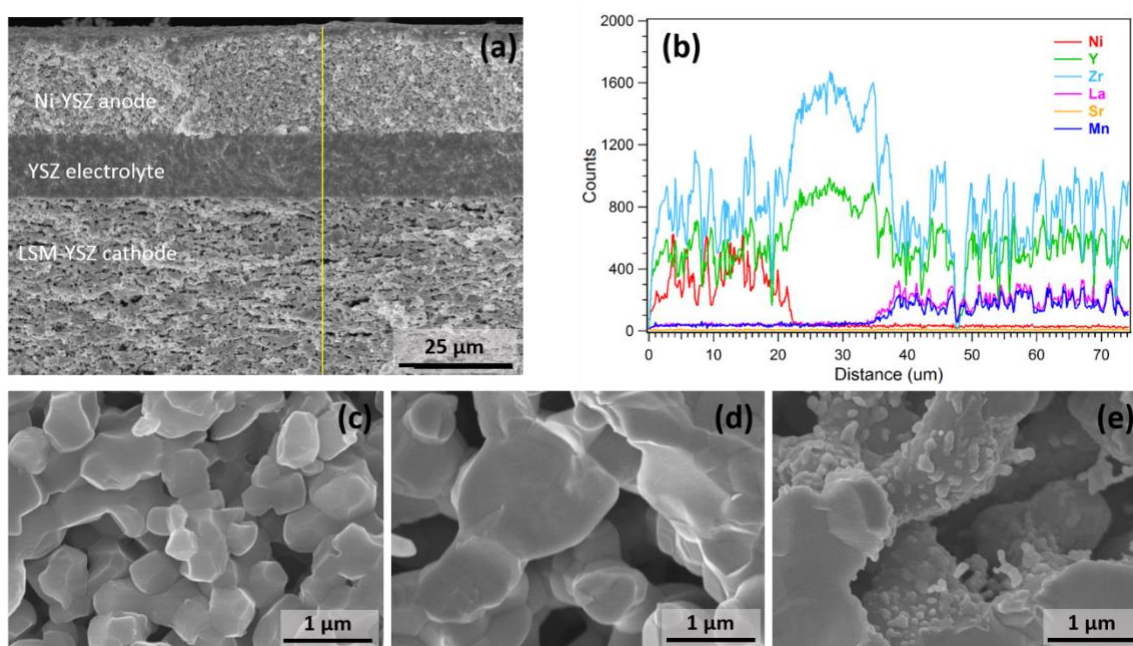


Figure 5.1. (a) Fracture cross-sectional SEM image of the non-infiltrated cell, taken after electrochemical testing. (b) EDS intensity line scan, taken along the line shown in (a). Magnified portion of the Ni-YSZ fuel-electrode (c), non-infiltrated (d) and SSC-infiltrated (e) LSM-YSZ oxygen-electrodes.

Figure 5.1b shows the EDS line scan, taken along the yellow line in Figure 5.1a. No detectable elemental interdiffusion was observed upon co-firing process. Figure 5.1c-e show the magnified portion of the Ni-YSZ fuel-electrode, non-infiltrated and SSC-infiltrated LSM-YSZ oxygen-electrodes, respectively. The Ni-YSZ and LSM-YSZ electrodes have similar structure with the ones reported previously under similar firing conditions.^{57, 115} SSC particles appear as nanoparticles with an average particle size of ~ 100 nm decorating LSM-YSZ surfaces in the infiltrated electrode.

5.3.2. Electrochemical performance

Figure 5.2 compares the voltage-current characteristics for the non-infiltrated and SSC-infiltrated cells operating at 800 °C, with humidified hydrogen as fuel and flow air or pure oxygen as oxidant. The non-infiltrated cell tested in hydrogen and air yields a maximum power density (P_{max}) of 325 mW/cm² at 800 °C, with a limiting current density of 0.9 A/cm². P_{max} increases to 575 mW/cm² when using pure oxygen as oxidant, ascribed to the improved gas diffusion and an increased exchange current density in the cathode. Incorporation of SSC nanoparticles into LSM-YSZ cathode increases P_{max} to 580 mW/cm² in hydrogen and air, with much smaller initial resistance compare to the non-infiltrated cell. However, the limiting current is similar to the non-infiltrated cell, ~ 0.9 A/cm², suggesting large gas diffusion limitation on the cathode. Changing the oxidant from air to pure oxygen results in significant improvement in cell performance, with P_{max} of 1405 mW/cm² and limiting current over 6 A/cm². The OCV values of all the cells shown in Figure 5.2 are ~ 1.05 V, slight lower than the calculated Nernst potential of 1.10 V (air) or 1.14 V (oxygen). This can be explained by the Ag seals used in the test setup, which usually exhibit slight leakage.¹⁰¹

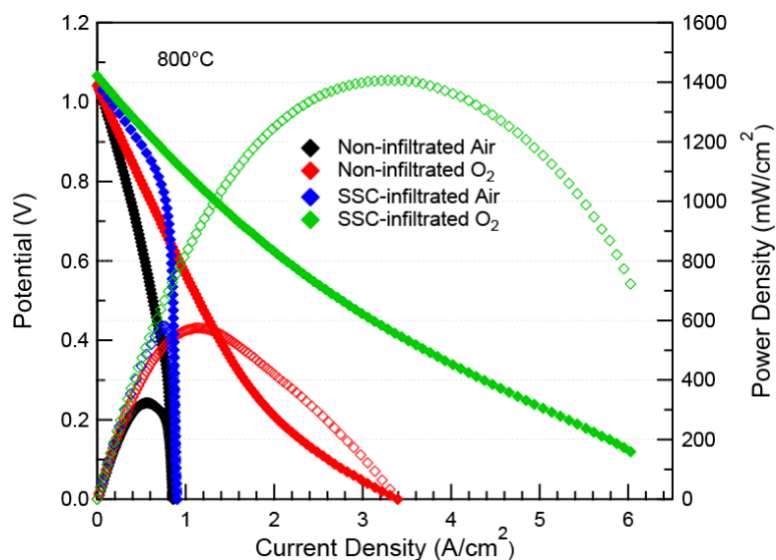


Figure 5.2. Voltage and power density versus current density for non-infiltrated and SSC-infiltrated cells operating at 800 °C, with humidified hydrogen at fuel-electrode and flow air or pure oxygen at oxygen-electrode.

Figure 5.3 presents Bode and Nyquist plots of the EIS data from the cells shown in Figure 5.2. The ohmic resistances are $\sim 0.11 - 0.15 \Omega\text{cm}^2$. The small variation is presumably due to slight difference in electrolyte thickness. Note that the ohmic resistances for the oxygen-electrode-supported cells are higher than the fuel-electrode-supported cells with similar compositions and electrolyte thickness,¹¹⁵ presumably due to higher electronic resistance from the thicker oxygen-electrodes. The total area specific resistance values for the non-infiltrated cells tested with hydrogen and air, hydrogen and oxygen, and the SSC-infiltrated cells tested with hydrogen and air, hydrogen and oxygen are $0.75 \Omega\text{cm}^2$, $0.51 \Omega\text{cm}^2$, $0.35 \Omega\text{cm}^2$ and $0.24 \Omega\text{cm}^2$, respectively, in good agreement with the trend in power density shown in Figure 5.2.

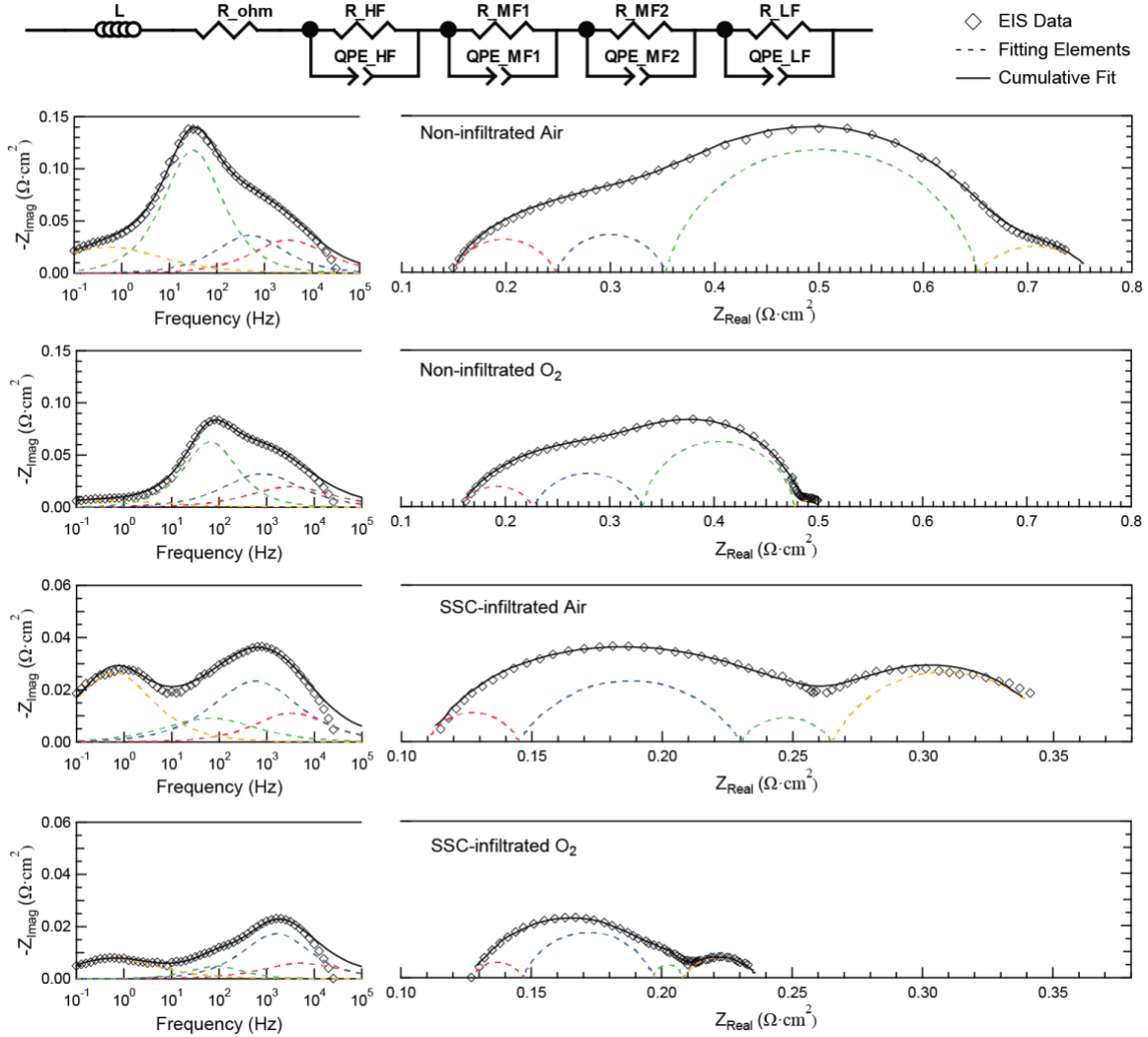


Figure 5.3. Bode (left) and Nyquist (right) plots of EIS data from non-infiltrated and SSC-infiltrated cells measured at 800 °C at OCV using humidified hydrogen as fuel and flow air or pure oxygen as oxidant. The four main responses are shown separately in dashed lines, along with the overall fits in solid lines.

The EIS data were modeled using an equivalent circuit, consisting of an inductor L , ohmic resistor R_{ohm} , and four resistor-constant phase element (R-CPE) units in series: $LR_{ohm}(RQ)(RQ)(RQ)(RQ)$ with $Z_{QPE} = (i\omega Q)^{-n}$. The four main responses are shown separately in dashed lines in Figure 5.3, along with the cumulative fits shown in solid lines. The low-frequency (LF) response centered at ~ 0.7 Hz is mostly eliminated when changing oxidant from air to pure

oxygen, suggesting that it is correlated to oxygen-electrode gas diffusion. The middle frequency (MF) response centered at ~ 60 Hz clearly decreases with increasing oxygen partial pressure and SSC infiltration, indicating that this MF response is from oxygen-electrode electrochemical process and can be explained by the increased active sites for electrode reactions due to SSC addition. Another MF response centered at ~ 900 Hz does not vary significantly with SSC infiltration or oxidant content, and hence can be ascribed to the fuel-electrode response. In fact, this frequency agrees well with the charge transfer process normally observed for Ni-YSZ fuel-electrodes.^{102, 103} Finally, the high frequency (HF) response centered at 10^3 - 10^4 Hz is probably associated with YSZ grain boundaries in the LSM-YSZ oxygen-electrode,⁵⁶ as it does not change with fuel composition (data not shown here), and only changes slightly with SSC infiltration and oxidant content. Based on the above electrochemical characterization, it can be concluded that for the oxygen-electrode-supported cells, the poor gas diffusion due to thicker oxygen-electrode can be greatly improved by using pure oxygen, and the oxygen-electrode electrochemical process can be enhanced by infiltration of SSC nanoparticles.

Figure 5.4 shows the voltage-current characteristics of the SSC-infiltrated cell at varying temperatures, with humidified hydrogen as fuel and pure oxygen as oxidant. Power densities are decent, with P_{max} of 1406 mW/cm², 717 mW/cm², 413 mW/cm² and 215 mW/cm² at 800 °C, 750 °C, 700 °C and 650 °C, respectively. For comparison, the LSM-YSZ|YSZ|Ni-YSZ fuel-electrode-supported cells made by single-step firing yield P_{max} of 900 mW/cm², 500 mW/cm² and 300 mW/cm² at 800 °C, 750 °C and 700 °C, respectively.¹¹⁵ Bode and Nyquist plots of EIS data taken at these temperatures are shown in Figure 5.5. The LF response remains small and constant at all temperatures. The lack of temperature dependence is consistent with the oxygen-electrode gas

diffusion process noted above. The two MF responses, corresponding to oxygen-electrode electrochemical process and fuel-electrode charge transfer process as described above, increase greatly with decreasing operating temperature. The observed strong temperature dependence of the HF response at 10^3 - 10^4 Hz is also consistent with it being the YSZ grain boundaries in the LSM-YSZ electrode.

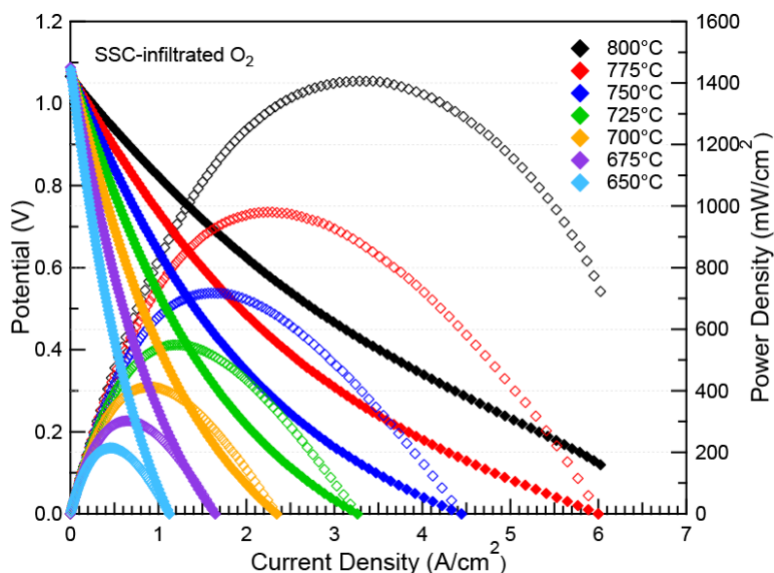


Figure 5.4. Voltage and power density versus current density for SSC-infiltrated cell measured at different temperatures in pure oxygen and humidified hydrogen.

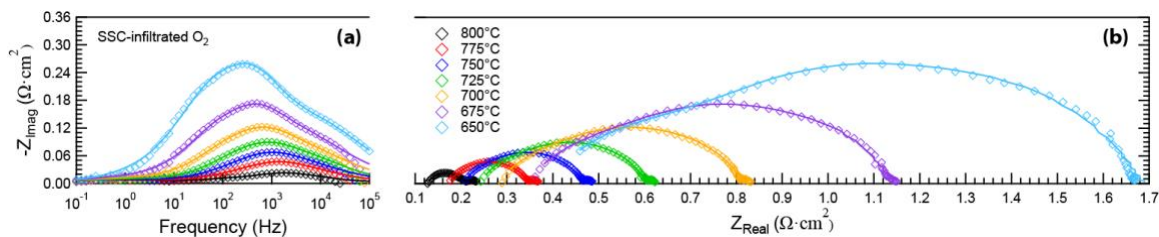


Figure 5.5. Bode (a) and Nyquist (b) plots of EIS data from SSC-infiltrated cell measured at different temperatures in pure oxygen and humidified hydrogen. The points represent the measured data, and the solid lines represent the overall fits made using the equivalent circuit shown in Figure 5.3.

5.3.3. H_2O electrolysis

Figure 5.6a shows voltage versus current density for SSC-infiltrated cell at different temperatures under electrolysis conditions, i.e., with 50 vol.% H_2 /50 vol.% H_2O on the fuel side and pure oxygen on the other. The curves are fairly linear in the SOEC region at all temperatures, yielding current densities of 0.8 A/cm^2 at 800 °C and 0.2 A/cm^2 at 700 °C at 1.3 V. The same cell was tested at 800 °C at varying H_2O partial pressures from 0.03 atm to 0.7 atm, shown in Figure 5.6b. Decrease in the limiting current density in SOEC mode with decreasing H_2O content is not evident even at 0.03 atm H_2O , as normally observed in fuel-electrode-supported cells.^{94, 116} The current density decreases only from 0.9 A/cm^2 to 0.7 A/cm^2 at 1.3 V when reducing H_2O content from 0.7 atm to 0.03 atm, indicating high steam utilization ascribed to thin fuel-electrode. The use of thin fuel-electrode also allows high fuel utilization when operating under SOFC mode, as no gas diffusion limitation was observed at reduced H_2 content. Based on the above results, the oxygen-electrode-supported cells could potentially be used at different positions in a stack system for reversible operations due to the high steam and fuel utilizations.

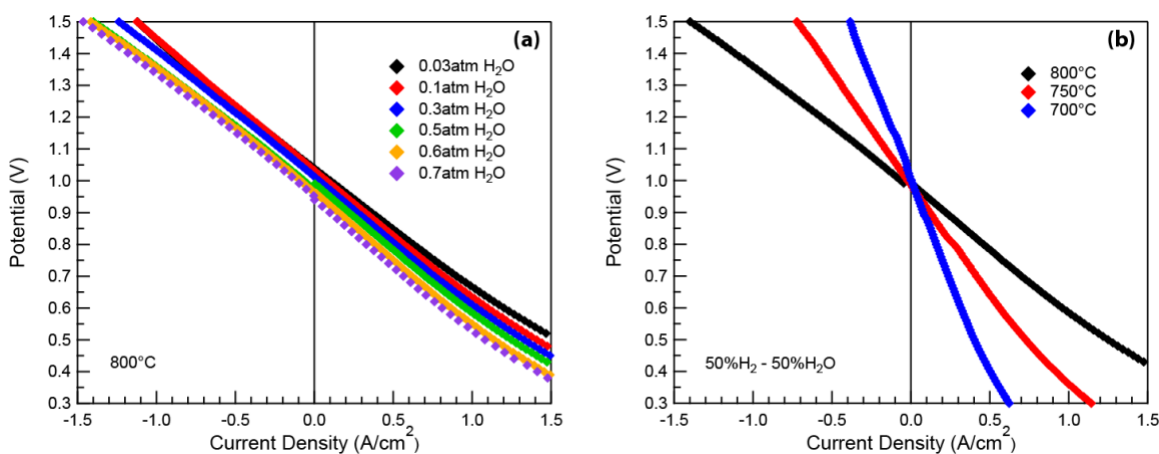


Figure 5.6. (a) Voltage versus current density for SSC-infiltrated cell measured at different temperatures in pure oxygen and 50 vol.% H_2 /50 vol.% H_2O . (b) Voltage versus current

density for SSC-infiltrated cell measured at 800 °C, with pure oxygen at oxygen-electrode and different H₂O partial pressures (balanced by H₂) at fuel-electrode.

5.3.4. Preliminary life testing

Preliminary life tests were carried out for the SSC-infiltrated cells at operating temperature of 800 °C, with fuel-electrodes exposed to 50 vol.% H₂/50 vol.% H₂O and oxygen-electrodes exposed to pure oxygen. The cell was operating under fuel cell or electrolysis mode, with a 1 A/cm² direct current running through. The corresponding voltage responses over time are shown in Figure 5.7. In fuel cell mode, the voltage decreases from ~ 650 mV to ~ 400 mV in the first 40 h, and becomes stable thereafter. Whereas a continuous increase in voltage has been observed, from an initial value of ~ 1300 mV to ~ 1650 mV at 110 h, when operating under electrolysis mode.

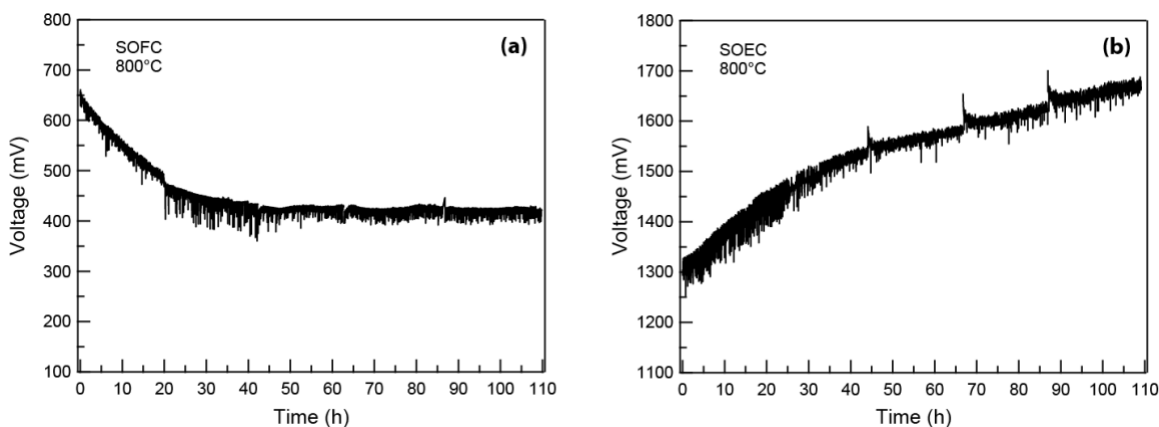


Figure 5.7. Voltage responses of the SSC-infiltrated cells during life tests under fuel cell (a) and electrolysis (b) modes, with 1 A/cm² direct current loading.

The EIS data obtained at selective time spots during the fuel cell and electrolysis life tests are shown in Figures 5.8 and 5.9, respectively. The same equivalent circuit model mentioned above

were used to fit the data. The changes in each response over time are plotted in Figure 5.10. The LF gas diffusion and HF grain boundary responses stay almost unchanged for both operating conditions. The MF fuel-electrode resistance only increases in the first 40 h, from $0.1 \Omega\text{cm}^2$ initially to $0.135 \Omega\text{cm}^2$ at 42 h, when running under fuel cell mode. Under electrolysis mode, the fuel-electrode resistance increases from $0.1 \Omega\text{cm}^2$ to $0.12 \Omega\text{cm}^2$ at 67 h, and then stays unchanged. The main change in the impedance seen in the Bode and Nyquist plots is mostly contributed by the change in the MF response associated with oxygen-electrode. Under fuel cell mode, the oxygen-electrode resistance increases rapidly from $0.04 \Omega\text{cm}^2$ to $0.23 \Omega\text{cm}^2$ in the first 40 h, before a much slower increase to $0.257 \Omega\text{cm}^2$ at 110 h. Whereas under electrolysis mode, the oxygen-electrode resistance continuously increases from $0.023 \Omega\text{cm}^2$ to $0.43 \Omega\text{cm}^2$ over the period of the life test.

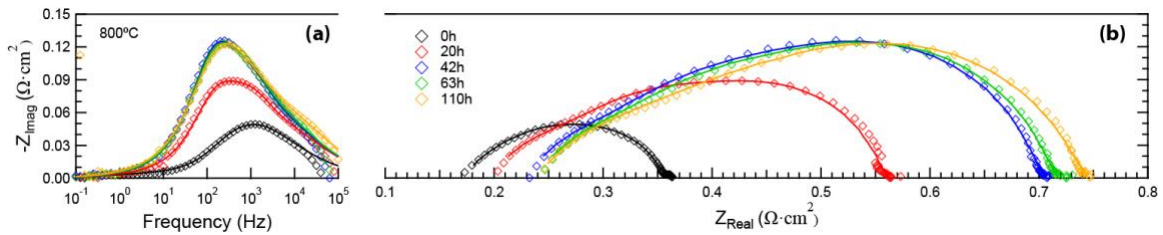


Figure 5.8. Bode (a) and Nyquist (b) plots of EIS data taken at different times during the life test under fuel cell mode. The points represent the measured data, and the solid lines represent the overall equivalent circuit fits.

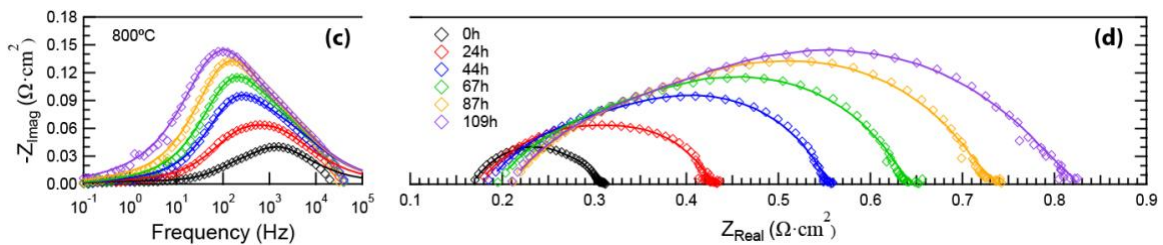


Figure 5.9. Bode (a) and Nyquist (b) plots of the EIS data taken at different times during the life test under electrolysis mode.

The higher initial value of the cell running under fuel cell mode is probably due to longer time being maintained at 800 °C before taking the measurement, where SSC particles coarsened to a greater extent. The degradation in the oxygen-electrode under fuel cell mode appears to be related to SSC particle coarsening, as it slows as particles grow. While in addition to particle coarsening, there tends to have another degradation mechanism when running under electrolysis mode, as the resistance continuous to increase over time. It could be due to oxygen bubble formation in YSZ grain boundaries and $\text{La}_2\text{Zr}_2\text{O}_7$ phase formation at YSZ-LSM interfaces, which would contribute to weakening and delamination near the oxygen-electrode-electrolyte interface, as reported in the literature.^{117, 118}

The ohmic resistance increases in the first 42 h and 87 h for fuel cell and electrolysis mode, respectively. The reasons for this are unclear, but it could be due to intergranular fracture of the YSZ electrolyte induced by current.¹¹⁹

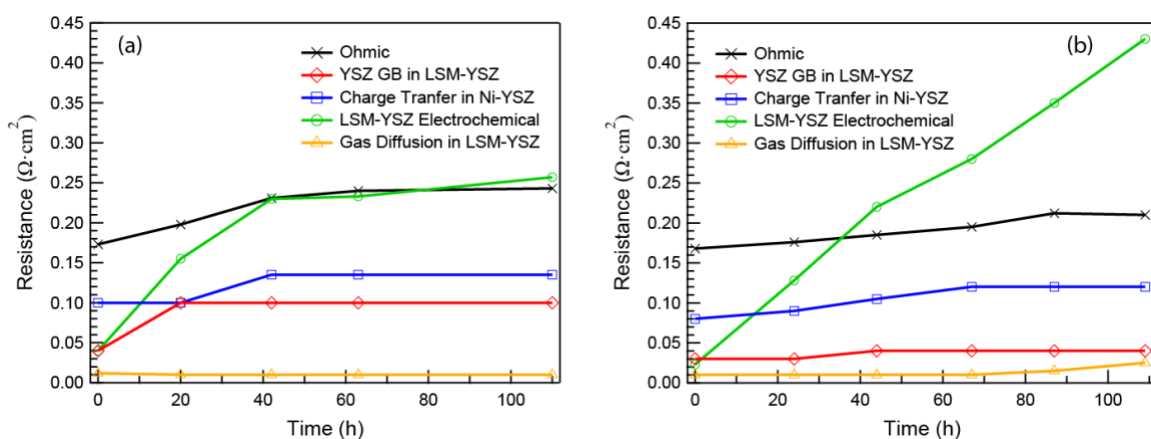


Figure 5.10. Resistance over time for each response in the oxygen-electrode-supported cells under fuel cell (a) and electrolysis (b) modes.

5.4. Conclusions

Oxygen-electrode-supported SOCs with LSM-YSZ oxygen-electrode, YSZ electrolyte, and Ni-YSZ fuel-electrode have been successfully fabricated via single-step firing at 1250 °C, utilizing Fe₂O₃ as YSZ sintering aid. Large gas diffusion limitation was observed when operating with flow air on the oxygen-electrode, due to slow binary diffusivity of O₂-N₂ in the thick oxygen-electrode compared to much faster H₂ diffusion in the traditional fuel-electrode-supported cells. The gas diffusion was greatly improved by using pure O₂ at the oxygen-electrode. Although SOFCs are normally operating with air fed to oxygen-electrodes, the oxygen-electrode-supported cells can be potential applicable to reversible SOCs (ReSOCs), where oxygen is being produced during electrolysis and can be utilized during fuel cell operation. Even with pure O₂ at the oxygen-electrode, the large polarization loss from the thick oxygen-electrode yielded poor performance. Infiltrating the LSM-YSZ oxygen-electrode with nano-sized SSC substantially increased the overall cell performance, from ~ 600 mW/cm² to ~ 1400 mW/cm² at 800 °C with pure O₂ at oxygen-electrode and humidified H₂ at fuel-electrode. This is due to increased TPBs provided by the SSC nanoparticles. The thin fuel-electrode geometry in the oxygen-electrode-supported cells also exhibited high fuel utilization under fuel cell operation and high steam utilization under electrolysis operation, allowing them to be potentially used at different positions in a ReSOC stack system. However, preliminary life tests at 800 °C showed fast degradation under both fuel cell and electrolysis modes. EIS measurements suggested that the main degradation was associated with electrochemical processes in the LSM-YSZ electrode, presumably due to SSC particle coarsening. In order to improve cell stability, cells need to be operated at lower temperatures, or using more stable infiltration materials, such as Sr(Ti_{0.3}Fe_{0.7-x}Co_x)O_{3-δ} (STFC).

5.5. Acknowledgements

This work is financially supported by the US National Science Foundation (Grant # DMR-0907639 and DMR-1506925). The authors also acknowledge the assistance of the Electron Probe Instrumentation Center (EPIC) at the NUANCE Center-Northwestern University, which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); and the State of Illinois, through the IIN.

Chapter 6

Mechanisms of Performance Degradation of (La,Sr)(Co,Fe)O_{3-δ} Symmetric-electrode Cells

In this work, the chemical etching method for quantifying Sr surface segregation on porous LSCF electrodes was developed in collaboration with Dr. Ghislain Rupp, Prof. Andreas Limbeck and Prof. Jürgen Fleig from Vienna University of Technology in Vienna, Austria. The XPS measurement was performed by Dr. Kyle Yakal-Kremiski.

6.1. Introduction

Mixed ionic-electronic conducting (MIEC) materials have been studied and developed as solid oxide cell (SOC) oxygen electrodes, due to their high activity for the oxygen reduction and evolution reactions at intermediate temperatures ($< 800\text{ }^{\circ}\text{C}$).¹²⁰⁻¹²⁵ However, many MIEC materials contain Sr and exhibit Sr surface segregation at elevated temperatures, which has been proposed to hinder the oxygen surface exchange process.^{9, 60-63} This is believed to be an important issue for the stability of advanced SOFCs utilizing MIEC cathodes. Still, most of the Sr segregation observations have been made on thin film samples, where it is straightforward to measure surface composition using techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy ion scattering (LEIS), and secondary ion mass spectrometry (SIMS).^{9, 64-67, 126} Recently Rupp *et al.*⁶⁸ reported a novel technique utilizing chemical etching with on-line inductively coupled plasma optical emission spectrometry (ICP-OES) detection to successfully quantify Sr-rich surface phases on dense La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC) thin films. There is

only two reports of a measurement of a practical porous LSCF electrode that showed Sr segregation, measured via XPS, along with electrochemical performance degradation.^{9, 60}

The distinction between thin film and bulk electrode samples is potentially important. Thin films are often characterized by columnar growth with very high grain boundary densities, they may exhibit significant stress, and the thermal history is usually very different from that of porous electrodes (preparation mostly below 800 °C). Although the measured properties of well-prepared polycrystalline thin-film electrodes normally agree reasonably well with values from bulk materials,³⁶ in some cases such as epitaxial thin film electrodes, properties may deviate significantly.¹²⁷ Also, SOFC stacks with LSCF cathodes have been shown to provide reasonably stable long-term performance,¹²⁸ an observation that appears to be at odds with the Sr segregation and related degradation observed for thin-film LSCF.

In this chapter, the degradation mechanisms, especially Sr surface segregation, of porous LSCF cathodes under various thermal ageing conditions is investigated. Particle coarsening effects, that can become important at sufficiently high temperatures, are also studied. LSCF symmetric-electrode cells with $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) electrolytes were maintained in ambient air at different temperatures ranging from 550 to 950 °C for different periods of time up to 1400 h, without current/polarization. For cells aged at 700, 750 and 800 °C, electrochemical evolution was monitored using impedance spectroscopy once per day at testing temperature of 700 °C. The electrode morphology was examined utilizing 3D tomography via FIB-SEM and Sr surface segregation was measured using XPS and chemical etching with ICP-OES detection. The Adler-Lane-Steele (ALS) model³⁷ was applied, making use of the measured impedance data and 3D

calculated microstructural parameters, to examine the effect of Sr surface segregation on the oxygen surface exchange and diffusion processes.

6.2. Experimental Procedures

6.2.1. Cell preparation

Symmetric-electrode cells were prepared on dense $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) electrolytes obtained by uniaxial dry-pressing from GDC powder followed by firing at 1450 °C for 6 h. A pure $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) ink, made by mixing LSCF powder with a vehicle (Heraeus V-737) in a three-roll mill, was screen printed on both sides of the GDC pellets, and fired at 1100 °C in ambient air for 1 h. For the cells used for life testing, gold contact grids were screen printed on the surfaces of both electrodes as current collectors.

6.2.2. Cell ageing and electrochemical evaluation

Life tests were carried out at three different ageing temperatures, 700, 750 and 800 °C, for 800 h. LSCF symmetric-electrode cells were maintained at the ageing temperatures with both electrodes exposed to ambient air. No current or polarization was applied. Electrochemical impedance spectroscopy (EIS) measurements were taken at 700 °C in all cases, once per day. For ageing at 750 and 800 °C, the furnace temperature was reduced and stabilized at 700 °C for the EIS measurement, and then returned to the ageing temperature; the entire measurement process took ~ 1 h. The EIS spectra were collected using a Zahner IM6 electrochemical workstation over a frequency range of 100 mHz – 1 MHz with a 5 mV AC signal amplitude at a 0 bias voltage.

Some identically-prepared cells were used for ageing-only experiments, *i.e.*, with no EIS measurements, with the cells maintained in ambient air at 550 and 650 °C for various periods of time up to 1400 h. The EIS measurements were omitted in this case because a measurement at 700 °C (to be comparable to the other results) was expected to significantly affect the segregation results for these lower ageing temperatures. EIS measurements were not conducted on the 950 °C-aged cells either, due to the ageing temperature being close to the melting point of silver contacting wires.

6.2.3. Microstructural characterization

Microstructural analysis was done on the aged cells and an as-prepared reference cell using 3D FIB-SEM tomography. The cell was prepared for FIB-SEM serial sectioning by fracturing, low-viscosity epoxy infiltration to provide good contrast from the solid phase, and polishing, as described in detail elsewhere.^{56, 99} Analysis was done on a FEI Helios system with 1kV electron beam energy and backscattered electron (BSE) detector. Image segmentation and 3D reconstruction were done as described elsewhere.⁹⁹ Microstructural parameters including phase volume fraction, tortuosity, surface area, and particle size distribution were then calculated based on the 3D data sets.

6.2.4. Chemical characterization

Each as-prepared and aged cell was fractured into three fragments. The cell fragments were separately stirred in ultrapure H₂O for 10 min. Subsequently, the samples were transferred into a 12 mol·L⁻¹ HCl solution and stirred until the electrodes were completely dissolved. The ultrapure H₂O solution was centrifuged at 2000 rpm for 5 min and only the upper part was used to eliminate

any loose LSCF particles. The H₂O and concentrated HCl solutions were mixed with the appropriate amounts of H₂O/HCl/HNO₃ to yield 0.36 mol·L⁻¹ HCl/0.72 mol·L⁻¹ HNO₃ solutions for ICP-OES analysis.

The chemical analysis of the solutions was done using a Thermo Scientific iCAP 7600 spectrometer. A certified stock solution (10.00 µg·mL⁻¹ from Inorganic Ventures) containing La, Sr, Co and Fe was used to prepare the calibration standards for quantification. The following background corrected emission lines were chosen for evaluation: La (379.478 nm; 412.323 nm), Sr (216.596 nm; 407.771 nm; 421.552 nm), Co (228.616 nm; 237.862 nm), Fe (238.204 nm; 239.562 nm; 240.488 nm).

XPS spectra were collected on a Thermo Scientific ESCALAB 205Xi to determine surface cation changes. Both as-prepared and aged samples were analyzed, with characteristic electron energy windows for all cations, as well as oxygen, collected. Copper tape was used to ground the samples to the stage to prevent sample charging. Gold, present from the current collector, was used as an internal standard for experimental energy offsets, as it is not expected to react with the electrode samples. Comparative analysis was performed by determining the relative integrated intensities for the present peaks for each cation for each sample. Changes in these intensities can suggest differences in relative amounts of valence for particular cations in a sample. However, quantitative analysis between samples, and indeed within a given sample, was not performed due to inconsistent variations between spots, as discussed below. Additionally, cobalt spectra were ignored due to the very low signal to noise ratio, likely due to the low concentration of cobalt in LSCF.

6.3. Results

6.3.1. Life testing and electrochemical characterization

Figure 6.1 shows the Bode and Nyquist plots of EIS data taken at different times during the 800-h life test at 700 °C. Only the 700°C-aged cell is shown here, since the cells aged at 750 and 800 °C yielded similar results. The ohmic resistance (R_o), which comes primarily from the electrolyte and is given approximately by the high frequency intercept with the real axis in the Nyquist plot, did not change measurably during the test. The polarization resistance (R_p), determined approximately by the difference between the high and low frequency intercepts, increased with time, approximately doubling by the end of the life test. The peak frequency decreased with ageing time, from ~ 126 Hz initially to ~ 10 Hz at 800 h, indicating a substantial increase in capacitance due to ageing.

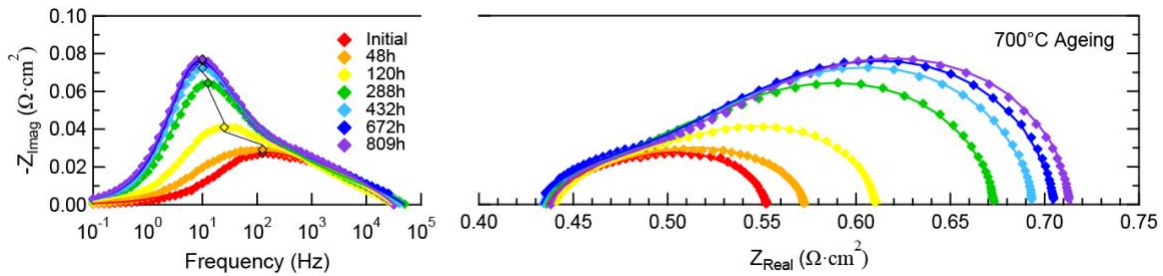


Figure 6.1. Bode and Nyquist plots of EIS data measured at 700 °C in ambient air from a LSCF symmetric-electrode cell during ageing at 700 °C over ~ 800 h. Fits are shown as solid lines on the plots and the peak frequency is outlined on the Bode plot.

The equivalent circuit used to model the EIS data consists of an inductor (L) primarily associated with measurement setup wires, the ohmic resistance (R_o), an R//CPE element at high frequency (HF), and a modified Gerischer element (GE), given by:

$$Z_G = R_G \sqrt{\frac{1}{1 + (j\omega t_G)^\alpha}} \quad , \quad [6.1]$$

used to model the low frequency (LF) response. R_G is the Gerischer resistance, t_G is the time constant, and α , which is < 1 , represents the degree of modification on the Gerischer response. The fits are shown as solid lines in Figure 6.1. Figure 6.2 shows the breakdown of individual elements in a typical fit, where it is clear that the LF response is the main contribution to the electrode polarization. The Gerischer element suggests co-limiting oxygen surface exchange and bulk diffusion processes, as expected for porous MIEC electrodes.^{36, 37, 129} The HF response has a smaller resistance R_{HF} , and may relate to oxygen ion transfer across the LSCF/GDC interface as reported previously for similar LSCF cathodes.¹³⁰⁻¹³²

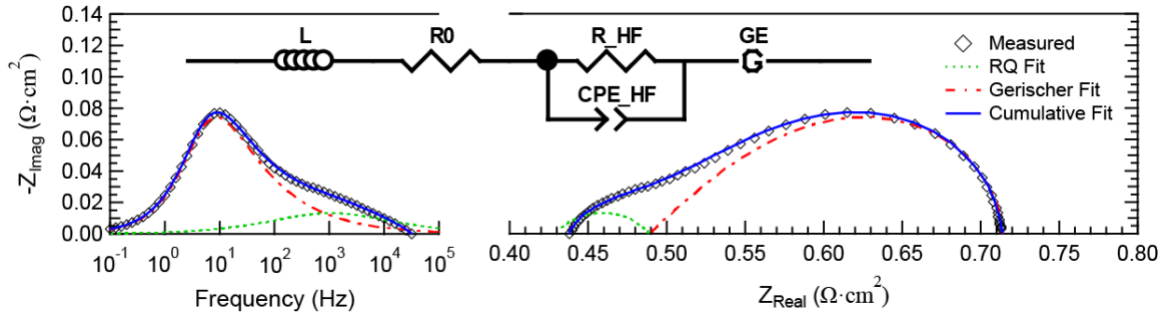


Figure 6.2. Equivalent circuit fits of the EIS data obtained at 700°C in ambient air for the 700°C-800h cell. The points represent the measured data, the dashed lines represent the R//CPE and Gerischer elements (the inductive element is not shown), and the solid lines represent the overall fitting.

Figure 6.3 shows the evolution of R_O and $R_P (= R_G + R_{HF})$ with ageing time, obtained from EIS measurements taken periodically during life tests at 700, 750 and 800 °C. Initial R_O values are slightly different for the three cells, presumably due to slight difference in electrolyte thickness. R_O is stable throughout the test for all three cells, suggesting that there was no electrolyte or

electrical contact degradation during the test. The initial R_P values are almost identical for the three cells, $0.11 \Omega \cdot \text{cm}^2$, indicating good electrode reproducibility. R_P increased with time and then reached a saturation value for each of the ageing temperatures, but the rates of increase were much different, with the time to saturation decreasing from ~ 500 h at 700°C to ~ 150 h at 750°C to ~ 50 h at 800°C . The R_P values increased to similar saturation values of 0.27 , 0.23 and $0.25 \Omega \cdot \text{cm}^2$ after 800 h at 700 , 750 and 800°C , respectively, with $\sim 90\%$ of the increase attributed to the increase in R_G .

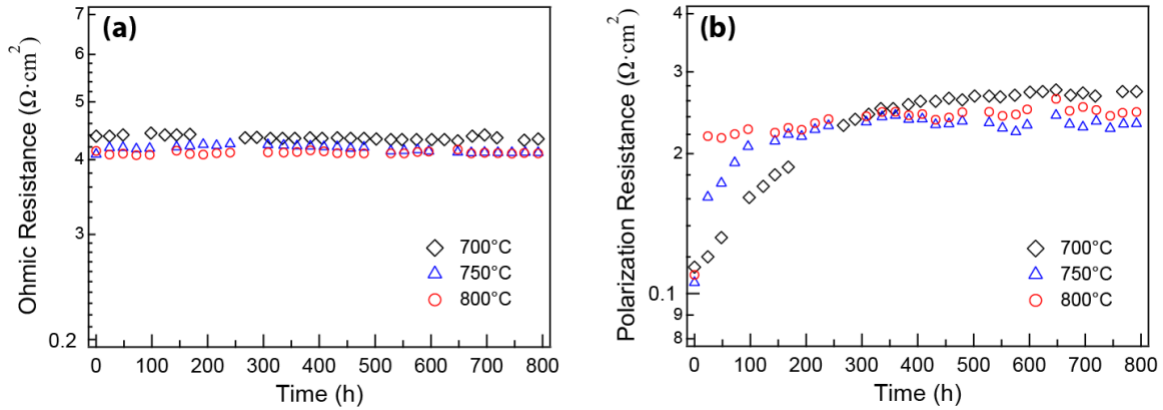


Figure 6.3. Evolution of cell ohmic resistance (a) and polarization resistance (b) with time for three identically-prepared LSCF symmetric-electrode cells during life tests at 700 , 750 and 800°C . The temperature was temporarily reduced to 700°C when taking the EIS measurements and back to the ageing temperatures afterwards. The R_O and R_P values were obtained using the intercept method, which was found to be in good agreement (deviations $< 4\%$ for R_O , $< 10\%$ for R_P) with the values obtained from the EIS fits.

6.3.2. Microstructural analysis

Figure 6.4a presents a low-magnification fracture cross-sectional SEM image of a portion of the as-prepared LSCF-electrode cell. The LSCF electrode is porous as needed to facilitate gas transport, and is $\sim 20 \mu\text{m}$ thick. The GDC electrolyte is dense, with only a few closed pores.

Higher-magnification SEM images were taken from the as-prepared and aged LSCF electrodes and were shown in Figure 6.4b-f. There is no significant change on the particle surface for cells aged at 700 and 750 °C, compared to the as-prepared sample. However, some particles forming isolated 3D islands were observed for the 800°C-800h aged cell, as indicated by arrows in Figure 6.4e. These isolated 3D islands were also present in the 950°C-800h aged electrode (Figure 6.4f), but with much lower density and smaller size. The presence of the 3D islands is likely related to surface segregated Sr and will be discussed in the later section.

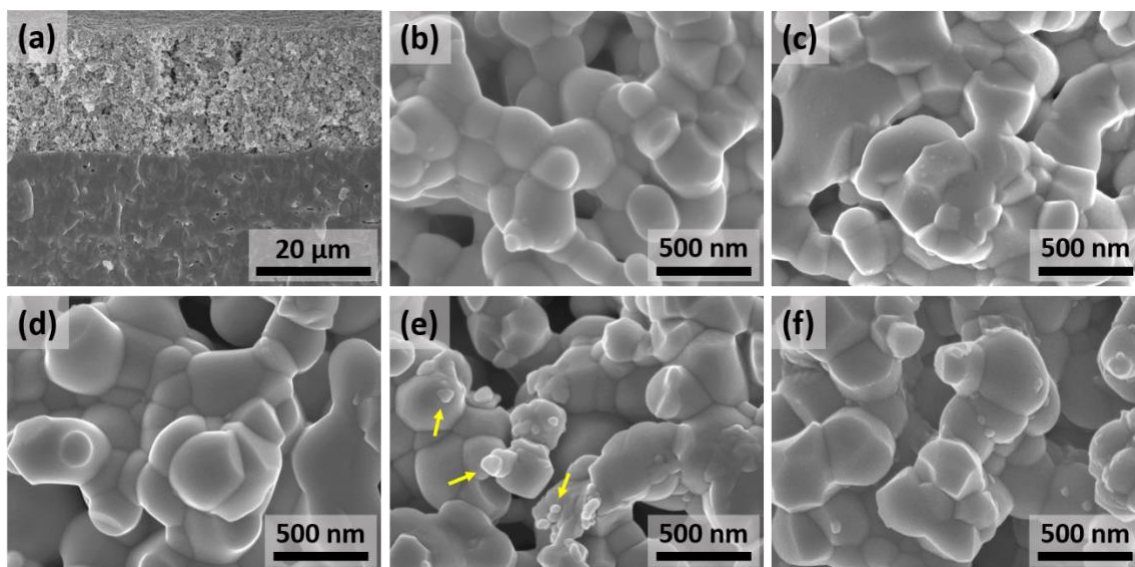


Figure 6.4. Low-magnification fracture cross-sectional SEM image of the as-prepared cell (a); and higher-magnification SEM images of the LSCF electrodes from the as-prepared (b), 700°C-800h (c), 750°C-800h (d), 800°C-800h (e) and 950°C-800h (f) cells.

Figure 6.5 shows typical 2D cross-sectional images of the FIB-milled surface from the as-prepared (a), 800°C-800h (b), and 950°C-800h (c) aged cells. The black regions are epoxy-filled pore space while the lighter areas are LSCF particles. The corresponding 3D reconstructions are also shown, with LSCF particles in green and pores transparent. Macrohomogeneous structural

parameters were obtained from the image data sets and are summarized in Table I. The changes in porosity and surface area are $\sim 2\%$ for the 800°C -800h aged electrode, well within the segmentation error.⁵⁶ Whereas there is an $\sim 15\%$ decrease in porosity, from 33.1% to 28.0%, for the electrode aged at 950°C for 800 h, suggesting particle sintering is likely present under this ageing condition. The decrease in LSCF particle surface area per unit electrode volume a is also substantial, from 3.31 to $2.50\ \mu\text{m}^{-1}$. The LSCF specific surface area a_s , which provides a more statistically relevant measure of LSCF microstructure since local porosity variations are cancelled out in dividing a by the solid volume, also shows an $\sim 30\%$ decrease, from 4.95 to $3.48\ \mu\text{m}^{-1}$, for the 950°C -800h aged electrode. The increase in average particle size, from 500 nm for the as-prepared and 800°C -800h aged sample to 620 nm for the 950°C -800h aged sample, is consistent with the surface area decrease. The solid tortuosity is close to unity, ~ 1.1 , for both as-prepared and aged samples. This is expected given the relatively high volume fraction of LSCF ($\sim 70\%$). Based on the above results, it can be concluded that LSCF particle sintering and coarsening occur at ageing temperature of 950°C , whereas there is no detectable change in microstructure upon ageing at 800°C for 800h. Hence, the measured electrochemical degradation for the LSCF electrodes aged at 700, 750 and 800°C cannot be explained by particle coarsening/sintering.

Note that there are two small regions with a darker grey contrast in the 800°C -800h aged electrode in Figure 6.5b. These were not seen in the FIB-SEM images for other conditions. EDS element mapping (not shown here) shows that these are Sr-rich. Based on prior SEM observations of Sr-rich islands on LSCF electrodes¹³³ and the SEM results shown in Figure 6.4, these are presumably SrO or another Sr-rich phase that has formed from surface segregated Sr. The volume fraction of this phase, obtained from the 3D image data, is only $\sim 0.06\%$.

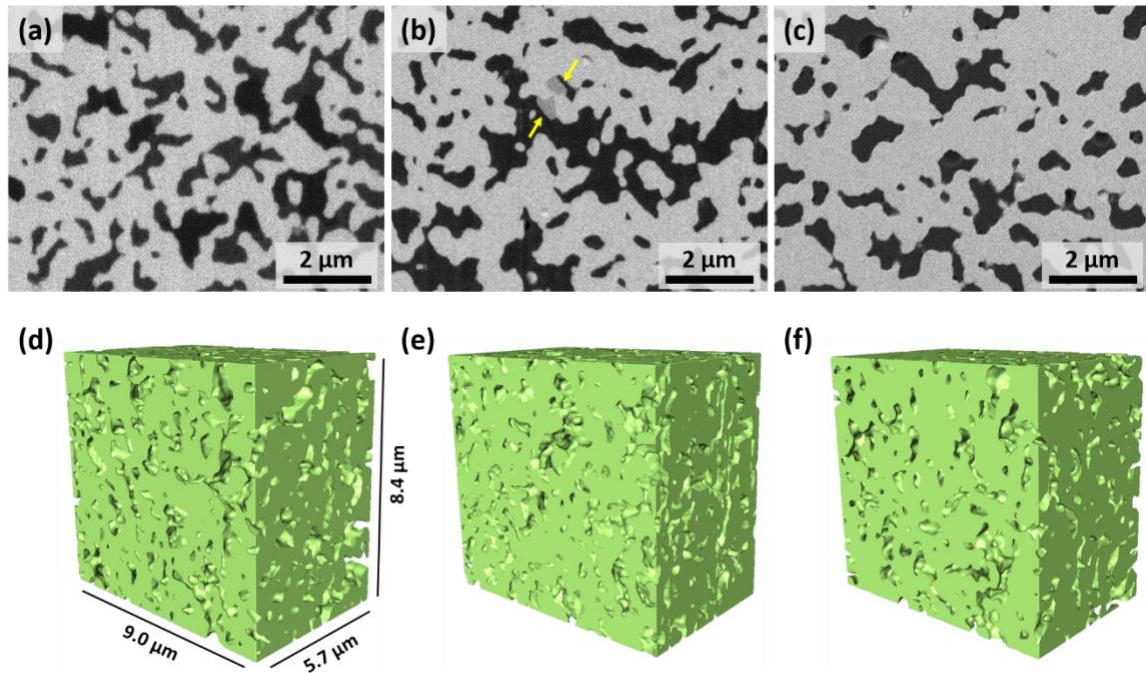


Figure 6.5. 2D micrographs (a, b, c) and the corresponding 3D reconstructions (d, e, f) from the FIB-SEM 3D data set of the as-prepared (a, d), 800°C-800h aged (b, e) and 950°C-800h aged (c, f) LSCF electrodes. The arrow in (b) indicates regions with darker grey contrast.

Table 6.1. Summary of calculated microstructural parameters for the as-prepared, 800°C-800h and 950°C-800h aged LSCF electrodes.

Microstructural Parameter	As-prepared	800°C-800h	950°C-800h
Porosity ε (%)	33.1	33.8	28.0
LSCF Surface Area a (μm^{-1})	3.31	3.35	2.50
LSCF Specific Surface Area a_s (μm^{-1})	4.95	5.05	3.48
Average Particle Size (nm)	500	500	620
LSCF Tortuosity τ	1.10	1.09	1.08

6.3.3. Sr surface segregation

6.3.3.1. ICP-OES analysis

Figure 6.6 shows the cation amounts dissolved in ultrapure water for the as-prepared and aged cells, detected by ICP-OES. The amounts were normalized to the LSCF electrode volume, obtained from the ICP-OES measured bulk LSCF in combination with 3D data given in Table 6.1. The amounts of La, Co and Fe cations were insignificant in the leaching solutions, whereas significant amounts of water-soluble Sr were detected for all samples. This is in agreement with the previous results showing the presence of a water-soluble Sr-rich layer on the surface of the LSCF particles while the bulk LSCF is insoluble in water.¹³⁴ At ageing temperatures ≤ 650 °C for 800 h, no significant increase in surface Sr was observed. Cells aged for 400-h and 1400-h at ≤ 650 °C, not shown in the figure, also exhibited no increase in segregated Sr. On the other hand, the amount of Sr increased with increasing ageing temperature above 650 °C, from $0.43 \pm 0.02 \times 10^5$ nmol/cm³ for the as-prepared cell to $0.72 \pm 0.12 \times 10^5$ nmol/cm³ for the 700°C-800h cell and $1.36 \pm 0.09 \times 10^5$ nmol/cm³ for the 750°C-800h aged cell. However, increasing the ageing temperature to 800 °C resulted in a similar surface Sr amount, $1.32 \pm 0.04 \times 10^5$ nmol/cm³, as the 750 °C aged case. Increasing the temperature to 950 °C reduced the Sr content to $0.77 \pm 0.03 \times 10^5$ nmol/cm³.

If we assume that the Sr detected by ICP-OES is in the form of SrO (prior research has shown that LSCF is primarily SrO terminated,⁶² the SrO volume fraction can be calculated. The additional y-axis scale bar on the right in Figure 6.6 indicates these amounts. The amount of SrO for the 800°C-800h electrode corresponds to ~ 0.27 vol.%. On the other hand, Sr-rich regions with

a volume fraction of $\sim 0.06\%$ were detected by FIB-SEM in the 800°C -800h aged electrode (this amount is depicted by the cross-hatched area in Figure 6.6). The difference between these amounts, $\sim 0.2 \text{ vol.}\%$, is presumably Sr either present in islands too small to be observed by FIB-SEM or as material segregated on the LSCF surface. For the other ageing conditions where no Sr-rich regions were observed by FIB-SEM, it appears that all or most of the ICP-OES-detected Sr is present in thin segregated layers on the LSCF surfaces or in very small islands.

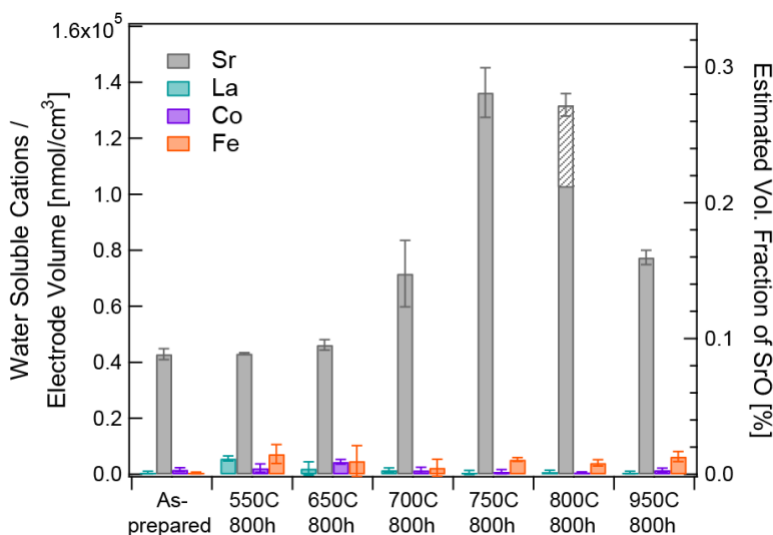


Figure 6.6. The amount of cations dissolved in ultrapure water for the as-prepared and aged cells. The detected amount was normalized by LSCF electrode volume and the error bars were calculated from standard deviation of 3 measurements. Volume fraction of SrO was estimated and shown on the additional y-axis. The cross-hatched region indicates the SrO volume detected by FIB-SEM.

In agreement with ref. ¹²⁶, we can present this additional Sr in terms of SrO layers with a SrO monolayer being defined by a dense homogenous SrO coverage with a (100) orientation (lattice parameter of 0.516 nm). The values are obtained by dividing the SrO volume fractions by the LSCF surface area values given in Table 6.1. For example, the 0.09 vol.% observed in the as-prepared electrode corresponds to a SrO thickness of 0.27 nm or 1.3 monolayer. This suggests that

the as-prepared LSCF particles are terminated by a single SrO rocksalt layer. A similar result was obtained by the same method on as-prepared LSC thin films^{68, 135} and by low energy ion scattering measurements on as-prepared LSCF thin films,¹²⁶ despite different thermal history. For conditions where some of the Sr is present in islands, such coverage values should be viewed as over-estimates.

The Sr amounts at different times during life test at 750 °C were measured and plotted in Figure 6.7. The Sr content increases with ageing time over the first 400 h, and then stays almost unchanged from 400 to 800 h. The measured Sr generally tracks the change in polarization resistance shown in Figure 6.3b, indicating that Sr segregation is the main degradation mechanism under the current ageing conditions.

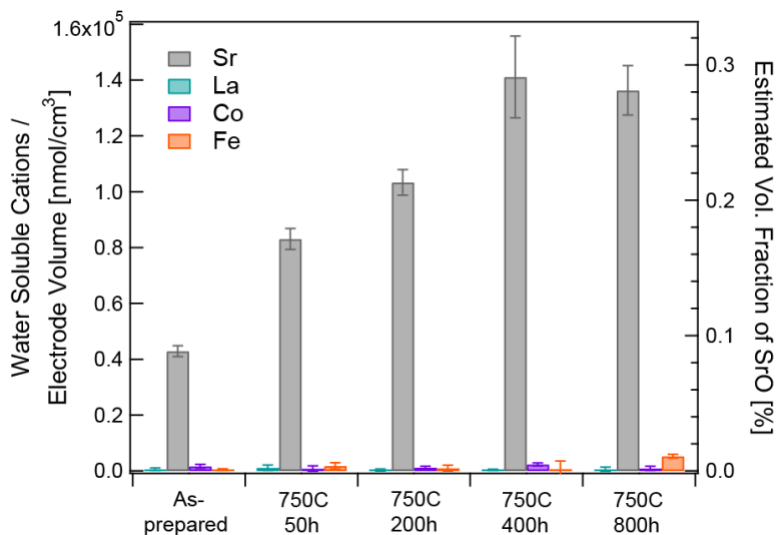


Figure 6.7. The amount of cations dissolved in ultrapure water for cells aged at 750 °C for different times.

6.3.3.2. XPS measurements

Figure 6.8 shows representative XPS spectra, in the regions where the Sr 3d peaks are observed, obtained from the as-prepared and 800°C-800h aged LSCF electrodes. The basic peak positions and intensities are similar to those reported previously for LSCF electrodes.¹³⁶ There was minor increase at the low energy satellite peak at 131.8 eV after ageing, but it is difficult to attribute this to a change in Sr surface coverage or Sr cation coordination. Measurements of the other cation peaks, not shown here, also showed peak positions and intensities similar to previous reports.¹³⁶ However, the peak intensities were inconsistent between probed X-ray spots, even on the same sample, making it impossible to observe changes in surface composition. It seems reasonable to conclude that the roughness and inhomogeneous porous electrode surface was not ideal for XPS measurements, so only the ICP-OES measurements are discussed below.

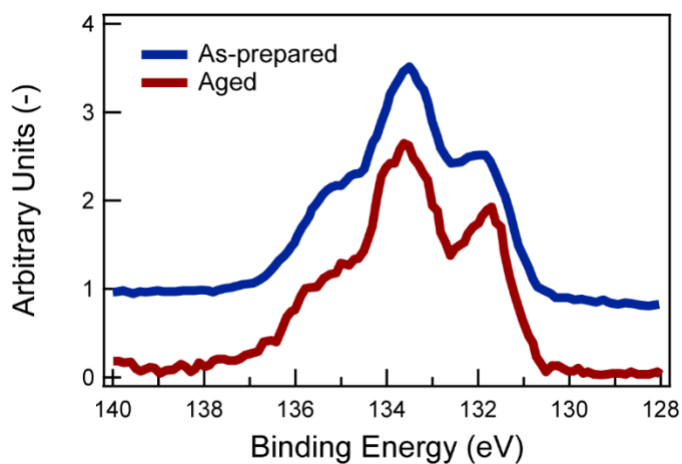


Figure 6.8. Sr 3d peaks from XPS analysis for the as-prepared and 800°C-800h LSCF electrodes.

6.4. Discussion

The above results show that there is little increase in the amount of surface Sr over 800 h at ageing temperatures ≤ 650 °C, relative to the initial amount of $0.43 \pm 0.02 \times 10^5$ nmol/cm³. Further increases in temperature up to 750 °C result in significant increases up to $1.36 \pm 0.09 \times 10^5$ nmol/cm³. That is an $\sim 220\%$ increase compared to the as-prepared electrode, but a further increase to 800 °C yields no additional increase in the Sr amount, and at 950 °C the amount is reduced to $0.77 \pm 0.03 \times 10^5$ nmol/cm³. This suggests that segregation at lower temperature is limited by kinetics, presumably related to out-diffusion of Sr from the LSCF bulk to the surface, leading to the rapid increase in final Sr content on going from 650 to 750 °C. The results also indicate that the surface Sr content increases with time during life tests, generally tracking the increase in polarization resistance. Thus, the much more rapid increase in R_P at the higher aging temperatures (Figure 6.3b) probably reflects faster Sr out-diffusion kinetics. The R_P value appears to have saturated by the end of the 800 h test at 750 °C, in accord with the saturation of the segregated Sr amount in Figure 6.7. Thus, the 0.28 vol.% SrO measured after 800 h at 750 °C, corresponding to ~ 3 monolayers of SrO, probably represents the equilibrium Sr surface segregation. If this is the case, the data suggests that the equilibrium Sr amount remains constant or even decreases slightly with increasing temperature. A decrease with increasing temperature seems reasonable given that the surface Sr amount observed after firing at 1100 °C (*i.e.*, the as-prepared electrode) is only 0.43×10^5 nmol/cm³.

The present observation of Sr-rich particles at a relatively high ageing temperature of 800 °C is in basic agreement with a prior report showing that the amount of sub-micron-sized

precipitates on LSCF after ageing at 600 °C was quite small, but increased with increasing ageing temperature up to 900 °C.¹³³ The present results generally mirror those for Sr surface segregation on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) thin films prepared by pulsed laser deposited (PLD). Cai *et al.*⁶⁶ found the phase separation of a $\text{SrO}/\text{Sr}(\text{OH})_2$ -rich structure out of the originally Sr-rich LSC surface after ageing at 600 °C, and increases with ageing time from 3 to 72 h. Similarly, Kubicek *et al.*⁶⁷ showed Sr segregation on the LSC thin film surface after thermal treatment at 600 °C for 72 h, correlated with an increase in the surface polarization resistance. The higher temperature required for Sr segregation in the present porous LSCF electrodes compared to LSC thin films is presumably a result of the different composition and different microstructure.

The ALS model was applied in order to provide more detail on how Sr surface segregation affects the oxygen reduction reaction. In this approach, the R_G and t_G values are obtained from fits to EIS data as shown, for example, in Figure 6.2. These values are given by the ALS model as:

$$R_G = \frac{RT}{4F^2} \sqrt{\frac{\tau A_0^2}{4a(1-\varepsilon)D_{chem}k_{chem}c_{mc}^2\chi_v}} (pO_2)^{-0.25} \quad [6.2]$$

$$t_G = \frac{(1-\varepsilon)\chi_v}{4ak_{chem}} (pO_2)^{-0.5} \quad [6.3]$$

where τ is the solid tortuosity, a is the pore-electrode interfacial area, and ε is the porosity, all of which were obtained in the 3D FIB-SEM measurements (Table 6.1). The oxygen concentration c_{mc} is approximated as 0.083 mol/cm³ at 700 °C for this LSCF composition.¹³⁷ Based on oxygen nonstoichiometry, the oxygen vacancy concentration χ_v and the thermodynamic factor A_0 are estimated to be 0.035 and 1.85, respectively.^{48, 50, 51} Using these values along with the R_G and t_G

values from the EIS fits, the values of k_{chem} and D_{chem} can be calculated from Eqs. [6.2] and [6.3]. The resulting values for the as-prepared and aged cells are plotted in Figure 6.9. The k_{chem} values after ageing are substantially lower than for the as-prepared electrode, in agreement with prior results.¹³⁴ It is reasonable to assume that a Sr surface segregated layer up to 3.5 monolayers thick should have a negative impact on the oxygen surface exchange process. On the other hand, the change in D_{chem} upon ageing is minor, indicating that the oxygen bulk diffusion process is less affected by the Sr surface segregation. No clear trend in k_{chem} or D_{chem} was found between the 700, 750 and 800 °C ageing temperatures, despite the different amounts of segregated Sr. Note that care must be taken in directly associating the apparent Sr surface coverage with changes in k_{chem} , because the ICP-OES measurement cannot distinguish between a uniform coverage of the LSCF surface and Sr-containing islands.⁶⁷ Segregated Sr present as isolated 3D islands is expected to have little impact on k_{chem} compared to a uniform surface coverage.⁶⁴

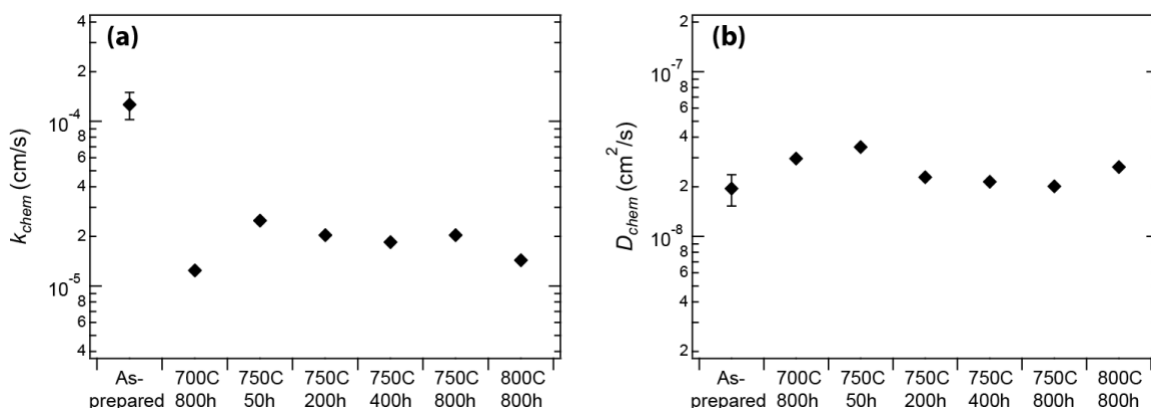


Figure 6.9. Plots of oxygen surface exchange coefficients (a) and oxygen diffusion coefficients (b) for the as-prepared and life-tested cells. The error bar of the as-prepared cell was calculated from standard deviation of the three cells used for life testing.

Table 6.2 compares the present k_{chem} and D_{chem} values with literature values. Note that the the k_{chem} values after ageing are in reasonably good agreement. The present D_{chem} values are

substantially lower than the literature value. This deviation may arise from comparing results from dense LSCF thin film^{50, 138} with the present porous LSCF electrodes.

Table 6.2. Comparison of the calculated and literature values of oxygen surface exchange and diffusion coefficients for LSCF.

	$k_{chem} \text{ (cm} \cdot \text{s}^{-1}\text{)}$	$D_{chem} \text{ (cm}^2 \cdot \text{s}^{-1}\text{)}$
Literature	1.05E-5 ¹³⁹	2.04E-6 ⁵⁰
	1.49E-6 ⁵²	6.03E-6 ¹³⁸
	1.04E-6 ¹²⁴	
This work (as-prepared)	1.26E-4	1.95E-8
This work (aged, average)	1.83E-5	2.58E-8

Coarsening of the porous LSCF structure is only observed at 950 °C, the highest temperature tested here and well above the typical temperature range, 700 – 800 °C, for operation of a SOC with LSCF electrode. However, it is unclear whether significant coarsening should be expected at these temperatures during the > 40 kh expected cell operation time. In order to estimate this, we apply a prior LSCF coarsening model developed to fit degradation results from infiltrated nano-scale electrodes.¹⁴⁰ A power-law coarsening expression is used, where the LSCF feature size l_C grows with time t from an initial size $l_{C,0}$:¹⁴¹

$$l_C^n - l_{C,0}^n = tK_{D,0} \exp\left(-\frac{E_D}{kT}\right) \quad [6.4]$$

where the power $n = 4$ is used for the case of porous materials, E_D is the cation diffusion activation energy, $K_{D,0}$ is the diffusion coefficient pre-factor, k is Boltzmann's constant, and T is the ageing temperature. Eq. [6.4] was used in a transmission line electrode model to fit measured increases in LSCF R_p values with time, yielding $K_{D,0} = 7 \times 10^{-13}$ cm/s and $E_D = 2.8$ eV.¹⁴² Using these values in Eq. [6.4] with $l_{C,0} = 500$ nm predicts an increase to $l_C = 590$ nm after 800 h at 950 °C, but only

502 nm for 800 h at 800 °C. These values are in reasonable agreement with the measured feature sizes in Table 6.1. Applying Eq. [6.4] for 800 °C over 40,000 h, a feature size increase to 600 nm is predicted, but the increase is to only 505 nm at 700 °C for 40,000 h. This model needs to be improved by comparison with more experimental data, and these predicted feature size increases are clearly approximate, but they provide a preliminary idea of the LSCF coarsening that can be expected over the full life of a solid oxide cell.

6.5. Conclusions

LSCF symmetric-electrode cells with GDC electrolytes aged at 700, 750 and 800 °C showed an increase in polarization resistance with time. LSCF particle coarsening/sintering was only observed at ageing temperature of 950 °C. For ageing at temperatures ≤ 800 °C, where there were no measurable electrode microstructural changes, the increase in polarization resistance of the LSCF electrodes is attributed mainly to an increased amount of segregated Sr. The Sr amount does not increase during ageing at temperatures ≤ 650 °C, but increases with increasing temperature from 700 °C to 750 °C. These results, along with the faster increase in the polarization resistance with increasing temperature from 700 °C to 800 °C, suggest that the segregation is limited by Sr out-diffusion kinetics. Increasing the ageing temperature from 750 to 950 °C resulted in reduced Sr segregation, suggesting that there may be an equilibrium for Sr surface segregation and the equilibrium amount decreases at high temperature. Segregated Sr appears to be present mainly in a uniform coverage of LSCF surfaces, but isolated Sr-rich islands were detected in some cases. Oxygen surface exchange rate k_{chem} and bulk diffusion coefficient D_{chem} values were determined using the ALS model based on the measured impedance response and measured microstructural parameters. k_{chem} decreased by ~ 10 times after ageing at 700 – 800 °C, with little

change in D_{chem} , suggesting that Sr surface segregation mainly hinders the oxygen surface exchange process.

6.6. Acknowledgements

The authors at Northwestern University gratefully acknowledge financial support by the Department of Energy (Grant # DE-FG02-05ER46255), which mainly supported the ageing and electrochemical testing, and the US National Science Foundation (Grant # DMR-0907639 and DMR-1506925), which mainly supported the tomography work. For collaboration on chemical analysis, the work in Vienna is financially supported by the Austrian Science Fund (FWF) project P4509-N16 and W1243-N16. The authors also acknowledge the assistance of the Electron Probe Instrumentation Center (EPIC) at the NUANCE Center-Northwestern University, which has received support from the soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. The metal analysis was performed at the Northwestern University Quantitative Bio-element Imaging Center.

Chapter 7

Effect of High-Temperature Ageing on (La,Sr)(Co,Fe)O_{3-δ} Cathodes in Microtubular Solid Oxide Fuel Cells

This work was done in direct collaboration with Dr. Hirofumi Sumi from AIST in Nagoya, Japan. All the microtubular cells were fabricated and electrochemically tested in Japan. The high-temperature ageing experiments, together with FIB-SEM 3D analysis and Sr surface segregation measurements were done at Northwestern.

7.1. Introduction

(La,Sr)(Co,Fe)O_{3-δ} (LSCF) is an important cathode material for solid oxide fuel cells (SOFCs), providing low polarization resistance R_P at temperatures well below 800 °C.³⁹ However, LSCF can be susceptible to degradation by mechanisms including reactions with YSZ electrolytes, Sr surface segregation,¹³⁴ Cr poisoning from steel stack components,⁷⁻⁹ and microstructural coarsening.^{59, 140} In the present chapter, the focus is on degradation mechanisms intrinsic to LSCF independent of the electrolyte type and the interconnect material,¹⁴³ *i.e.*, coarsening and Sr segregation. Coarsening and sintering of porous electrodes are expected at sufficiently high temperatures, long times, and small particle sizes. However, it is difficult to predict whether a given electrode will be susceptible to coarsening/sintering because of the strong dependence of coarsening rate on initial feature size. For example, coarsening of initially ~ 50-nm-diameter infiltrated LSCF to > 100 nm after ageing for ~ 1000 h at ≥ 700 °C has been shown to measurably increase R_P .^{59, 140} On the other hand, LSCF electrodes with larger feature sizes do not coarsen

measurably: *e.g.*, no coarsening was observed for LSCF with ~300 nm particle size aged for ~1000 h at up to 800 °C,^{134, 144} or for LSCF with 550 nm feature size aged for 1000 h at 600 – 900 °C.¹³⁹ In the latter study, an increase in R_P was observed after ageing at 600 and 750 °C, despite no change in microstructure;¹³⁹ this may have been due to Sr segregation, which was not tested in that study. Indeed, Sr surface segregation and increased R_P have been observed on model thin-film LSCF electrodes¹²⁶ and on LSCF porous electrodes.^{134, 144} More results on LSCF electrodes with different feature sizes are needed to understand the respective roles of coarsening and Sr segregation on electrode stability.

Here we present results on LSCF cathodes on tubular SOFCs with ageing at 700 – 1000 °C for up to 700 h. Since these cells are projected to operate at temperature ≤ 600 °C,¹⁴⁵ these higher temperatures are expected to accelerate degradation. The cells utilize GDC electrolytes, so there is no issue with LSCF/YSZ reactions. No Cr was present during the ageing experiments, in order to avoid Cr poisoning and thereby focus on the segregation and coarsening/sintering effects. EIS data taken before and after ageing under various conditions is analyzed using distribution of relaxation time methods to isolate the cathode response. 3D tomographic measurements and Sr surface segregation measurements on as-prepared and aged cells are used to understand the effects of ageing on LSCF electrochemical performance. The fabrication and EIS measurement of the tubular cells were performed by Dr. Hirofumi Sumi from AIST in Japan.

7.2. Experimental Procedures

7.2.1. Sample preparation

Anode microtubes were made from NiO (Sumitomo Metal Mining), $(\text{Ce}_{0.9}\text{Gd}_{0.1})\text{O}_{1.95}$ (GDC; Anan Kasei), pore former (acrylic resin; Sekisui Plastic) and binder (Cellulose; Yuken Kogyo) powders. The weight ratio of NiO to GDC was 6:4. A pore former of acrylic resin with a grain size of ca. 5 μm was added before sintering to increase anode porosity. These powders were mixed mechanically for 2 h in a kneading machine with the proper amount of water added. The anode microtubes were extruded using a piston cylinder with a metal hole of 2.4 mm (outside diameter) and 2.0 mm (inside diameter). After extrusion, the tubes were dried overnight in air at room temperature. An electrolyte slurry was prepared by mixing GDC, a binder (polyvinyl butyral; Sekisui Chemical), a dispersant (tallow propylene diamine; Kao) and a plasticizer (dioctyl adipate; Wako Pure Chemical Industries) into ethanol and toluene solvents for 48 h. The GDC electrolyte was formed by dip-coating. The GDC thin-film electrolyte and NiO anode microtube were co-sintered in air 3 h at 1450 °C. The $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF; Kusaka Rare Metal) cathode was coated by a similar manner. The cathode thin-film layers were sintered sequentially in air for 1 h at 1050 °C. The outside diameter of microtube was 1.8 mm, and the cathode length was 10 mm after sintering. The thickness of the anode, electrolyte and cathode were ca. 200, 5, and 20 μm , respectively.

7.2.2. Cell ageing and electrochemical evaluation

Cells were aged at 700, 800, 900 and 1000 °C in a tube furnace exposed to ambient air. Two ageing times, 300 and 700 h, were used at each temperature. An as-prepared cell was used as

a reference sample, for comparison with the aged cells. The characteristics of power generation and AC impedance were evaluated with a potentiostat/galvanostat and an impedance analyzer (Bio-Logic Science Instruments VSP). A silver wire was used as a current collector on the LSCF cathode. A mixture of $\text{H}_2:\text{H}_2\text{O}:\text{N}_2 = 20:3:77$ was supplied as fuel at a flow rate of 100 mL/min to the anode side, and a mixture of $\text{O}_2:\text{N}_2 = 21:79$ was supplied as oxidant at 100 mL/min to the cathode side. The operating temperature was 550 °C. Current-voltage (i-V) characteristics were measured from OCV to 0.4 V at a sweep rate of 5 mV/s. The AC impedance was measured at OCV in the frequency range from 1 MHz to 0.1 Hz with 20 steps per logarithmic decade. The distribution of relaxation time (DRT) analysis was done as described in detail in Refs.¹⁴⁵⁻¹⁴⁸. The polarization processes are considered as an equivalent circuit composing an infinite series connection of parallel RC elements. The inductance components were removed by the same method as described in Ref.¹⁴⁵ before DRT analysis for the impedance spectra in this study. The software package FTIKREG¹⁴⁹ was used to solve an ill-posed inverse problem in DRT analysis by Tikhonov regularization.

7.2.3. Microstructural measurements

The microstructure of the as-prepared and aged cells was analyzed by FIB-SEM 3D tomography. The procedures are as described in Section 7.2.3.

7.2.4. Chemical characterization

The Sr surface segregation was quantified by ICP-OES. The procedures are as described in Section 7.2.4.

7.3. Results & Discussion

7.3.1. Electrochemical properties of LSCF cathodes

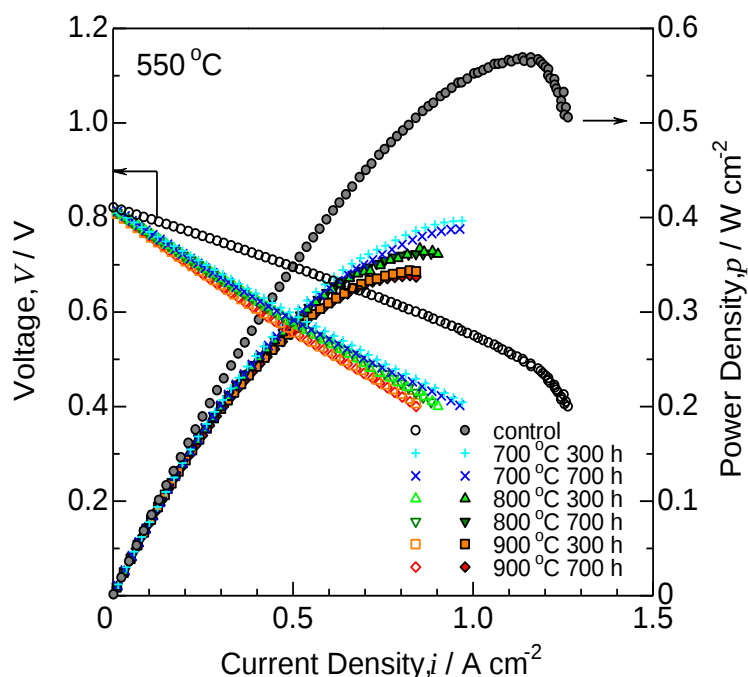


Figure 7.1. Voltage and power density versus current density measured at 550 °C for the control and aged microtubular cells.

Figure 7.1 shows the current-voltage and power characteristics at 550 °C for the control and aged microtubular cells. The OCV was 0.82 V for all cells, lower than the theoretical values derived from Nernst equation due to current leakage in the GDC electrolyte. The maximum power density for the control cell, 0.57 Wcm⁻², decreased to 0.39, 0.36, and 0.34 Wcm⁻² for the cells aged at 700, 800 and 900 °C, respectively. At each temperature, increasing the ageing time from 300 to 700 h yielded only a very small decrease in power density. There appears to be a significant concentration loss for the control sample (aged samples didn't show limiting current at the testing current range), which is presumably due to testing under low H₂ partial pressure, *i.e.*, 0.2 atm.

Figure 7.2 shows the Nyquist plot of AC impedance at 550 °C for the control and aged microtubular cells measured at OCV. The ohmic loss for the aged samples was slightly larger than that for the control sample. There was a substantial increase in the polarization resistance after ageing that increased with increasing ageing temperature. As shown in the Bode plot in Figure 7.3a, this was due to significant increases in the impedance responses at frequencies < 10 Hz and at ~ 100 Hz after ageing. Note that ageing at 1000 °C damaged the cell structure to a point where no electrochemical measurement results could be obtained.

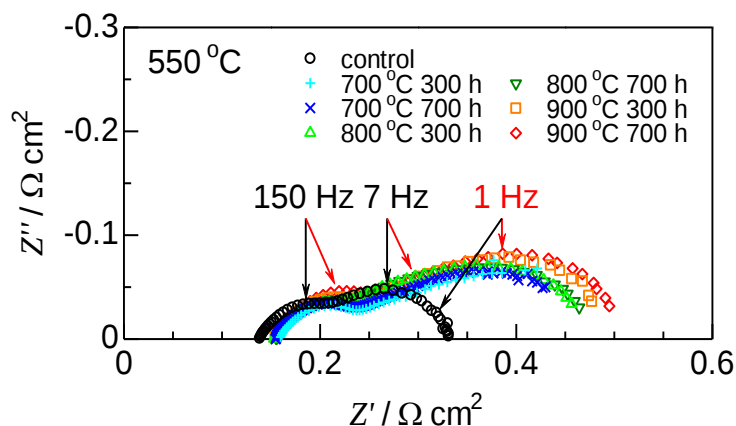


Figure 7.2. Nyquist plot of AC impedance measured between the anode and cathode under OCV at 550 °C for the control and aged microtubular cells.

DRT analysis was applied to this impedance data to separate each response – the results are shown in Figure 7.3b. Three large peaks were detected at 0.1 – 100 Hz by the DRT analysis for all samples. The small DRT peak around 1 kHz (P_1^a) was ascribed to the fuel oxidation process on the anode for microtubular cells.^{145, 150} On the other hand, we confirmed by another experiment that the DRT peak around 7 Hz (P_1^d) increased with decreasing hydrogen concentration in the anode.¹⁴⁵ This peak is ascribed to gas diffusion process for anode-supported cells. After ageing, the DRT peak around 1 Hz (P_2^d) appeared. This peak is also related to gas diffusion with

consideration of frequency. Thus, the increase in impedance at ~ 1 Hz is presumably caused by a change in the anode morphology during ageing. It was previously confirmed that the impedance at 1-10 Hz varied by a change of anode porosity for microtubular cells.¹⁴⁵ The large response at these frequencies confirms that the concentration loss present in Figure 1 mainly comes from the gas diffusion limitations in the anode. However, since the focus of this study is the LSCF cathode, not the anode, this is not discussed further here.

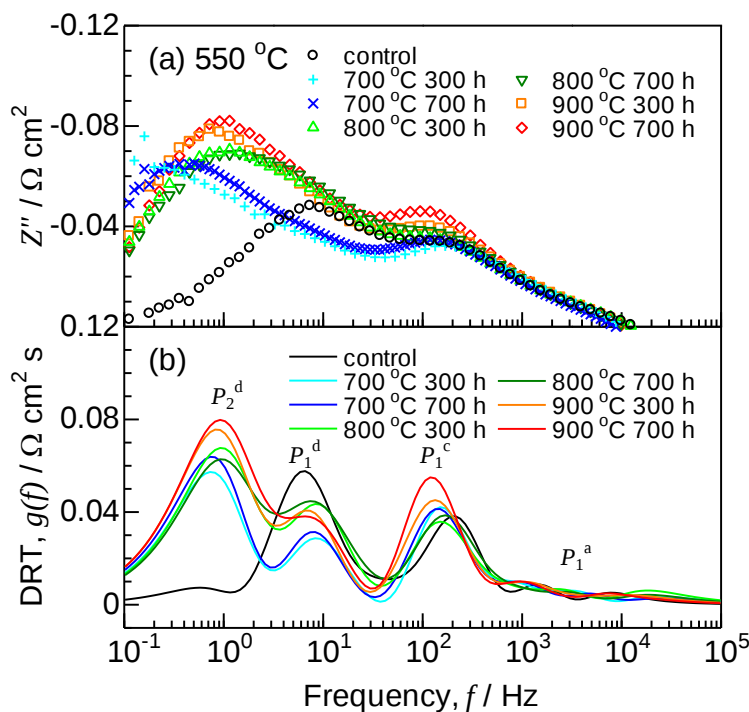


Figure 7.3. Bode plot of AC impedance and DRT spectra at 550 °C for the control and aged microtubular cells.

The peak around 100 Hz (P_1^c) was ascribed to the oxygen reduction reaction on the LSCF electrode.^{36, 37} In this study, we focus on the chemical resistance (R_{chem}) and time constant (t_{chem}) of P_1^c . Prior studies in the literature have shown that the impedance of porous mixed-conducting

cathodes with fast electronic transport, such as LSCF, is co-limited by the oxygen surface exchange and solid-state oxygen ion diffusion processes, and can be expressed as^{36, 37}

$$Z_G = \frac{R_{chem}}{\sqrt{1 + j\omega t_{chem}}} \quad [7.1]$$

Figure 7.4 shows the R_{chem} and t_{chem} of P_1^c derived by fitting as a Gerischer impedance. Both R_{chem} and t_{chem} increased after ageing. The values of R_{chem} for the samples aged at 900 °C were larger than those at 700 and 800 °C, while the values of t_{chem} was independent on the ageing temperature from 700 to 900 °C.

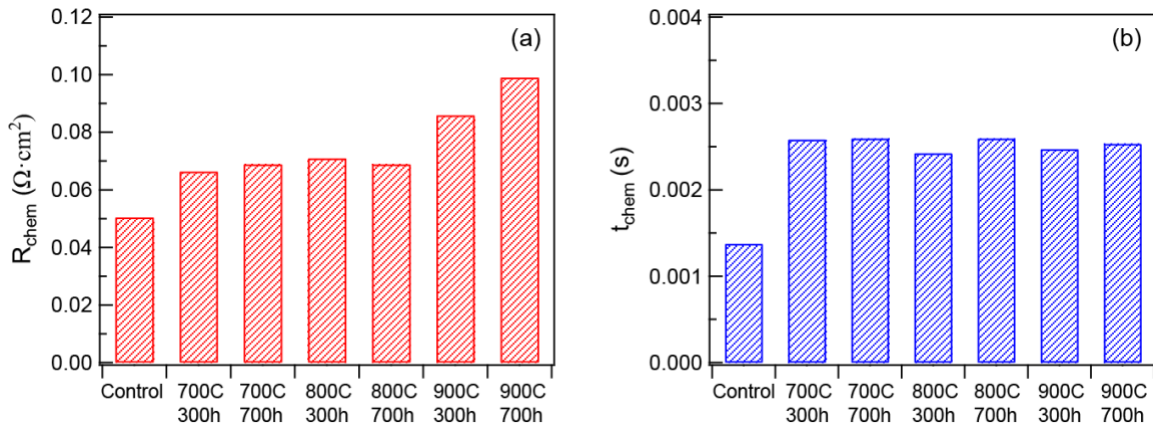


Figure 7.4. Chemical resistance (a) and time constant (b) of P_1^c for the control and aged microtubular cells.

7.3.2. SEM and FIB-SEM observation of LSCF cathodes

Figures 7.5a and b show the low-magnification fracture cross-sectional SEM images of the control and 800C-700h cells. The GDC electrolytes are dense enough to ensure gas tight. The LSCF cathode porosity is from partial sintering, while the porosity of the Ni-GDC anodes is provided by pore former and NiO reduction. No clear changes were observed between the control

and the aged samples. Higher-magnification SEM images of the corresponding LSCF cathodes are shown in Figures 7.5c and d. There are some finer particles deposited on the 800C-700h aged LSCF surface. However, they are too small and appear as nano-scale particles covering the larger LSCF particle, so that EDS cannot confirm whether they are Sr-rich particles.

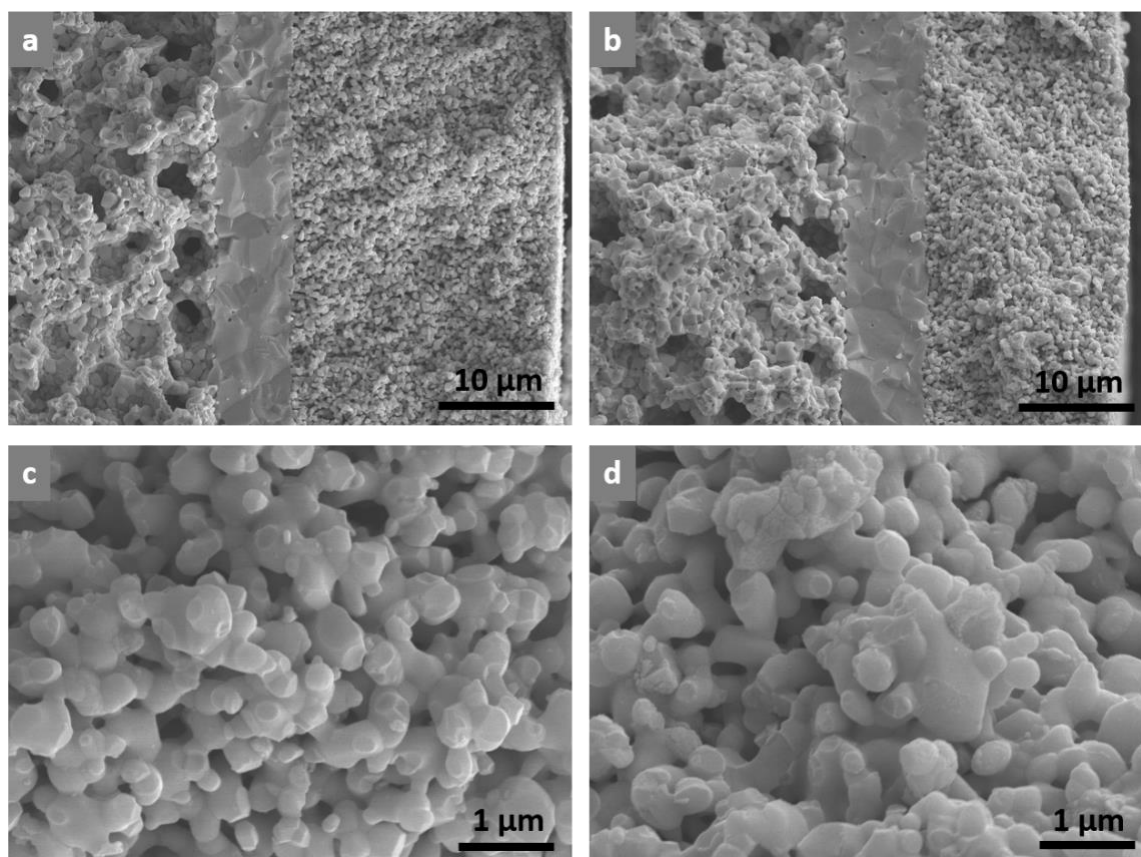


Figure 7.5. Low-magnification fracture cross-sectional SEM images of the control (a) and 800C-700h aged (b) cells; and higher-magnification SEM images of the LSCF cathodes of the control (c) and 800C-700h (d) cells.

Figure 7.6 presents 2D FIB-SEM cross-sectional images from the control and aged LSCF electrodes. Only the 700 h samples are shown here, since the 300 h samples have similar structure. The lighter contrast particles are identified as LSCF, whereas the darker contrast indicates pore. It

can be clearly seen that the LSCF particles of the sample aged at 1000 °C for 700 h have significantly larger size relative to the others, indicating substantial coarsening of LSCF at this temperature. Regions with intermediate grey contrast, indicated by white arrows, are apparent in the 800C-700h and 900C-700h images, suggesting that another phase is present. These are not seen in the 700C-700h image. EDS element mapping, conducted on the area indicated in Figure 7.6d and shown in Figure 7.6f, shows that the third phase contains primarily Sr.

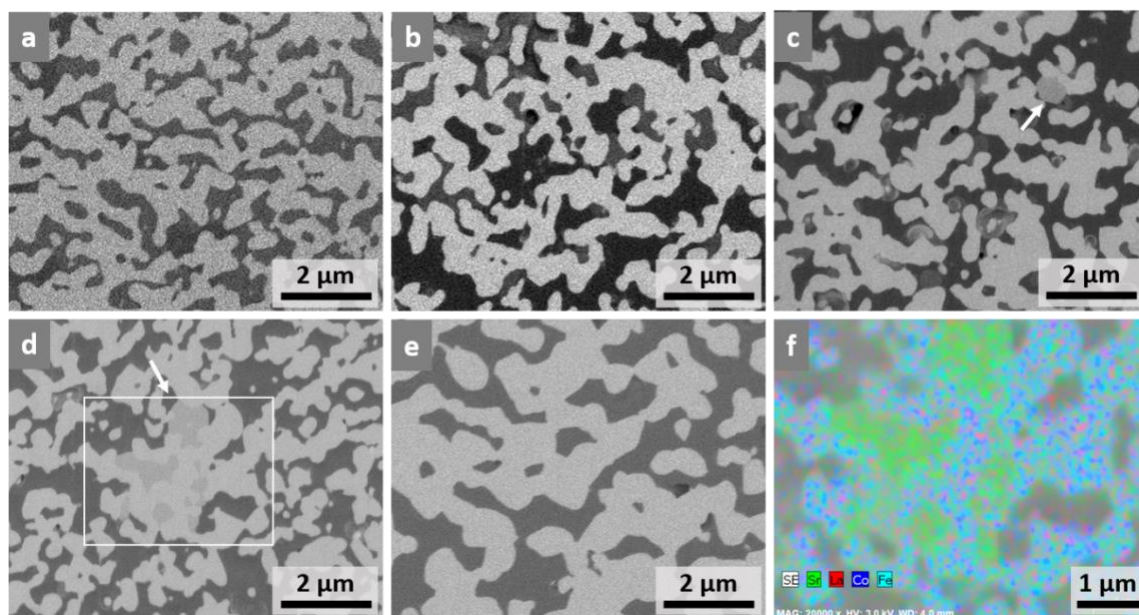


Figure 7.6. SEM images of the control (a), 700C-700h (b), 800C-700h (c), 900C-700h (d) and 1000C-700h (e) aged LSCF electrodes. (f) EDS element mapping of the boxed area shown in (d).

The macrohomogeneous microstructural parameters obtained from the 3D image data are summarized and plotted in Figure 7.7. The error bars were calculated based on the 5% accuracy expected for 3D FIB-SEM data.⁵⁶ Note that 2% accuracy was used in the error calculation for tortuosity, since it is less sensitive to experimental and segmentation errors. The porosity ε varied between 36 and 43% for all cathodes; while this variation is slightly greater than the 5% accuracy,

it is difficult to establish any meaningful trend. The decrease in ϵ with increasing ageing temperature might indicate sintering, but the trend is much less clear for 300 versus 700 h ageing. The lower porosity of the as-prepared electrode is difficult to explain by any reasonable mechanism, and so it is attributed to experimental errors. Tortuosity was calculated for both LSCF and pore phases from the 3D image data using the method described in Ref.⁸². As shown in Figure 7.7b, tortuosity values followed the trend expected, *i.e.*, decreasing with increasing phase volume fraction. Thus tortuosity was lower, ~ 1.1 , for LSCF (~ 60 % volume fraction) compared to ~ 1.2 for the pore phase (~ 40 % volume fraction). The LSCF surface area per unit electrode volume a_v , shown in Figure 7.7c, decreased by > 30 % for 1000C-300h and 1000C-700h samples, respectively, indicating LSCF coarsening likely occurred under these ageing conditions. The LSCF specific surface area a , shown in Figure 7.7d, provides a more statistically relevant measure of LSCF microstructure since local porosity variations are cancelled out in dividing a_v by the solid volume.¹³⁴ There is also a clear decrease in a after ageing at 1000 °C. Although there appears to also be smaller decreases in a_v and a with increasing ageing temperature below 1000 °C, at least for the 700 h case, it is difficult to be sure of this trend given experimental errors.⁵⁶

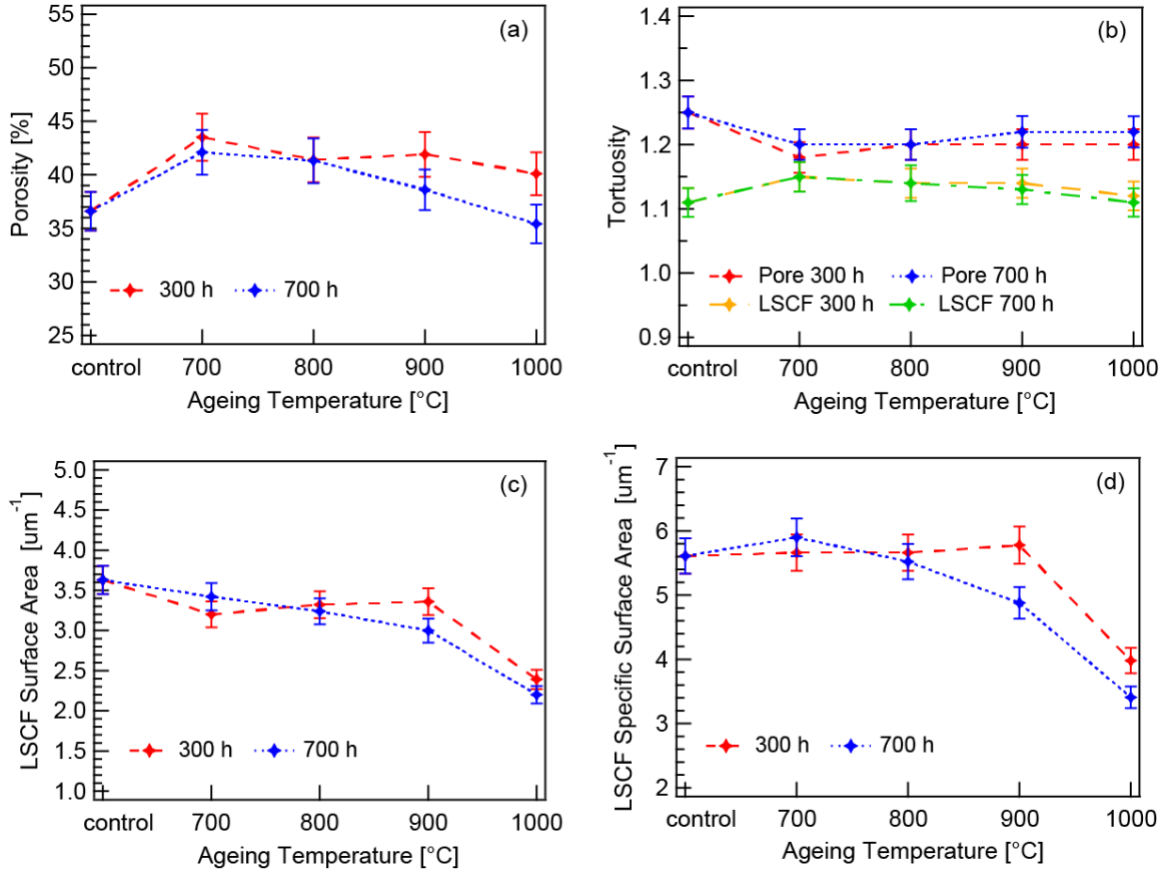


Figure 7.7. Porosity (a), pore and LSCF phase tortuosity (b), LSCF surface area per unit electrode volume (c), and LSCF specific surface area (d), versus temperature for cells aged for 300 and 700h, determined from measured 3D structural data.

Figure 7.8 shows the LSCF feature size distributions, calculated using the method reported by Holzer.⁷⁸ LSCF particles grew measurably only after ageing at the highest temperature, 1000 °C, and further increased in size with increasing ageing time from 300 to 700 h, which is in good agreement with the observed changes in LSCF specific surface area. The 900C-700h sample did not show change in average particle size relative to the control sample, but had slightly increased volume fraction at ~ 1150 nm. Again, these large particles are likely due to treating Sr-rich phase as LSCF particles during segmentation. Based on the above results, it can be concluded that the

LSCF did not coarsen significantly at ≤ 900 °C, consistent with the surface area results in Figure 7.7.

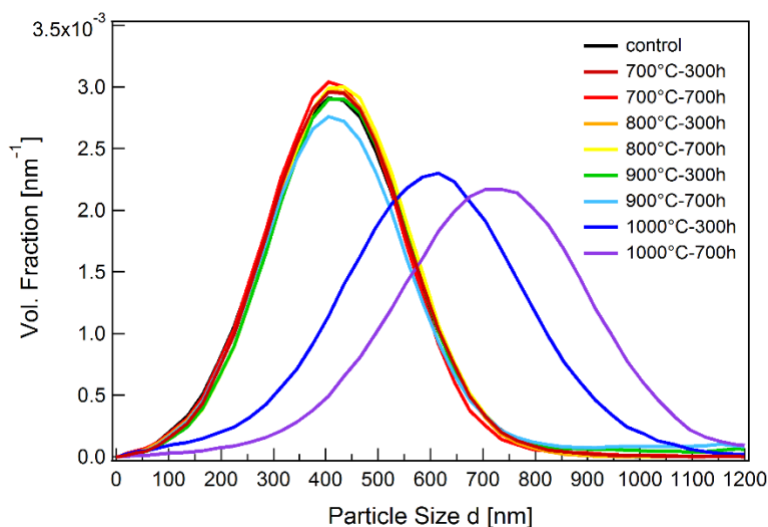


Figure 7.8. LSCF particle size distributions calculated from 3D tomographic images.

7.3.3. ICP-OES analysis of LSCF cathodes

Figure 7.9a shows the amount of Sr dissolved in ultrapure water for the control and aged cells, detected by ICP-OES, normalized to the measured electrode volume. Previous results show that only Sr-rich surface layers or phases are water-soluble, while the bulk LSCF is insoluble in water,^{68, 134} so the detected Sr amount can be used as a measure of the total amount of surface segregated Sr and the Sr-rich phase. The amount of Sr increased with increasing ageing time and temperature up to 900 °C, from $0.28 \pm 0.03 \times 10^5$ nmol/cm³ for the control sample to $1.28 \pm 0.17 \times 10^5$ nmol/cm³ for the 900C-700h cell. However, increasing the ageing temperature from 900 to 1000 °C resulted in much smaller surface Sr amount, $0.45 \pm 0.02 \times 10^5$ nmol/cm³ for the 300 h cell and $0.52 \pm 0.02 \times 10^5$ nmol/cm³ for the 700 h cell. It is plausible that this high ageing

temperature suppresses the Sr surface segregation, an explanation that is consistent with the low surface Sr amount observed for the control sample, which was fired at 1050 °C. It is estimated that most of the Sr detected was segregated on LSCF surfaces, versus in Sr-rich particles. Using this and assuming that the segregated phase is a dense homogeneous SrO coverage with a (100) orientation, the nominal SrO monolayer (ML) coverage increases from ~ 0.8 ML for the control electrode up to ~ 3.5 ML for 900C-700h aged electrode, but decreases to ~ 1.9 ML for 1000C-700h electrode (Figure 7.9b).

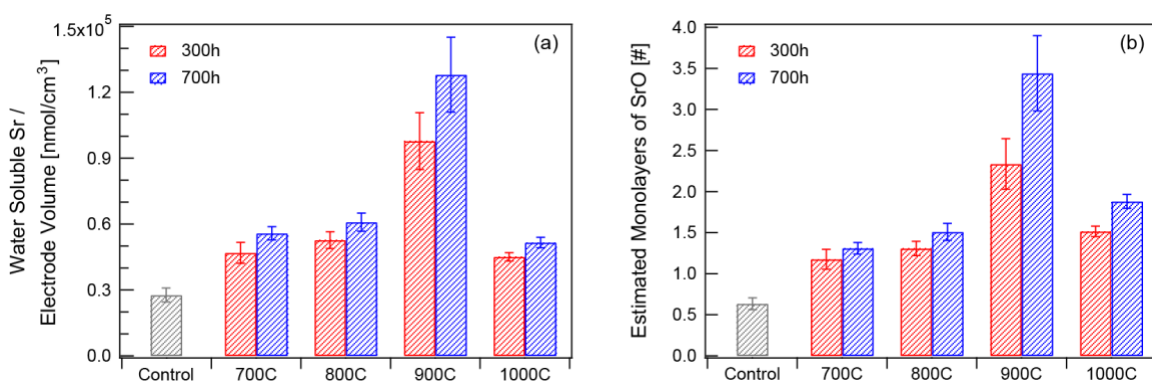


Figure 7.9. (a) The amount of Sr dissolved in ultrapure water for the control and aged cells normalized to the measured electrode volume. (b) The corresponding nominal number of SrO monolayers estimated assuming dense homogeneous SrO coverage with a (100) orientation. The error bars were calculated from standard deviation of 3 measurements.

7.3.4. ALS model prediction

Based on the electrochemical and microstructural data, the ALS model was applied to examine the effect of ageing on the oxygen reduction reaction. The values of R_{chem} and t_{chem} are related to the microstructural, thermodynamic and kinetic properties of the electrode

$$R_{chem} = \left(\frac{RT}{4F^2} \right) \sqrt{\frac{\tau_s A_0^2}{4a_v(1-\varepsilon)k_{chem}D_{chem}c_{mc}^2\chi_v}} (pO_2)^{-0.25} \quad [7.2]$$

$$t_{chem} = \frac{(1-\varepsilon)\chi_v}{4a_vk_{chem}} (pO_2)^{-0.5} \quad [7.3]$$

where τ_s , ε , and a_v are given in Figure 7.7. The oxygen lattice site concentration c_{mc} , oxygen vacancy fraction χ_v , and thermodynamic enhancement factor A_0 for this LSCF composition at operating temperature of 550 °C are found in the literature to be 0.083 mol/cm³, 0.0037, and 1.11, respectively.^{48, 49, 151} With the values of these parameters known, and R_{chem} and t_{chem} values obtained from the DRT analysis, the oxygen surface exchange coefficient k_{chem} and oxygen bulk diffusion coefficient D_{chem} were obtained, and are shown in Figure 7.10.

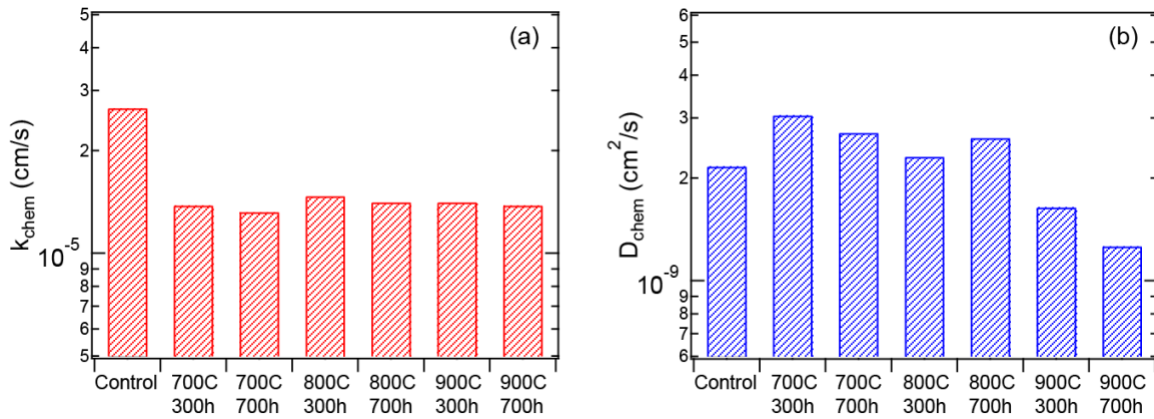


Figure 7.10. Surface exchange (a) and oxygen diffusion (b) coefficients for the control and aged microtubular cells.

The k_{chem} values after ageing are substantially lower than for the control sample, indicating that the Sr surface segregation inhibited the oxygen surface exchange. However, there is no clear trend in k_{chem} between 700, 800 and 900 °C ageing temperatures. Although increase in Sr surface

segregation with temperature and time has been observed by ICP-OES measurement, it cannot be directly associated with the change in k_{chem} , as the measurement cannot distinguish between a uniform coverage of the LSCF surface and Sr-rich 3D islands. The isolated 3D islands, which were observed for samples aged at 800 and 900 °C, are expected to have little impact on k_{chem} . On the other hand, the change in D_{chem} is small for samples aged below 900 °C, indicating that Sr surface segregation has relatively small impact on the oxygen diffusion process. However, D_{chem} decreases with ageing time for samples aged at 900 °C. This might be due to change in the LSCF composition resulted from Sr surface segregation, given the slightly increased La/Sr ratio measured by ICP-OES. Comparison with Figure 7.4 shows that the R_{chem} increase after ageing at 700 – 800 °C was mainly due to the decrease in k_{chem} , whereas the further increase at 900 °C was due to the decrease in D_{chem} .

7.4. Conclusions

Microtubular SOFCs with LSCF cathodes were aged at elevated temperatures ranging from 700 to 1000 °C, for 300 and 700 h. EIS measurements with DRT analysis revealed a response associated with co-limiting oxygen surface exchange and oxygen diffusion processes in the LSCF cathode. The chemical resistance and time constant associated with this response increased after ageing. 3D tomographic measurements done by FIB-SEM serial sectioning indicated that the LSCF surface area did not decrease significantly until ageing temperatures were increased above 900 °C, such that LSCF coarsening cannot be used to explain the observed increase in chemical resistance. The EIS data, analyzed using the ALS model together with measured microstructural data, indicate that ageing under any condition decreases the oxygen surface exchange coefficient by a factor of ~ 2 , whereas the oxygen diffusion coefficient decreased only for 900 °C ageing. Sr

surface segregation, measured by a chemical etching technique, increased with increasing ageing temperature up to 900 °C, but decreased with further increase in temperature to 1000 °C. The segregated Sr was present mainly as a thin layer covering LSCF surfaces, with a smaller amount present as Sr-rich particles. Thus, Sr surface segregation appears to be the primary mechanism causing degradation of LSCF electrodes. However, the polarization resistance increase does not correlate directly with the amount of Sr detected by ICP-OES, perhaps because it measures both surface Sr that directly impacts surface exchange, and Sr-rich particles that do not.

7.5. Acknowledgements

Special thanks to Dr. Jürgen Fleig and Dr. Ghislain M. Rupp for development of the chemical etching method for measuring Sr surface segregation. The work was supported in part by Minister of Economy, Trade and Industry, under the Japan–U.S. Cooperation Project for Research and Standardization of Clean Energy Technologies. The authors at Northwestern gratefully acknowledge financial support from the National Science Foundation under grant Number DMR-1506925. The FIB-SEM tomography data was collected at the Electron Probe Instrumentation Center (EPIC) at the NUANCE Center-Northwestern University, which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); and the State of Illinois, through the IIN.

Chapter 8

Degradation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ Oxygen Electrodes on $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$

Electrolytes during Reversing Current Operation

This work was done in collaboration with Dr. Justin Railsback. The cell fabrication, life testing, and SEM/EDS analysis were performed by Dr. Justin Railsback.

8.1. Introduction

Reversible solid oxide cells (ReSOCs) are a promising technology for large scale energy storage, needed to stabilize the electrical grid against fluctuations introduced by an increasing fraction of renewables in the electricity supply.¹⁵²⁻¹⁵⁴ Good long-term durability is a critical issue for the economic viability of ReSOC technology, but little is known about the effects of current switching operation. Previous work has focused on LSM-YSZ oxygen electrodes,¹⁵⁵⁻¹⁵⁷ where degradation at the electrode-electrolyte interface leading to cracking and delamination has been observed. A similar mechanism is observed during DC electrolysis, although degradation is more rapid than in current switching.^{156, 158} Degradation rates $\lesssim 1\%/ \text{hr}$ have been reported during reversing current operation for LSM-YSZ, but only for low current density/overpotential¹⁵⁵ or for current switching with very low electrolysis duty fraction.¹⁵⁸ Thus, it is important to determine whether other oxygen electrode materials can provide low degradation rates at higher current density j than LSM-YSZ. Furthermore, energy storage involving co-electrolysis is predicted to be substantially more efficient and economical if the ReSOC operates at lower operating temperatures,^{152, 153} so low temperature electrodes are of particular interest.

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSCF) has been under intense investigation for solid oxide fuel cell cathode applications.³⁹ LSCF is typically implemented in cells with YSZ electrolytes, with $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ (GDC) barrier layers used to reduce LSCF-YSZ interactions.^{93, 94} The durability of LSCF oxygen electrodes under current switching operation has not been reported previously, except for a short (total 72 hours) test¹⁵⁹ which showed some degradation that was attributed to the LSCF electrode. DC electrolysis operation of cells with LSCF electrodes has been studied¹⁶⁰⁻¹⁶⁴ and, given the general similarity of degradation during current switching and DC electrolysis, these latter results are discussed briefly here. DC electrolysis degradation has been mainly attributed to mechanisms similar to those occurring during fuel cell operation – diffusion of Sr or Co through the GDC barrier layer to the underlying YSZ electrolyte allowing zirconate formation reactions,^{162, 164} or a phase change in the resulting Sr and Co depleted LSCF.¹⁶⁰ Sr surface segregation has also been reported to impair LSCF electrode performance during fuel cell operation,^{39, 134} but it is not known if a similar effect occurs during electrolysis. In one report of LSCF on YSZ, degradation during electrolysis occurred by the delamination mechanism commonly seen in LSM-YSZ electrodes, but the effect was minimized with an added GDC interlayer.¹⁶⁰ There are no reports that systematically compare the effect of j or overpotential η on either electrolysis or current switching degradation of LSCF electrodes.

Here we present life tests on symmetric LSCF/GDC/LSCF cells operating under current switching, showing the effect of varied j and η on degradation. This is the first detailed study of LSCF electrode degradation during current switching, to our knowledge. As discussed previously,^{155, 156} symmetric cells have the advantage of isolating degradation of the oxygen electrode, without the need to deconvolute from a fuel electrode. These cells further focus on

degradation in the LSCF and the LSCF/GDC interface; since there is no YSZ electrolyte, the Co and Sr diffusion/reactions noted above are eliminated. Microstructural evaluation is presented and compared with the electrochemical degradation in order to provide insights into the nature of the degradation mechanisms.

8.2. Experimental Procedures

8.2.1. Cell fabrication

GDC was pressed into 0.5 g, 19 mm diameter pellets and sintered at 1450 °C for 6 hours. Commercial $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSCF) powder was mixed with Heraeus V-737 in a 1:1.18 ratio on a three roll mill and screen printed on both sides of the sintered pellets. The symmetric cells were then fired at 1100 °C for 2 hours resulting in an electrode thickness of $\sim 40 \mu\text{m}$.

8.2.2. EIS measurements and fitting

Electrical contacts to both electrodes were made with porous 0.4-cm-diameter $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) pellets. A paste composed of LSM and Heraeus V-373 was used to affix the LSM pellet to the electrode, and a weight of $\sim 20 \text{ g}$ provided a contact force. The LSM pellets avoid possible contamination effects associated with precious-metal¹⁶⁵ or steel¹⁶⁶ connections. A LabView controlled Keithley sourcemeter abruptly switched the current with a 12-h cycle period, with the current density j maintained equal and opposite for 6 h in each direction, with j values ranging from 0.7 - 1.5 A/cm². The sourcemeter was disconnected periodically (approximately every 24 h) for $\sim 15 \text{ min}$, during which time impedance spectra were collected using a Zahner IM6 workstation in the frequency range of 10^5 - 10^{-1} Hz . ZView software was used to fit the data using

L-R-RQ-G equivalent circuits, in order to separate the ohmic and polarization resistance contributions.

In the following, we use a definition of degradation rate for reversing current operation that is similar to that usually used for constant current operation: the time rate of change in cell operating voltage V normalized to V , $(1/V)(dV/dt)$.^{161, 163} In general, $V = V_{OC} \pm \eta_T$, where V_{OC} is the open circuit potential, η_T is the total cell overpotential, and the “-” sign represents fuel cell mode and the “+” sign electrolysis mode. If V_{OC} is constant, as expected for a good cell, then $dV/dt = \pm d\eta_T/dt$ and the degradation rate can be written as:

$$\frac{1}{V} \frac{dV}{dt} = \pm \frac{1}{V_{OC} \pm \eta_T} \frac{d\eta_T}{dt} \quad [8.1]$$

where the first $\pm$ signifies that degradation increases the voltage in electrolysis, and decreases the voltage in fuel cell mode. Note that in Eq. [8.1], a given $d\eta_T/dt$ yields a lower degradation rate magnitude for the electrolysis operating voltage $V_{OC} + \eta_T$ and a higher degradation rate for the fuel cell operating voltage $V_{OC} - \eta_T$. Thus, for reversing current operation it seems reasonable to report the degradation rate as:

$$\frac{1}{V} \frac{dV}{dt} \approx \pm \frac{1}{V_{OC}} \frac{d\eta_T}{dt} \quad [8.2]$$

Which gives an average of the electrolysis and fuel cell degradation rates.

Eq. [8.2] is used below to provide degradation rates that are relevant to full cells; the $d\eta_T/dt$ values measured from the present symmetric cells should correlate well with similar electrodes in full cells. However, the present degradation rates are only for the oxygen electrode-electrolyte

combination. The degradation rates reported below assume a typical full-cell $V_{OC} = 1.0$ V. The aim here is to provide a reasonable value of degradation rate applicable to real stacks. The 1 V value is used as a typical approximate OCV for a reversible SOC. Note that actual stack OCV values may vary, e.g., from 0.9 to 1.1 V, depending on the fuel composition.

8.2.3. SEM/EDS

Symmetric cells were fractured and vacuum infiltrated with EpoThin epoxy (Buehler) and polished to $1.0\ \mu\text{m}$ with a diamond slurry (Buehler). Specimens were then coated with 7 nm of Os and contacted with carbon tape. The electrodes were imaged using a Hitachi SU 8030 scanning electron microscope at 25 kV and 20 nA using a lower secondary electron detector at a 15 mm working distance.

8.2.4. FIB-SEM

A control sample, a $0.7\ \text{A}/\text{cm}^2$ post-test fragment, and a $1.5\ \text{A}/\text{cm}^2$ post-test fragment were prepared for FIB-SEM serial sectioning by epoxy infiltration and mechanical polishing.^{56, 99} The procedures for FIB-SEM data collection are as described in Section 7.2.3.

8.2.5. ICP-OES analysis

Each of the three samples (control, $0.7\ \text{A}/\text{cm}^2$ and $1.5\ \text{A}/\text{cm}^2$) were fractured into three fragments. The cell fragments were separately stirred in ultrapure H_2O ($18.2\ \text{M}\Omega/\text{cm}$) for 10 min. Subsequently, the samples were transferred into a 12 mol/L HCl solution and stirred until the electrodes were completely dissolved. The tubes with ultrapure H_2O were then centrifuged and only the upper part of the solution was used in order to eliminate any loose powders coming from

the LSM pellets. The ultrapure H_2O and the concentrated HCl solutions were mixed with the appropriate amounts of $\text{HCl}/\text{HNO}_3/\text{H}_2\text{O}$ to yield 0.36 mol/L HCl /0.72 mol/L HNO_3 solutions for ICP-OES analysis. The chemical analysis of the solutions was done using a Thermo Scientific iCAP 7600 spectrometer. A certified stock solution (Inorganic Ventures, 10.00 $\mu\text{g}/\text{mL}$) containing La, Sr, Co, Fe and Mn was used to prepare the calibration standards for quantification. The following background corrected emission lines were chosen for evaluation: La (333.749 nm; 379.478 nm; 412.323 nm), Sr (216.596 nm; 407.771 nm; 421.552 nm), Co (228.616 nm; 237.862 nm), Fe (238.204 nm; 239.562 nm; 259.940 nm), Mn (257.610 nm; 259.373 nm; 279.82 nm).

8.3. Results

Figure 8.1 shows the cell voltage versus time for each of the current switched life tests. Within each 6 h cycle, the voltage starts high and eventually stabilizes at a value ~ 10 mV lower, indicating that there is some slow process that decreases the cell resistance slightly. Figure 8.2 shows the voltage degradation rate of each life test in %/kh as defined in Eq. [8.2], with an assumed OCV of 1.0 V. For the 0.7 A/cm^2 test, there was a very slight decrease in absolute cell voltage over 1000 h, but this was largely due to an initial voltage decrease in the first few cycles. We assume that the voltages changes after this initial break-in period will provide a better measure of the long-term degradation rate; after the first 50 h of the test, the total voltage increase is < 10 mV, corresponding to < 10 mV/kh. This suggests an average degradation rate over the test of $< 1.0\%$ /kh, which appears to be consistent with the degradation rate versus time shown in Figure 8.2. The apparent increase in degradation rate later in this test appears to be caused by noise in the measurement, propagated in the analysis. The cell voltage increases about 60 mV over the course of the 1.0 A/cm^2 test including an anomalous ~ 20 mV jump in the voltage; the reason for this

change is not known. The degradation rate for 1.0 A/cm^2 starts at about 8%/kh but decreases steadily to $\sim 2\%/kh$ at the end of the test; the average rate is 3.1%/kh. The cell voltage increasing by about 60 mV in the first 500 h of the 1.5 A/cm^2 test, but then stabilizing during the remainder of the test. This corresponds to an initial voltage degradation rate of 10-15%/kh, dropping steadily to $\sim 0\%/kh$ by ~ 500 h. The degradation rate average over the entire 1.5 A/cm^2 test was 6.0%/kh.

The EIS data provides information on the electrode and electrolyte contributions to the cell degradation. Figures 8.3 and 8.4 show Nyquist and Bode plots of selected impedance spectra collected over the course of current switched life tests. The ohmic resistance is dominant, as expected because of the thick GDC electrolyte, and two distinct polarization responses can be observed – a dominant one at $\sim 30 - 1000$ Hz and a smaller one at ~ 1 Hz. The model fits overlaid on the data are based on a L-R-RQ-G equivalent circuit. The inductor accounts for inductance in the test setup, while the series resistor models the ohmic resistance of the electrolyte. The inductance is small enough that the high frequency intercepts in the Nyquist plots are a good approximation of the ohmic resistance. The main higher frequency response is fitted using the Gerischer element predicted by the Adler-Lane-Steele model,³⁷ associated with co-limiting oxygen surface exchange and diffusion in porous mixed conducting electrodes such as LSCF. The RQ element accounts for the small response at ~ 1 Hz visible in all the 0.7 A/cm^2 test data and at early times in the 1.5 A/cm^2 data. Although the origin of this response is not fully clear, the evidence suggests it is related to gas diffusion through the thick LSM pellet and paste contacting the LSCF. First, this RQ response is not observed in similar LSCF/GDC/LSCF symmetric cells contacted with silver wires³⁹ instead of LSM pellets. Second, the response remains relatively constant at $\sim$

$0.01 \Omega \cdot \text{cm}^2$ throughout all tests, although it is not obvious at late times in the 1.5 A/cm^2 case because it overlaps with the larger ORR response.

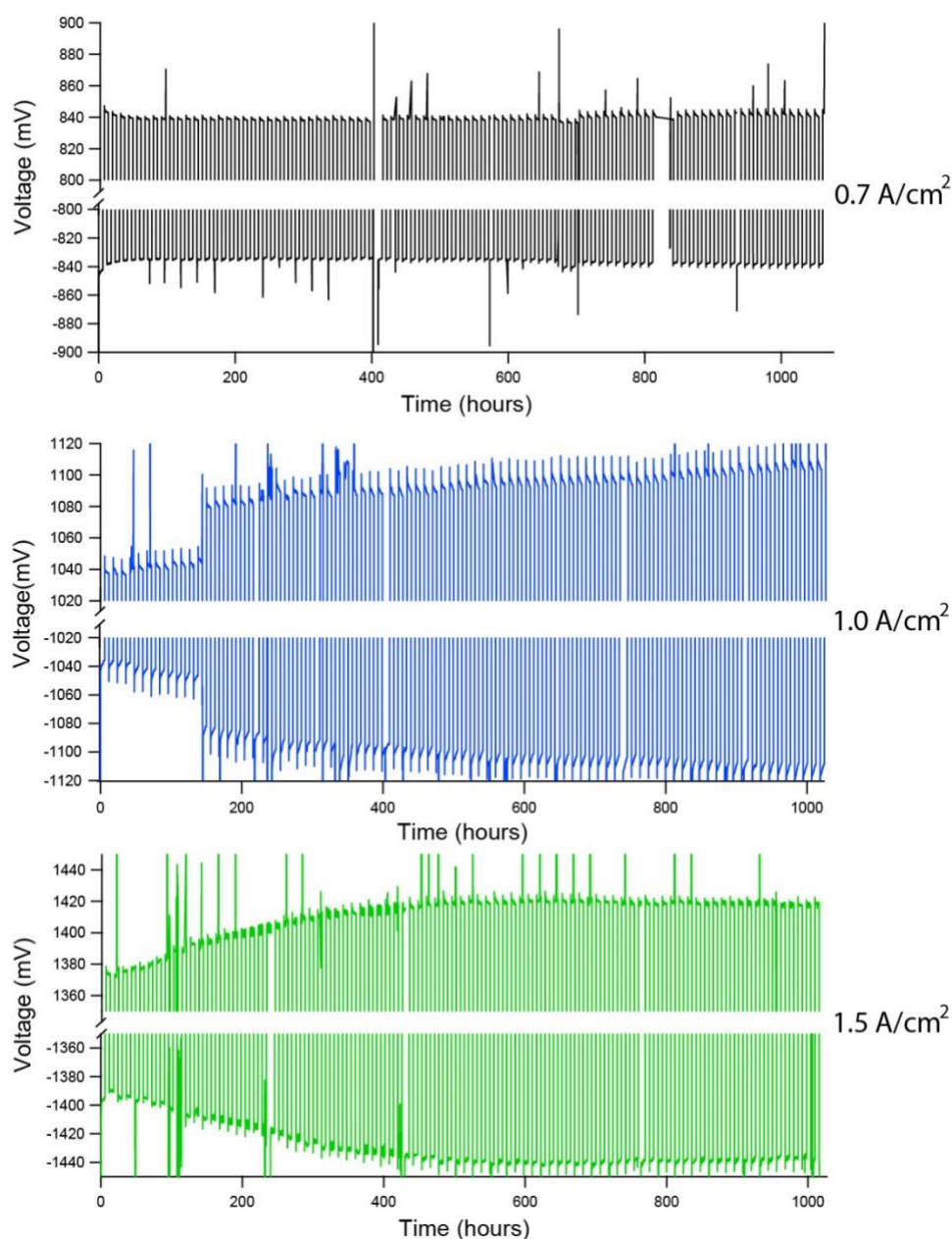


Figure 8.1. Voltage data for current switched life tests performed at 0.7 , 1.0 , and 1.5 A/cm^2 . The data were cropped to 100 mV ranges for each current direction in order to make the degradation obvious. The occasional voltage spikes correspond to program stops and starts where EIS measurements were taken.

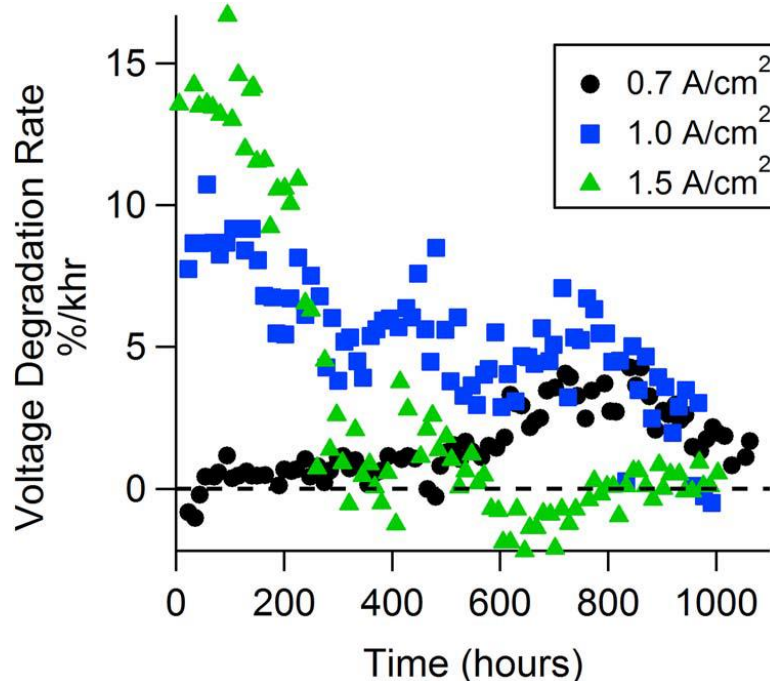


Figure 8.2. Voltage degradation rate versus time for each of the three life tests. Each point is a moving average taking into account the nearest neighbors in a 100 h window because the degradation rate calculated from point to point is excessively noisy.

The impedance spectra from the 0.7 A/cm² life test (Figure 8.3) show an increase in the Gerischer resistance R_G with time, which is mostly offset by a decrease in the ohmic resistance R_Ω , such that the total resistance R_T remains approximately constant. The R_G increase appears over a large frequency range from $\sim 20 - 1000$ Hz. The initial ~ 100 h appears to be a break-in period during which the changes are rapid. At longer times the same changes occur but much more slowly, *i.e.*, the cell becomes much more stable. In the 1.5 A/cm² life test (Figure 8.4), the initial polarization responses are similar, but not identical, to that shown in Figure 8.3, due to cell to cell variations. R_Ω decreased by $\sim 0.02 \Omega \cdot \text{cm}^2$ during the early stages before stabilizing, similar to the 0.7 A/cm² test. However, the R_G increase is much larger throughout the life test at the higher current density. As shown in the Bode plot in Figure 8.4, the dominant response grows and shifts

to lower frequency during the life test. The impedance spectra of the 1 A/cm² life test, not shown, was intermediate between those shown in Figures 8.3 and 8.4.

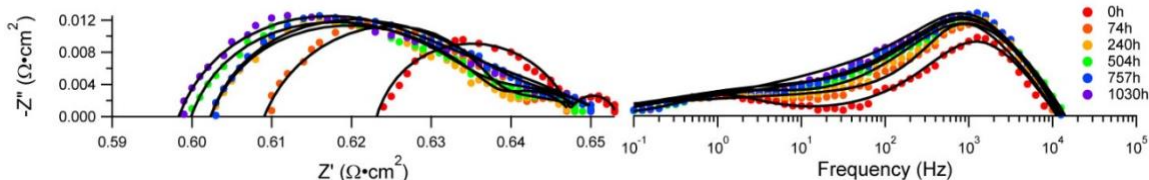


Figure 8.3. Nyquist and Bode plots at selected time points of the current switched life test performed at a current density of 0.7 A/cm².

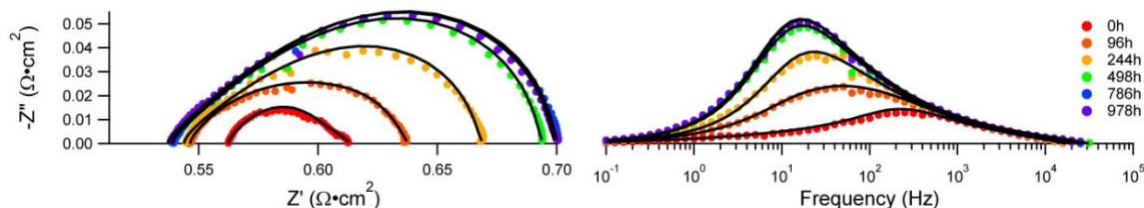


Figure 8.4. Nyquist and Bode plots at selected time points of the current switched life test performed at a current density of 1.5 A/cm².

The ohmic, Gerischer, and total resistance values were obtained from equivalent circuit fits to the EIS data over the course of life tests. Figure 8.5 shows the changes in the R_Ω (a), R_G (b), and R_T (c) relative to the values at the start of the test (given in Table 8.1). The R_Ω values (Figure 8.5a) show minimal change or even decrease slightly, in the 0.7 and 1.5 A/cm² cases, during the life tests. Most of the degradation occurs as an increase in R_G (Figure 8.5b) for all the cells. The degradation rate of R_G increased with increasing j ; the increase was especially pronounced for $j = 1.0$ and 1.5 A/cm², and during the first ~ 400 h. The net increase in R_G over the 1000 h tests was 3-4 times greater for 1.5 compared to 0.7 A/cm². For the 0.7 A/cm² case, the increase in R_G is small enough that it is almost completely cancelled by the slight decrease in R_Ω , such that R_T is almost constant. The trends in the R_T are similar to R_G , with degradation increasing with increasing current

density. However, the unexplained increase in resistance at ~ 150 h of the 1.0 A/cm^2 test helps to make its total resistance increase similar to that of the 1.5 A/cm^2 test.

Table 8.1. Initial resistance values for current switched life tests.

Sample	Initial R_{ohmic} ($\Omega \cdot \text{cm}^2$)	Initial R_{pol} ($\Omega \cdot \text{cm}^2$)	Initial R_{total} ($\Omega \cdot \text{cm}^2$)
0.7 A/cm^2	0.62	0.03	0.65
1.0 A/cm^2	0.54	0.12	0.66
1.5 A/cm^2	0.56	0.05	0.61

Figure 8.6 shows polished SEM cross-sections of the cells after life testing, showing the region near the electrode/electrolyte interface. For all j values, the electrodes are well connected to the electrolyte, with none of the material depletion near the interface that was observed after current switching tests of LSM-YSZ electrodes.¹⁵⁵ There is no evidence of delamination at the interface, as commonly observed for LSM-YSZ electrodes.^{167, 168} Although there are numerous pre-existing pores in the GDC electrolytes, there does not appear to be oxygen bubble or crack formation in the electrolyte near the interface, as reported previously for high electrolysis currents.¹⁶⁸⁻¹⁷⁰ Overall, there does not appear to be any obvious change in the electrode or electrolyte in these relatively low magnification images.

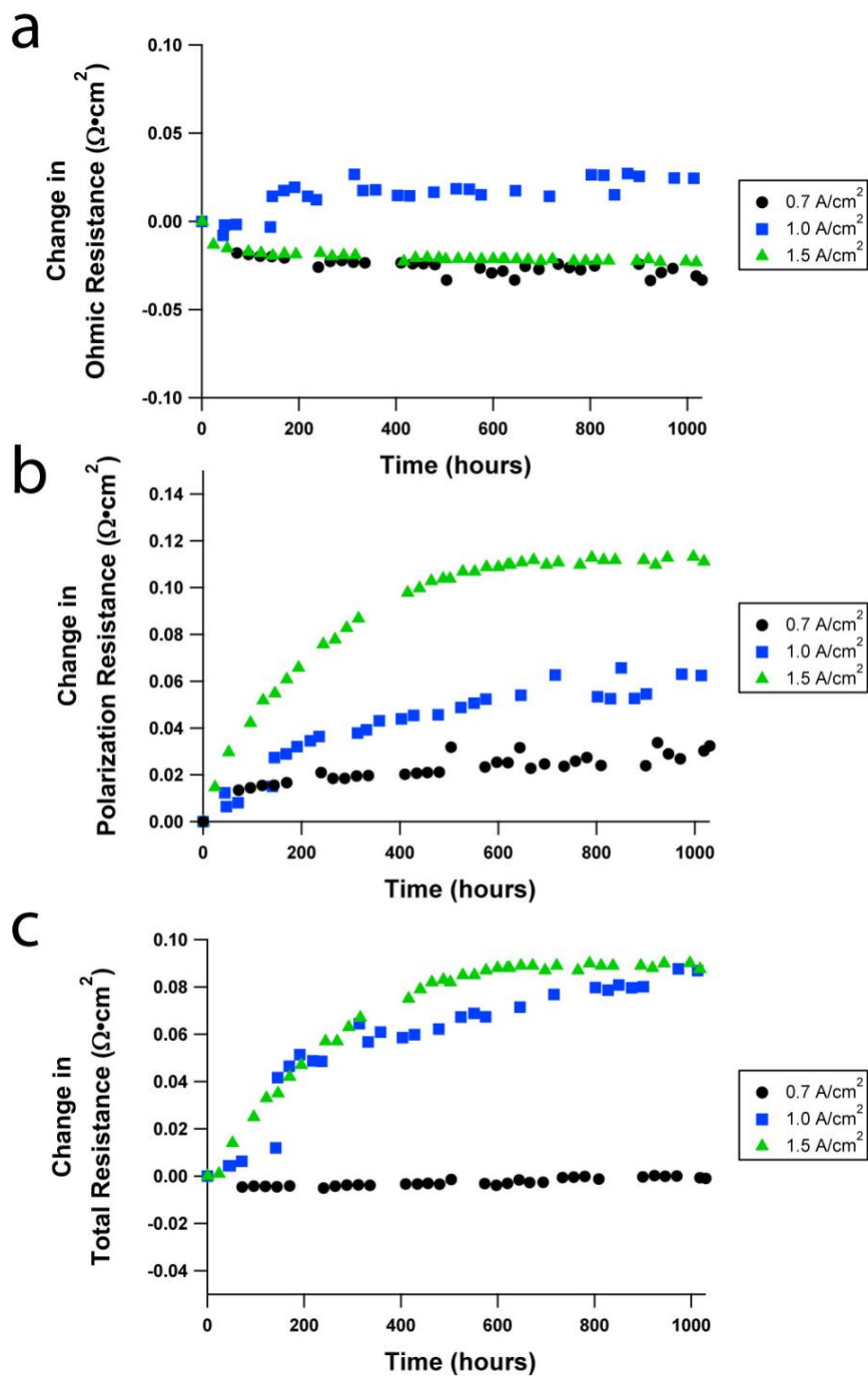


Figure 8.5. Change in a) Ohmic resistance, b) R_p , and c) Total resistance of the current switched life tests performed at 0.7, 1.0, and 1.5 A/cm². Data points show circuit model values. Initial values are shown in Table 8.1.

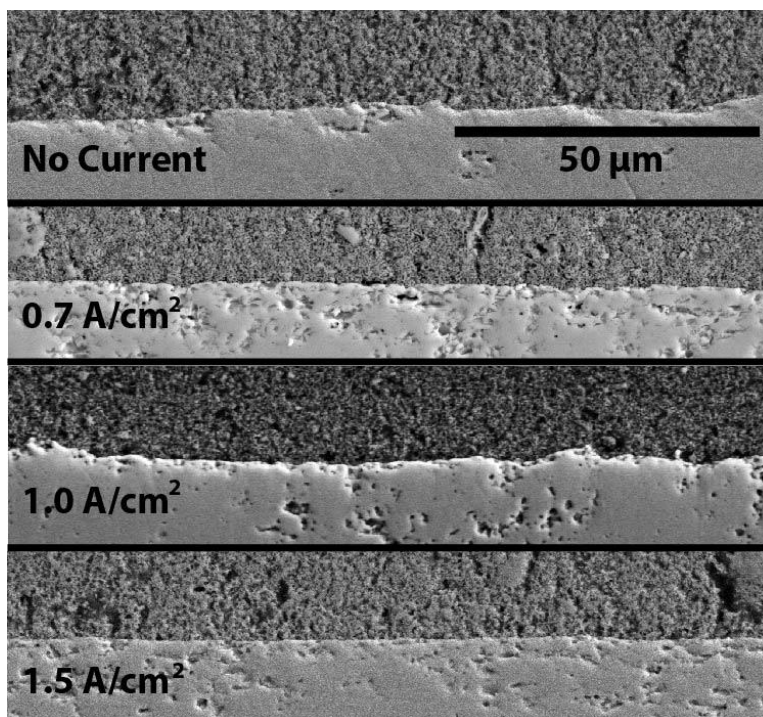


Figure 8.6. Polished cross-sections of LSCF symmetric cells operated at zero, 0.7, 1.0, and 1.5 A/cm².

Figure 8.7 shows representative FIB-SEM cross sections and 3D reconstructions of an as-prepared control, the 0.7 A/cm² cell, and the 1.5 A/cm² cell. The GDC electrolyte is visible on the left side of each cross-sectional image, and the black portions of the image are epoxy filled pores. In the 3D reconstructions, the blue represents the GDC electrolyte, the green represents the LSCF electrode, and the pore area is transparent. The cross-sectional views generally agree with the SEM images in Figure 8.6, showing no obvious electrolyte defects, interfacial delamination or degradation, or changes in electrode structure. However, the 3D image data does provide evidence of minor changes in electrode microstructure. Table 8.2 provides a summary of the electrode 3D tomographic data including the porosity, solid phase tortuosity, and LSCF particle specific surface

area per. There is no difference between the control and 0.7 A/cm² samples, within experimental error of ~ 5%, but the porosity and surface area are clearly lower for 1.5A/cm²–operated electrode.

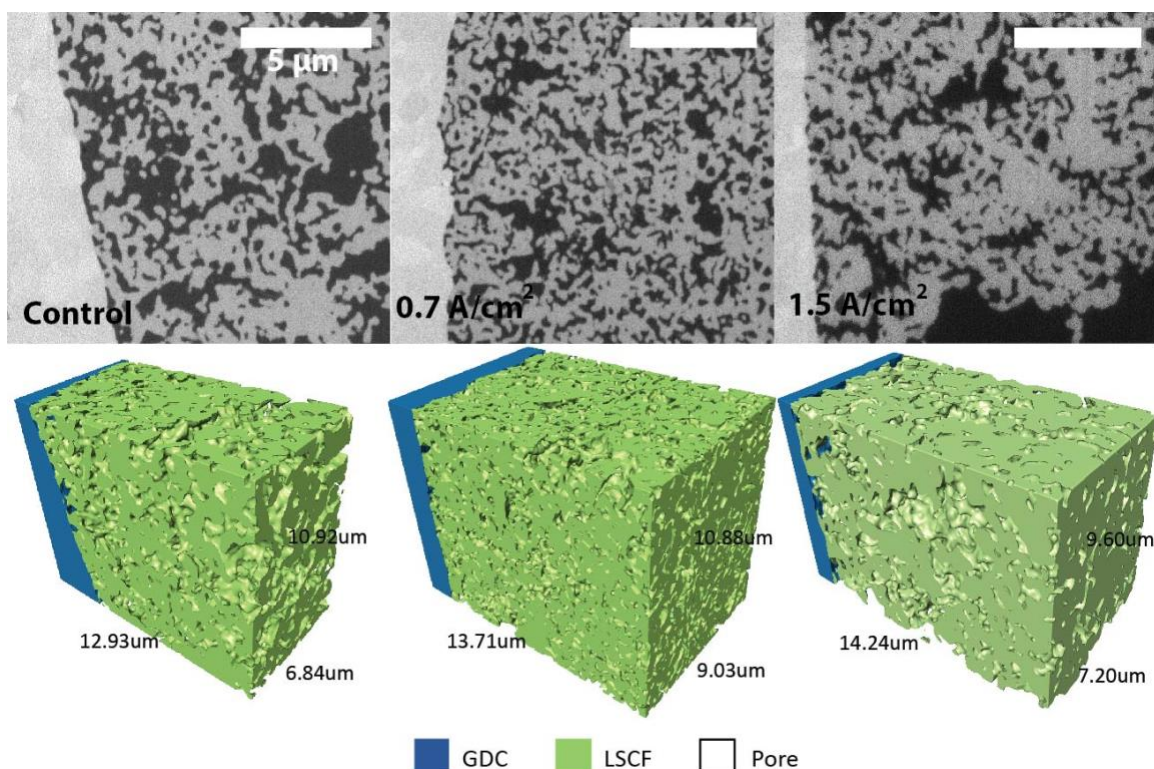


Figure 118.7. FIB-SEM cross-sections and corresponding reconstructed volumes of the control (no current), 0.7 and 1.5 A/cm² post-test electrodes.

Table 8.2. Summary of microstructural parameters in post-test LSCF electrodes.

Sample	No Current	0.7 A/cm ²	1.5 A/cm ²
Porosity, ϵ (%)	39.69	39.59	34.03
Tortuosity, τ	1.12	1.12	1.10
Specific Surface Area, a (µm ⁻¹)	5.62	5.96	4.47

Figure 8.8 shows the water soluble cation concentrations of Sr, La, Co, and Fe measured by ICP-OES for the as-prepared control, the 0.7 A/cm² current switched test, and the 1.5 A/cm²

test. Also shown for comparison is data from a previous study¹³⁴ of an identical as-prepared cell annealed at 700 °C for 800 h. The amount of segregated strontium in the current switched cells is increased relative to the as-prepared and annealed cells. Note, however, the amount of segregated Sr in the 0.7 and 1.5 A/cm² current switched cells is similar. In general, the other cation amounts are low because they are not water soluble.

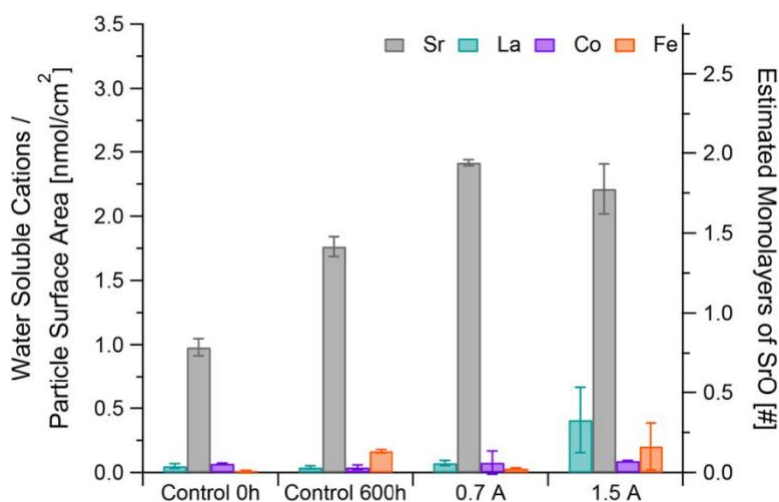


Figure 8.8. Concentration of water soluble cations measured by ICP-OES, for an un-aged control sample, a control annealed at 700 °C for 600 h, the 0.7 A/cm² current switched cell, and the 1.5 A/cm² current switched cell. The concentration values are normalized to the LSCF surface areas, and are also given as a nominal number of monolayers of SrO.

8.4. Discussion

We consider first how the total cell resistance and voltage varies with time. For the 0.7 A/cm² case, the voltage degradation rate remains relatively low, with some fluctuations, with an average degradation rate of < 1 %/kh. These results suggest that these LSCF electrodes can work with voltage and resistance degradation rates $\leq 1.0\%/kh$ at ≤ 0.7 A/cm², especially if the degradation rate slows at longer times and lower j ,¹⁶⁰⁻¹⁶⁴ as observed in our voltage degradation

data. The 1.0 and 1.5 A/cm² case show a different behavior, with much higher initial degradation rates that gradually decrease over time. At the highest current density, the initial rate is very high but drops off more rapidly than at 1.0 A/cm². It is possible that the degradation rate would drop to zero for the 1.0 A/cm² case, if the test were continued beyond 1000 h. Additional life test will be important to verify that these trends, and particularly the very low late-stage degradation rate, continue to longer times at the higher current densities. Note, for example, that if the cell voltage held stable after ~ 500 h in the 1.5 A/cm² case, the total increase in voltage would be only 40 mV, corresponding to a voltage degradation rate over 40,000 h of only 0.1%/kh.

One notable observation from the microstructural and electrochemical data is the lack of obvious electrolyte degradation. Prior work suggests that electrolyte degradation is driven by the high effective oxygen potential at the electrode/electrolyte interface for large electrode overpotentials η . The theory reported by Virkar^{168, 170} can be used to predict a critical electrode overpotential η_{cr} value sufficient to yield fracture in the electrolyte:

$$\eta_{cr} = \frac{RT}{4F} \ln \left\{ \sqrt{\frac{\pi}{(1-v)^2 c} \frac{K_{Ic}}{2p_o}} \right\} \quad [8.3]$$

where the fracture toughness $K_{Ic} = 1.53 \text{ MPa}\sqrt{m}$ ¹⁷¹ for GDC, the initial defect size c is estimated to be between 1 and 10 μm , the Poisson ratio $\nu = 0.33$, the oxygen pressure $p_o = 21.3 \text{ kPa}$, and R , T , and F have their usual meanings. $\eta_{cr} = 0.24\text{-}0.22 \text{ V}$ is obtained for GDC using these values. Approximate η values during the life tests are obtained by multiplying the current density j by the electrode resistance. Note, however, that the EIS-measured resistance values are at low current, and that the electrode j - V response is likely nonlinear, such that these overpotential values are

overestimated. The values range from ~ 0.02 V at the beginning of the 0.7 A/cm^2 life test to 0.12 V at the beginning of the 1.5 A/cm^2 test. The highest η value reached is ~ 0.22 V at the end of the 1.5 A/cm^2 life test. Thus, η values in all cases were below that expected to cause degradation, in agreement with the observation that the electrolyte does not degrade.

Figure 8.4 shows that the degradation arises almost entirely from increases in the R_G , suggesting that the majority of the changes are in the electrode. The initial increase in the R_G becomes faster with increasing j , and also correlates reasonably well with increasing η . One possible explanation is the electrode microstructural change quantified in the 3D tomography data in Table 8.2. Note that coarsening and sintering of LSCF electrodes has not been observed in similar LSCF electrodes maintained at 700°C without current.¹³⁴ The present observation suggests that current switching accelerates coarsening.

The Adler-Lane-Steele (ALS) model is used here to assess the impact of the observed microstructural changes on R_G , which can be related to the chemical and physical descriptors of the LSCF electrodes:³⁷

$$R_G = \frac{RT}{4F^2} \sqrt{\frac{\tau}{4a(1-\epsilon)R_0c_0D_{chem}}} \quad [8.4]$$

where ϵ is the electrode porosity, a is the internal specific surface area of the solid phase, τ is the tortuosity of the solid phase, c_0 is the concentration of oxygen sites involved in diffusion, x_δ^0 is the molar fraction of interstitial or vacancy defects at equilibrium, A_0 is the thermodynamic factor, D is the oxygen bulk diffusivity, and R_0 is the molar surface exchange rate given by:

$$R_o = \frac{k_{chem}}{A_0} (pO_2)^{0.5} c_0 \quad [8.5]$$

Using the microstructural parameters from Table 8.2 in Eq. [8.4] yields an R_G value that is $0.004 \Omega \cdot \text{cm}^2$ higher for the 1.5 A/cm^2 electrode compared to the control; this is less than 10% of the observed increase of $0.11 \Omega \cdot \text{cm}^2$. That is, the increase in R_G is only partially explained by the change in microstructure.

Another possible cause of electrode degradation is the observed increase in Sr segregation (Figure 8.8). As discussed by Wang *et al.*¹³⁴ in a study of LSCF electrodes similar to those in the present study, an increase in the amount of segregated Sr from ~ 1 to 3 monolayers (assuming the surface compound formed is SrO) caused by high-temperature ageing yielded an increase in R_P at 700°C by $0.15 \Omega \cdot \text{cm}^2$. This is consistent with the present observation of an R_G increase by $0.11 \Omega \cdot \text{cm}^2$ associated with an increase in surface Sr from ~ 0.75 to 1.75 monolayers. The ALS model can be used to fit the apparent change in k_{chem} and D_{chem} to the observed change in resistance since the microstructure is known.¹³⁴ Here we employ a somewhat simpler approach, using Eqs. [8.4] and [8.5] to calculate the $k_{chem}D_{chem}$ product, which quantifies the overall oxygen transport kinetics of the LSCF electrode. This analysis shows that the $k_{chem}D_{chem}$ product decreases from 1.27×10^{-14} for the as-prepared electrode to $2.04 \times 10^{-15} \text{ cm}^3/\text{s}^2$ after the 1.5 A/cm^2 life test. (This can also be expressed in terms of k^*D^* , which decreases from 2.3×10^{-16} to $3.68 \times 10^{-17} \text{ cm}^3/\text{s}^2$ after testing; these are the vacancy-content-normalized versions that can be directly compared to LSCF k^*D^* ranges given, for example, in Ref. ³⁹.) These changes in $k_{chem}D_{chem}$ product, apparently due to Sr segregation on LSCF, are somewhat comparable to those reported previously for an annealed case, where k^*D^* decreased by ~ 2 times.¹³⁴

The increased Sr segregation in the current switched cells relative to the annealed cell (Figure 8.7) indicates that current cycled operation accelerates Sr segregation in LSCF electrodes. It is unclear whether the increased rate of Sr segregation occurs while the electrode is in fuel cell mode or electrolysis mode, or both. The amount of segregated Sr observed after the 0.7 A/cm² and 1.5 A/cm² life tests is similar (Figure 8.8), whereas the degradation rates are much different (Figure 8.5). This apparent discrepancy might be explained by differences in the morphology of the segregated Sr and how it influences oxygen exchange and diffusion kinetics; for example, Sr-rich islands may be less detrimental than a complete Sr-segregated layer.

These segregation and coarsening degradation mechanisms have been shown in previous reports to show similar time dependence to the present results. That is, when degradation is fast, rapid initial increases in electrode resistance are followed by slow degradation at longer times,^{134, 140} similar to the present 1.0 and 1.5 A/cm² life test. Slower degradation by these mechanisms often appears to be linear with time.^{59, 140} Thus, a combination of microstructural changes and surface chemical changes is consistent with the present results.

8.5. Conclusions

Current switched life tests of LSCF electrodes in GDC-electrolyte symmetric cells showed increasing degradation with increasing current density j from 0.7 to 1.5 A/cm². The degradation rate at 0.7 A/cm² was $\sim 1.0\%/kh$, indicating good potential for long term cell operation if j is kept ≤ 0.7 A/cm². While the initial degradation rate increased substantially with increasing j , the rate decreased with time. For $j = 1.5$ A/cm², the cell became quite stable after ~ 700 h. Thus the

interpretation of the results at higher j remains unclear – while the initial degradation is fast, if the late-stage stabilization continues to long times, there may be potential for good durability.

Impedance spectroscopy analysis showed that the degradation was mostly attributed to an increase in electrode resistance. Analysis of the EIS data using the ALS model along with measured electrode microstructural and chemical changes suggested that Sr surface segregation induced by current-switching operation was the primary cause of polarization resistance increase, whereas current-switching-induced coarsening yielded a smaller contribution. No significant electrolyte degradation was observed, either as a resistance increase or a microstructural change, consistent with the fact that estimated electrode overpotentials were below the values predicted to cause fracture of GDC electrolytes. Finally, based on prior work showing that reversible and electrolysis degradation effects are similar, the present results should provide a qualitative idea of LSCF degradation during electrolysis.

8.6. Acknowledgements

The authors gratefully acknowledge support from NSF PIRE grant # 1545907, and NSF grant # DMR-1506925 for support of the 3D tomography work. This work made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR- 1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. This work made use of the MatCI Facility which receives support from the MRSEC Program (NSF

DMR-1121262) of the Materials Research Center at Northwestern University. The authors thank Gareth A. Hughes for his early input on the cell testing and helpful discussions.

Chapter 9

Study on O₂-Reduction Reaction and Degradation Mechanisms Operating on La_{0.5-x}Pr_xBa_{0.5}CoO_{3-δ} Cathodes for LT-SOFCs

The selective chemical etching method with ICP-OES detection can also be applied to study surface segregation in systems other than LSCF, such as Ba segregation in (La,Pr,Ba)CoO_{3-δ} (LPBC) electrodes. Ba surface segregation has been observed for (La,Ba)MnO₃, to a larger extent than Sr surface segregation due to larger size mismatch between the dopant and the host cations.¹⁷² Since BaO is water-soluble and the bulk LPBC material is insoluble in water, the quantification of Ba surface segregation can follow the same procedures. This work is in direct collaboration with Dr. Diana Garcés and Dr. Liliana Mogni from CONICET/CNEA in Bariloche, Argentina. Powder synthesis and characterization, cell fabrication, and electrochemical testing were done in Argentina. The cells were then brought to Northwestern for FIB-SEM analysis and surface cation characterization.

9.1. Introduction

The large-scale commercialization of SOFCs is currently constrained by a combination of cost and durability issues. In order to address these concerns, much effort has been focused on developing low-temperature SOFCs (LT-SOFCs), with cell operating temperature < 700 °C.³⁹ One of the major issues to achieve this goal is the development of cathode materials with low polarization resistance and good stability over time.

Cobaltites with the perovskite structure such as, the Strontium-Barium cobaltites $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}(\text{BSCF})$,¹⁷³ are promising cathode materials for LT-SOFCs. Despite the good performance of Sr-containing perovskites, one major issue is the long-term instability due to Sr-surface segregation.⁹ Yildiz group pointed out, from the study of thin film electrodes, that the cation surface segregation increases due to the size mismatch between the dopant and host cations, being more important the Ba surface segregation than Sr and Ca surface enrichment for $(\text{La},\text{M})\text{MnO}_3$ with $\text{M} = \text{Ba}, \text{Sr}$ or Ca electrodes.¹⁷² However, there is not enough information about Ba-segregation in Ba-cobaltites porous electrodes. In these perovskites, the Ba plays a key role since its large cation radii mismatch also distorts the cubic crystal structure promoting the oxygen vacancy formation and migration,¹⁷⁴ thus reducing the $R_{c,p}$ due to the improvement of the O-surface exchange and the O-ion diffusion. However, the same structural distortion, also induces a slow segregation of a hexagonal perovskite phase¹⁷⁵⁻¹⁷⁷ which deteriorates the O_2 reduction kinetics with time.¹⁷⁸ Recent works have shown that $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ is a promising cathode materials for LT-SOFCs because of their low cathode polarization resistance.¹⁷⁹⁻¹⁸¹ Besides, in this oxide we did not observe the hexagonal phase formation suggesting that La^{+3} ions play an important role stabilizing the cubic phase because of its charge and ionic radii.

With these ideas, in this work, the La content of the perovskite oxide $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ is partially substituted with Pr as $\text{La}_{0.5-x}\text{Pr}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ (LPBC), with $0 \leq x \leq 0.5$ to improve even more the cathode performance. Samples exhibit a combination of cubic and tetragonal symmetry for $x \leq 0.1$, whereas above this value the cation ordering produces a layering structure with tetragonal symmetry. The Electrochemical Impedance Spectroscopy (EIS) as a function of temperature (T), oxygen partial pressure ($p\text{O}_2$) and time, in combination with 3D FIB-SEM

tomography and the ICP-OES studies, were used to analyze the mechanism of O₂ reduction and the origin of degradation with time.

9.2. Experimental Procedures

9.2.1. Powder Synthesis

Powders with nominal composition $\text{La}_{0.5-x}\text{Pr}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ (LPBC) were synthesized via a combined EDTA-citrate complexing sol-gel process. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Pr}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ were dissolved into EDTA- $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution ($\text{pH} \approx 6$) under heating and stirring conditions. A proper amount of citric acid- $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution ($\text{pH} \approx 6$) was added at a mole ratio of 1:1:2 for EDTA: total metal ions: citric acid. The mixed solution was firstly evaporated at 80 °C to form a red transparent gel and then heated at 150 °C for several hours to obtain a dark dry foam structure. After decomposition on a hot plate, the powders were calcined at 400 °C (4 h, in air) and then at 1000 °C (4 h, in air). Each sample of the LPBC series was labeled according to its corresponding lanthanum content, i.e., La30 represents the $\text{La}_{0.30}\text{Pr}_{0.20}\text{Ba}_{0.50}\text{CoO}_{3-\delta}$ compound.

9.2.2. XRD characterization

The crystal structure was studied by X-ray diffraction at the D10B-XPD beamline of the LNLS (Brazilian Synchrotron Light Laboratory, Campinas, Brazil) in static air. The wavelength was set at 1.5495(4) Å. Data in the angular region of $2\theta = 20 - 90^\circ$ were collected at room temperature in a step-scanning mode, with a step length of 0.02 and a step-counting time of 3 s.

9.2.3. Cell fabrication

Symmetrical cell configuration was used in this study. The cells consist of a dense $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) electrolyte (area $\sim 0.8 \text{ cm}^2$, thickness $\sim 0.1 \text{ cm}$), where firstly a porous layer of GDC and afterwards a porous layer of LPBC were deposited on both sides by spin coating. The inks were prepared by mixing the corresponding ceramic powders (GDC or LPBC) with ethanol, α -terpineol, polyvinyl butyral, and polyvinyl pyrrolidone in a 40:40:27:2:1 mass ratio. The porous layer of GDC improves the adherence of LPBC cathode onto the GDC dense electrolyte.¹⁸² After deposition, the porous GDC layer was heat treated at 1400°C during 1 h in air, while the LPBC porous electrode was heat treated at 1000°C 1 h in air.

9.2.4. Electrochemical measurements

The electrochemical performance was evaluated by (EIS on symmetrical cells (LPBC/GDC/LPBC) by using an AUTOLAB PGSTAT30 (EcoChemie) potentiostat coupled to a FRA2 analyzer. The EIS measurements for all samples were carried out in air in a temperature range between 400 and 800°C . At 600 and 700°C the EIS spectra were collected varying the $p\text{O}_2$ between 1 and $5 \times 10^{-3} \text{ atm}$ by using a home-made device to test symmetrical cells coupled to an electrochemical oxygen pump and sensor. In addition, EIS spectra were also collected at 0.2 and 0.05 atm varying the temperature, with 50°C step, between 500 and 800°C . Life testing was performed at 700°C in air for La35 sample.

9.2.5. Microstructural analysis

The electrode microstructure was analyzed by FIB-SEM 3D tomography. The procedures are as described in Section 7.2.3.

9.2.6. Chemical characterization

The Ba surface segregation was quantified by ICP-OES. The procedures are the same as measurement of Sr surface segregation described in Section 7.2.4. The following background corrected emission lines were chosen for evaluation: La (379.478 nm; 412.323 nm), Pr (414.311 nm; 417.939 nm; 422.535 nm), Ba (233.527 nm; 455.403 nm; 493.409 nm), Co (228.616 nm; 237.862 nm)

9.3. Results & Discussion

9.3.1. Structure and microstructure characterization

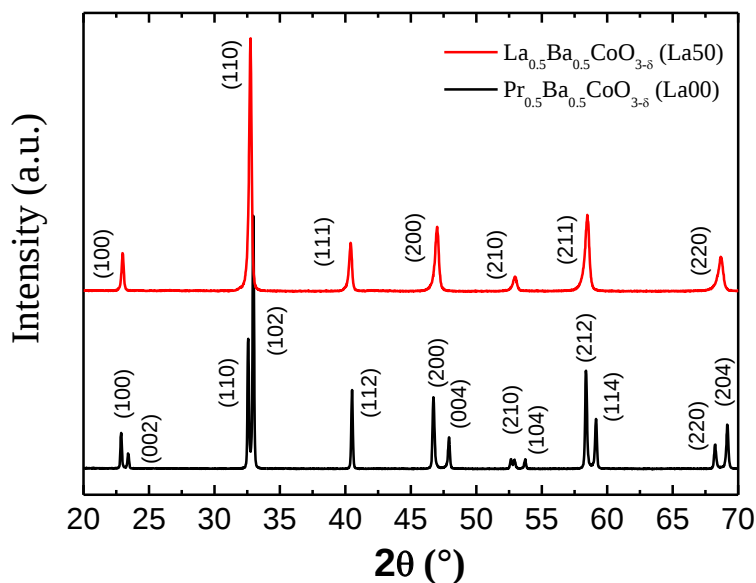


Figure 9.1. XRD pattern of La00 and La50 sample.

Figure 9.1 shows the XRD pattern of La50 and La00 samples where Bragg index of each peak was included in the graphic. The analysis of XRD data shows that above the La content of

0.15 samples can be indexed as cubic perovskite (space group $Pm\bar{3}m$), otherwise a peak splitting indicates the formation of a tetragonal phase below 0.15.

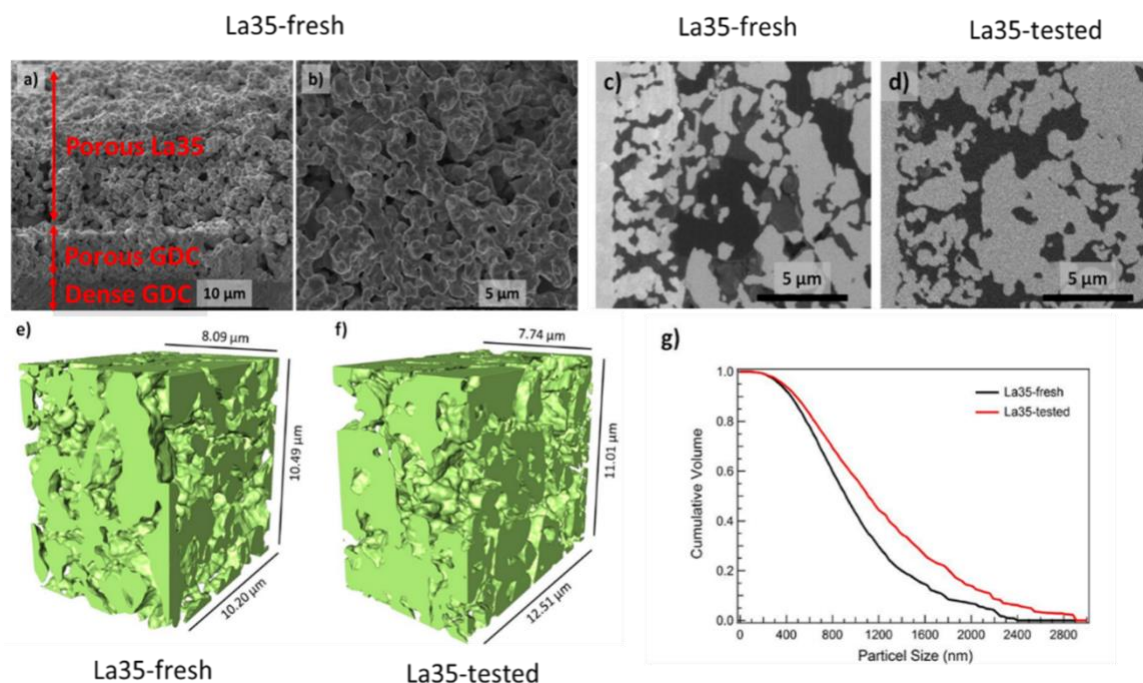


Figure 9.2. SEM images of La35 symmetrical cell, a) cross and b) top section. Typical 2D FIB-SEM cross-sectional image of c) La35-fresh and d) La35-tested with pore phase infiltrated by epoxy. The corresponding 3D reconstruction of e) La35-fresh and f) La35-tested with LPBC particles shown in green and pores transparent. Note that the 3D view only shows the electrode region. g) Cumulative particle size distribution of LPBC calculated from obtained 3D data sets.

Figures 9.2a and b present SEM images showing cross sectional and electrode surface view of the symmetrical cell La35/GDC/La35, respectively. Figures 9.2c and d illustrate 2D FIB-SEM cross-sectional image of the La35-fresh and tested sample, respectively. The bright phase represents the particles and the dark phase is the epoxy-infiltrated pores. The corresponding 3D reconstructed structures are shown in Figures 9.2e and f. The structure is typical of SOFC cathode electrode produced by firing of particle compacts, showing reasonably uniform particle sizes and

good necking between particles. Table 9.1 indicates the microstructural parameters, solid phase fraction (ε), solid phase and pore phase tortuosities (τ_s , τ_p), specific surface area (a) and the mean particle size determined from the analysis of the 3D data and the cumulative particle size distribution (Figure 9.2g) of La35 before and after life testing.

Table 9.1. Microstructural parameters for La35 electrode.

Sample	solid phase fraction (ε)	solid phase tortuosity (τ_s)	pore phase tortuosity (τ_p)	specific surface area (a)	mean particle size
La35-fresh	52.4 %	1.28	1.22	$3.78 \mu\text{m}^{-1}$	900 nm
La35-tested	53.7%	1.28	1.25	$3.12 \mu\text{m}^{-1}$	1100 nm

9.3.2. Electrochemical characterization

Figures 9.3b and c show typical examples of impedance spectra, Nyquist and Bode plots (data points), measured at 600 °C and 0.05 atm for the symmetrical cell La30/GDC/La30. Figures 9.3d and 9.3e show the same information at 700 °C. All data collected were normalized to the geometric area of the electrodes in the symmetrical cell configuration. All spectra show two arcs denoting two different processes, one occurring at high frequency that is well fitted using a Gerischer-type element and the other occur at low frequency that is well fitted using a R//CPE element. Similar results were reported for Pr-free La-Ba cobaltite.¹⁷⁹ The two arcs are observed at temperatures above 600 °C, but only one EIS arc is observed at lower temperature. All cathode compositions present similar behavior shown in Figure 9.3.

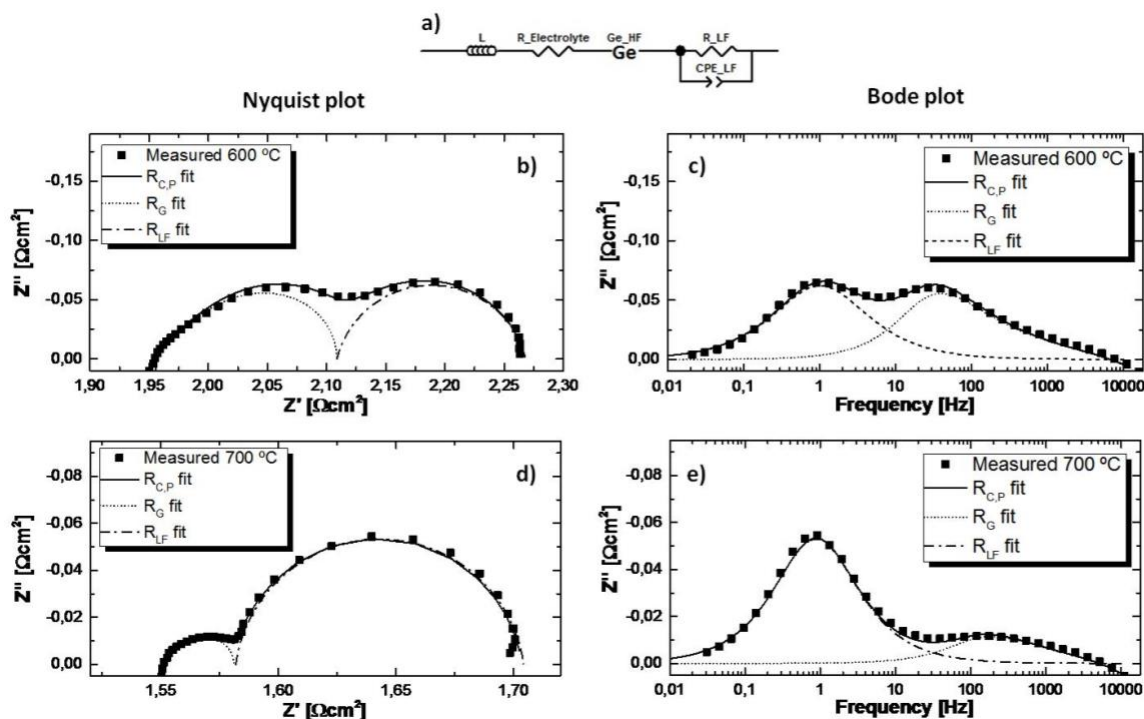


Figure 9.3. a) Equivalent circuit used for fitting the EIS spectra in the whole frequency range. b,d) Nyquist and c,e) Bode plot obtained for La30 sample in a $pO_2 = 0.05$ atm at 600 and 700 °C, respectively. Data point represents the measured data, solid line represent the arcs resulting of fitting data with equivalent circuit proposed and dashed lines indicating the different contributions.

In order to study the mechanism of the ORR, the electrochemical response of the cubic La30 electrode was analyzed as a function of T and pO_2 . The EIS spectra were fitted using the electrical equivalent circuit approximation. This circuit is composed by the inductance of connectors (L) and the electrolyte resistance ($R_{electrolyte}$), whereas the electrode response is fitted by the combination of a Gerischer for high frequency (HF) arc and a resistance (R_{LF}) in parallel with a capacitor (C_{LF}) for the low frequency arc (HF) (see Figure 9.3a). The resulting fits show good agreement with the measured spectrum.

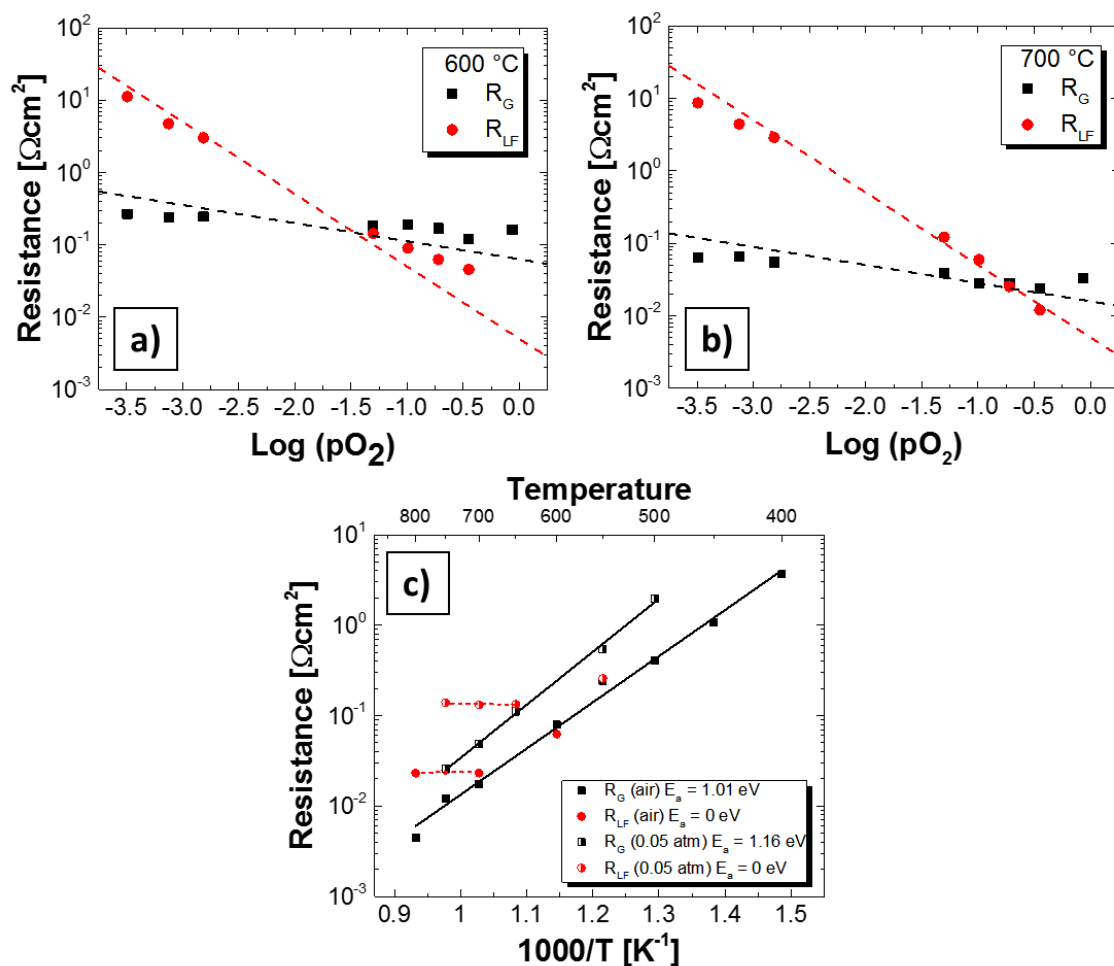


Figure 9.4. a) and b) Log-log plot of the high frequency Gerischer resistance (R_G) and the low frequency resistance (R_{LF}) with pO_2 at 600 and 700 °C for La₃₀ sample. Dotted lines indicate the pO_2 dependences $R_G \propto (pO_2)^{-0.25}$ and $R_{LF} \propto (pO_2)^{-1}$. b) Arrhenius plot for the Gerischer resistance (R_G) and the low frequency resistance (R_{LF}) in air and 0.05 atm. The activation energies are indicated on the graphs.

Figures 9.4a and b show the log-log plot for the high frequency Gerischer resistance (R_G) and the low frequency resistance (R_{LF}) vs pO_2 at 600 and 700 °C for the La₃₀ sample. The pO_2 dependences of R_G and R_{LF} fit approximately to $R_G \propto (pO_2)^{-0.25}$ and $R_{LF} \propto (pO_2)^{-1}$. Figure 9.4c shows the Arrhenius plot of R_G and R_{LF} obtained from the fitting of EIS spectra collected as a function of T in air and $pO_2 = 0.05$ atm. Both process shows markedly different activation energies.

Whereas the R_G has an activation energy ~ 1 eV. The O_2 -gas diffusion is almost independent of T . These results suggest that the electrochemical response is limited by one or both of two mechanisms, depending on the conditions. At temperatures ≤ 600 °C, the target T for low temperature SOFC,³⁹ the high frequency contribution R_G associated with co-limiting O-surface exchange and O-bulk diffusion^{37, 54} is dominant. Whereas at higher temperatures ($T > 700$ °C), R_G becomes small enough, or at very low pO_2 the low frequency R_{LF} response increases being in both cases the O_2 -gas diffusion the main responsible of the cathode polarization losses. A previous work in cathode with similar composition showed that the polarization resistance associated to O_2 -gas diffusion takes similar values independently of microstructure for electrodes with significant differences in particle size.¹⁷⁹ This result suggested that the O_2 gas transport limitation due to the gas diffusion is through the pores but also through the layer boundary between the porous electrode and the gas phase.

9.3.3. Life Testing

Figure 9.5 shows the time evolution of R_G and R_{LF} , measured by EIS at 700 °C in air, and their sum, for the La35 electrode. The results reveal an increase of the total polarization resistance by ~ 67 % over 280 hours. The overall rate of change over this time, defined as $\frac{1}{R_{C,P}^0} \frac{dR_{C,P}}{dt}$, is 0.002 h^{-1} . As it can be observed from Figure 9.5, the low frequency contribution (R_{LF}) is the major contribution to the polarization resistance, but it changes only $\sim 20\%$ at the end of the test ($\frac{1}{R_{LF}^0} \frac{dR_{LF}}{dt} = 0.0009$ h^{-1}). Whereas the low frequency R_G triples its value ($\frac{1}{R_G^0} \frac{dR_G}{dt} = 0.009$ h^{-1} , increasing ~ 200 %). The little increase of R_{LF} can be attributed to the particle coarsening reported in Table 9.1 which reduce the pore fraction ($\varepsilon_p = 1 - \varepsilon$) and increases the pore phase tortuosity

(τ_p) - i.e. $R_{LF} \propto \frac{\tau_p}{\varepsilon_p}$ ³⁷ - whereas the increases of R_G cannot be totally explained by the reduction of the specific surface area - i.e. $R_G \propto \frac{1}{\sqrt{a}}$ ³⁷

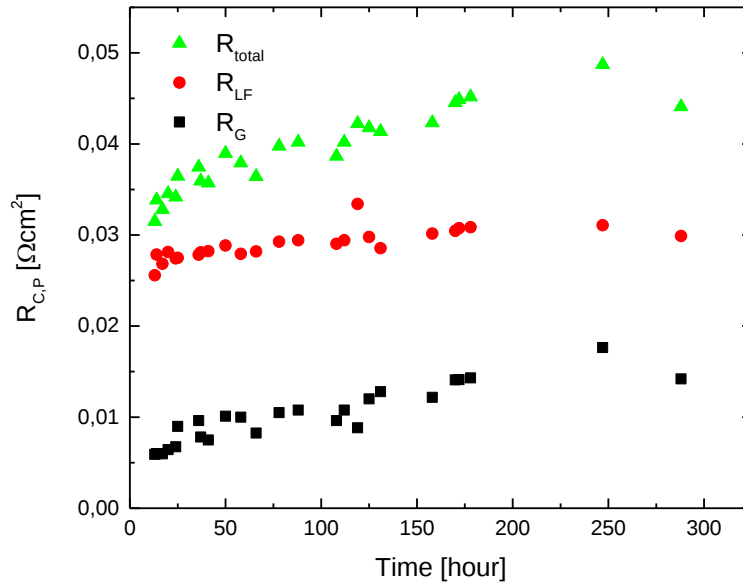


Figure 9.5. Evolution of $R_{C,P}$, R_G and R_{LF} values with aging time for La35 sample at 700 °C in air.

The amount of Ba segregated on the electrode surfaces after the La35 life test was measured using ICP measurements of BaO preferentially solubilized in water, and compared with the as-prepared electrode. As shown in Figure 9.6, the amount of surface Ba is doubled, which can explain the increase of R_G during the life test. Comparing these results with previous works where the Sr-surface segregation was evaluated for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathode,¹³⁴ it can be conclude that the segregation of Ba produces a greater degradation of the cells. This conclusion is based not only to the increases of Ba surface concentration - i.e. Ba surface concentration is duplicated in the half of time that Sr concentration due it - but also for the larger cation surface concentration.

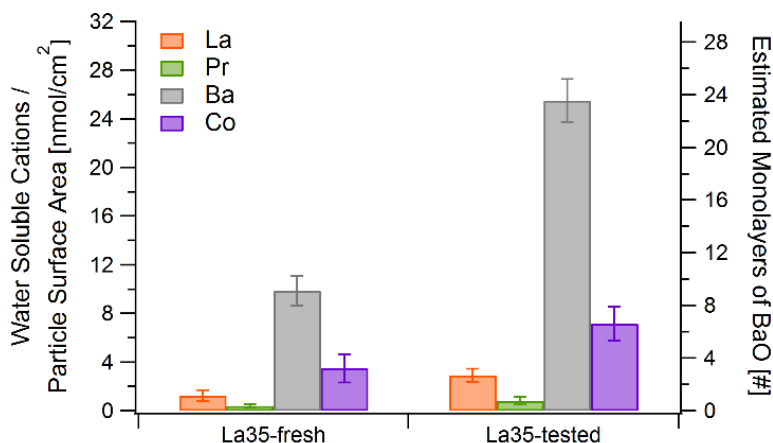


Figure 9.6. Amounts of water-soluble cations detected by ICP-OES. The cation amounts were normalized to LPBC surface area, obtained by 3D FIB-SEM as shown in Table 9.1.

9.4. Conclusions

A soft chemical route was used to obtain $\text{La}_{0.5-x}\text{Pr}_x\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ powders. The study of electrode performance by EIS as a function of temperature, $p\text{O}_2$ and time suggested that two processes contribute to $R_{C,P}$: 1) The low frequency resistance (R_{LF}) that is associated to O_2 gas diffusion. This contribution dominates the cathode polarization resistance as T increases or $p\text{O}_2$ decreases. The O_2 gas transport resistance shows little changes with time which is in agreement with small change of microstructure. 2) The high frequency Gerischer-resistance (R_G) that is in agreement with the ALS approximation. This R_G considers that the O_2 -reduction reaction is co-limited by O-surface exchange and O-bulk diffusion. This mechanism is mostly determined by the crystal structure, microstructure and surface conditions. The R_G is the contribution showing the largest evolution with time.

Ageing of La35 symmetric-electrode cells with GDC electrolytes, carried out at 700 °C for 280 hours in air, resulted in an increase of the electrode polarization resistance by about 67 %. 3D

tomographic analysis indicated no significant microstructural changes due to ageing. ICP-OES measurements of selectively dissolved surface species shows that the amount of surface Ba increased by ~ 2 times after the thermal ageing. Therefore, it is reasonable to conclude that Ba surface segregation, rather than microstructural changes, caused the increased La35 polarization resistance.

9.5. Acknowledgements

Author want to acknowledge the support of CONICET-NSF collaborative project. Conventional XRD studies were performed at the X-ray Diffraction Laboratory, Department of the Condensed Matter Physics, GIyA, GAIyANN-CAC-CNEA. The authors also acknowledge the assistance of the Electron Probe Instrumentation Center (EPIC) at the NUANCE Center-Northwestern University, which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); and the State of Illinois, through the IIN. Metal analysis was performed at the Northwestern University Quantitative Bio-element Imaging Center.

Chapter 10

Future Work: Coarsening Study of LSCF

Ageing study of LSCF with an initial particle size of ~ 500 nm was conducted at temperatures ranging from 550 °C to 950 °C (Chapter 6). Coarsening of LSCF particles was only observed at 950 °C, the highest ageing temperature. The work in Chapter 7 has demonstrated that no coarsening was observed for LSCF with ~ 450 nm particle size aged ≤ 900 °C for 700 h, while increase in particle size with increasing ageing time was shown at 1000 °C. Although these temperatures are well above the typical operating temperatures, $700 - 800$ °C, for cells with LSCF electrodes, it is unclear whether significant coarsening will occur during the whole expected operation time, usually $> 40,000$ h. As discussed in Chapter 6, by applying a coarsening model which was originally developed to predict coarsening of nano-sized LSCF, the predicted change in particle size was found to be generally in good agreement with the experimental observations. In addition, an increase in particle size from 500 nm to 600 nm was estimated for $40,000$ h at 800 °C, but to only 505 nm for $40,000$ h at 700 °C. To improve the model's accuracy, more experimental data at various temperatures and times are needed, preferably be able to see particle coarsening. For example, some high-temperature (probably ≥ 1000 °C) ageing over shorter times and one or two longer-time ageing at lower-temperatures (probably between 850 and 950 °C). Note that we need to take into account the $\sim 5\%$ error usually existed in FIB-SEM 3D tomographic technique.

10.1. Preliminary Results

Table 10.1. Summary of calculated microstructural parameters for the as-prepared, 950°C-400h and 950°C-800h aged LSCF electrodes.

Microstructural Parameter	As-prepared	950°C-400h	950°C-800h
Porosity ε (%)	33.1	33.1	28.0
LSCF Surface Area a (μm^{-1})	3.31	2.70	2.50
LSCF Specific Surface Area a_s (μm^{-1})	4.95	4.04	3.48
Average Particle Size (nm)	500	560	620
LSCF Tortuosity τ	1.10	1.10	1.08

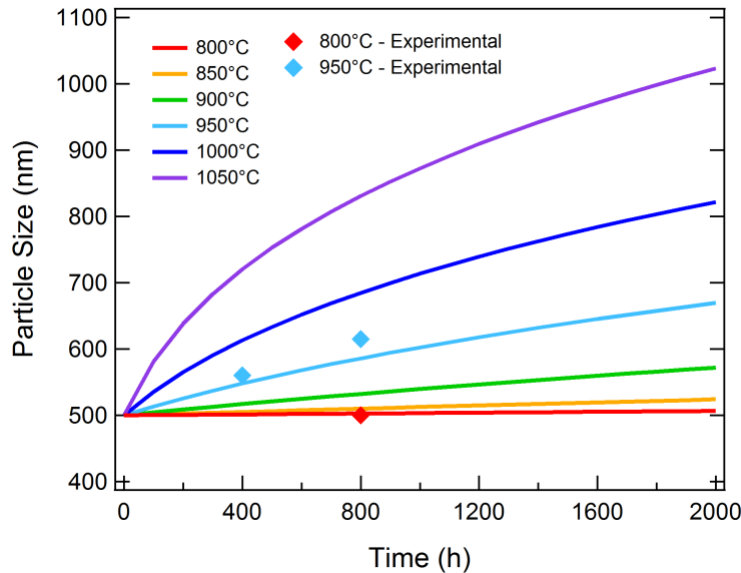


Figure 10.1. Coarsening prediction of LSCF with 500 nm initial particle size. Experiment results at 800 and 950 °C were shown as markers.

Ageing experiments for LSCF with 500 nm initial particle size have been conducted at 950 °C for 400 and 800 h. The microstructural parameters obtained from FIB-SEM 3D tomography data are shown in Table 10.1. It clearly shows particle coarsening, with increase in particle size and decrease in particle surface area with ageing time. The predicted coarsening of the LSCF particles at ageing temperatures from 800 to 1050 °C are shown in Figure 10.1, together with the

experimental data at 800 and 950 °C. In general, the prediction agrees reasonably well with the experimental results, but more data points are needed to improve the coarsening model, and eventually, to determine the activation energy for LSCF.

10.2. Future Experiments

Based on the approximate prediction in Figure 10.1, several ageing conditions were chosen and listed in Table 10.2. Again, symmetric-electrode cells, with identical LSCF electrodes screen-printed on both sides of GDC electrolyte, will be a key tool as they are more readily interpreted without any concerns of influence from other cell components. The ageing will be conducted in ambient air at the selected temperature. Since the temperatures are too high for contacting wires (silver and gold), in situ EIS measurements will not be carried out. Instead, EIS measurements will be conducted on cells after ageing treatment, followed by FIB-SEM 3D analysis. In addition to microstructural evaluation, Sr surface segregation will also be measured using ICP-OES. The obtained electrochemical data in combine with the microstructural parameters will be used to examine the effect of Sr migration and morphological changes on the oxygen surface exchange and oxygen bulk diffusion processes, based on ALS model.

Table 10.2. Ageing conditions for LSCF coarsening study.

Ageing Condition	Temperature (°C)	Time (h)
#1	900	1600
#2	1000	800
#3	1000	1600
#4	1050	400

Electrode life testing at elevated temperatures are able to accelerate degradation, facilitating collection of data needed in a manageable timeframe. However, to extrapolate the data from accelerated testing to predict long-term stability under normal operating conditions, mechanistic models implemented with underlying degradation mechanisms are required. A number of models have been developed to perform electrochemical simulations on SOFC cathodes. The Fanner-Fung-Virkar (TFV) model is a useful first step to relate the microstructure of an electrode to its resistance. Shah, *et al.* developed a power law model applied to infiltrated LSCF cathodes.⁵⁹ The model allows prediction of polarization resistance versus time based on microstructural evolution. Recently, electrochemical simulations using lattice Boltzmann methods with measured 3D microstructure on the LSCF cathode have been developed by Matsuzaki, *et al.*, which yielded good agreement with measured electrode polarization characteristics.¹⁸³

In our case, the experimentally measured initial 3D structure will be used in the predictive models utilizing phase-field simulation, developed by collaborators in Prof. Katsuyo Thornton group at the University of Michigan. The simulated microstructural evolution will be compared to the experimentally measured data. Further modifications may be performed to improve accuracy of the models. Modeling of the effect of Sr surface segregation on cell performance is sought to be developed as well. Electrochemical simulations including observed degradation mechanisms may be used to predict the electrode polarization behavior and compare with the measured ones. This allows prediction of electrode durability over a much longer timescale.

Chapter 11

Conclusions

In this work, fabrication and electrode performance evaluation of SOFCs/SOCs have been conducted. The focus was on electrochemical performance and degradation of cathodes (or oxygen-electrodes in SOCs). Two main categories of cathode materials were investigated: LSM-YSZ two-phase composite and single-phase MIECs, including LSCF, LPBC, and SSC.

By using Fe_2O_3 as a sintering aid for YSZ electrolyte, the anode-supported SOFCs with Ni-YSZ anodes and LSM-YSZ cathodes, as well as oxygen-electrode-supported SOCs with Ni-YSZ fuel-electrodes and LSM-YSZ oxygen-electrodes were successfully fabricated at reduced-temperature via single-step firing. However, the requirement of co-firing LSM-YSZ electrodes at relatively high temperature, in this case 1250 °C, resulted in a relatively large polarization loss. The slight oversintering caused reduction in TPB density, and hence an increase in the electrode resistance. In anode-supported SOFCs, reducing the firing time from 4 h to 2 h increased the LSM-YSZ cathode TPB density, yielding improved cathode performance. Nevertheless, the thick LSM-YSZ oxygen-electrodes in the oxygen-electrode-supported SOCs showed large gas diffusion limitation, and required further reduction in the oxygen-electrode electrochemical resistance. These were achieved by supplying pure oxygen instead of air to the oxygen-electrodes, and infiltrating nano-scale SSC particles, an MIEC material. The SSC particles provided additional TPBs for electrochemical reactions, but coarsening has been observed to happen quite rapidly at 800 °C, the testing temperature used in the study. The oxygen-electrode-supported SOCs were also tested under electrolysis mode, and demonstrated relatively high fuel and steam utilizations,

presumably due to the use of thinner fuel-electrodes. They were potentially applicable for SOC stack systems where fuel and steam contents may vary at different positions.

Compared to the two-phase composite structure, cathodes utilizing single-phase MIEC materials have increased reaction sites, and thus are suitable for lower-temperature operations. The performance and degradation of LSCF, the most common MIEC material for SOFC cathodes, were extensively studied in this work. Two types of experiments were carried out: high-temperature ageing and reversing current loading. The high-temperature ageing was conducted on both symmetric-electrode cells and full microtubular cells. Performance degradation was found to mainly relate to Sr surface segregation at temperatures $< 900\text{ }^{\circ}\text{C}$, which caused decrease in the oxygen surface exchange process, according to ALS model calculation. The segregated Sr present in both a uniform coverage of LSCF surfaces and 3D isolated Sr-rich particles. Coarsening of LSCF particles was only observed at sufficiently high temperatures, $\geq 950\text{ }^{\circ}\text{C}$. Although the electrodes aged at lower temperatures did not show coarsening within the testing period, it is unclear whether significant coarsening will occur at longer times. The degradation induced by reversing current operation was also found to primarily associate with Sr surface segregation, with a smaller contribution from current-switching-induced coarsening.

The selective chemical etching method was originally developed to quantitatively measure Sr surface segregation on porous LSCF electrodes, but it was found to generally applicable to cation surface segregations, as long as the segregated species are water soluble while the bulk materials are insoluble in water. One study in this work demonstrated the measurement of Ba surface segregation on LPBC cathodes. There was a 67% increase in the cathode polarization

resistance after life test at 700 °C for 280 h. 3D tomographic analysis ruled out the changes in microstructure. On the other hand, the surface Ba increased by ~ 2 times after testing.

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