NORTHWESTERN UNIVERSITY

Ceramic Anode Materials with Nanoscale Electrocatalysts

for Solid Oxide Fuel Cells

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

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EVANSTON, ILLINOIS

December 2007

ABSTRACT

Ceramic Anode Materials with Nanoscale Electrocatalysts for Solid Oxide Fuel Cells

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The work presented in this dissertation focuses on ceramic anode materials for solid oxide fuel cells (SOFCs). The primary goal was to characterize the anode and relate the electrochemical behavior to the microstructure. The anode that was most extensively studied in this work was a composite of $Gd_{0.10}Ce_{0.90}O_{1.95}$ (GDC) and $La_{0.80}Sr_{0.20}Cr_{1-x}Ru_xO_3$ (LSCrRu, x = 0.05 - 0.25). SOFCs with LSCrRu-GDC anodes achieved high power densities, > 500 mW/cm², and low polarization resistances, $\approx 0.16 \ \Omega cm^2$, at 800°C. When the cells were tested at constant current, the voltage increased significantly with time. In powders that were reduced in H₂ at 800°C, transmission electron microscopy images revealed the presence of nanometer-scale Ru particles on the surface of lanthanum chromite. Up to 300 h, the Ru particle diameter remained less than 5 nm. The high surface area of Ru, the catalyst phase, was determined to be the main cause for the time-dependent increase in voltage over time.

Detailed studies were carried out to determine the effect of anode current collector thickness, Ru content, operating current and temperature on the behavior and overall performance of cells with LSCrRu-GDC anodes. The performance of the cells increased with increasing current collector thickness, Ru content, operating current and temperature. The rate at which the performance improved and reached a maximum or stable voltage also increased. However, the onset of voltage degradation occurred earlier for cells with higher Ru content and those operated at higher temperature. SOFCs with LSCrRu-GDC anodes were also tested with hydrocarbon fuel, fuels containing sulfur and reduction-oxidation cycling. The anode did not suffer significant damage immediately after reduction-oxidation cycling. Cells tested with fuel containing sulfur showed a relatively high degradation rate but the performance was fully recovered by reduction-oxidation cycling. Overall, the LSCrRu-GDC anode material yielded high performance SOFCs and is a good candidate as an alternative anode material.

Similar anodes were tested and exhibited time-dependent behavior similar to cells with LSCrRu-GDC. However, the performance was unsatisfactory. Microscopy results showed that nano-catalyst particles precipitated from the host lattice upon reduction, demonstrating that the technique of nanometer-scale catalyst particle precipitation can be adapted to other materials.

ACKNOWLEDGEMENTS

I would like to express my gratitude and deep appreciation to Professor Scott Barnett for his guidance, support and patience. His knowledge and true interest in the science and engineering of fuel cells has kept me inspired throughout the years. Thank you also to my dissertation committee members, Prof. David Dunand, Prof. Laurie Marks, and Dr. Erica Murray, for their time and expertise.

I am indebted to Dr. Brian Madsen, who is not only a friend, but also a mentor for most of my graduate school years. I owe much of my knowledge to him, and I thank him also for his patience in answering all my questions. I am also deeply grateful to Dr. Yingmin Wang, for taking the time to do transmission electron microscopy work, even when he had much more important duties to attend.

My time at Northwestern was also truly enriched by having such a great group with which to work. I would like to thank members of the Barnett group, past and present: Jiang Liu, Zhongliang Zhan, Tammy Lai, James Wilson, Yuanbo Lin, Megna Shah, Blake Stevens and David Bierschenk. A special thank you also to Dr. Manoj Pillai and Dr. Ilwon Kim, for taking the time to discuss fuel cells, among other things, with me.

Finally, I am most deeply indebted to my family and friends for their infinite love and support. I thank my mom, dad and brother for their unconditional love and support, for their patience with me and their words of encouragement. I could not have done it without them. My husband, Kurt, is my rock and my world. Words cannot express how grateful I am to have him in my life. His love and support has pushed me through. I am grateful too to Chuck and Donna

Ruthe, Joanne and Ron Martin, Julie and Jack and the Breslins, and Scott, Chelsea and Erin Ruthe, for their love and support.

And finally, my experience at Northwestern University would not be the same without the friendships that I have developed. I am immensely grateful for my friendship with Mark Seniw. His love means the world to me. Thank you also to my good friend Pam who has had to put up with me ever since the beginning of our journey to the United States.

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Chapter 1

Introduction

In recent years, the rise in gas prices, the increased public awareness of global warming and concerns about national security have brought increased attention to renewable energy. Hydrogen fuel, in particular, has received much interest among researchers from both the industrial and academic sectors. This is partly due to the fact that hydrogen can be produced from a wide range of sources including biomass, coal, and natural gas. In addition, when hydrogen is used as fuel for fuel cells, the products are only water and heat which can be used for other applications. For these reasons, in spite of the associated technological and infrastructural challenges, hydrogen gas and fuel cells together remain an attractive method of obtaining clean energy. An example of the optimism in the potential that fuel cells hold is the \$1.2 billion Hydrogen Fuel Initiative launched by President George W. Bush in a 2003 State of the Union address. Since then, the United States government has appropriated several hundred million dollars to hydrogen and fuel cell research, development and demonstration [1].

Although there are several types of fuel cells, the specific type that is of interest in this dissertation is the solid oxide fuel cell (SOFC). Fuel cells are typically named after the material of which the electrolyte is made. The term "solid oxide" in SOFC therefore refers to the ceramic electrolyte. The anode and cathode of SOFCs are either ceramic or ceramic-metal composites (cermet). These materials allow SOFCs to be operated at high temperatures, typically 600-1000°C, compared to as low as 80°C for polymer electrolyte membrane fuel cells [2]. There are numerous advantages to the high operating temperature of SOFCs, including the ability to utilize

hydrocarbon fuels and, combined with gas turbines in hybrid power generation systems, the ability to yield high efficiency. That SOFCs can function on hydrocarbon fuels is of great significance, as the current infrastructure for hydrocarbon fuel delivery, e.g., natural gas, propane, *etc.* in the United States is already in place or can be easily adapted, while that for hydrogen still requires major development.

The work presented in this dissertation is concerned with the material that is used as the anode in SOFCs. The traditional SOFC anode material is a nickel metal and zirconia composite (Ni-YSZ). While this cermet can yield high anode performance, there are several known problems associated with Ni, such as particle coarsening, poor reduction-oxidation stability, sensitivity to fuel impurities such as sulfur, and susceptibility to carbon deposition during hydrocarbon fuel operation. Ni-YSZ and the other anode materials that have been investigated for use in SOFCs are discussed in Chapter 2. The purpose of this research was to characterize a unique new alternative material, a ceramic composite of doped lanthanum chromite and doped ceria, which has the potential to improve upon Ni-YSZ anode. The material was tested as an SOFC anode using electrochemical characterization methods, *i.e.*, electrochemical impedance spectroscopy (EIS) and current-voltage measurements. Also presented in this dissertation are results from various microstructural characterization. The goal was to determine the feasibility of this type of material as a replacement for Ni-YSZ.

The results and discussion in this dissertation are divided into four main chapters. The first two chapters (chapters 3 and 4) concern a Ru-doped lanthanum chromite based anode. Chapter 3 presents results from characterization, both microstructural and electrochemical, of the

Ru-doped anode utilizing hydrogen gas as fuel. Chapter 4 covers the anode performance under more harsh conditions, i.e., reduction-oxidation cycling, hydrocarbon fuel utilization, sulfur tolerance and operation under electrolysis mode. Chapter 5 discusses experimental results from similar anodes, for example, an anode doped with Ni rather than Ru. Finally, chapter 6 consists of a brief summary of the results and future work.

Chapter 2

Background

2.1 Fuel Cell Background

A fuel cell is an electrochemical device that converts chemical energy into electrical energy via the reaction between a fuel, e.g., hydrogen, and oxidant, e.g., oxygen. A basic fuel cell unit consists of a porous anode and cathode and a dense electrolyte. Unlike batteries, fuel cells are not energy storage devices. Therefore, in theory they can operate as long as fuel and oxidant are supplied to the anode and cathode, respectively [1]. In order to achieve a practical voltage level, several fuel cells must be joined together, forming a fuel cell stack. This requires an additional component, the interconnect, which conducts electrons between the fuel cells. Interconnects may also serve as mechanical support and a physical barrier between fuel and oxidant to prevent combustion. Figure 2.1 shows a simple schematic of a single fuel cell unit (Fig. 2.1a) and a sample schematic of a fuel cell stack (Fig. 2.1b). Note that these are flat-plate designs. Other fuel cells designs include tubular and segmented-in-series designs.



Figure 2.1: Schematic of a single fuel cell unit (a) [2] and a fuel cell stack of 115 cells (b) [1].

There are five types of fuel cells, classified by the electrolyte material: phosphoric acid fuel cell (PAFC), alkaline fuel cell (AFC), polymer electrolyte membrane fuel cell (PEFC, PEMFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). The differences among the types of fuel cells shall not be discussed in detail, but the major distinguishing factors are compared in Table 2.1.

	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated polymeric ion exchange membranes	Mobilized or immobilized potassium hydroxide in asbestos matrix	Immobilized liquid phosphoric acid in SiC	Immobilized liquid molten carbonate in LiAlO ₂	Fluorites, Perovskites (ceramics)
Electrodes	Carbon	Transition metals	Carbon	Ni and NiO	Oxide and oxide/ metal cermet
Catalyst	Pt	Pt	Pt	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Ni	Ni, ceramic, or steel
Operating Temperature	40-80°C	65-220°C	205°C	650°C	600-1000°C
Charge Carrier	H^+	OH	H^{+}	CO ³⁻	O ⁻
External Reformer for Hydrocarbon Fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell designs
Prime Cell Components	Carbon- based	Carbon- based	Graphite- based	Stainless steel-based	Ceramics

Table 2.1: Comparison of the five types of fuel cells. Adapted from [1].

2.2 History of SOFCs

In 1893, it was already known that platinum is a catalyst for the reaction between hydrogen and oxygen. Using this knowledge, William R. Grove invented a gas battery by submerging two platinum electrodes into a sulfuric acid electrolyte bath. One of the electrodes was covered with an inverted tube filled with hydrogen and the other with oxygen gas. Upon submerging the electrodes, a galvanometer indicated the flow of electrons. This was the first fuel cell invented, though at the time Grove named the device a "gaseous voltaic battery" [3].

During that period, coal was used to fuel steam engines. However, due to the enormous amount of energy lost in burning the coal, steam engines were able to convert only 10% of the chemical energy in coal into mechanical energy [3]. In 1894, Ostwald proposed that electrochemistry, using galvanic cells, was a more efficient method of extracting energy from coal than steam engines [4]. Then in 1896, William W. Jacques reported that he had produced electricity directly from coal using an electrochemical cell. This was done by using a molten potassium hydroxide electrolyte contained in a platinum crucible (positive electrode) and suspending a lump of coal in the electrolyte with platinum wire (negative electrode). Several studies followed the work by Jacques, using different materials for the electrodes, e.g., iron (Haber and Brunner, 1904), and the molten electrolyte, e.g., mixtures of potassium hydroxide and sodium hydroxide (Baur and Ehrenberg, 1912) [3].

It was not until 1937 that a solid electrolyte was used in a fuel cell developed by Baur and Preis, who were driven by the desire to replace the less-practical molten electrolyte cells [3]. The electrolyte material used was the "Nernst mass", a material identified almost 40 years earlier by Wilhem Nernst. Nernst observed that when zirconia was doped with certain oxides, such as

calcia and yttria, the material was insulating at room temperature, but conducted ions between 600 - 1000°C. At approximately 1500°C, the material conducted both electrons and ions. The Nernst mass was in this group of materials, with a particular composition of 85% zirconia and 15% yttria, and yielded an exceptionally high conductivity. According to the 1937 study by Baur and Preis, the Nernst mass had a low resistance of $1 - 4 \Omega$ at 1050°C, compared to 90 Ω for pure zirconia and 60 Ω for 10% magnesia-doped zirconia [4]. However, the performance of the cells when connected in parallel was unsatisfactory. The steady-state voltage was 0.83 V for eight connected cells, which was 0.2 V below the value obtained from a single cell. In addition, the voltage dropped even more when current was drawn from the cells, providing a volumetric power density of only 0.18 kW/m³, compared to the 10 kW/m³ required for power production at the time [3].

With the help of new characterization techniques, such as x-ray crystallography, the first detailed studies of SOFCs finally took place in the 1950s. The specific details of these investigations are not pertinent to the work presented in this dissertation. In brief, the studies concerned the structure and conductivity of the Nernst mass and other mixed oxides. With a better understanding of the conduction mechanisms in SOFCs, thermodynamic calculations were used alongside empirical results to further explain the effects that various factors, e.g. gas types and concentrations and operating temperature, had on cell behavior.

The advances in SOFC technology spurred a rapid rise of interest in SOFCs. In the United States alone, four companies applied for patents related to SOFCs between 1961-1962 [4]. To this day, there are over 30 SOFC companies around the world, two of which are publicly traded (Ceramic Fuel Cells, Ltd., Australia and Ceres Power, UK) [5]. There are also several large

companies, such as Mitsubishi, Rolls Royce, etc., that have significant SOFC efforts. The National Energy Technology Laboratory (NETL), under the U.S. Department of Energy (DOE), initiated the Solid State Energy Conversion Alliance (SECA) to bring together government-funded research from the private and academic sectors in an effort to reduce the cost and improve the efficiency of SOFCs. SECA's target goal for 2010 is to produce 3 - 10 kW SOFC power generation systems at a cost of \$400/kW (based on a 250 MW annual electricity production). Currently, the projected system costs are in the range of \$724 - \$775/kW [6].

2.3 SOFC Operation with Hydrogen Fuel

SOFCs are fuel cells that consist of all solid-state materials, typically ceramics. In operation, the anode is supplied with H_2 gas as fuel and the cathode is supplied with an oxidant, i.e., O_2 or air. In the anode, the H_2 gas dissociates and the electrons travel through an external circuit to the cathode, while the hydrogen cations react with oxygen anions at the anode/electrolyte interface as follows:

$$H_2 + O^{2-} \rightarrow H_2 O + 2e^- \tag{2.1}$$

At the cathode/electrolyte interface, oxygen gas combines with electrons from the external circuit to form oxygen ions:

$$\frac{1}{2}O_2 + 2e^- \to O^{2-} \tag{2.2}$$

The oxygen ions travel through the electrolyte to combine with the hydrogen ions at the anodeelectrolyte as mentioned above. Combining the two reactions above (Eqs. 2.1-2.2), the overall reaction for the basic operation of an SOFC is obtained:

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$$H_2 + \frac{1}{2}O_2 \to H_2O \tag{2.3}$$

As can be seen from the overall reaction, water is the only product. Since this is an exothermic reaction, heat is generated as well ($\Delta H = -241.82 \text{ kJ/mol}$) [2, 4]. A schematic of a single SOFC utilizing H₂ fuel is shown in Fig. 2.2. Note that CO can be used as fuel as well, yielding CO₂ as the final product ($\Delta H = -282.99 \text{ kJ/mol}$) [4]. The detailed reactions paths are complex and usually not known. Further discussion on the reaction paths can be found in refs. [7-11].

On the microstructural level, the sites where the electrode reactions (Eq. 2.1 - 2.2) take place are called the triple-phase boundaries (TPB). A TPB is where the fuel or oxidant gases, present in the electrode pores, meet with the ionically- and electronically- conductive phases. An SOFC electrode should have highly interconnected TPBs to allow for a large number of reaction sites and transport paths for the gas phases, ions and electrons.



Figure 2.2: Basic schematic of an SOFC operating with H₂ fuel.

2.4 The Nernst Potential

The maximum electrical work, W_{el}, that can be derived from a fuel cell is given by:

$$W_{el} = \Delta G = -nFE \tag{2.4}$$

 ΔG is the change in Gibbs free energy, n is the number electrons involved in the reaction, F is Faraday's constant (96485.309 ± 0.029 C/g-mol electron) and E is the ideal potential of the cell. For standard conditions (25°C, 1 atm), Eq. 2.17 can be written as:

$$\Delta G^{\circ} = -nFE^{\circ} \tag{2.5}$$

The change in Gibbs free energy for a given reaction can be expressed as follows:

$$\Delta G = \Delta G^o + RT \ln(K) \tag{2.6}$$

where K is the reaction equilibrium constant. For the following reaction,

$$\alpha A + \beta B \to \chi C + \delta D \tag{2.7}$$

K is expressed as:

$$K = \frac{\begin{bmatrix} C \end{bmatrix}^{\chi} \begin{bmatrix} D \end{bmatrix}^{\delta}}{\begin{bmatrix} A \end{bmatrix}^{\alpha} \begin{bmatrix} B \end{bmatrix}^{\beta}}$$
(2.8)

The square brackets denote the concentration of each component.

By substituting Eqs. 2.4, 2.5 and 2.8 into Eq. 2.6, an expression for the Nernst potential, E, is obtained:

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{[A]^{\alpha} [B]^{\beta}}{[C]^{\chi} [D]^{\delta}}$$
(2.9)

For hydrogen operation (see Eq. 2.3) in SOFCs, the reactants and product are in gas phase, the expression for the Nernst potential can therefore be written using the partial pressures of each component.

$$E = E^{o} + \frac{RT}{2F} \ln \frac{(pH_2)(pO_2)^{\frac{1}{2}}}{(pH_2O)}$$
(2.10)

The Nernst potential, also called the open circuit voltage (OCV), is the maximum ideal voltage that the SOFC can achieve at a given temperature and partial pressures [1, 4].

2.5 SOFC Electrochemical Characterization

The electrochemical behavior of the SOFCs in this research was characterized by two main methods: current-potential (I-V) measurements and electrochemical impedance spectroscopy (EIS).

2.5.1 I-V Characteristics

The I-V curves presented in this dissertation were obtained by supplying the cell with a range of potentials, typically from 20-30 mV above the OCV to 0 V (short-circuit condition), and measuring the corresponding current level. Figure 2.3 illustrates a generic voltage versus current density (current divided by electrode active area) plot that may be obtained from an SOFC. Note that an I-V curve is generally plotted together with the power density (the product of voltage and current density) on the right axis.

The I-V plot can be divided into three regions based on the different sources of polarization, or voltage loss as illustrated in Fig. 2.4. At low current levels, near the OCV, the voltage drop from the ideal value is due to the activation energy of the electrode reactions on the microstructural level. For example, slow charge-transfer processes at the electrode/electrolyte interfaces can lead to high activation polarization. The Tafel equation is a semi-empirical



Figure 2.3: A generic I-V plot.



Figure 2.4: Actual and theoretical I-V characteristics of a fuel cell [1].

equation that can be used to approximate the voltage drop when the activation polarization (η_{act}) is $\geq 50 - 100$ mV:

$$\eta_{act} = \frac{RT}{\alpha nF} \ln \frac{I}{I_o}$$
(2.11)

The electron transfer coefficient is represented by α , and I_0 is the exchange current density.

At intermediate current levels, the voltage loss is due to ohmic resistances, mostly from the electrolyte. By decreasing electrolyte thickness and improving its ionic conductivity, the ohmic resistance can be reduced. The types of materials used (for all cell components), the cell geometry (which affects the ionic/electronic conduction path length) and the operation temperature are also factors that affect the cell ohmic resistance. The ohmic resistance is simply represented by Ohm's Law, R = V/I.

At high current levels, concentration polarization dominates. This is caused by slow mass transport of the reactant and/or products gases at the electrode surface or at the pores of the electrodes. For example, insufficient flow of fuel and/or oxidant to the electrodes can cause large voltage losses at high current. The concentration polarization is therefore related to diffusion, which is in turn a function of the bulk (C_B) and surface (C_S) concentrations of the diffusing species. The concentration polarization can be expressed as follows:

$$\eta_{conc} = \frac{RT}{nF} \ln \frac{C_s}{C_B}$$
(2.12)

The total polarization of the electrodes are the sum of the anode and cathode polarization as follows:

$$\eta_{electrode} = \eta_{anode} + \eta_{cathode}$$
(2.13)

where

$$\eta_{anode} = \eta_{act,anode} + \eta_{conc,anode}$$
(2.14)

and

$$\eta_{cathode} = \eta_{act,cathode} + \eta_{conc,cathode}$$
(2.15)

The effect of polarization is that the potential of the anode (V_{anode}) is increased from the ideal potential (E_{anode}) and the potential of the cathode ($V_{cathode}$) is decreased from the ideal cathode potential ($E_{cathode}$).

$$V_{anode} = E_{anode} + \left| \eta_{anode} \right| \tag{2.16}$$

$$V_{cathode} = E_{cathode} - \left| \eta_{cathode} \right| \tag{2.17}$$

Finally, the measured cell voltage is a contribution of the anode and cathode voltage and the ohmic loss:

$$V_{cell} = V_{cathode} - V_{anode} - IR \tag{2.18}$$

Note that as the polarization losses from the anode and cathode are decreased, the cell voltage becomes closer to the ideal voltage, $E_{cathode} - E_{anode}$ [1].

As shall be presented in the results chapters, in the I-V curves taken from laboratory experiments, the regions of activation and concentration polarization are not immediately obvious. In several cases, the entire I-V curve appears to concave up or down with no apparent "ohmic" region where the slope should be constant (following Ohm's law). In other cases, only two major slopes can be seen from the curves, such as a small slope at low to intermediate currents and a steep slope at high currents. These I-V curves should be analyzed on a case-to-case basis as the cells may have been processed differently or the operating conditions are not
identical. A useful tool in separating the sources of voltage loss is electrochemical impedance spectroscopy, discussed in the following section.

2.5.2 Electrochemical Impedance Spectroscopy (EIS or IS)

Impedance spectroscopy is a useful tool in characterizing SOFCs, particularly because while an I-V curve is useful in determining the overall cell performance, it does not provide information regarding the reactions and mechanisms within an SOFC. Although the interpretation of impedance spectra is by no means a simple task, at the very least, the technique allows one to distinguish the ohmic resistance (from the electrolyte) from the polarization resistances (from the electrodes) because of their different frequency dependences.

Impedance is a measure of the ability of a material to prevent current flow. Impedance is measured by supplying an AC potential at different frequencies to the material under investigation and recording the corresponding current response, which is phase-shifted from the signal. An excitation signal $E(t) = E_0 \sin(\omega t)$ yields a current response $I(t) = I_0 \sin(\omega t + \phi)$, where E_0 and I_0 are the magnitude of the voltage and current signals, respectively, ω is the frequency and ϕ is the phase shift. The impedance is given by [12]:

$$Z(\omega) = \frac{E(t)}{I(t)} = |Z| \exp(j\phi) = |Z| (\cos\phi + j\sin\phi)$$
(2.19)

Impedance data is collected over a wide range of frequencies, typically 100 kHz – 0.1 mHz [13]. The results can be plotted as $Z^{\prime\prime}$ vs. Z^{\prime} (Nyquist plot) (Fig. 2.5a) or phase shift and amplitude vs. frequency (Bode plot) (Fig. 2.5b).



Fig. 2.5: An example of (a) a Nyquist plot and (b) a Bode plot for the same set of IS data.

With regards to SOFCs, the ohmic resistance of the cell is a real number, i.e., no imaginary component. It corresponds to the high-frequency intercept with the real (Z') axis in a Nyquist plot. The polarization resistance of the cell can be found by subtracting the high-frequency intercept from the low-frequency intercept. Therefore, the total cell resistance (ohmic + polarization resistance) is the value of the low-frequency intercept with the real axis. The reactions and transport mechanisms within an SOFC can, in theory, be distinguished using impedance spectra as their timescales are different. Thus, the response signals from a given excitation frequency range, e.g., an arc, can be related to a specific process within the SOFC.

Analysis of impedance spectra are commonly modeled using "equivalent circuits". The circuits typically consist of a combination of resistors, capacitors and inductors. Typically, an

impedance spectrum is modeled using a resistor and constant phase element (CPE) connected in parallel, forming an "arc", or semi-circle, in the Nyquist plot. A constant phase element is usually used in place of a capacitor as most materials do not exhibit behaviors resembling an ideal capacitor. The impedance of a CPE is $Z = 1/(Y_o)(j\omega)^{-n}$. Y_o is the admittance, which is equal to 1/|Z|, at $\omega = 1$ rad/s, j is the imaginary unit, ω is the frequency and n represents the deviation from ideal capacitor behavior. For an ideal capacitor $Y_0 = C$ (C is the capacitance) and n = 1. A value of n < 1 indicates that the semi-circle is depressed below the x-axis. When the material behavior is more complex, more than one arc may be necessary to obtain a realistic model. In the work presented in this dissertation, the impedance spectra were modeled by connecting 2 - 3 sub-circuits, each consisting of a resistor and CPE connected in parallel, connected in series. In addition, the inductance, which mainly resulted from the interaction between wires for current collection, was accounted for by connecting it in series with the rest of the circuit. Note that the inductance is the source of the tail on the high frequency end (below the x-axis) of the spectrum as shown in the Nyquist plot (Fig. 2.5a). Finally, a resistor representing the ohmic resistance is connected in series. This shifts the entire spectrum along the x-axis.

The software used in fitting of the impedance spectra presented in this work was EQUIVCRT, written by Boukamp [14]. The software utilizes a non-linear least squares (NLLS) fitting method. The measure of the fit quality is the chi-squared value (χ^2), which is an indication of the deviation of the fit from the measured spectrum. All of the equivalent circuit fitting results in this dissertation have a χ^2 between $10^{-4} - 10^{-5}$. The notation used in EQUIVCRT for each relevant element is as follows: L for inductor, R for resistor and Q for CPE. A simple

model consisting of an inductor a resistor (ohmic) and one arc is written as LR(RQ). This circuit is illustrated in Fig. 2.6 along with a generic arc that may be generated by this circuit. Note that the fit for the data presented in the Nyquist and Bode plots in Fig. 2.5 above were obtained using LR(RQ)(RQ)(RQ) model circuit, i.e., three arcs. The admittance, Y^{*} and impedance values for the three circuit elements used in this work are shown in Table 2.2 [15].



Figure 2.6: A model circuit represented as LR(RQ) (a) and a generic arc that may be generated by this circuit (b).

Element	Admittance (Y [*])	Impedance (Z)
L	-j/ωL	jωL
R	1/R	R
Q	$Y_o \omega^n (\cos \frac{1}{2} n\pi + j \sin \frac{1}{2} n\pi)$	$\omega^n(\cos\frac{1}{2}n\pi - j\sin\frac{1}{2}n\pi)/Y_o$

Table 2.2: The admittance and impedance for each relevant circuit element.

The peak frequency (f_{max}) for each arc is given by $\frac{1}{2\pi}(RY_o)^{-1/n}$ and the capacitance at any

frequency is equal to $Y_o(2\pi f)^{n-1}\sin\frac{1}{2}n\pi$ [16].

2.6 Traditional SOFC Materials

2.6.1 Electrolyte

The electrolyte material for SOFCs must (1) be structurally and chemically stable in both reducing and oxidizing atmospheres at SOFC operation temperatures, (2) be chemically compatible with both the anode and cathode materials, (3) have high ionic conductivity and low electronic conductivity to prevent current leakage through the cell, and (4) form a dense, leak-tight layer to prevent the fuel and oxidant from mixing.

As mentioned in Section 2.2, the first electrolyte material used in an SOFC was 15 mol% Y_2O_3 -doped ZrO₂, i.e., the Nernst mass. To this day, YSZ is still the most commonly used electrolyte material in high temperature SOFCs (800-1200°C). The conductivity of undoped ZrO₂ is low due to the low concentration of oxygen ion vacancies and interstitial oxide ions [4]. Doping the Zr site with tetravalent cations such as Y⁴⁺ not only stabilizes the structure of the material (cubic fluorite) but also improves the ionic conductivity by increasing the number of oxide ion vacancies. The following equation (Eq. 2.20) shows the substitution of Y₂O₃ into ZrO₂ using the Kroger-Vink notation [2]:

$$Y_2 O_3 \xrightarrow{(ZrO_2)} 2Y'_{Zr} + V_O^{\bullet \bullet} + 3O_O^x$$
(2.20)

The conductivity of YSZ improves with the doping level up to ~ 9-10 mol% Y_2O_3 . The decrease in conductivity at higher doping levels is thought to be due to ordering of defects, clustering of vacancies or electrostatic interactions. This trend of conductivity with doping level has also been found in ZrO₂ doped with other tetravalent cations, such as Yb⁴⁺ and Gd⁴⁺. It is worth noting that stabilization of ZrO₂ with Y₂O₃ does not yield the highest conductivity but is preferable due to the low cost and availability of Y_2O_3 [2, 4]. The conductivity of doped ZrO_2 materials is highest in Sc₂O₃-doped ZrO₂. At only 780°C its conductivity is equal to that of YSZ at 1000°C (0.14 S/cm) [17].

Another common fluorite-structured electrolyte material is doped CeO₂. Like ZrO₂, undoped CeO₂ has low ionic conductivity. CeO₂ is typically doped with Sm₂O₃, Gd₂O3, Y₂O₃ and CaO [4]. 10% SrO-doped CeO₂ has also been shown to have conductivity similar to 20% Gd₂O₃-doped CeO₂ [18, 19]. Doped CeO₂ is mainly of interest for intermediate to low temperature SOFC applications, i.e., 400-800°C. For example, at 600°C the conductivity of a 10 mol% Sm₂O₃-doped CeO₂ (~ 0.02 S/cm) is approximately an order of magnitude larger than that of a 10 mol% Y₂O₃-doped ZrO₂ (~ 0.002 S/cm) [4]. One known issue with doped CeO₂ is it exhibits mixed conductivity, both electronic and ionic, at temperatures above 550-600°C and low oxygen partial pressures (< 10^{-11} atm [19]). This is due to the reduction of Ce⁴⁺ to Ce³⁺ leading to n-type electronic conduction, according to Eq. 2.21 [20].

$$O_{O}^{x} + 2Ce_{Ce}^{x} \rightarrow \frac{1}{2}O_{2}(g) + V_{O}^{\bullet \bullet} + 2Ce_{Ce}^{\prime}$$
 (2.21)

The electronic conduction of doped CeO₂ at the anode side (where pO₂ is $\sim 10^{-18}$ atm) decreases the performance of the SOFCs due to current leakage between the anode and cathode.

More recently, materials with the perovskite structure (ABO₃) have received much interest for their potential as electrolyte materials. Figure 2.7 shows the lattice structure of a cubic perovskite structure. The A and B sites have a total charge of +6 (+3 and +3), so these materials are very flexible in terms of the dopant oxidation state, which increases the number of options for dopant materials. The cations substituting the A and B sites can be a combination of 1+5, 2+4 or 3+3. Several perovskites, such as $LaCrO_3$, are stable over a wide range of pO_2 and temperatures, making them suitable for SOFC applications [4].

Nearly all of the results presented in this dissertation are based on doped LaGaO₃, specifically $La_{1-x}Sr_xGa_{1-y}Mg_yO_3$ (LSGM), electrolyte-supported SOFCs. Compared with other alkaline earth cations, Ca^{2+} and Ba^{2+} , doping the A site with Sr^{2+} yields the highest conductivity between 500-1000°C as shown in Fig. 2.8.

Doping Mg^{2^+} into Ga^{3^+} sites further increases the conductivity of the material and the increase is more significant compared to doping with In^{2^+} and AI^{2^+} [21]. In addition, Mg^{2^+} ions have a larger radius than do Ga^{3^+} ions (65 and 62 pm for Mg^{2^+} and Ga^{3^+} , S respectively [22]). This causes the LSGM lattice to expand, allowing for a higher solubility of Sr^{2^+} on the La site from 10 mol% without Ga^{3^+} doping to 20 mol% with Ga^{3^+} doping [4]. The increase in ionic conductivity of Sr- and Mg-doped LaGaO₃ is due to the increase in oxygen ion vacancies according to the following defect equations [22]:

$$2SrO \xrightarrow{(LaO_{1.5})} 2Sr'_{La} + V_O^{\bullet\bullet} + 2O_O^x$$
(2.22)

$$2MgO \xrightarrow{(GaO_{1.5})} 2Mg'_{Ga} + V_O^{\bullet\bullet} + 2O_O^x$$
(2.23)

Figure 2.9 compares the conductivity of LSGM to other oxide ion conductors. Although Y_2O_3 -doped Bi_2O_3 has the highest conductivity, Bi-based electrolytes have been found to exhibit high electronic conductivity due to the reduction of Bi^{3+} to Bi^{2+} [17] and they also tend to decompose in fuel.



Figure 2.7: Cubic perovskite lattice structure [23].



Figure 2.8: Plot of conductivity versus temperature for A site doped LaGaO₃

using Sr^{2+} , Ca^{2+} and Ba^{2+} [4].



Figure 2.9: Comparison of LSGM conductivity with other oxide ion conductors [17].

Since the electrical conductivity of LSGM is competitive with other oxide ion conductors in the 600-800°C range, it is studied mainly for utilization in intermediate temperature SOFCs (IT-SOFCs). LSGM also has negligible electron and hole conduction over a wide pO_2 range. At 800°C, the range of pure oxide ion conduction is between 0.25 - 10^{-25} atm. The boundaries of electronic (n-type and p-type) and oxide ion conductivity with respect to pO_2 and temperature, studied by Kim and Yoo [24], are shown in Fig. 2.10.



Figure 2.10: Boundaries of ionic and electronic conduction as functions of temperature and pO_2 . Figure adapted from Kim and Yoo [24].

A commonly known problem with LSGM is the difficulty in synthesizing a phase pure sample. Impurity phases such as LaSrGaO₄ and LaSrGa₃O₇ have been reported [25]. An excess of Sr can also lead to the formation of SrGaO₃ and La₄SrO₇, therefore, these samples must be prepared with care. In addition, for SOFCs with Ni-containing anodes a barrier layer must be used between the electrolyte and anode as Ni may react with the La in LSGM to form LaNiO₃ [25, 26].

2.6.2 Electrodes

The requirements for both SOFC electrodes are similar. Both anode and cathode must be (1) porous to allow for gas transport, (2) electronically- and ionically-conductive to ensure a large number of reaction sites, (3) compatible with the electrolyte and, if applicable, the interconnect material and (4) stable in oxidizing (for the cathode) and reducing (for the anode) environments at high temperatures. In addition, the cathode and anode must have a high catalytic activity for oxygen reduction and fuel oxidation, respectively (see eqs. 2.1 and 2.2).

The least complex electrode structure consists of a single electronic-conducting phase. With this structure, the TPB sites are limited to the electrode/electrolyte interface. The fuel and oxidant gases also have to travel long distances to reach the reaction site, resulting in electrode performances that are less than optimal. The schematic for this type of electrode is represented in Fig. 2.11a.

There are two main strategies for improving upon this simple electrode structure. The first is by adding another ionically-conductive phase to the anode (Fig. 2.11c), such as the same material as the electrolyte. In this case, the contact area between the electronically- and ionically-conductive phases is increased, thereby increasing the number of possible reaction sites

[7]. It is important, however, that all the phases are networked to form interconnected, rather than isolated, TPBs [27].

The second strategy is by using a mixed ionic and electronic conductor (MIEC) (Fig. 2.11b). This allows for bulk transport of oxide ions in the electrode, effectively extending the TPBs from the electrode/electrolyte interface into the electrode itself [8].

The type of anode presented in this dissertation does not fit exactly into any one of these three categories of electrodes. Upon reduction, the anode consists of an electronically- and ionically-conductive phase and, in addition, a small amount of metal catalyst. The exact structure of this anode will be discussed in detail in a later section.



Figure 2.11: Schematic of an anode with (a) a single-phase electronic conducting material, (b) a mixed-conducting material and (c) a composite of electronic and ionic conducting materials (the darkest phase represents an ionic conductor and the medium gray represents an electronic conductor). Figure adapted from [7].

2.6.2.1 Cathode

In the initial years of SOFC development, the cathodes used were typically noble metals such as platinum [1]. However, because noble metals are not economically viable, conductive oxides were explored as an alternative. Nowadays, the traditional cathode material is a ceramic composite of Sr-doped LaMnO₃ (LSM) and YSZ. LaMnO₃ is a perovskite with intrinsic p-type conductivity. When a divalent cation such as Sr^{2+} is doped into the A site, the electronic conductivity is enhanced. This is because to preserve charge balance within the lattice, Mn^{3+} must transition to Mn^{4+} according to [2]:

$$LaMnO_{3} \xrightarrow{SrO} La_{1-x}^{3+} Sr_{x}^{2+} Mn_{1-x}^{3+} Mn_{x}^{4+}O_{3}$$

$$(2.24)$$

Therefore, the hole concentration (Mn_{Mn}^{\bullet}) increases with Sr doping. The electronic conduction occurs via small polaron hopping, where holes "hop" between the Mn ions. Figure 2.12 shows the temperature dependence of the conductivity of LSM with different levels of Sr doping.



Figure 2.12: Electrical conductivity of LSM with temperature and amount of Sr dopant [4].

In high temperature SOFCs (operating temperature $\geq 1000^{\circ}$ C) where YSZ is commonly used as electrolyte, LSM is an appropriate cathode material as it yields high reaction rates (for oxygen reduction). It can also be mixed with YSZ. The similar thermal expansion coefficients of LSM and YSZ, the high ionic conductivity of YSZ and the high catalytic activity for oxygen reduction of LSM are factors that make LSM-YSZ a suitable cathode material.

One known issue with LSM is if an excess of La₂O₃ is present after the synthesis step, it can combine with humidity in the environment to form La(OH)₃. This can be catastrophic if it occurs during SOFC operation as the formation of a hydrated compound within the cathode can lead to its disintegration [2]. The excess La may also react with ZrO₂ which to form La₂Zr₂O₇ which is electronically insulating (2.5 orders of magnitude lower conductivity than YSZ [2]), thus degrades cathode performance. To address this issue, an A site-deficient LSM can be used, which ensures that there is no excess La. Lower conductivity has been observed in La-deficient lanthanum manganite, e.g., at 800°C the conductivity decreased from \approx 112 S/cm LaMnO₃ to \approx 90 S/cm for La_{0.9}MnO_{3+δ} [4]. However, with all factors taken into account, LSM-YSZ is still the choice material for high temperature SOFC cathodes.

At intermediate SOFC operation temperatures (600-800°C), the catalytic activity of LSM is relatively low due to decreased oxide ion conductivity [28]. Alternative cathode materials are therefore considered. Two widely-studied IT-SOFC cathode materials are Sr-doped LaCoO₃ (LSC) and Sr-doped LaFeO₃ (LSF). At 800°C, the catalytic activity of LSC is much higher than that of LSM. One measure of catalytic activity for oxygen reduction is the oxygen surface exchange coefficient. This is a measure of the rate at which oxygen can be transferred from the pores to the oxide (in this case, LSC or LSM) surface. For LSC this value is approximately 100

times larger than that of LSM [4]. However, LSC is known to have a high thermal expansion coefficient (CTE; $16 - 22 \times 10^{-6} \text{ K}^{-1}$ for LSC compared to $10 - 12 \times 10^{-6} \text{ K}^{-1}$ for YSZ) and reactivity with YSZ electrolyte.

LSF has a lower conductivity than LSC, but when doped with Co on the Fe site to form LSCF, the conductivity is improved. For example, the conductivity at 800°C in air for La_{0.6}Sr_{0.4}CoO_{3- δ}, La_{0.6}Sr_{0.4}FeO_{3- δ} and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} are 1585, 129 and 269 S/cm, respectively. LSF also has a lower CTE than LSC (12 x 10⁻⁶ K⁻¹) and when doped with Co this increases to 15-17 x 10⁻⁶ K⁻¹, which is still an improvement from LSC alone [29]. In brief, the choice of LSCF comes as a compromise between the low CTE and reactivity of LSF and the high conductivity of LSC. Finally, an additional advantage of LSCF over LSM is that LSCF is a mixed ionic and electronic conductor. As discussed earlier, the advantage of a mixed ionic and electrode, i.e., more reaction sites are available for oxygen reduction.

2.6.2.2 Anode

One of the most extensively studied materials related to SOFCs is the traditional Ni-YSZ anode. Compared to several other metals, e.g., Co, Fe, Pt and Ru, Ni has the highest electrochemical activity for hydrogen oxidation [30]. It is still considered the most successful anode material up to date despite the many problems associated with the presence of Ni.

Prior to SOFC operation, the anode material is NiO-YSZ. Upon exposure to reducing atmospheres at high temperature, NiO reduces to Ni metal. Due to the large decrease in volume upon reduction to Ni (theoretically \approx 41% volume change), the anode structure is left with pores which allow for gas transport. The reduction of NiO to Ni occurs rapidly, only requiring a few

minutes for a 100 μ m thick anode. The microstructure of a typical Ni-YSZ anode after reduction and testing in H₂ is shown in Fig. 2.13.

Though the conductivity of Ni-YSZ is mainly a contribution of the Ni component, the microstructure of each individual component and the network that they form are significant factors that affect the ability of the anode to oxidize hydrogen. Based on percolation calculations, it was predicted that at least 30 vol% of Ni is needed in the cermet in order for electronic conductivity to be dominant over the ionic conductivity. Indeed, experimental results show that the electrical conductivity of Ni-YSZ is three orders of magnitude higher when the Ni content is above at least 30 vol%. The conductivity decreases with increasing temperature, confirming that electronic conduction is the dominant mechanism [2]. There is also a dependence of conductivity on the particle size ratio of Ni to YSZ [30]. Interestingly, sintering the anode at high temperature (1400°C) even appears to aid the formation of both the YSZ-YSZ and Ni-Ni network, thus reducing the ohmic and polarization resistance [31].

As to be expected, the porosity also affects the anode performance as the pores are the transportation path of fuel to Ni/YSZ interface and also of the product gas, such as steam, to escape the cell. Based on two-dimensional calculations, Tanner *et al.* [32] studied the effect of electrode porosity on the charge-transfer resistance (between Ni and YSZ) and determined that resistance decreases with decreasing porosity. The minimum charge-transfer resistance occurred at 20% porosity, below which concentration polarization (i.e., gas diffusion loss) became an issue. Since the dominant mechanism of conduction in Ni-YSZ is electronic, the rate-limiting process is ionic transport. With decreasing porosity, the cross-sectional area in which ions may be transported increases, effectively reducing the resistance.



Figure 2.13: Typical structure of a Ni-YSZ anode after hydrogen operation observed by FIB-SEM (Zeiss 1540XB SEM). The light, medium and dark areas are Ni, YSZ and pores, respectively. Image courtesy of James Wilson.

In addition, the charge-transfer resistance decreases with increasing anode thickness. This can be predicted using the relation:

$$R_{ct} = \frac{\rho_{ct} \cdot \delta}{l \cdot \varepsilon} \tag{2.25}$$

where R_{ct} is the charge-transfer resistance, ρ_{ct} is resistivity, δ is the TPB thickness, 1 is the TPB length and ϵ is the TPB width. A schematic showing this geometry is shown in Fig. 2.14.



Figure 2.14: The geometry used in calculating the charge-transfer resistance at a TPB [32].

Simply put, the decrease in charge-transfer resistance with increasing anode thickness is due to the increase in total TPB length assuming all other factors remain unchanged.

The study of the effects of TPB length and structure on anode performance is an ongoing challenge due to the complex nature of the anode microstructure. Most studies in literature have been on the two-dimensional (2D) scale, e.g., using secondary electron microscopy (SEM). Since the microstructure is three-dimensional (3D), these 2D techniques cannot provide sufficient microstructural information. Studies on electrodes where the TPB length is clearly

defined, e.g., patterned Ni electrodes [33, 34], Ni point electrodes [35, 36] and porous Ni electrodes [37], have been done. The results from these studies do shed some light on the effect of TPB length but the TPB structure is not taken into account. Recent microscopy results obtained with a combined focused ion beam and secondary electron microscope (FIB-SEM) have shown that 3D reconstructions of the Ni-YSZ anode can be obtained [27]. The reconstructions allow for more realistic calculations of TPB length and structural characteristics such as tortuosity. In theory, this and other microstructural details can be related to the anode performance, which will help in the future engineering of anodes.

A state-of-the-art anode-supported SOFC with Ni-YSZ anode, YSZ electrolyte and LSM-YSZ cathode operating with hydrogen fuel and air oxidant can yield very high power densities, up to 1.8 W/cm² at 800°C. Figure 2.15 shows representative results for a button cell made from traditional SOFC materials.



Figure 2.15: Representative cell test results from a button cell made with Ni-YSZ anode, LSM-YSZ cathode and YSZ electrolyte. Voltage vs. current density is shown in (a) and the corresponding power density vs. current density is shown in (b) [38].

2.7 Disadvantages of Ni-YSZ Anode

Unfortunately, as noted earlier, the Ni-YSZ anode has several major disadvantages. These issues are (1) Ni coarsening, (2) Ni susceptibility to carbon deposition during hydrocarbon operation, (3) instability under reduction-oxidation (redox) cycling, and (4) low sulfur tolerance.

2.7.1 Ni Coarsening

The earliest known problem is the coarsening of Ni. Originally, pure Ni metal was used as the anode material. It was observed that when tested at high temperature, the Ni particles tended to agglomerate over time. This reduced the surface area for reactions to occur, thus decreasing the overall anode performance. YSZ was mixed with Ni in order to address this issue. That is, YSZ acted as the core structure for the anode and, to some degree, prevented Ni However, even with further development of the Ni-YSZ microstructure, this coarsening. problem persists. A detailed study of the effect of Ni coarsening on the conductivity of Ni-YSZ was done by Simwonis et al. [39]. After reduction in 4% H₂/3% H₂O/balanced Ar at 1000°C for 1000 h, it was found that the average diameter of Ni particles increased 13.2% (from 2.04 to 2.31 um), while the room-temperature conductivity dropped 10.3% (from 3900 to 3500 S/cm). After 4000 h, the average diameter increased further to 26% (2.57 µm) of the original diameter and the conductivity decreased by a total of 33.3% (2600 S/cm). This study was done on sintered pellets of Ni-YSZ, rather than on a fuel cell. Therefore, no current was passed through the cermet. It has been observed that the coarsening of Ni is more pronounced at high current densities [40]. It has also been observed that the Ni coarsening occurs to a lesser extent when the Ni particle size distribution is narrow and the steam content in the fuel is low, though the reason for this is not clearly understood [41].

2.7.2 Carbon Deposition

Because of the high operating temperature, SOFCs can operate directly on hydrocarbon fuels, via internal reforming or partial or full oxidation of the fuel. Hydrocarbon fuels are more practical than hydrogen since they are easier to obtain, store and deliver. For SOFC operation using hydrocarbons, an external fuel reformer, which outputs H₂ and/or CO, is not required. In contrast, PEM fuel cells require an external reformer along with shift reactions (eq. 2.29), for example, to remove impurities and CO, since they can only operate on pure hydrogen. Because an external reformer is not needed, the cost and complexity of the fuel cell system may be significantly reduced.

The internal reforming of a general hydrocarbon fuel in an SOFC occurs via the following reaction:

$$C_n H_{2n+2} + nH_2 O \to nCO + (2n+1)H_2$$
 (2.26)

Note that steam contents are often increased well above the stoichiometry given in eq. 2.26, in order to prevent hydrocarbon pyrolysis which leads to carbon deposition, according to Eq. 2.27:

$$C_n H_{2n+2} \to nC + (n+1)H_2$$
 (2.27)

The disproportionation of CO, i.e., the Boudouard reaction, can also cause carbon deposition on the anode [4]:

$$2CO \to C + CO_2 \tag{2.28}$$

Another reaction that may occur when CO, CO_2 , H_2 and H_2O are present is the water gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 (2.29)

SOFCs are also capable of directly oxidizing the hydrocarbon fuel without steam or any additional source of oxygen besides the oxygen ions provided to the anode via the electrolyte. If the hydrocarbon is "fully oxidized", the reaction product is CO₂, and if it is "partially oxidized", the product is CO, according to Eqs. 2.30 and 2.31, respectively [4]. A combination of both partial and full oxidation is possible as well.

$$C_n H_{2n+2} + (3n+1)O^{2-} \to nCO_2 + (n+1)H_2O + 2(3n+1)e^{-}$$
 (2.30)

$$C_n H_{2n+2} + nO^{2-} \to nCO + (n+1)H_2 + 2ne^-$$
 (2.31)

As with the case of internal reforming, carbon deposition on the anode is a major issue when the hydrocarbon fuel is partially and/or fully oxidized. Carbon deposition is a well-documented problem with Ni-containing anodes as Ni is a catalyst for both reforming and pyrolysis reactions (see, for example, [42]). An anode that is less susceptible to coking compared to Ni-containing anodes, e.g., Ni-YSZ, is therefore highly desirable.

Using thermodynamics, the minimum steam-to-carbon ratio at which carbon deposition will not occur can be calculated for a given temperature and pressure. Figure 2.16 shows the boundary above which carbon deposition occurs. However, experimentally, carbon deposition can, and often does, occur at these "preferred" conditions. Generally, carbon deposition is less likely to occur at a high steam-to-carbon ratio (> 2), but this also reduces the Nernst potential due to the increased pO₂ on the anode side. Lower operating temperature, higher Ni content and additives such as CeO₂, alkaline earth oxides, Mo, Pt and Ru have all been shown to suppress the deposition of carbon during methane operation [42, 43]. There are, of course, drawbacks associated with these proposed solutions. Lowering the operating temperature also results in reduced conductivity, especially for YSZ, and Ni is more likely to oxidize to NiO at temperatures below 700°C [30]. A higher Ni content reduces the reduction-oxidation stability of the anode even further (due to the large volume difference between Ni and NiO). And finally, the addition of another phase could add significant materials cost to the SOFC, especially if the additive is a precious metal.



Figure 2.16: The area in which carbon deposition takes place at 1 atm and between 900-1200°C according to thermodynamic calculations [44].

The mechanism of carbon formation in the Ni-YSZ anode is not clearly understood. Research has shown that the structure of carbon that forms in the anode, e.g., adsorbed, polymeric, graphitic, carbide, varies depending on the temperature and types of reactant [45]. When carbon is adsorbed onto the anode surface, the degradation is typically fully reversible. Recovery is done by increasing the amount of oxide ions to the anode, e.g., by increasing the current flow, which results in the formation of CO or CO_2 gases. However, when carbon forms within the pores and on Ni particles, this not only blocks the gas channels but also deactivates the Ni catalyst. This results in a loss of cell performance and may not be fully recoverable. For example, in wet methane operation the carbon forms as graphite and cannot be completely eliminated by oxygen permeation [30].

The problem of carbon deposition is one of the strongest drives for the development of an alternative anode material. Methane is the main component in natural gas, which is one of the most easily accessible and abundant alternative fuels at this time. However, methane is known to cause catastrophic coking in Ni-YSZ. An anode material that is less susceptible to coking should reduce the overall cost of maintaining the fuel cell system due to its longer lifespan.

2.7.3 Reduction-Oxidation Instability

Ni oxidation to NiO during SOFC operation causes a reduction in electrocatalytic activity, electrical conductivity and can result in mechanical failure of the anode. At 800°C, oxidation of Ni occurs at $pO_2 \ge 10^{-14}$ atm. There are several possible reasons why pO_2 can rise at the anode during SOFC operation. A disruption in the flow of fuel, such as when there is a power failure, allows air from the cathode or surrounding environment to enter the fuel stream. The gas seals should prevent most of the leakage of air, but there is always a very small amount of air that enters on the anode side. Oxidation can occur accidentally during start-up as well [46]. In order to avoid Ni oxidation during routine shut-down, SOFC stacks are typically purged with an inert gas.

Since NiO can be reduced back to Ni, the conductivity of the Ni-YSZ anode can be recovered (assuming all the NiO reduces to Ni). However, it has been observed that there is a shape change as well. Upon reduction, Ni tends to forms a near-spherical shape to minimize surface energy. This may not be an issue during the initial reduction. However, should oxidation occur, the resulting NiO has a different morphology from the initial pre-reduction form. This can cause cracking or spalling of the anode layer. In addition, when reduced back to Ni again, the microstructure of the pores, Ni and YSZ may not be as interconnected as they were originally. In fact, it has been found that Ni tends to coalesce into larger Ni particles during reduction, which reduces the surface area, thus reducing TPB length. Upon re-oxidation, this results in a larger volume than the initial NiO-YSZ composite [47]. Microcracks have been found in Ni-YSZ anodes after four redox cycles. This occurred when the anode was sintered at high temperature (1400°C) which leaves less porous areas that accommodate the expansion upon formation of NiO [48].

Overall, reduction-oxidation cycling instability is a major issue with this type of anode and any other Ni-based anode. The problem is further complicated by the contradictory results obtained from several studies. Other factors affecting the stability of Ni-YSZ that have been reported are Ni content, Ni-to-YSZ particle size ratio, Y_2O_3 content in YSZ, porosity, sintering temperature and oxidation temperature and environment [48].

2.7.4 Sulfur Poisoning

In natural gas, hydrogen sulfide (H₂S) and carbonyl sulfide (COS) are naturally present in very small amounts. Sulfur-containing compounds such as dimethyl sulfide ((CH₃)₂S) are also added to natural gas as odorants. Overall, natural gas contains a few parts per million of sulfur up to 1%, mostly H₂S, depending on the origin of the gas. Gasoline in the United States also contains an average of 300 pm of sulfur [3]. Diesel contains between < 15 ppm to > 500 ppm and propane contains 10 - 200 ppm of sulfur [49].

When reformed, the sulfur contaminants are converted to H_2S . Ni-YSZ has low tolerance for H_2S , which results in performance degradation over time. As little as 5-10 ppm of H_2S causes poisoning of the anode at 950-1000°C, and even lower levels can be tolerated at lower temperatures, e.g., 0.05 ppm at 750°C [50, 51]. For fuels containing low levels of sulfur (< 20 ppm), the performance degradation is usually reversible, at least partially, by supplying a clean, sulfur-free fuel to the anode. The level of performance recovery improves with increasing temperature in the 700-900°C range [50, 52]. The degradation, caused by the decrease in active Ni surface area, can be reversed at least partially by supplying the anode with a sulfur-free fuel. The level of recovery depends on the stability of the adsorbed species, which is higher at lower temperatures [50, 52]. It was also found that the tolerance limit above which severe poisoning occurs is much lower at lower temperatures, e.g., at 1000°C the anode can tolerate up to 2 ppm, while at 750°C the tolerance limit is only 0.05 ppm [51]. It was found that with the addition of 5 ppm of H_2S in a $H_2/3\%$ H_2O fuel stream at 950°C, the polarization resistance of a cell with Ni-YSZ anode increased to twice the original value [53].

However, at levels greater than 100 ppm, sulfur poisoning can cause permanent damage to the Ni-YSZ anode [54]. The sulfur is likely to react to the anode, especially the catalyst component. This form of sulfur-poisoning may cause a phase transformation in the anode microstructure and/or delamination of the anode from the electrolyte, both of which lead to irrecoverable damage to the cell performance [52].

There are several theories on the mechanism of sulfur poisoning. At low H_2S levels, the sulfur is thought to be physically (as H_2S on Ni) or chemically adsorbed onto the anode surface.

The chemisorption of sulfur on the anode occurs by the dissociative adsorption of sulfur according to the following equation [50, 52]:

$$H_2S(g) \leftrightarrow HS_{ads} + H(g/ads) \leftrightarrow S_{ads} + H_2(g/ads)$$
 (2.32)

At high levels of H₂S, the irreversible poisoning of Ni as likely due to the formation of Ni-S compounds, especially Ni₃S₂ according to [54]:

$$3Ni(s) + 2H_2S(g) \rightarrow Ni_3S_2(l) + 2H_2(g)$$
 (2.33)

The melting point of Ni₃S₂ is 789°C at pH₂S = 1 atm and 727°C at pH₂S ~ $10^{-2} - 10^{-3}$ atm. Ni₇S₆ and possibly NiS have also been found in poisoned Ni-YSZ anodes at 950°C [54]. However, sulfur poisoning may occur experimentally despite the insufficient levels of H₂S based on thermodynamic calculations. This suggests that the formation of Ni-S compounds is influenced by additional factors, such as surface roughness, particle size and current level [52].

Peterson and Winnick [55] proposed the following possible reactions at the anode when a sulfur-containing fuel is utilized. It should be noted that the following equations do not directly address reasons for degradation of the Ni-YSZ anode. These are rather the possible reactions in which a sulfur contaminant can be involved.

$$H_2 S + O^{2-} \to H_2 O + \frac{1}{2}S_2 + 2e^-$$
 (2.34)

$$H_2S + 3O^{2-} \to H_2O + SO_2 + 6e^-$$
 (2.35)

In addition, above 827°C, H₂S decomposes according to:

$$H_2 S \to H_2 + \frac{1}{2}S_2 \tag{2.36}$$

Both products from Eq. 2.36 can be oxidized. H_2 oxidizes forming water, and S_2 oxidizes to form SO_2 as shown in Eq. 2.37.

$$\frac{1}{2}S_2 + 2O^{2-} \to SO_2 + 4e^-$$
(2.37)

Finally, SO₂ can also react with H₂S to form yet more S₂ according to:

$$2H_2S + SO_2 \leftrightarrow \frac{3}{2}S_2 + 2H_2O \tag{2.38}$$

Since SO_2 is more thermodynamically stable than H_2S and S_2 , the reactions in Eqs. 2.35 and 2.37 are preferred. This can be achieved by increasing the O^{2-} levels at the anode/electrolyte interface, e.g., by adding an additional component with high ionic conductivity to the anode and/or electrolyte.

2.8 Alternative Anode Materials for IT-SOFCs

The search for a novel anode material is not only motivated by the aforementioned drawbacks of the Ni-YSZ anode, but also by the drive towards a lower SOFC operating temperature. An intermediate operating temperature, 600-800°C, has several advantages. First, the choices of materials are widened due to the less stringent requirement on thermal stability. For example, less expensive metals such as steel can be used as the interconnect. Metal interconnects are preferred over ceramics since they are easier and less expensive to fabricate and shape. Secondly, since reaction kinetics are slower at lower temperatures, the reactions that form products that are potentially detrimental to SOFC performance may be suppressed. Of course, the SOFC reaction kinetics are also slowed, but proper materials may be chosen to compromise the rates of the desired and undesired reactions. Finally, the start-up and ramp-down phases are shortened when the operating temperature is lowered.

One of the major requirements for SOFCs is that the combined (electrolyte and electrodes) area-specific resistance (R_{as}) should be $\leq 0.5 \ \Omega \text{cm}^2$, preferably as low as $0.1 \ \Omega \text{cm}^2$, in order to meet the target power density of 1 W/cm³ often quoted for transport applications [56]. Due to the decrease in conductivity in the electrolyte and the increase in polarization resistance of the electrodes at 600-800°C compared to 1000°C, it is necessary to develop new SOFC materials that meet this requirement. This problem is commonly addressed by using a thin electrolyte (10-30 μ m) on a thick anode support (300-500 μ m). An anode "active" layer, where most of the anode electrochemical activity occurs, is deposited between the anode support and electrolyte. This SOFC configuration minimizes ohmic losses from the electrolyte, thus in anode-supported SOFCs the major performance losses are from the anode and/or cathode [57].

There are still numerous studies on Ni-containing cermets (in addition to Ni-YSZ) as potential candidates for IT-SOFC anodes, for example, Ni-(Sm₂O₃-doped CeO₂) (SDC) [58], (Ni-Fe alloy)-SDC [59], (Ni-Co-Fe alloy)-SDC [60] and Ni-LSGM [25]. However, with the goal of eliminating or minimizing the amount of Ni in the anode, significant research effort has been invested into the development of ceramic anodes. Satisfactory R_{as} values have been achieved using these types of anodes. For example, 0.1 to 0.25 Ωcm^2 for Sr₂Mg_{1-x}Mn_xMoO_{6- δ} (x = 0-1) at 800°C [61], 0.25 Ωcm^2 for La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃ anodes at 925°C (with a Ce_{0.8}Gd_{0.2}O_{2- δ} interlayer) [62], 0.2 Ωcm^2 for cerium-modified (La,Sr)(Ti,Ce)O₃ anodes at 850°C [63] and \leq 0.2 Ωcm^2 for (La,Sr)(Cr,Ru)O₃-GDC anodes at 800°C (presented in this dissertation) [64]. In addition, these anodes may have better prospects for hydrocarbon operation than the traditional Ni-YSZ anode. For example, a (La,Sr)(Cr,Ni)O_{3- δ} anode was shown to have some catalytic activity towards methane reforming (28% methane conversion), but the highlight was that no

carbon deposition was found at a steam-to-carbon ratio of < 1 between 750-850°C [65]. Tao and Irvine [66] observed 68% methane conversion at 900°C using a (La,Sr)(Cr,Fe)O_{3- δ} anode when a O₂/CH₄ molar ratio of 1 was added to the reactor and up to 96% conversion was obtained when O₂/CH₄ was increased to 2:1.

An intermediate operating temperature also allows for a major change in the microstructure of the anodes. Specifically, the particles in the anode can be reduced down to the nanometer scale. In high temperature SOFC applications, nanometer-sized particles, e.g., Ni particles would sinter or coarsen significantly and quickly due to the drive to lower the energy associated with high surface energies. At intermediate temperatures, though coarsening or sintering still occurs, the rate should be reduced significantly. The interfacial area for the reactions to occur increases significantly when the catalyst, ionically- or electronically-conducting phase is nanometer-sized compared to the typical micron-sized particles. In other words, by reducing the particle radius by three orders of magnitude, the surface-to-volume ratio also increases three orders of magnitude, which should enhance the anode performance.

The most common method of introducing a nanoscale phase into the anode is wet impregnation or infiltration. This is typically done by dropping a suspension of nanoparticles, such as a nitrate, into a porous skeleton structure followed by a heat treatment step. The amount of nanoparticles can be increased by infiltrating the structure with the precursor multiple times. The average diameter of the nano-particles produced by this method is 100-300 nm [57]. This technique has been used successfully with a number of anode materials, yielding good performance, including Ni-SDC (Ni impregnated into SDC skeleton) [67], Ni-GDC (GDC impregnated into Ni skeleton) [68], Ru-SDC (SDC skeleton) [69, 70] and Cu-YSZ and (Cu-

SDC)-YSZ (YSZ skeleton) [71, 72]. Drawbacks of this method are: (1) Impregnation requires an additional processing step which increases the processing cost and time; (2) In anodesupported SOFCs the nanoscale material cannot be selectively added to only the anode active layer but rather to both the anode support and active layer. This increases the material cost unnecessarily as the nanoparticles are typically only needed in the active layer; (3) The heat treatment step may require high temperatures, as high as 1000°C to decompose the precursor, and has to be done after each impregnation step. This may result in the coarsening of the other materials and the previously-deposited nanoscale phase.

Other less common methods of obtaining a nanoscale anode structure include spray pyrolysis [73], plasma spraying [74] and polymeric routes (such as the Pechini method) [75, 76]. The development of these techniques specifically to form nanometer-scale structures in IT-SOFC electrodes is very much in the initial phase.

Chapter 3

(La,Sr)(Cr,Ru)O₃-GDC Anode Characterization

3.1 Introduction

In this chapter, a novel method and the results of introducing a nanoscale phase into a lanthanum chromite and GDC composite anode is studied in detail. LaCrO₃ was traditionally used as an interconnect material in high temperature SOFCs. This is due to its stability and high electronic conductivity in both reducing and oxidizing environments. LaCrO₃ is an intrinsic p-type conductor [2]. When doped with a divalent cation such as Sr^{2+} in the La site, the charge in the lattice is balanced by the change in oxidation state of Cr^{3+} to Cr^{4+} (small polaron hopping) and the formation of oxygen vacancies [77].

In this study, a Ru catalyst phase was added into the Cr site of a $La_{1-x}Sr_xCrO_3$ lattice, forming $La_{1-x}Sr_xCr_{1-y}Ru_yO_3$ (LSCrRu). This was done not only to enhance the conductivity of the oxide, but also to improve its catalytic activity for fuel oxidation. The mechanism by which this occurs is examined in this chapter. Ru was chosen due to its sintering resistance, high catalytic activity for hydrocarbon oxidation and reforming, carbon deposition resistance [78, 79]. Ru has been added as a catalyst phase and shown good performance in several types of SOFC anodes, such as Ru-YSZ, Ru-SDC and Ru-Ni-GDC [78-86]. Note that all the LSCrRu compositions studied here consisted of 20 mol% Sr (x = 0.20) in the A site, while the composition of Ru is between 5 – 25 mol% (y = 0.05 – 0.25) on the B site. For simplicity, the composition of the LSCrRu phase is denoted by the four digits following "LSCrRu". The first two indicate the dopant level in the A site and the last two indicate that in the B site. For example, $La_{0.80}Sr_{0.20}Cr_{0.82}Ru_{0.18}O_3$ is written as LSCrRu2018.

The choice of material added to the B site, Ru, was due to the fact that, similar to Ni, Ru has a high catalytic activity for hydrogen dissociation and fuel oxidation. Ru has been tested quite extensively and showed high performance as a catalyst material in SOFC anodes [70, 78-80, 82-85, 87, 88] using various fuels, e.g., H_2 , $H_2/H_2O/CO_2$, CH_4 and natural gas. In addition, compared to other platinum group metals (e.g., Ir, Rh, Pd and Pt) which are also known to be effective catalysts for fuel oxidation, Ru is significantly less expensive [86, 89].

The GDC phase was added to the anode in order to increase the ionic conductivity of the anode. The conductivity of lanthanum chromite tends to be lower in reducing atmospheres due to the formation of additional oxygen vacancies, which results in reduction of Cr^{4+} to Cr^{3+} to maintain charge balance [90]. Since GDC is a mixed conductor at low pO₂, the addition of GDC should also improve the anode electronic conductivity. Finally, GDC was chosen over the other common ionic conductor, YSZ, because it does not form secondary phases with lanthanum chromite. YSZ and Sr-doped lanthanum chromite tend to react to form $La_2Zr_2O_7$ and $SrZrO_3$. An added advantage is doped CeO_2 is known to have high resistance to carbon deposition [91-93].

The SOFCs in this study were all electrolyte-supported, with $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) as the electrolyte material. In general, electrode-supported cells exhibit higher conductivity due to the thinner electrolyte (minimizing the ohmic losses). However, electrolyte-supported cells are easier to fabricate as there are less processing steps. In addition, the thermal expansion mismatch of the components is less of an issue as the electrolyte is dense and thick

and the electrodes are only $\sim 25 - 50 \,\mu\text{m}$ thick. Even if cracking or spalling of an electrode was to occur, it can be resolved by adjusting processing factors, such as sintering temperature and composition. Fortunately, in this study, there did not appear to be significant CTE mismatch among the components.

The cathode material chosen was $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-6}$ -GDC (LSCF-GDC) as it has been shown to exhibit good conductivity (see Chapter 2, Section 2.6.2.1) and compatibility with the electrolyte material. The cathode had a current collection layer of the electronicallyconducting phase LSCF deposited on top to assist in the lateral conduction of electrons. Without the current collector, the poor conduction should be reflected in the higher ohmic resistance of the cell.

In most cells described here, the LSCrRu-GDC anode had a $La_{0.8}Sr_{0.2}CrO_3$ (LSCr) current collection layer as well. The effect of the addition of a current collector and its thickness is presented in this chapter.

3.2 Experimental Procedures

The electrolyte and both electrodes were made using standard ceramic processing procedures. $La_{1-x}Sr_xCr_{1-y}Ru_yO_3$ was synthesized by solid-state reaction. The starting powders, La_2O_3 (99.99%; Alfa Aesar), SrCO_3 (99.99%; Alfa Aesar), Cr_2O_3 (99%; Alfa Aesar) and RuO_2 (99.95%; Alfa Aesar), were weighed in appropriate amounts according to the desired stoichiometry in the final compound. The powders were ball-milled in deionized water using zirconia grinding media for approximately 24 h. This wet mixture was dried at room temperature and hand-mixed (with mortar and pestle) briefly to ensure thorough mixing of the phases. The powders were then reacted at 1200°C for 3 h in air to form LSCrRu.
To form LSCrRu-GDC, the LSCrRu and GDC (Gd_{0.1}Ce_{0.9}O₂₋₆; Fuel Cell Materials) powders (1:1 weight ratio) were ball-milled in ethanol using zirconia grinding media for approximately 24 h. The mixture was dried at room temperature and mixed further using mortar and pestle. To form an ink, the LSCrRu-GDC powder was mixed with a polymeric vehicle (Heraeus) using a three-roll milling machine. The typical solids loading in the ink was 20 - 25 vol%. Note that, prior to mixing with LSCrRu, the GDC powder was calcined at 800°C for 4 h in air in order to increase the average particle size. Since the as-received GDC powder had an average particle size of 5 - 10 nm (surface area > 100 m²/g), the surface area was too high to form a printable ink, i.e., the ink was too thick since the vehicle could not coat all the particle surfaces. The average GDC particle diameter after calcination was $0.2 - 0.4 \mu$ m. The LSCr current collector ink was made using similar procedures as LSCrRu, but without the addition of Ru.

The cathode was produced by mixing LSCF (Praxair) with GDC (Fuel Cell Materials) in a 1:1 weight ratio, then ball-milling for 24 h in ethanol. The powder was dried at room temperature and hand-mixed using a mortar and pestle. This was made into an ink using the same procedures as the anode. An LSCF current collector ink was also made using the same LSCF powder.

The LSGM electrolyte was made by mixing the starting powders, La₂O₃ (99.99%; Alfa Aesar), SrCO₃ (99.99%; Alfa Aesar), Ga₂O₃ (99.9%; ProChem) and MgO (99.95%; Alfa Aesar), in the appropriate amounts. The starting powders were ball-milled in ethanol using zirconia grinding media for 24 h, then the mixture was dried at 60°C. This powder mixture was sieved through a -120 mesh sieve ($\approx 125 \ \mu m$ opening) before being reacted at 1250°C for 12 h. The

reacted powder was sieved again through a -200 mesh (\approx 76 µm opening). The LSGM discs, which acted as supports for the SOFCs, were made by uniaxially pressing the powder into 3/4" (1.9 cm) diameter discs. The green discs were sintered at 1450°C for 6 h then ground lightly using 240 grit SiC paper in order to improve the adhesion of the electrodes on the electrolyte. The discs were then ultrasonically cleaned in ethanol or acetone for 5 – 10 min.

Finally, the SOFC was assembled by screen printing the anode and LSCr current collector (if applicable) onto the electrolyte. The anode was sintered at 1200°C for 3 h. The cathode and LSCF current collector were then screen printed on the other side of the electrolyte and cosintered at 1000°C for 3 h. Both the anode and cathode had an area of approximately 0.5 cm² (\approx 0.4 cm radius circle), which is considered the active area in all future calculations. A current collection grid was screen printed onto both the anode and cathode using Au paste (Heraeus). Screen printing is a common method of depositing a film of material onto a substrate. It is similar to silk screening of graphics onto fabric. For screen printing, an ink is pushed through a stainless steel screen (325 mesh; 28 µm wire diameter; 50 µm opening) by a rubber squeegee. The substrate is placed beneath the screen, thus as the squeegee travels across the substrate, the ink is deposited onto the substrate. The resulting (dried) film is 25 – 50 µm thick. Ag wires were connected to the Au grid using Au and Ag paste.

The button cell was sealed onto an Al_2O_3 tube of similar diameter using a copious amount of Ag paste to prevent cross leakage of the fuel and oxidant. The anode faced inside the tube and the fuel was supplied via a smaller tube that was inserted into the Al_2O_3 tube close to the anode. Ambient air was the oxidant in all of the experiments. Figure 3.1 shows a schematic of a cell (Fig 3.1a), an image of a cell prior to testing (Fig 3.1b) and the fuel cell test set-up (Fig. 3.1c)







Figure 3.1: Schematic of a single SOFC used in this work (a); Top view image of an SOFC with Au grid; Note that the electrode in this image is square, though most of the SOFCs in this study were circular (b); Schematic of the test set-up (c).

To test each cell, the furnace was ramped up to an operating temperature of 800°C in either air or Ar atmosphere. Once the thermocouple reading indicated that the cell temperature reached 800°C, the fuel supply, typically $H_2/3\%$ H_2O at a flow rate of 50 sccm, was supplied to the anode. After 5 – 10 min, the first IS measurement was then taken using a BAS-Zahner IM-6 impedance analyzer. The times given in discussions and figures are relative to the start of fuel flow. IS data was taken at OCV, 50 mV and 500 mV bias using a 20 mV amplitude within a frequency range of 100 mHz – 1 MHz. I-V plots were also obtained using the impedance analyzer. The IS and I-V measurements were taken at different times. To obtain life test data, the SOFC was supplied with a constant current and the voltage was measured.

3.3 Behavior of Cells with (La,Sr)(Cr,Ru)O₃-GDC Anodes

3.3.1 Cell Test Results for cells with (La,Sr)(Cr,Ru)O₃-GDC Anodes

The results in this section illustrate the typical behavior expected from this type of anode. Figure 3.2 shows the life test results for a representative cell with an LSCrRu2018-GDC anode operated in H₂/3% H₂O. This particular cell did not have an anode current collector and the life test was done at a constant current of 600 mA/cm². The voltage increased by 5% over a period of 96 h, from ≈ 0.59 V at 15 min to 0.62 V at 96 h. The most significant increase appears to be during the first 3 h of testing, when the voltage increased by $\approx 14\%$ from the initial value. In another cell (not shown here), the voltage increased by nearly 300% over 93 h, with a 90% increase in the first 3 h. The voltage for this cell reached a fairly stable value between 75-96 h. Although the most rapid improvement occurred during the first 3 h for most cells, the time required to reach a relatively stable or maximum voltage varied. For example, a relatively stable voltage (within $\pm 1\%$ of the nominal voltage) was reached in < 10 h for some cells. On the other hand, some cells never reached a stable or maximum voltage within a period of 100 - 300 h (depending on the length of the cell test), i.e., the voltage was still increasing at the end of the test.

Note also that the voltage for this cell began to decrease after 96 - 100 h. The voltage degradation between 96 - 311 h was $\approx 2\%$. The onset of degradation was also observed between 90 - 100 h in some other cells. This cause of this degradation is discussed in more detail later in this section.



Figure 3.2: Life test data obtained from a cell with LSCrRu2018-GDC anode at 800°C and 600 mA/cm². Courtesy of Dr. Brian Madsen.

Based on these observations, the general behavior of a cell according to its life test results can be divided into three regions (Fig. 3.2). Region I is where the most rapid improvement of voltage is observed, during the first 3 h. In Region II, the voltage still improves, but at a slower rate. For example, the rate of improvement for this cell in Region I was nearly 20 times larger than that in Region II. The behavior in Region III is not clearly defined as several trends have been observed. In this cell, the voltage appeared to reach a relatively stable value before slowly declining. Although rare in cell tests that are longer than 90 h, some cells remained at a relatively stable voltage for the duration of the test. Of course, this is also dependent upon the length of the cell test itself. Finally, as mentioned earlier, in some cases the voltage still exhibited an upward trend by the end of the cell test. It is noteworthy that the duration and time at which each of the regions is observed vary from cell to cell.

Figure 3.3 shows the I-V characteristics measured at various times for this same cell. The OCV increased from 0.97 V at 15 min to a maximum OCV of 1.02 V, which was stable between 96 - 311 h. The maximum OCV was slightly lower than the theoretical OCV value of 1.10 V. The I-V results agree well with the life test results in that the maximum power density increases most significantly between 15 min and 3 h. The maximum power density obtained for this cell was 398 mW/cm² measured at 96 h, which is a 100% increase from the value measured at 15 min. The maximum power densities achieved from cells with these anodes vary between 250 mW/cm² to > 500 mW/cm². The performance depended upon the Ru content, operating temperature and operating current.

The I-V curve measured at 15 min exhibited some curvature and then became fairly linear thereafter. This behavior, where the I-V becomes more linear, was commonly observed in these



Figure 3.3: The I-V characteristics at 800°C for a cell with LSCrRu2018-GDC anode.

Courtesy of Dr. Brian Madsen.

cells. The increase in OCV, the decrease in slope (which corresponds to the total cell area specific resistance, R_{as}) and the increase in linearity after 3 h indicate that the total cell polarization is reduced over time. Though not evident in this particular cell, it is not uncommon among these cells to exhibit concentration polarization at longer times (larger slope at high current densities). Once the cell has reached a certain level of performance, the gas diffusion kinetics becomes the rate-limiting mechanism.

The impedance spectra obtained from this cell at 800°C at different times are shown in Fig. 3.4. The locations of certain frequencies are marked. For simplicity, the frequencies (Hz) are denoted by the exponent of 10, e.g., "5" represents 10⁵ Hz. The ohmic resistance (high frequency intercept with the Z' axis; R_{ohm}) varied between $0.37 - 0.44 \ \Omega cm^2$. The conductivity of LSGM was shown to be ≈ 0.1 S/cm at 800°C [94]. Assuming an electrolyte thickness of \approx 400 μ m, this gives an expected ohmic R_{as} of 0.4 Ω cm². Therefore, the experimental ohmic resistance is within a reasonable range from the literature value. The ohmic resistance drifted towards larger values with time. However, the zoomed view of the IS data at 500 mV between 96 - 311 h (Fig. 3.5) shows that the drift in the high frequency intercept, i.e., ohmic resistance, is accompanied by a drift in the low frequency intercept. This indicates that the polarization resistance (R_{pol}) did not increase significantly within this period of time. The voltage degradation of the cell after 96 h shown in the life test (Fig. 3.2) was therefore not due to electrode effects. One possible cause of degradation is the peeling of the Au grid, most likely on the anode side as this was visually observed in several cells post-testing. Should this happen, the effective active area of the SOFC is reduced since current collection would not be as effective as it originally was.

The smallest cell R_{as} obtained was $\approx 0.60 \ \Omega cm^2$ measured at 96 h and 500 mV bias, giving an electrode R_{pol} of $\approx 0.20 \ \Omega cm^2$. Since the initial value was $\approx 0.62 \ \Omega cm^2$ at 15 min, the R_{pol} decreased by nearly 70%. The R_{pol} has reduced to as little as 20% of the original value in other cells. The smallest R_{pol} ever obtained from these cells was $< 0.2 \ \Omega cm^2$. Based on an IS study of LSCF-GDC symmetrical cells on LSGM and GDC electrolytes, the cathode R_{pol} at 800°C was found to be $0.04 - 0.05 \ \Omega cm^2$ ([64] and Appendix A). Therefore, most of the electrode resistance stemmed from the anode.

It should also be noted that the irregular shape of the spectra measured at low frequency at 15 min is likely due to the rapid changes in impedance during the initial period of testing. The spectra were all obtained from high to low frequency, thus the inward curving of the spectrum indicated a decrease in impedance during the measurement. The irregularity was not observed after longer times.

The impedance spectra were fitted using a non-linear least squares (NLLS) fitting software, EQUIVCRT, developed by Boukamp [14] (see Chapter 2, Section 2.5.2). It was determined from analysis of impedance spectra obtained from LSCF-GDC cathode symmetric cells (on LSGM) with LSCF current collection layers that the cathode contribution to R_{pol} was \approx 0.04 Ω cm² at 800°C. The peak frequencies of the two fitted arcs were located at 196 and 302 Hz. The high frequency peak was larger, with $R_{pol} \approx 0.03 \Omega$ cm². Details on the NLLS fitting of the cathode symmetric cell can be found in Appendix A.



Figure 3.4: Impedance spectra obtained from a typical cell with LSCrRu-GDC anode at 800°C. The spectra were taken at OCV (a) and 500 mV (b).



Figure 3.5: Zoomed view of the impedance spectra measured at 500 mV between 96 and 311 h. The high and low frequency intercepts both shifted to higher values.

Table 3.1 summarizes the results obtained from fitting the impedance spectra of the cell with LSCrRu2018-GDC anode (Fig. 3.4) at OCV (Table 3.1a) and 500 mV (Table 3.1b) at various times. The best fit was obtained when using a $LR_{ohm}(R_1Q_1)(R_2Q_2)(R_3Q_3)$ model circuit (illustrated in Fig. 3.6) for spectra obtained between 3 – 311 h. Because of the irregular shape at low frequencies of the spectra obtained at 15 min, the circuit $LR_{ohm}(R_2Q_2)(R_3Q_3)$ was utilized.



Figure 3.6: Equivalent circuit diagram corresponding to LR(RQ)(RQ)(RQ).

Time (h)	R _{ohm} (Ωcm ²)	R ₁ (Ωcm ²)	n ₁	f ₁ (Hz)	R_2 (Ωcm^2)	n ₂	f ₂ (Hz)	R ₃ (Ωcm ²)	n ₃	f ₃ (Hz)
0.25	4.15E-01	-	-	-	6.91E-01	0.75	1.96	4.14E-02	0.75	454.75
3	3.97E-01	3.93E-02	0.94	0.29	1.75E-01	0.78	13.30	4.14E-02	0.75	454.75
48	4.09 E-01	4.04E-02	0.91	0.28	1.67E-01	0.74	20.28	2.95E-02	0.82	481.62
96	4.21 E-01	3.93E-02	0.94	0.29	1.60E-01	0.76	24.85	4.14E-02	0.75	454.75
239	4.32 E-01	2.95E-02	1	0.41	1.99E-01	0.75	28.99	2.82E-02	0.77	422.71
311	4.36 E-01	3.13E-02	1	0.09	2.43E-01	0.69	30.30	6.37E-03	1	1035.56

Table 3.1a: Equivalent circuit fitting results (OCV) from a cell with LSCrRu-GDC anode

based on LR_{ohm}(R₁Q₁)(R₂Q₂)(R₃Q₃) model circuit.

Time (h)	R _{ohm} (Ωcm²)	R ₁ (Ωcm ²)	n ₁	f ₁ (Hz)	R ₂ (Ωcm ²)	n ₂	f ₂ (Hz)	R ₃ (Ωcm ²)	n ₃	f ₃ (Hz)
0.25	3.72E-01	-	-	-	5.61E-01	1	2.15	1.24E-01	0.49	31.20
3	3.82E-01	1.53E-02	1	0.85	2.16E-01	0.85	8.95	6.09E-02	0.51	474.48
48	4.00E-01	2.36E-02	1	0.99	1.41E-01	0.82	30.39	4.26E-02	0.62	1281.27
96	4.34E-01	7.45E-02	0.57	0.20	1.07E-01	0.85	27.97	2.86E-02	1	227.99
239	4.18E-01	3.90E-02	1	0.81	1.17E-01	0.89	33.51	6.20E-02	0.67	435.89
311	4.23E-01	3.89E-02	1	2.15	1.13E-01	0.93	40.54	5.63E-02	0.70	505.68

Table 3.1b: Equivalent circuit fitting results (500 mV) from a cell with LSCrRu-GDC anode

based on $LR_{ohm}(R_1Q_1)(R_2Q_2)(R_3Q_3)$ model circuit.

The induction component, L, (not shown in Table 3.1) had values of ~ 10^{-7} H at all times. Based on the peak frequency, it is possible that the cathode arcs were highly overlapped with that of the high frequency arc (R₃Q₃). Considering the R_{pol} associated with the cathode high frequency arc was 0.03 Ω cm², it was determined that the cathode was more responsible for the high frequency arc than was the anode.

For both the impedance spectra measured at OCV and 500 mV, the intermediate frequency arc ($f_2 \approx 9 - 40$ Hz) had the highest resistance, ~ 0.1 – 0.2 Ω cm² from 3 – 311 h. This arc also appeared to decrease in size most significantly with time. The lowest frequency arc, though the size fluctuated over time, appeared to decrease as well. This indicated that the mechanism associated with these two arcs were primarily responsible for the cell performance improvement. These are similar to the findings by previous work on (La,Sr)(Cr,V)O₃-GDC-Ni anodes by Madsen [16, 95] where the intermediate and low frequency arcs were found to be most significantly related to the anode performance. The arcs were also strongly negatively correlated as observed by Madsen as well. The correlation factor between the two arcs were as high as -0.98. Therefore, the absolute values of the low and intermediate frequency resistances should be taken with a grain of salt, though the sum of the two should still be considered.

Adler *et al.* [7, 8] studied the impedance of mixed conducting oxides extensively, focusing on processes that are not dominated by charge-transfer, which typically occur at high frequency. These processes include solid-state oxygen transport, O_2 surface exchange and gas phase diffusion. It was determined that these processes, especially in mixed-conducting oxides, are difficult to resolve using equivalent circuits due to their similar time constants, i.e., frequency range. The reaction kinetics were thought to be co-limited by these processes, which explain the strong correlation between the low and intermediate frequency arcs. The peak capacitance of such processes were expected to be in the range of $10 - 10^{-3}$ F/cm², larger than typical double layer capacitances ($10^{-4} - 10^{-6}$ F/cm²) [8]. The peak capacitances calculated from the NLLS fitting results of the cell with LSCrRu2018-GDC anode (Tables 3.1a and 3.1b) were ~ $10^{-1} - 10^{-2}$ F/cm² for the intermediate frequency arcs and 2 - 14 F/cm² for the low frequency arcs. The high frequency arcs generally had lower peak capacitances, on the order of 10^{-3} F/cm². As mentioned earlier, the high frequency arc was attributed largely to the cathode, at which the non-charge transfer processes most likely dominated as well (see Appendix A, Table A.1).

The specific processes associated with the low and intermediate frequency arcs in this study are not clear. It is possible that they are associated with hydrogen dissociation and diffusion of H^+ and/or O^{2^-} in or on the surface of the lanthanum chromite and GDC. The diffusion of oxygen vacancies within the anode is also a possible source of the arc. Oxygen vacancies are known to form in lanthanum chromite in reducing atmospheres. The activation energies for the low and intermediate frequency arcs calculated from NLLS fitting between 600 – 800°C were 2.46 eV and 1.17 eV, respectively. Unfortunately, literature values for such processes in a similar anode could not be found.

Referring back to Tables 3.1a and 3.1b, the cause of degradation at larger times (96 - 311 h) was determined to be mostly from the increased ohmic resistance as speculated earlier. However, there were contributions from the electrodes as well. The high frequency arc, in particular showed an increasing trend. As the high frequency arc is likely associated with charge transfer, whether in the anode or cathode, it is possible that the coarsening of the microstructure may have lead to a decrease in the efficiency of charge transfer (reduced TPB length).

3.3.2 Anode Microstructural Characterization

In order to gain further understanding of the behavior of LSCrRu-GDC anodes, the microstructure was characterized using x-ray diffraction (XRD; Rigaku 0.8 kW Dmax and 18 kW ATX-G diffractometers), x-ray photoelectron spectroscopy (XPS; PHI electronics, Dual-Anode X-ray Source (Al Ka) with Spherical Electron Energy Analyzer), secondary electron microscopy (SEM; Hitachi S-3400N-II variable-pressure SEM and Hitachi S-3500 SEM) and transmission electron microscopy (TEM; JEOL JEM-2100F Fast TEM, Tokyo, Japan). X-ray diffraction was done on powders smeared onto scotch tape or krypton film. Background reduction was carried out using JADE software (MDI, Livermore, CA). XPS was done on powders packed onto Cu or carbon tape. SEM was performed on both powders, which were loosely dispersed on carbon film attached to an SEM stub, and on anodes that had been screen printed onto an LSGM electrolyte (pre- and post-test). Finally, TEM was done on powders (LSCrRu, no GDC) prepared using the ultrasonic method without pulverization. The powders were dispersed in water/acetone by ultrasonic agitations, then the suspension was dropped onto a lacey carbon film, which covered a TEM Cu grid (Ted Pella). The samples were allowed to dry in air prior to TEM observations. Special care was taken into fully removing the water/acetone and any other possible contaminants, which may cause deterioration of the vacuum and produce artifacts during TEM studies.

3.3.2.1 As-Reacted Anodes

Figure 3.7 shows a typical XRD pattern from an LSCrRu powder after solid-state reaction at 1200°C using a Rigaku 0.8 kW Dmax diffractometer. The powder had a cubic perovskite



Figure 3.7: X-ray diffraction pattern of an LSCrRu2018 powder after solid-state reaction.

structure similar to $La_{0.8}Sr_{0.2}CrO_3$ (JCPDS card # 74-1980) as indicated by the vertical lines. There were no significant secondary phases.

However, some powders had 2 – 3 very low intensity peaks between $2\theta = 20 - 30^{\circ}$ (indicated by the two arrows in Fig. 3.7). This phase is possibly SrCrO₄, which has been observed in other studies on LSCrRu [78, 96, 97]. It is thought to be due to the oxidation of Cr³⁺ to Cr⁶⁺ during solid state reaction in air. Cr⁶⁺ then reacts with SrCO₃, which was a starting powder, to form SrCrO₄ [96]. The presence of SrCrO₄ implies that there was a Sr and Cr deficiency in the LSCrRu phase. However, the exact stoichiometry of the LSCrRu powders was not determined. Note that these peaks were also observed in the XRD pattern for a La_{0.8}Sr_{0.2}CrO₃

powder made in the laboratory. This indicates that the addition of Ru in the B site was not the cause of the formation of the SrCrO₄ phase.

The XRD pattern from a sintered LSCrRu2018-GDC anode was also obtained (not shown here). The pattern showed peaks for the two separate phases (LSCrRu and GDC) without any additional phases, indicating that the chromite and GDC did not react to form a secondary phase. The peaks for SrCrO₄ were not observed, possibly because the amount of SrCrO₄ was below the x-ray detection limit (\approx 1%). Since SrCrO₄ is stable up to 1808°C (at 1 atm) [98], it was unlikely that it disintegrated into SrO, Cr₂O₃ and O₂ during anode sintering (1200°C).

Figure 3.8 shows an SEM image (Fig. 3.8d) and elemental maps of Ru, Cr, and Ce (Fig. 3.8a-c) obtained by energy dispersive x-ray spectroscopy (EDS) of a screen printed and sintered LSCrRu2018-GDC anode prior to testing. The particle size varies between $< 1 \mu m$ to $3 \mu m$ in diameter. The larger particles appeared to be sintered GDC particles as seen from the Ce map (Fig. 3.8c). The average diameter of the lanthanum chromite particles was $\approx 1 \mu m$. The chromite and GDC phases were fairly well mixed, though better mixing may be obtained if the agglomeration of GDC particles can be prevented. A separate Ru or RuO₂ phase was not detected by this method as shown in the Ru map (Fig. 3.8a). However, with longer collection time, it was expected that Ru should be observed. In this particular map, the collection time was no longer than 30 min.

Based on a Brunauer-Emmett-Teller (BET) measurement using a Micromeritics ASAP 2010 surface analyzer on an anode powder before and after firing at 1200°C for 3 h, the average particle diameter increased by \approx 50%. For GDC, the as-received powder surface area was 198 m²/g and the approximate particle diameter was 5 – 10 nm according to the manufacturer. After



Figure 3.8: SEM image (d) and the corresponding elemental maps of Ru (a), Cr (b) and Ce (c) obtained from an LSCrRu2018-GDC anode prior to testing. The arrows indicate the locations of some of the GDC agglomerates, while the surrounding areas correspond to the LSCrRu phase.

calcination at 800°C for 4 h (prior to mixing with LSCrRu powder), the BET surface area decreased to $12.242 \pm 0.073 \text{ m}^2/\text{g}$. Upon sintering, the average grain diameter appeared to be \approx 1.5 µm, which corresponds to a BET surface area of ~ 0.3 m²/g. After the two heat treatments, the surface area of GDC increased by nearly 100 %.

Sample TEM images of different magnifications obtained from an as-reacted LSCrRu2018 powder are shown in Fig. 3.9. The particle diameter ranged between $0.1 - 1 \mu m$. The structure was determined to be cubic with a lattice parameter of ≈ 0.38 nm. This information is in agreement with the SEM observations and XRD data. No other phases besides the chromite were detected.



Figure 3.9: TEM images obtained from an as-reacted LSCrRu2018 powder. Images courtesy of Dr. Yingmin Wang.

3.3.2.2 Tested or Reduced Anodes

Figure 3.10 is a SEM image obtained from an anode after a cell test at 800°C for \approx 100 h. There is a large distribution of particle sizes. The GDC agglomerates, identified by EDS mapping (not shown here), grew from the pre-test size (< 3 µm) to 3 – 5 µm in diameter. The diameter of the chromite particles is \leq 1 µm as seen in the pre-test microstructure, though some particle sintering was observed as well. EDS mapping only showed the two phases, chromite and GDC.



Figure 3.10: SEM image obtained from an anode tested at 800°C for 96 h.

The XRD patterns of LSCrRu powders after annealing in H₂ at 800°C for 3 - 311 h were obtained using an 0.8 kW Rigaku diffractometer. There was no difference in these patterns from that of an as-reacted powder (Fig. 3.7) except the SrCrO₄ peaks generally had much lower intensities. Based on thermodynamic calculations, SrCrO₄ was not expected to disintegrate into SrO, Cr₂O₃ and O₂ at 800°C and pO₂ = 10^{-18} atm [97]. However, it is possible that SrCrO₄ was partially reduced to SrCrO₃. This would result in a lower SrCrO₄ peak intensity and the concentration of SrCrO₃ was likely below the x-ray detection limit.

When an 18 kW Rigaku ATX-G thin film diffraction system was used to obtain a normal scan around the strongest Ru peak (the (101) reflection at $2\theta = 44.016^{\circ}$ based on JCPDS card # 70-0274), the peak was observed in a powder reduced for 1000 h (Fig. 3.11). This small peak was only observable by using a powder reduced for as long as 1000 h and the sample was prepared by dropping a solution of the powder (isopropanol as solvent) onto a zero-background Si substrate. Because no other phases were observed in the diffraction pattern besides the chromite phase, the peak was determined to be from Ru metal despite the $\approx 0.6^{\circ}$ shift (to larger 20) from the expected position. This shift may have been partially due to poor alignment of the sample or equipment. Another possibility is that there may have been a slight compression of the lattice (between (101) planes), causing a decrease of the lattice parameter from 2.054 Å to 2.028 Å.

The average Ru particle diameter can be calculated using the Scherrer Equation [99]:

$$D_{hkl} = \frac{0.89\lambda}{(FWHM)\cos\theta}$$
(3.1)



Figure 3.11: A detailed XRD scan in the vicinity of the strongest metallic Ru peak obtained from an LSCrRu2018 powder reduced for 1000 h. The inset shows the wide scan to illustrate that no other phase was observed aside from the chromite phase.

where λ is the x-ray wavelength (1.54 Å for CuK α), FWHM is the full width at the halfmaximum peak intensity (radian), and θ is the peak location. Based on a FWHM of (4.2 ± 0.1) x 10⁻³ rad (0.24° ± 0.01°), the average diameter of Ru particles was calculated to be 35.4 ± 2.0 nm.

TEM studies were carried out in order to gain a clearer view of the structure of the Ru phase. LSCrRu powders were annealed in H₂ at 800°C for various amounts of time and then examined by TEM (by Dr. Yingmin Wang). The images obtained from LSCrRu2018 powders reduced in H_2 atmosphere for 1 - 1000 h are shown in Fig. 3.12. The as-reacted TEM image is also shown (Fig. 3.12a) for comparison. In the powder reduced for 1 h (Fig. 3.12b), small particles were observed on the surface, which were not found in the as-reacted powder (Figs. 3.9 and 3.12a). The approximate diameter of these particles was $\approx 1 - 2$ nm. The particle density was relatively low, especially compared to that observed in the powders reduced for 311 h and 1000 h (Fig. 3.12c and d, respectively). After 1000 h of reduction, the Ru particles appeared to be larger (1-6 nm diameter) than that observed after 1 and 311 h of reduction. Ru particles as large as 8 nm in diameter were observed in other areas of the powder. However, the particle sizes are still much smaller compared to the average diameter calculated from the XRD pattern (\approx 35 nm; Fig. 3.7). The discrepancy between the particle diameter observed by TEM and from the XRD pattern may be due to the fact that the Scherrer equation was derived for spherical and ellipsoidal particles, which was clearly not the case here [100]. It can also be seen in the TEM images that the particle size distribution also broadened with time, which is especially apparent in the powder reduced for 1000 h. The diffusion rate and paths are discussed in more detail in Section 3.3.3.

The lattice fringes of these nanometer-scale particles yielded atomic spacings of 1.35 and 2.14 Å in the (110) and (002) directions, respectively. This agrees within 1% of the lattice spacings of hexagonal Ru according to XRD values (JCPDS card # 70-0274). Because of these observations along with the significant improvement in the performance of cells with this type of anode, it was concluded that the nanoscale particles were Ru metal as predicted.

This was also confirmed by XPS results obtained from an LSCrRu2018 powder reduced for 45 h compared to that from an as-reacted powder (Fig. 3.13). The reduction in binding energy in the reduced powder corresponds to the formation of Ru metal from another binding state, such as Ru oxide. The reduced LSCrRu powder was also re-oxidized *in situ* at 500°C and the spectrum (not shown here) was unchanged, indicating that Ru remained in metallic form. Thermodynamically, at 500°C, Ru is expected to oxidize at $pO_2 > 10^{-12}$ atm (see Appendix C) [101]. That Ru remained in the metallic state indicates that the oxidation of Ru may have been kinetically-limited.

Based on literature [102], the position of the Ru $3d_{5/2}$ peak is at 280.2 eV. The binding energies of Ru $3d_{5/2}$ for RuCl₃ (Ru oxidation state is +3), RuO₂ (+4) and RuO₃ (+6) are 281.8, 280.8 and 282.6 eV, respectively. For the as-reacted powder, the Ru3d_{5/2} peak position was \approx 282 eV, which is closest to the peak position for Ru in RuCl₃. However, it cannot be immediately concluded that the Ru in LSCrRu exists as Ru³⁺ for the following reasons. First, raw XPS data is typically shifted due to reasons such as instrument error or uneven surface charging. Since carbon is present as a contaminant from the surroundings in most materials, the C 1s peak is often used as a standard for calibrating scans. However, the positions of the C 1s



Figure 3.12: TEM images of LSCrRu2018 powders as-reacted (a) and reduced in H_2 at 800°C for 1 h (b), 311 h (c) and 1000 h (d). Courtesy of Dr. Yingmin Wang.



Figure 3.13: XPS results obtained for the Ru $3d_{3/2}$ and $3d_{5/2}$ peaks as-reacted and reduced for 45 h. Courtesy of Dr. Yingmin Wang.

and Ru $3d_{3/2}$ peaks are statistically identical ($\approx 284 \pm 1 \text{ eV} [102]$). Therefore, in these scans, the alignment was done using the Cr $2p_{3/2}$ peak (574.1 eV). Though the relative positions of the two scans (as-reacted and reduced powders) should not be significantly affected, the exact peak positions may be slightly shifted from their expected values. Note also that the Cr $2p_{3/2}$ peak position did not shift significantly ($\approx 0.1 \text{ eV}$ difference) (Fig. 3.15) before and after reduction, which indicates little, if any change in the oxidation state of Cr (presumably Cr³⁺). Thus, this method of calibration should not be a large source of error in the data.

However, the other reason for the inconclusive oxidation state of Ru in LSCrRu is it is likely that more than one oxidation state exists. This would result in a separate peak in the XPS data, but it is possible that the peaks are highly convoluted. Peak deconvolution was not carried out for this study.

Sauvet *et al.* [78] speculated that the Ru oxidation state in LSCrRu is +4, which is the starting material, RuO₂. The Ru⁴⁺ ions substitute for Cr^{4+} , which form from the substitution of Sr^{2+} in the La³⁺ site (Section 3.1). In addition, Ru⁴⁺ has higher stability toward reduction than Cr^{4+} . Thus, Cr^{4+} is the species that is more likely to reduce in reducing atmospheres. Finally, the estimated ionic radius of Ru⁴⁺ (0.62 Å) in an oxide, compared to that of Ru³⁺ (0.68 Å), is closer to that of Cr^{3+} (0.615 Å) and Cr^{4+} (0.55 Å) [103], which results in a less distorted lattice. Regardless of the oxidation state of Ru in the LSCr lattice (prior to reduction), it was concluded from XPS spectra that Ru at the surface was in metal form upon reduction.

Figure 3.14 shows the XPS data obtained from the Sr 3d peak region. After reduction, the Sr peak shifted to a higher binding energy, which may be a result of Sr bonding with other elements such as oxygen. However, it is unlikely that SrO formed, since the peak position after reduction was 133.5 eV while that of Sr in SrO is 135.3 eV [104]. Despite possible inaccuracies from peak calibration using the Cr 2p peak, the observed peak position is much too far from that of Sr in SrO. Shin *et al.* observed a similar shift by comparing the Sr peak position of SrRuO₃ before and after annealing at 800°C at 10^{-11} atm [104]. The peak was attributed to the formation of Sr₂RuO₄. The presence of this phase could not be confirmed in this study. Since SrCrO₄ was observed in the XRD pattern after anode sintering (Fig. 3.7), it was possible that the shift in Sr peak position was associated with a change of oxidation state of Sr in the Sr-Cr-O phase (SrCrO₄ and/or SrCrO₃). However, the Cr 2p peak before and after reduction remained in the same



Figure 3.14: XPS data obtained within the Sr 3d peak region for an as-reacted and reduced LSCrRu2018 powder.

position (presumably Cr^{3+} position), which suggests that this may not have been the explanation for the Sr peak shift.

Based on a study on an LSCrRu anode by Sauvet *et al.*, the shift in the Sr 3d peak was attributed to Sr segregation to the near-surface regions. Under reducing conditions, oxygen vacancies form near the surface, causing Sr to diffuse to those areas to balance the charge near and at the surface [78].

Figure 3.15 shows the XPS data obtained around the Cr 2p peaks of LSCrRu2018 powder. For ease of comparison, the data was shifted such that the Cr $2p_{3/2}$ peaks were aligned. However, as mentioned earlier, the peaks in the as-reacted and reduced samples were only shifted by ≈ 0.1 eV, considering the FWHM of Cr $2p_{3/2}$ peaks are 1.5 - 3.0 eV [105], the peak locations (between reduced and as-reacted powders) were considered identical.



Figure 3.15: XPS results for Cr $2p_{1/2}$ and $2p_{3/2}$ peaks obtained from an LSCrRu2018 powder as-reacted and after reduction for 45 h. Courtesy of Dr. Yingmin Wang.

According to literature, XPS studies done on $La_{0.8}Sr_{0.2}CrO_3$ reveal that prior to reduction, Cr has at least two oxidation states, Cr^{3+} and Cr^{6+} [106, 107]. Cr^{4+} is also likely to be present, as postulated by Sauvet *et al.* [78], but the binding energy is similar to that of Cr^{3+} and the peaks are broad, making its existence difficult to confirm. Yan *et al.* [106] also observed that upon reduction in 10% H₂/Ar at 600°C for 2 h, all of the Cr^{6+} was reduced to Cr^{3+} . Temperatureprogrammed reduction of $La_{0.8}Sr_{0.2}CrO_3$ doped with Ru showed that the reduction temperature of Cr reduced with Ru loading (0 – 1 wt%), from > 500°C to as little as $\approx 350°C$.

Based on the XPS results obtained from the LSCrRu2018 powder in this study (Fig. 3.15), the Cr 2p peaks indicate that Cr^{6+} was not present, i.e., the binding energies corresponded to Cr^{3+}

(583.8 eV and 574.1 eV for Cr $2p_{1/2}$ and $2p_{3/2}$, respectively [102]). This was true for both the asreacted and reduced powder. However, when the spectra was obtained for a powder with lower Ru content, LSCrRu2008, Cr⁶⁺ was observed prior to reduction (Fig. 3.16). The expected peak positions of Cr⁶⁺ were 587.7 eV and 578.7 eV for Cr $2p_{1/2}$ and $2p_{3/2}$, respectively [105]. Similar to results found for LSCr by Yan *et al.*, the Cr⁶⁺ was reduced to Cr³⁺ completely after 45 h of reduction at 800°C.

To summarize the above results, when LSCr is not doped with Ru or doped with a small amount of Ru (at least up to 8 mol% in the B site, which is 4.5 wt% in LSCrRu), Cr has at least two oxidation states, +3 and +6. However, when the Ru content is increased to at least 18 mol% in the B site (10 wt% in LSCrRu), Cr exists as Cr^{3+} and possibly Cr^{4+} . Based on these findings, it is postulated that the addition of 10 wt% Ru to LSCr effectively lowered the reduction temperature of Cr to approximately room temperature, such that the oxidation state of Cr was only +3. In other words, by doping LSCr with Ru, the Cr is stabilized in the +3 state. It must be noted that in all these cases, Cr^{4+} may be present as well, due to the substitution of 20% of the La³⁺ sites with Sr^{2+} . However, upon reduction, Cr^{4+} reduces to Cr^{3+} , regardless of Ru content, to maintain electroneutrality [65, 108].

The XPS results in the O 1s peak region is shown in Fig. 3.17. The data was obtained from an as-reacted LSCrRu2018 powder and a reduced powder (45 h) that was re-oxidized *in situ* at 500°C. In all three cases, there are peaks at \approx 528.8 and 530.7 eV. This is a common observation in perovskites and other metal oxides. The peak at lower binding energy corresponds to O²⁻ ions within the lattice. The larger binding energy peak is thought to be



Figure 3.16: XPS results around the Cr 2p peaks for an LSCrRu2008 powder as-reacted and reduced for 45 h.

associated with adsorbed O_2 or other oxygen-containing species, e.g., carbonates and hydroxyls, at near-surface regions (~ 20 Å) at the grain boundaries [109-112]. It is possible that the adsorption of oxygen species occurred during the cool down period of the furnace after annealing as this was observed in La_{1-x}Sr_xCoO_{3-δ} by Imamura *et al.* [112]. They also determined that La₁. xSr_xCoO_{3-δ} could accommodate more adsorbed oxygen species than an undoped LaCrO₃ due to the larger amount of oxygen vacancies. However, upon re-oxidizing at 500°C, the oxygen species desorbed returning the O 1s spectrum to still showed a strong peak at higher binding energy. This is an indication that the O species, most likely a hydroxyl group (OH⁻) was strongly bound to the chromite surface. One possible cause of this is that La₂O₃ may have been present in LSCrRu. La₂O₃ is has a strong tendency towards hydration, forming La(OH)₃, which may



Figure 3.17: XPS results obtained in the O 1s peak region for an as-reacted, reduced and re-oxidized LSCrRu powder. Courtesy of Dr. Yingmin Wang.

have been the source for the high binding energy O 1s peak. On the other hand, neither La_2O_3 nor $La(OH)_3$ were observed by TEM, EDS or XRD. Overall, based on these results alone, it cannot be determined whether the structure and/or oxidation state of oxygen was significantly altered by reduction in H₂.

To summarize the observations from cell tests and microstructural characterizations, the large improvement in performance over time was a result of the diffusion of Ru out of the lanthanum chromite lattice. The Ru phase, which is a known catalyst for hydrogen oxidation, formed nanometer-scale particles on the surface of the chromite particles. The large surface area of the nanoscale catalyst particles further enhanced the cell performance since the number of

reaction sites and total TPB length are increased. The Ru particles did not grow significantly over 1000 h. This is thought to be at least partially due to the refractory nature of Ru (meltin temperature = 2334° C). The kinetics of Ru diffusion out of the chromite lattice is investigated in more detail in the following section.

3.3.3 Kinetics of Nano-catalyst Precipitation

Based on the microstructural observations before and after reduction, it is likely that the Ru nanoparticles formed by diffusing out from the LSCrRu lattice upon reduction. In order to determine the diffusion coefficient of Ru through the chromite lattice, Ru particle dimensions and density were estimated based on TEM images of an LSCrRu2018 powder reduced for 45 h. Figure 3.18 shows the image obtained by scanning transmission electron microscopy (STEM), which was used to obtain particle density since the Ru particles were easily observed. However, the high resolution TEM (HREM) image (Fig. 3.18b) was more useful for obtaining Ru particle size as the particle edges were more clearly defined. Based on the powder reduced for 45 h and assuming the Ru particles were hemispherical, the particle diameter was ≈ 5 nm and the particle density was $\approx 4 \times 10^{16} \text{ m}^{-2}$ (i.e., 4 hemispheres per 100 nm²). Using an approximate LSCrRu spherical particle diameter of 1 µm, this size and density of particles comes from 12.5% of the bulk Ru. This amount of Ru would have to diffuse from a 22 nm-thick shell within the LSCrRu particle. Using the relation $D \sim L^2/t$ where D is the diffusion coefficient, L is the distance (22) nm) and t is time (45 h), the diffusion coefficient was calculated to be $\approx 3.0 \times 10^{-21} \text{ m}^2/\text{s}$. This value is in agreement with the literature value for cations bulk diffusion coefficients in lanthanum chromite extrapolated to 800°C ($\approx 10^{-21} - 10^{-20} \text{ m}^2/\text{s}$) [113, 114]. Details of the above



Figure 3.18: Images obtained by STEM (a) and HREM (b) for an LSCrRu2018 powder reduced in H_2 at 800°C for 45 h. Courtesy of Dr. Yingmin Wang.

calculation can be found in Appendix B.1. Note that this calculation is based on the assumption that all of the lattice Ru within the shell leaves the lattice to form Ru nanoparticles. This is most likely not the case because it would cause B site deficiency in the sub-surface regions, which could destabilize the lattice and result in phase decomposition.

A more detailed calculation was carried out (courtesy of Megna Shah) by solving the diffusion equation $\partial C/\partial t = D\nabla^2 C$, where C is the concentration of Ru, for a semi-infinite rod. The implication of the use of a semi-infinite rod is that the calculation is only valid for short times. When the depth from which Ru precipitates (L) is extremely small (i.e., L << 0.5 µm), the surface of the LSCrRu particle is approximately parallel to the surface of the inner sphere defined by C = C_{bulk} (C_{bulk} is the bulk concentration of Ru). See Appendix B.2 for details on this calculation. Using the same Ru hemisphere density as the previous calculation, the diffusion coefficient for Ru in LSCrRu was calculated to be ~ 10⁻²⁰ m²/s. Extrapolating the solution for

the diffusion equation to 311 h, the Ru particle radius was expected to be ~ 3.7 nm. This is clearly larger than the observed particles after 311 h of reduction (radius \leq 3 nm). Clearly, a more detailed model, which includes not only bulk, but also surface diffusion and coarsening via bulk and surface diffusion is needed to accurately describe the behavior of the Ru nanoparticles.

3.4 Comparison with (La,Sr)CrO₃-GDC-RuO₂ and (La,Sr)CrO₃-GDC

3.4.1 Cells with (La,Sr)CrO₃-GDC-RuO₂ Anode

To determine the effect of Ru addition to LSCr, two types of anodes were tested. One contained Ru as a separate phase, LSCr-GDC-RuO₂, and the other contained no Ru, LSCr-GDC. The LSCr-to-GDC weight ratio was kept at 1:1 as was done in the LSCrRu-GDC anodes. In order to compare the performance of LSCr-GDC-RuO₂ with that of LSCrRu2018-GDC, 5 wt% RuO₂ was used in the former anode, matching the calculated weight percentage of RuO₂ in LSCrRu2018-GDC.

Figure 3.19 is the life test result obtained from a cell with an LSCr-GDC- 5 wt% RuO₂ anode. The life test shows the three regions that were also observed in the cell with LSCrRu2018-GDC anode. The time required to reach a stable voltage was ~ 60 h, less than that observed in the cell with LSCrRu-GDC anode. The operating current for the cell with LSCr-GDC-RuO₂ anode was ~ 60% lower than that used for the cell with LSCrRu2018-GDC. Generally, for cells with LSCrRu-GDC anode, the time to reach stabilization increases with decreasing current. Therefore, if the mechanism which caused the performance improvement were the same for both types of cells, the time required to reach stabilization for the cell with LSCr-GDC-RuO₂ should have been longer. Because the catalyst was added as a separate phase, the improvement was thought to be at least partially due to the reduction of RuO₂ to Ru. As

 RuO_2 did not have to diffuse out of the chromite lattice to the surface, the improvement occurred at a faster rate.

Between 120 h to the end of the test, 239 h, the voltage degraded by 0.5%. Based on the I-V curves (Fig. 3.20), the maximum power density decreased from 261 mW/cm² at 96 h to 255 mW/cm² at 239 h. Note that the highest power density achieved was 262 mW/cm² at 152 h. The performance of these cells are significantly worse than cells with LSCrRu2018-GDC despite similar Ru contents. As seen from the impedance spectra (Fig. 3.21), R_{ohm} was not significantly different from cells with LSCrRu2018-GDC. However, the smallest R_{pol} achieved was 0.46 Ω cm² (at 500 mV and 96 h and 152 h), compared to < 0.2 Ω cm² for cells with LSCrRu2018-GDC.



Figure 3.19: Life test results obtained from a cell with LSCr-GDC-RuO₂ anode at 800°C and 340 mA/cm².


Figure 3.20: I-V curves obtained from a cell with LSCr-GDC-RuO₂ anode at 800°C.



Figure 3.21: IS results obtained from a cell with LSCr-GDC-RuO₂ anode at OCV (a) and 500 mV (b).

3.4.2 Cells with (La,Sr)CrO₃-GDC Anode

The life test result for a representative cell with LSCr-GDC anode is shown in Fig. 3.22. The voltage trend was dissimilar from that of typical cells with LSCrRu-GDC and LSCr-GDC-RuO₂ anodes. The major difference was the continuous increase in voltage for the duration of the \approx 320 h cell test. From 120 – 320 h, the voltage increase was 12%, a rate that was generally observed between 0 – 96 h in cells with LSCrRu-GDC anode. Thus, the voltage trend of cells with LSCr-GDC anode consists of only Region I and Region II as labeled in Fig. 3.22.



Figure 3.22: Life test results from a cell with LSCr-GDC anode measured at 800° C and 300 mA/cm^2 .



Figure 3.23: I-V curves obtained from a cell with LSCr-GDC anode at 800°C.

was the longest test performed on this type of cell, the time to reach stabilization could not be determined. It should also be noted that the large break in the life test measurement ($\sim 75 - 100$ h) was due to a power outage. During this period, the current supply to the SOFC was shut off, but the flow of fuel to the anode was uninterrupted. Upon re-starting the measurement (and current flow), the voltage rose fairly quickly and the voltage trend from prior to the power outage was continued.

One characteristic that was expected from this cell was its low performance compared to cells with Ru-doped anodes. As seen from the I-V curves (Fig. 3.23), the cell did indeed yield low power density, only achieving 202 mW/cm² after 312 h. Between 144 – 264 h, the maximum power density increased $\approx 3 \text{ mW/cm}^2$ every 24 h. However, between 264 – 312 h (48)

h), the rate slowed down to 1 mW/cm^2 per 24 h. It is unlikely that the cell could reach a power density as high as 500 mW/cm² observed from cell with LSCrRu-GDC.

The impedance spectra obtained from this cell (Fig. 3.24) showed high R_{pol} compared to cells with LSCrRu-GDC and LSCr-GDC-RuO₂ anodes. The minimum R_{pol} achieved was ≈ 0.7 Ωcm^2 measured at 239 – 311 h and 500 mV. The results from NLLS fitting of the impedance spectra to an LR_{ohm}(R₁Q₁)(R₂Q₂)(R₃Q₃) are presented in Table. 3.2.



Figure 3.24: IS results obtained from a cell with LSCr-GDC anode at 800°C and OCV (a) and 500 mV (b).

Time (h)	R _{ohm} (Ωcm²)	R ₁ (Ωcm²)	n ₁	f ₁ (Hz)	R ₂ (Ωcm ²)	n ₂	f ₂ (Hz)	R ₃ (Ωcm²)	n ₃	f ₃ (Hz)
0.25	3.72E-01	9.96E-01	0.92	0.17	7.75E-02	0.96	1.59	4.60E-01	0.54	10.12
3	3.68E-01	7.60E-01	0.94	0.21	5.35E-02	1	1.53	5.28E-01	0.50	7.07
96	3.74E-01	2.68E-01	0.99	0.28	2.22E-01	0.80	1.06	3.50E-01	0.51	21.48
239	3.68E-01	2.01E-01	1	0.35	8.43E-02	0.97	1.39	4.50E-01	0.46	11.75
312	3.70E-01	2.03E-01	1	0.35	7.54E-02	1	1.46	4.41E-01	0.47	12.76

Table 3.2: Results from NLLS fitting of the impedance spectra from a cell with LSCr-

GDC anode to a $LR_{ohm}(R_1Q_1)(R_2Q_2)(R_3Q_3)$ model circuit.

The decrease in R_{pol} was found to be mainly due to a decrease in the low frequency arc, where R_1 decreased from ~ 1 Ω cm² to 0.2 Ω cm². Note that the intermediate frequency arc size did not change significantly with time (with the exception of the value at 96 h). In contrast with the NLLS fitting results of the cell with LSCrRu2018-GDC anode, the low and intermediate frequency arcs were only weakly negatively correlated. Based on the peak frequencies and capacitances, the process associated with the low frequency arc were determined to be similar between cells with LSCrRu2018-GDC anode and those with LSCr-GDC anode. As discussed in Section 3.3.1, this is most likely not a charge transfer process. Note that the peak capacitance for both the low and intermediate frequency arc in the cell with LSCr-GDC was $\sim 1 - 2$ F/cm². On the other hand, the peak frequencies and capacitances associated with the intermediate frequency arc indicated that the process associated with this arc was different between the two types of cells. Overall, it was determined that the mechanism that caused the performance improvement in the cells with LSCrRu2018-GDC anode was different from those with LSCr-GDC anode. This was not unexpected as the addition of a high surface area catalyst phase, i.e., Ru, to the anode was expected to alter and improve the kinetics within the anode.

It is also worth noting that the cathode arc could not be clearly identified in these fittings. It is possible that the cathode arc was highly overlapped with the large high frequency arc ($f_3 = 7 - 21$ Hz). In addition, the inductance of this cell was twice as large as that observed in that with LSCrRu2018-GDC anode, which may have caused the cathode arc to shift to a negative y-axis position. An indication that the latter cause was likely the case is the lower R_{ohm} obtained by NLLS fitting ($\approx 0.37 \ \Omega cm^2$) compared to that observed in the spectra without fitting ($\approx 0.40 \ \Omega cm^2$). The unexpected behavior based on the test results, i.e., increasing voltage and decreasing R_{pol} over 312 h, (Fig. 3.22) warrants further discussion. That this was not observed in cells with LSCrRu-GDC and LSCr-GDC-RuO₂ anodes suggests that the addition of Ru had the effect of stabilizing lanthanum chromite, in addition to improving the anode catalytic activity. As observed from the XPS results for the Cr 2p peaks in LSCrRu, Ru allowed for stabilization of Cr in the +3 and possibly +4 oxidation state. For LSCr-GDC-RuO₂, it is possible that at least part of the Ru substituted for the vacancies, which exist in high concentration at the surface of lanthanum chromite in reducing atmospheres. This is likely to maintain mass balance at the surface. Yan *et al.* [106] speculated that Ru substituted for vacancies in (La,Sr)CrO₃ when it was impregnated with 0.05 – 0.1 wt% Ru.

In the case of LSCr, as Ru is not available to substitute for the vacancies at the surface, another species must diffuse to the surface to maintain electroneutrality and mass balance. As noted earlier in the discussion of XPS results on LSCrRu, Sauvet *et al.*, speculated that Sr^{2+} (Sr'_{La}) also segregates at the surface of lanthanum chromite, substituting oxygen vacancies $(V_o^{\bullet\bullet})$ [78]. Note that because LSCr is a p-type conductor, it is also likely that holes diffuse away from the surface to maintain charge neutrality within the entire lattice.

Akashi *et al.* [114] proposed that when LaCrO₃ is exposed to a reducing atmosphere, La vacancies $(V_{La}^{"})$ and holes $(h^{\bullet}$, such as Cr_{Cr}^{\bullet}) diffuse to the surface according to the following equation:

$$2V_{La}^{"} + 2Cr_{Cr}^{x} + 6O_{O}^{x} + 6h^{\bullet} \to Cr_{2}O_{3} + \frac{3}{2}O_{2}$$
(3.2)

Because the diffusion coefficient of holes (~ $10^{-19} \text{ m}^2/\text{s}$) is higher than La vacancy diffusion coefficient (~ $10^{-22} \text{ m}^2/\text{s}$), the diffusion process is limited by the diffusion of La vacancies. The surface charge must also be balanced according to $3[V_{La}^{"}] = [h^{\bullet}]$.

Regardless of the charged species that exists at the lanthanum chromite surface due to reducing atmosphere, an oppositely charged species must diffuse to the surface as a result. This is thought to be the main conduction mechanism for LSCr, thus, this may be the cause for the improvement in performance of the LSCr-GDC anode over 312 h. This hypothesis may be tested by an XPS study on an as-prepared and reduced LSCr powder. The surface enrichment of a particular species, e.g., Sr or Cr, after reduction could provide more information on the conduction mechanism. Unfortunately, XPS studies were not done on LSCr powders in this research work.

The main results presented in this chapter thus far are summarized as follows. Solid oxide fuel cells with LSCrRu2018-GDC anode were fabricated and tested, revealing that the voltage increased with time at a constant current. The cells also yielded high performance, with the best cell achieving over 500 mW/cm² and a low polarization resistance of $< 0.2 \ \Omega \text{cm}^2$ at 800°C. As the cathode contribution to the polarization resistance was small, $0.04 - 0.05 \ \Omega \text{cm}^2$, it was determined that most of the electrode resistance stemmed from the anode. The impedance spectra were fitted to an equivalent circuit, which show that the arcs at low frequency (0.1 – 2 Hz) and intermediate frequency (9 – 40 Hz) decreased most significantly with time. This indicated that the process(es) associated with these arcs were the source of the performance improvement. The source of these arcs were unclear, though they were possibly due to the dissociation and/or diffusion of H₂ and O²⁻.

Microstructural characterization was carried out utilizing TEM, SEM, XRD and XPS. XRD patterns revealed that the LSCrRu powder had a cubic perovskite structure. A small amount of secondary phase peaks were identified as SrCrO₄. SEM results reveal that the GDC particles had coarsened significantly over time, and was a possible cause of the degradation of the anode performance over time. TEM observations reveal that Ru nanoparticles formed on the surface of the lanthanum chromite particles upon reduction. The particles were roughly hemispherical with < 5 nm diameter after up to 311 h of reduction at 800°C. The particles grew to as large as 8 nm in diameter after 1000 h of reduction and the particle size distribution was wider than observed at shorter times. XPS results confirm the TEM observations in that the binding energy of Ru decreased after reduction, indicating Ru was in the metallic state. The presence of Ru nanoparticles explains the large improvement in performance over time. Ru is an excellent catalyst and is known to have a high activity for H₂ dissociation, thus the microstructural observations agree well with the results obtained from electrochemical characterization. Diffusion calculations based on the Ru particle density observed by TEM after 45 h of reduction yielded a diffusion coefficient for Ru in LSCrRu of ~ $10^{-21} - 10^{-20}$ m²/s. The value was consistent with that found in literature for cation diffusion in lanthanum chromite.

The performance of cells with LSCrRu-GDC anode were compared to those with LSCr-GDC-RuO₂ and LSCr-GDC anodes. Overall, cells with LSCrRu-GDC yielded the highest performance. Cells with LSCr-GDC-RuO₂ and LSCr-GDC yielded maximum power densities of only $\approx 260 \text{ mW/cm}^2$ and 200 mW/cm², respectively. Cells with LSCr-GDC-RuO₂ and LSCr-GDC anodes both showed time-dependence of voltage at a constant current density. The time-dependence for cells with LSCr-GDC-RuO₂ anode was thought to be due to the reduction of

RuO₂ to Ru, which is stable under the SOFC operating conditions. Cells with LSCr-GDC anode showed a constant increase in voltage over 300 h, a behavior that was not observed in the other types of cells. It was speculated that this was due to the instability of LSCr in reducing atmospheres. This causes oxygen vacancies to form at the surface of the chromite particle, which is compensated by the diffusion of Sr to the surface and likely the diffusion of holes away from the surface. In addition, it is possible that lanthanum vacancies diffuse to the surface upon reduction, which causes holes to diffuse to the surface in order to maintain charge neutrality. The rate limiting mechanism is the diffusion of ions/vacancies. As hole diffusion is likely to accompany ion/vacancy diffusion, this would explain the slow but constant improvement in voltage over time in cells with LSCr-GDC anode. Anodes doped with Ru were determined to be less susceptible to this process because Ru is thought to stabilize the chromite lattice.

A comparison of the average maximum power densities and minimum polarization resistance values obtained at 800°C for cells with LSCrRu2018-GDC, LSCr-GDC-RuO₂ and LSCr-GDC is shown in Fig. 3.25.



Figure 3.25: The average maximum power density (a) and average minimum polarization resistance (b) obtained from cells with three types of anodes at 800°C.

3.5 Detailed Studies of Cells with (La,Sr)(Cr,Ru)O₃-GDC Anodes

3.5.1 Effects of Anode Current Collection Layer on Cell Performance

3.5.1.1 Effect of the Addition of an Anode Current Collection Layer

The test results presented thus far are for cells that had a cathode current collector but no anode current collector. The conductivity of LSCrRu-GDC was likely to be relatively poor in H₂ at 800°C, based on the conductivity of LSCr (≈ 6.2 S/cm) [115] and GDC (≈ 0.26 S/cm) [116, 117] under those conditions. Therefore, it was possible that the performance could be enhanced by the addition of an anode current collector. To determine the effect of an anode current collection layer on cell performance, some cells were tested with an additional LSCr layer that had been screen printed and co-sintered with the anode. Figure 3.26 shows maximum power density versus time for cells with LSCrRu2018-GDC anode with and without a current collection layer. The maximum power density for the cell without a current collector reached 400 mW/cm^2 after 96 h, compared to 460 mW/cm² with a LSCr current collector. The inset in Fig. 3.26 shows the I-V curves for the cells measured at 96 h. Both the OCV and short circuit current of the cell with the anode current collector were higher than those of the cell without current collector. Note that the cell R_{as} (slope of the I-V curve) are similar at low current densities, up to ~ 500 mA/cm^2 . At higher current densities, the cell R_{as} is slightly lower for the cell with an anode current collector. This is also reflected in the IS results measured at 96 h (Fig. 3.27b). When measured at OCV (Fig. 3.27a), the R_{as} of both cells were similar, $\approx 0.65 \ \Omega \text{cm}^2$, but the R_{ohm} was significantly lowered, from 0.43 to 0.33 Ω cm², when an anode current collector was used.



Figure 3.26: Comparison of maximum power density vs. time for SOFCs with and without an anode current collector. The inset shows the I-V curves measured at 96 h.



Figure 3.27: Impedance spectra obtained from cells with and without anode current collector at 800°C and 96 h; (a) OCV, (b) 500 mV.

However, this also means that R_{pol} was larger when LSCr was utilized. The higher R_{pol} (0.32 Ωcm^2) appeared to be a result of the enlarged higher frequency arc.

At 500 mV bias, both types of cells exhibited lower R_{as} . Though R_{pol} is still higher for the cell with LSCr ($\approx 0.25 \ \Omega \text{cm}^2$ compared to $\approx 0.20 \ \Omega \text{cm}^2$ for the cell without LSCr), the cell R_{as} is smaller ($\approx 0.54 \ \Omega \text{cm}^2$ vs. $\approx 0.60 \ \Omega \text{cm}^2$ for the cell without LSCr).

Based on these results, it was concluded that the anode current collector improves the cell performance mainly by improving the ohmic resistance of the cell. The increase in R_{pol} is offset by the decrease in R_{ohm} , especially at higher current densities (lower voltage).

3.5.1.2 Effect of Thickness of Anode Current Collection Layer

The thickness of the anode current collector can be increased by screen printing additional layers of LSCr then co-firing with the anode. The effect of anode current collector thickness was tested by comparing the performance of cells with one (25 μ m thick) and two (50 μ m) layers of LSCr. The time-dependence of maximum power density and R_{pol} measured at 500 mV are shown in Fig. 3.28. Both the cell power density and R_{pol} were enhanced when a thicker LSCr layer was used. However, the rate of increase of maximum power density and decrease of R_{pol} did not depend upon the current collector thickness. This was an expected result as the current collector should not have an effect on the diffusion rate of Ru nanocatalysts. The cell with the thick current collector achieved a power density of 503 mW/cm² and R_{pol} of 0.16 Ω cm².

Based on the IS measurements made at OCV after 96 h of testing (Fig. 3.29a), the higher frequency arc (peak frequency = 40 Hz), which was the dominant arc, was much smaller for the cell with the thick anode current collector. The values of R_{pol} for the higher frequency arcs were ≈ 0.10 and 0.28 Ω cm² for the cell with thick and thin LSCr layer, respectively. For the low

frequency arc (peak frequency = 0.2 Hz) is present in both samples with $R_{pol} \sim 0.05 \ \Omega cm^2$. Though NLLS fitting was not performed on this set of data, the arc at higher frequency is likely an anode contribution. The cathode arc is most likely at a higher frequency, based on Table 3.1. This suggests that the thicker current collection layer allowed for improvement in kinetics of a process that does not involve charge transfer, possibly transport of oxygen and/or hydrogen ions.

Increasing the LSCr thickness also reduced R_{ohm} by $0.02 - 0.03 \ \Omega cm^2$. For the cell with thick LSCr, the low frequency arc was not observed in the IS measurement at 500 mV (Fig. 3.29b) possibly due to scattered data at low frequency.

Overall, the additional thickness of LSCr current collector improved the cell performance by decreasing both the ohmic and polarization resistances. The power density increased by ~ 50 mW/cm^2 when the thickness of LSCr was increased by 25 µm. This improvement is consistent with that observed in the previous section, where the power density improved by 60 mW/cm^2 in a cell with an anode current collector compared to one without the current collector.



Figure 3.28: Effect of anode current collector thickness on the maximum power density (a) and R_{pol} measured at 500 mV (b) over time.



Figure 3.29: Comparison of IS results from cells with thick and thin anode current collectors measured at OCV (a) and 500 mV (b) at 96 h.

3.5.2 Effects of Precipitation Temperature on Cell Performance

Since the improvement of the cell performance was determined to be due to the outdiffusion of Ru from the LSCrRu particles, the rate of improvement was also likely to have a strong dependence on the SOFC operation temperature. To test this theory, cells with LSCrRu2018-GDC anode were tested at 600, 700 and 800°C. The time-dependence of the R_{as} for these cells is shown in Fig. 3.30.

As expected, the R_{as} decreased with increasing operating temperature. This is due partially to higher overall conductivity in the materials as the ionic and electronic conduction processes are thermally-activated. The R_{ohm} measured at 48 h and 500 mV were 2.52, 0.70 and 0.36 Ω cm² for the cell tested at 600, 700 and 800°C, respectively. In addition, the diffusion of Ru out to the LSCrRu particle surface is presumably significantly faster. As seen in Fig. 3.30, the time required for the cells to reach a relatively stable R_{as} decreased with increasing temperature. The cell tested at 600°C was fairly stable after 80 h, while those tested at 800°C required less than 10 h to stabilize.

The breaks observed in the plots occurred when the life test data acquisition was interrupted for IS and I-V measurements. It is apparent that, upon restarting the life test, the R_{as} improves. This behavior was observed in all cells with LSCrRu-GDC anode. The exact cause for this behavior is not currently understood. It is speculated that the cause is a current effect, as the cell is cycled through a wide range of currents during the I-V measurement. The general trend in R_{as} of each cell was not affected significantly by these breaks.

At the end of the test for each cell operated at 700°C (\approx 96 h), the IS and I-V characteristics of the cell were measured at 800°C. Figure 3.31 compares the I-V curves measured at 800°C for cells tested at 700°C and 800°C after 96 h of testing. The cell that was tested at 700°C had a larger maximum power density (495 mW/cm²) than the cell tested at 800°C (426 mW/cm²).

If it is assumed that a specific mass or volume of precipitated Ru is required to obtain a relatively stable voltage, then this amount is achieved in ~ 8 h and 50 h for an operating temperature of 800 and 700°C, respectively. Based on work by Sakai *et al.* [113], the extrapolated bulk diffusion coefficients of a cation in lanthanum chromite at 700°C ($6.7 \times 10^{-23} \text{ m}^2/\text{s}$) is ~ 20 times smaller than that at 800°C ($1.4 \times 10^{-21} \text{ m}^2/\text{s}$). Therefore, the time required for the same amount of Ru to diffuse to the surface should also be 20 times larger at 700°C (i.e., 160 h). That it only took 50 h at 700°C to achieve stable R_{as} suggests that there are other factors involved. For example, Ru may be transported via other diffusion paths, such as surface or grain



Figure 3.30: Time-dependence of R_{as} for cells tested at 600-800°C.



Figure 3.31: I-V curves measured at 800°C for cells tested at 700°C and 800°C.

boundary diffusion. The size distribution or total surface area of the Ru particles may also affect the rate of improvement. Given the same amount of time, the Ru particles in the cell tested at 800°C may have grown more significantly than those in the cell tested at 700°C. Assuming that the average LSCrRu particle size is approximately equal at 700°C and 800°C, for the same total volume (or mass) of precipitated Ru, the ratio of surface area or surface coverage of Ru on LSCrRu is related to the ratio of Ru particle radii according to:

$$\frac{A_s(r_1)}{A_s(r_2)} = \frac{r_2}{r_1}$$
(3.3)

Where A_s is the surface area or surface coverage, and r_1 and r_2 are the radii of the Ru particles in cells tested at 700°C and 800°C, respectively. In addition, the ratio of the total length (L) of the LSCrRu/Ru interfaces, i.e., sum of circumferences of Ru hemispheres, is:

$$\frac{L(r_1)}{L(r_2)} = \frac{r_2^2}{r_1^2}$$
(3.4)

If $r_1 < r_2$ as expected, the larger surface coverage and TPB length would explain the higher power density of the cell tested at 700°C compared to that tested at 800°C when measured at 800°C (Fig. 3.31). An additional explanation is if more Ru diffuses out of the lattice at 800°C, the particle density would be higher, which may enhance the rate of particle coarsening due to shorter diffusion distances.

3.5.3 Effects of Ru Content on Cell Performance

Anodes with different amounts of Ru in LSCrRu were tested for comparison. The cells were operated at 800°C and 300 mA/cm². Figure 3.32 shows the time-dependence of cell R_{as} for representative cells with 5, 8, 18 and 25 mol% Ru in the B site of LSCrRu. The R_{as} generally

decreased with increasing Ru content, though the Ru content dependency is small at higher Ru contents. The average final R_{as} of cells with 5, 8 and 18 mol% Ru were similar, 0.72 ± 0.04 Ωcm^2 . The cells with LSCrRu2005-GDC anode reached an average of $0.82 \pm 0.05 \Omega \text{cm}^2$.

For each cell, R_{as} decreased with time and the decrease was most rapid during the initial period of the test. Similar to the behavior seen in the cells tested at different temperatures (Section 3.4.2), the rate of change of R_{as} was dependent upon the Ru content. The time required for R_{as} to drop to a relatively stable or minimum value decreased as the Ru content increases. In general, R_{as} for the cells with LSCrRu2005- and LSCrRu2008-GDC anodes were continuously, but slowly, decreasing at 96 h. On the other hand, the R_{as} for cells with LSCrRu2025-GDC anodes reached a minimum within ~ 50 h then slowly increased thereafter. The inset of Fig. 3.32 shows this behavior for cells with LSCrRu2025-GDC anode.

The R_{as} of the cells with LSCrRu2018-GDC anode exhibited several different trends, but most showed slow increases after 20-96 h. Generally, the onset of the R_{as} increase occurred after longer times compared to the cells with LSCrRu2018-GDC anode. On the other hand, the R_{as} of some cells continued to decrease after ~ 100 h.

Figure 3.33 shows the IS results for the representative cells at 96 h and 500 mV. The large differences in ohmic resistance are likely due to variations in electrolyte thickness among the cells. The R_{pol} decreased with increasing Ru content. The values for the cells with 5, 8, 18 and 25 mol% Ru anodes were 0.50, 0.43, 0.24 and 0.21 Ω cm², respectively.



Figure 3.32: Time-dependence of R_{as} of representative cells with different levels of Ru doping tested at 800°C. The inset shows the data for the cells with LSCrRu2025-GDC anode.



Figure 3.33: Impedance spectra at 500 mV for cells with different levels of Ru doping measured at 800°C and 96 h.

TEM images obtained from LSCrRu2005 and LSCrRu2025 powders that were reduced in H₂ at 800°C for 1000 h are shown in Fig. 3.34. Two major observations were made based on the TEM images. First, the Ru particle density in LSCrRu2025 is higher than that found in LSCrRu2005 and LSCrRu2018 (Fig. 3.12). The second observation is that the Ru particle sizes are larger, with diameters as large as 10 nm. There was a wide particle size distribution, especially compared with LSCrRu2005, but this was also observed in LSCrRu2018. It is not clear whether the wide particle distribution is due to continuous nucleation and growth of new particles or coarsening of existing larger particles at the expense of smaller ones.



Figure 3.34: TEM images of LSCrRu2005 (a) and LSCrRu2025 (b) powders after 1000 h of reduction at 800°C.

3.5.4 Effects of Current Density on Cell Performance

To determine the effect of current density on cell performance, several cells were tested at different current densities: open circuit voltage (OCV), 100 mA/cm², 300 mA/cm² and 600 mA/cm². Figure 3.35 shows the time-dependence of R_{pol} obtained from IS data at 500 mV and the maximum power density for representative cells.



Figure 3.35: Time-dependence of R_{pol} for representative cells measured at 500 mV (a) and maximum power density (b).

 R_{pol} decreased significantly with time as expected from other test results. The rate and final value of R_{pol} varied with the operation current. Unlike the dependence on operation temperature and Ru content, the rate of change of R_{pol} and final values did not follow a specific trend. The final R_{pol} for the cells tested at OCV, 100, 300 and 600 mA/cm² were 0.38, 0.17, 0.23 and 0.14 Ω cm², respectively. The R_{pol} for cells tested at 100 mA/cm² and OCV reached a stable value in less time (~ 24 h) than cells tested at 300 mA/cm².

The time-dependence of maximum power density for the cells tested at OCV, 100 and 600 mA/cm^2 were similar. The largest change in maximum power density occurred between 15 min and 3 h, and little change was observed after 3 h. The extent of improvement between 15 min and 3 h also increased with the operation current. The improvement in power density of the cell tested at 300 mA/cm² was gradual and this improvement continued past 100 h of testing.

The maximum power density at 96 h increased with increasing operation current, from 322 mW/cm^2 for the cell operated at OCV to 521 mW/cm^2 for the cell operated at 600 mA/cm^2 . The latter cell reached its highest power density of 534 mW/cm^2 at 3 h. This is also the highest power density achieved from this type of cell up to date. In addition to these results, it was observed from several other cell tests that those operated at 600 mA/cm^2 tend to yield high performance. While the cells operated at lower current density did not show a decline in maximum power density within 96 h, the cell operated at 600 mA/cm^2 decreased by $\approx 2.5\%$ between 3-96 h.

The reason for the higher performance in cells operated at higher current density is not clearly understood. Anodes tested at OCV, 300 mA/cm² and 600 mA/cm² at 800°C were scraped off and examined by TEM (by Dr. Yingmin Wang). For the anode tested at OCV, Ru particles could not be found on the lanthanum chromite surface. Very few particles were observed in the anode tested at 300 mA/cm² and only slightly more were seen in that tested at 600 mA/cm². A TEM image obtained from the anode powder tested at 600 mA/cm² is shown in Fig. 3.36.



Figure 3.36: TEM image obtained from an LSCrRu2018-GDC anode tested at 600 mA/cm² at 800°C. The arrows indicate the locations of the observed Ru particles. Courtesy of Dr. Yingmin Wang.

The absence and low density of Ru particles may have been due to two reasons. The lanthanum chromite particles were thicker than average, as they were not ground prior to TEM examination, which was done on previously observed powders. This would make the Ru particles more difficult to observe, even if they were present. Also, because the powder was obtained from a tested anode, there were also GDC and LSCr particles (in addition to LSCrRu) included in the sample as well. This is in contrast with the typical untested powder, which was only LSCrRu. For this reason, the Ru particles may have been more difficult to locate.

The fact that Ru particles were most easily found in the anode tested at 600 mA/cm² may be an indication that the Ru particle density was higher at higher current, which would explain the high performance. Another possibility is, as a result of high current, more O^{2-} is pumped to the anode/electrolyte interface, decreasing the oxygen vacancy concentration on the anode side. To maintain charge neutrality, this would cause the hole concentration to increase according to the following equation for a fixed Sr concentration [77]:

$$[Sr_{La}] = 2[V_0^{\bullet}] + [Cr_{Cr}^{\bullet}]$$
(3.5)

An increase in hole concentration leads to higher conductivity and, presumably, higher performance. As this is mere speculation, the effect of current density on the performance of these anodes should be studied in further detail.

3.5.5 Effects of Attrition-Milling the Anode Powder on Cell Performance

Aside from the anode sintering temperature (1200°C) which was determined from previous work on similar anodes [16], the processing factors had not been adjusted to yield an optimal microstructure. As seen in SEM images (Figs. 3.8 and 3.10), the GDC particles are relatively large in comparison with the LSCrRu particles due to calcination and particle

aggregation upon sintering. It was thought that the anode performance could be improved by attrition-milling the LSCrRu and GDC powders prior to forming an ink for screen printing. Attrition-milling was expected to enhance mixing between the two phases and reduce the overall particle size. Both are factors that, in theory, increase the TPB length. The catalytic activity for fuel oxidation may also improve due to a larger surface area. The smaller LSCrRu particle size was expected to affect the time-dependence of Ru precipitation as well. Since the diffusion distance for Ru out of the LSCrRu particles should be smaller, the time required for the voltage to stabilize was expected to be lessened.

Attrition-milling was done by mixing LSCrRu2018 and GDC (198 m²/g; Fuel Cell Materials) in a 1:1 weight ratio then milling the powders in ethanol using zirconia milling media for 4 h. The mixture was then dried and made into an ink using standard procedures. The BET surface area of LSCrRu2018-GDC after attrition-milling was $17.62 \pm 0.06 \text{ m}^2/\text{g}$. This is a relatively large increase in surface area compared to that of the traditional mixture of LSCrRu2018 (1.95 ± 0.02 m²/g) and GDC (calcined at 800°C for 4 h; $12.24 \pm 0.07 \text{ m}^2/\text{g}$).

Figure 3.37 shows the life test results obtained from a cell with attrition-milled LSCrRu2018-GDC anode operated at 200 mA/cm². The cell was operated at a lower current density than was normally done (300 mA/cm²) because the initial short circuit current (the maximum operation current for a fuel cell) was only ~ 230 mA/cm². The voltage behavior shows the three regions as expected. The time to reach a relatively stable voltage (~ 120 h) was slightly longer than that observed in most cells of which anode was not attrition-milled (< 100 h), which may have been partially due to the lower operation current. Nevertheless, the longer stabilization time was unexpected. The large increase in voltage at \approx 230 h occurred after an

accidental exposure of the anode to Ar for a short period of time (< 10 min). As the anode was re-exposed to H₂, the voltage increased again but stabilized at a higher level, from 0.65 to 0.74 V. Since Ar is an inert gas, the only effect that the exposure to Ar for a short amount of time may have had on the SOFC was to slightly and temporarily raise the pO_2 on the anode side. The observed behavior was unexpected and cannot be explained at the present time. However, regardless of the increase in voltage, the power densities achieved from this cell were low compared to other cells (Fig. 3.38). The highest power density obtained was only 181 mW/cm² at 312 h, which is less than that achieved from the cell with LSCr-GDC (no Ru) anode. It is possible that a higher power density could have been achieved at longer times, but the stable voltage in the life test indicates that the cell was already at or near its optimum performance level at the time the cell test was ended.

The impedance spectra obtained from this cell at various times is shown in Fig. 3.39. Despite the significant decrease in R_{pol} over time, from 3.21 Ω cm² at 15 min to 0.94 Ω cm² at 312 h measured at 500 mV, the final resistance of the cell was still large. The cell also had an uncharacteristically large R_{ohm} of 0.69 Ω cm². The LSGM electrolyte thickness measured from an SEM image was $\approx 280 \ \mu$ m. The calculated ohmic resistance of the electrolyte was $\approx 0.28 \ \Omega$ cm², based on a conductivity of 0.1 S/cm at 800°C [94]. This value is nearly 2.5 times smaller than the R_{ohm} observed. The high R_{ohm} along with the low power density suggest that there may be an insulating phase in the SOFC. Since all other materials and processing steps were identical to other cells, it was highly likely that a contaminant was introduced into the anode during the attrition-milling step. As the container used for attrition-milling was made of alumina, it is highly possible that this was the contaminant. When added to GDC, Al₂O₃ has been found to



Figure 3.37: Life test results from a cell with attrition-milled LSCrRu2018-GDC anode tested at 200 mA/cm².



Figure 3.38: I-V characteristics for a cell tested with attrition-milled LSCrRu2018-GDC anode.



Figure 3.39: Impedance spectra obtained at OCV (a) and 500 mV (b) obtained from a cell with attrition-milled LSCrRu2018-GDC anode.

segregate to the grain boundaries decreasing its total conductivity [118, 119]. Al₂O₃ may also promote particle sintering, since Al_2O_3 has been shown to be an effective sintering aid in ceramics (see, for example, [120, 121]).

SEM images of the attrition-milled LSCrRu2018-GDC anode were obtained before (Fig. 3.40a) and after testing (Fig. 3.40b). The inset in Fig. 3.40a shows a zoomed view of the particles obtained from another area of the sample. The particles had sintered into clusters with irregular shapes even prior to testing. An EDS composition map was not obtained since particle charging caused constant shifting of the image, so the phase of individual particles could not be determined. In addition, the presence of Al₂O₃ could not be confirmed by EDS, but the amount of Al₂O₃ could have been below the detection limit (\approx 1%). After testing, the features appeared to grow slightly. Because the particles were fused into a network, it was difficult to determine an approximate particle size. The size of the spherically-shaped portions did increase from ~ 0.2 – 0.3 µm to ~ 0.4 – 0.5 µm in diameter. The larger extent of particle sintering in this anode compared to the anodes that were not attrition-milled is likely due to the smaller starting particle



Figure 3.40: SEM images of the attrition-milled LSCrRu2018-GDC anode before (a) and after cell testing (b).

size, which results in a larger driving force for surface area reduction. If Al_2O_3 was indeed present in the anode, it may have promoted particle sintering as well.

As the microstructure alone could not explain the poor performance of the cell, it was determined that the most likely cause was the Al_2O_3 contaminant. With respect to the GDC phase alone, the addition of only 0.5 mol% of Al_2O_3 decreases the electrical conductivity of GDC at 800°C by 54% (from 8.3 x 10⁻² S/cm to 3.8 x 10⁻² S/cm) [118]. In future work, attrition-milling should be done in a zirconia, or ideally ceria, container with milling media made of the same material to prevent cross-contamination.

An additional factor that possibly affected the performance was the thickness of the anode. Based on SEM observations, the anode thickness varied between $10 - 20 \mu m$. This likely contributed to the high R_{ohm} , as the cross-sectional area for current conduction was lower than average. In addition, the irregular surface may have lead to a decrease in contact area between the anode and Au current collection grid.

3.5.6 Long-Term Stability of Cells with (La,Sr)(Cr,Ru)O₃-GDC Anodes

Since the life expectancy of an SOFC is ~ 40,000 h, it is important that the anode is stable at high temperature in reducing atmosphere for an extended period of time. In order to test the stability of LSCrRu-GDC anodes, tests were run on cells with LSCrRu2018-GDC anode for 312 h. Figure 3.41 shows the life test results of a cell operated at 300 mA/cm² at 800°C. Note that this cell had an anode current collector (LSCr). Long-term test results for a similar cell without LSCr were presented in Section 3.3.1.



Figure 3.41: Life test results for a cell with LSCrRu2018-GDC anode operated at 300 mA/cm² and 800°C.

Based on the life test shown here, no degradation in voltage was observed over the length of the cell test. The voltage increased by 21% over 312 h and the most rapid improvement occurred during the first 3 h (Region I; 13% voltage increase). As seen in other cells, the increase of voltage in Region II was more gradual. From ~ 72 h to the end of the test at 312 h, the voltage was relatively stable, yielding a power density of 255 mW/cm². The power density was lower than that observed in the cell discussed in Section 3.3.1, but it was to be expected as the cell discussed here was operated at $\frac{1}{2}$ the current density.

The break in data between Regions II and III was due to a power outage. The fuel was still flowing, but no current was supplied to the cell for ~ 20 h. Upon restarting the current (~ 72 h), the voltage increased by 2.5% from the value prior to the power outage, ~ 20 h earlier. This behavior is similar to that observed in life tests in other cells, where the voltage jumped significantly after IS and I-V measurements were made (Section 3.4.2 and 3.4.3). However, unlike several other cells, it seemed unlikely that this cell would have reached the higher voltage had there not been an accidental interruption. As the cell was operated at OCV during the 20 h break in data, the significant improvement in performance was somewhat unexpected, based on the observed effect of current density on cell performance (Section 3.4.4). Interestingly, the behavior observed here was also similar to that of the cell with the attrition-milled anode. The difference is that the latter operated in Ar with constant current for a short period of time, while this cell ran in H₂ without current for a longer period of time. The relative increase in voltage upon restarting normal operation was more significant in the cell with the attrition-milled anode (~ 14% compared to 2.5%).

Based on observations from all cells tested, it was determined that the cell performance benefits from both interruptions in current and fuel, but the improvement is most significant when the cell has some level of current for most of, if not all, the time while fuel is supplied. On the other hand, an interruption in fuel flow for extended periods of time, especially when the cell is operating at high current, can cause permanent damage to the cell. For example, the voltage of a cell with LSCrRu-GDC anode dropped by ~ 0.05 V (from 0.76 to 0.71 V) after 2 h of anode exposure to air at 300 mA/cm², and the performance did not recover after the anode was supplied with fuel.

At high current densities, more oxide ions are supplied through the electrolyte to the anode. When there is an insufficient amount of fuel to oxidize, the materials within the anode are oxidized instead, which can cause permanent change in the stoichiometry and/or microstructure of the anode materials. This type of damage is also generally observed when an anode is exposed to oxygen, such as by leakage through the seal or reduction-oxidation cycling. As mentioned earlier, this is a known problem with Ni-YSZ anodes.

The I-V curves obtained from the cell are shown in Fig. 3.42. The highest power density achieved was 456 mW/cm² obtained at 96 h, though the power density obtained at 312 h, 451 mW/cm^2 , was not significantly lower, indicating that there was not substantial cell degradation with time.

The impedance spectra measured at OCV and 500 mV over time are shown in Fig. 3.43. At 500 mV, R_{pol} increased from 0.23 Ωcm^2 at 96 h to 0.23 Ωcm^2 at 312 h. The cell R_{as} increased from 0.55 to 0.65 Ωcm^2 as a result of an increase in both R_{ohm} and R_{pol} . The increase in R_{pol} may be associated with the LSCr/LSCrRu-GDC interface as the R_{pol} did not increase significantly



Figure 3.42: I-V characteristics for a cell with LSCrRu2018-GDC anode tested over 300 h at 800°C.



Figure 3.43: Impedance spectra at OCV (a) and 500 mV (b) obtained from a cell with LSCrRu2018-GDC anode tested at 800°C.

over time for the cell tested without LSCr (Section 3.3.1). The R_{pol} measured at OCV (Fig. 3.43a) even slightly decreased between 96 h and 312 h.

3.6 Summary and Conclusions

The performance of cells with LSCrRu-GDC anode were evaluated. The cells yielded high power densities (> 500 mW/cm²) and low R_{pol} (< 0.2 Ω cm²). The performance improvement was associated with the out-diffusion of Ru from the lanthanum chromite lattice. Ru formed nanoparticles on the surface of lanthanum chromite, increasing the catalytic activity of the anode over time. The cells were determined to be stable over 300 h. TEM results reveal that the nanoparticles did not grow significantly over time, due partially to the refractory nature of Ru.

More detailed studies were performed on cells with LSCrRu-GDC anode in order to optimize the performance. An additional anode current collector, LSCr, improved the performance of the cell and the performance improved further with a thicker current collector. The operation temperature had a significant effect on the performance of the cells as well. The polarization resistances of the cells improved with increasing temperature, as the conduction mechanisms in ceramics are typically thermally-activated. In addition, the rate of decrease of R_{pol} was higher at higher temperatures. This was consistent with the idea that the performance improvement with time of these anodes was attributed to the diffusion of Ru to the surface of lanthanum chromite. In other words, the slower diffusion rate of Ru yielded a slower improvement in performance.

The performance of cells improved with increasing Ru content in the anode. In addition, the rate of improvement increased with Ru content, a trend similar to that observed in the
temperature-dependence study. This may be due to the higher instability of Ru in the chromite lattice with increasing Ru content. Another possibility was that the amount of Ru exceeded the solubility limit, especially in the cell doped with 25 mol% Ru in the B site of the chromite lattice. It was also found that the stability of the cell over time decreased with increasing Ru content, as shown by the cells with LSCrRu2025-GDC anode. Thus, it was determined that the most suitable anode for further testing were LSCrRu2008-GDC or LSCrRu2018-GDC.

Cells with LSCrRu2018-GDC were tested at varying operation currents revealing that the performance can be improved significantly if operated at a high current density. This was thought to be due to the increased oxygen ion concentration in the anode. To maintain charge neutrality, the reduction of oxygen vacancy concentration must be accompanied by the increase in hole concentration, thus improving the overall conductivity of the chromite phase.

Attrition-milling of the anode powder was done in an attempt to decrease the overall particle size within the anode. Unfortunately, the cell with attrition-milled anode showed poor performance. SEM observations revealed that this may be due to Al_2O_3 contamination from the attrition-milling equipment. Al_2O_3 was thought to reduce the anode conductivity and enhance particle sintering, thus reducing the total TPB length. In addition to the Al_2O_3 contamination, the anode thickness was less than half of the typical anode thickness in this study (25 – 50 µm). Similarly to the LSCr-(Ru-GDC) anode, this was due to the extremely high surface area of the starting GDC powder, resulting in low solids loading in the anode ink.

Chapter 4

(La,Sr)(Cr,Ru)O₃-GDC Anode Extended Applications

4.1 Reduction-Oxidation Stability

As discussed in the background section (Section 2.7), one major drawback of Ni-YSZ anodes is its instability towards reduction-oxidation (redox) cycling due to the significant difference in volume between Ni and NiO. Since LSCrRu-GDC anodes have a significantly smaller amount of metal compared to Ni-YSZ, they are expected to be more stable under redox cycling. Ru is expected to oxidize to RuO₂ at $pO_2 \ge 10^{-10}$ atm at 800°C [104]. Therefore, Ru should remain in the metallic state during SOFC operation.

The redox stability of cells with LSCrRu-GDC anode was tested by subjecting a cell to multiple cycles of reducing (H₂/3% H₂O) and oxidizing (air) atmospheres at 800°C. Figure 4.1 shows the voltage versus time results for a cell with LSCrRu2005-GDC anode. To ensure that the cell voltage was stable before testing its redox stability, redox cycling was done after ~ 168 h of normal cell operation at 800°C and 300 mA/cm². Each redox cycle was done with 25 min in air and 60 min in H₂ with 5 min Ar flushing before each change in atmosphere. There were a total of four redox cycles, with IS and I-V data taken after the 2nd and 4th cycle. Then the cell was allowed to run in H₂ at 300 mA/cm² for another 14 h before a final set of IS and I-V data was taken.

The voltage in H_2 during redox cycling was worse than that prior to redox cycling (0.72 V), but the values increased with each cycle. During the periods of H_2 exposure, the voltage also increased slightly with time.



Figure 4.1: Redox cycling performance of a cell with LSCrRu2005-GDC anode.

The impedance spectra measured at 500 mV before redox cycling (168 h), after the 2nd (172.5 h) and 4th (176 h) cycles and after 14 h (190 h) of restarting normal operation in H₂ is shown in Fig. 4.2. The ohmic resistance remained fairly stable, at $0.55 - 0.57 \ \Omega \text{cm}^2$. The R_{pol} prior to redox cycling was $0.50 \ \Omega \text{cm}^2$ and did not increase significantly after two redox cycles. However, after the 4th redox cycle, R_{pol} increased to $0.63 \ \Omega \text{cm}^2$. After 14 h of continuous operation in H₂ at 300 mA/cm², R_{pol} nearly recovered to its original value, indicating that there was not significant permanent damage to the cell due to redox cycling. In fact, based on I-V measurements (Fig. 4.3) the performance improved from that prior to redox cycling. The maximum power density increased from 254 mW/cm² at 168 h to 262 mW/cm² at 190 h. The maximum power density measured after the 2nd and 4th redox cycles were similar, ≈ 242 mW/cm², but at higher current densities, the resistance became lower after the 4th redox cycle. This is in agreement with impedance spectra measured at 50 mV (not 500 mV) after the 2nd and



Figure 4.2: Impedance spectra obtained from a cell with LSCrRu2005-GDC anode before and after redox cycling.



Figure 4.3: I-V curves measured before and after redox cycling.

 4^{th} redox cycles (Fig. 4.4). R_{pol} decreased from $\approx 0.94 \ \Omega cm^2$ after the 2^{nd} redox cycle to 0.81 Ωcm^2 immediately after the 4^{th} cycle. Based on the redox cycling results, the LSCrRu-GDC anodes appear to be stable. Given sufficient time, the cells also benefit from the cycling. It is possible that the improvement in cell performance was a result of the current and fuel interruption rather than the actual cycling itself. However, the cell performance only improved after re-exposure to H₂ and current (normal cell operation) for 14 h. This is in contrast with the observations of cells that had a short current or fuel interruption, where the improvement in performance occurred immediately upon resuming normal operation.

The stability of the anode towards a longer period of oxidation was also tested. This was done by exposing the anode side of a cell (LSCrRu2008-GDC anode) to air at OCV for 24 h after



Figure 4.4: Comparison of IS results from a cell with LSCrRu2005-GDC anode after the 2nd and 4th redox cycles.



Figure 4.5: Life test results from a cell with LSCrRu2008-GDC anode showing the oxidation period from 312 – 336 h.

the cell had been tested under normal operating conditions for 312 h (Fig. 4.5). The cell was then restarted in H₂ and IS and I-V measurements were once again taken over time. After oxidation, the voltage decreased from the value prior to oxidation by 0.06 V to \approx 0.72 V. The performance could not be recovered even after an additional 96 h of operation and, during the final 45 – 50 h of the test, the cell appeared to be unstable. The poor cell performance after oxidation was also apparent in the I-V measurements (Fig. 4.6). Figure 4.6a shows the I-V curves taken from the initial start-up of the cell, i.e., before oxidation. Figure 4.6b is the I-V data collected after oxidation, therefore, the time shown in Fig. 4.6b is the amount of time after the second start-up of the cell. The highest power density obtained prior to oxidation was 330 mW/cm² (96 h), while that achieved after oxidation was only 260 mW/cm² (24 h). This was still



(a)



Figure 4.6: I-V curves measured before (a) and after (b) oxidation. The time in the post-oxidation data corresponds to the time after the second start-up of the cell.

much less than the maximum power density obtained at 312 h (320 mW/cm²), which was after the performance had degraded. The voltage recovery after the oxidation period was much quicker and the extent of the increase much smaller compared to the initial start-up. After only 3 h, the voltage had already reached 97% of the maximum voltage. If the Ru metal re-dissolved into the chromite lattice during oxidation, one would expect the time-dependence of voltage to be similar to that observed during the initial start-up. Based on the experimental results, it was determined that the oxidizing atmosphere did not cause Ru to re-dissolve into the bulk lattice. This does not exclude the possibility that Ru dissolved into the near-surface regions of the chromite phase. As the near-surface regions are likely to be more off-stoichiometry than the bulk due to oxygen vacancy formation, it may be energetically favorable for Ru to re-dissolve into those regions. Based on XPS results, upon re-oxidation of a reduced LSCrRu powder, the Ru 3d binding energies did not shift from the metal state (Fig. 4.7). Therefore, it is most likely that the Ru metal did not dissolve into the sub-surface regions of the lanthanum chromite upon oxidation.

The cause of the lower performance after oxidation is not known. One possibility is that the Ru particle morphology may have changed upon oxidation. Upon re-exposure to H_2 , the contact area of the Ru particles with the lanthanum chromite and/or GDC may have decreased. The lower TPB length would result in lower performance.



Figure 4.7: Comparison of XPS results obtained from an LSCrRu2018 powder as reduced and after oxidation.

4.2 Hydrocarbon Fuel Operation

Ru has been shown to be an effective catalyst for steam reforming of CH₄ because of its high electrocatalytic activity for fuel oxidation with less carbon deposition than Ni-containing anodes [86, 122]. Figure 4.8 shows the performance of a cell with LSCrRu2018-GDC anode tested in humidified CH₄ for 55 h (after 72 h of H₂ operation). The cell was operated at 150 mA/cm² as it was determined through earlier experiments that this current level approximately corresponded to its maximum power density in CH₄. In addition, the fuel flow rate was reduced from 50 sccm (typically used for H₂ flow) to 25 sccm for CH₄. Earlier work showed that a CH₄ flow rate of 50 sccm caused the cell voltage to decrease to zero in less than 10 min. Carbon deposition on the anode was visually observed in those cells.



Figure 4.8: Time-dependence of voltage for a cell tested with CH₄ fuel at 800°C.



Figure 4.9: I-V characteristics of a cell with LSCrRu2018-GDC anode

As seen from the life test (Fig. 4.8), at the end of CH₄ operation (55 h), the cell had reached a relatively constant voltage of ≈ 0.75 V (power density = 112.5 mW/cm²). The peak power density at 55h was ≈ 150 mW/cm², which is an increase of 32 mW/cm² measured after 5 h of CH₄ operation (Fig. 4.9).

The I-V curves were irregularly shaped, especially that measured at 55 h, which showed a region of high resistance between 0.46-0.26 V (290-320 mA/cm²). This kink was also observed in the data measured at 5 h in the same voltage range, but the effect was much less apparent. This indicates that as the cell performance improved, the microstructural process(es) associated with the kink became more prominent and was possibly the rate-limiting mechanism. Note that the cell resistance at high current densities (> 320 mA/cm²; voltage < 0.26 V) measured at 55 h, was also higher than that at 5 h.

The impedance measurements at 5 and 55 h measured at OCV, 500 mV and 50 mV are shown in Fig. 4.10. The most significant change was seen in the spectra measured at OCV, where the R_{pol} at 5 and 55 h were 0.75 and 0.55 Wcm², respectively. This is consistent with the decrease of slope in the I-V curves. Interestingly, the IS spectra measured at 500 mV were nearly identical, with $R_{pol} \approx 1.92 \ \Omega \text{cm}^2$. R_{pol} measured at 50 mV was the higher than that measured at OCV and 500 mV for both times, 2.42 and 2.62 Ωcm^2 at 5 h and 55 h. For both measurements at 5 and 55 h, R_{pol} at 50 mV > R_{pol} at 500 mV > R_{pol} at OCV. The higher R_{pol} with increasing current indicates that there is high concentration polarization. The improved cell performance with time is likely a result of the increase of Ru electrocatalyst density with time as observed in cells tested with H₂ fuel. The cell became more fuel-deprived causing an even higher concentration polarization.



Figure 4.10: Impedance spectra measured after 5 and 55 h of CH₄ operation at (a) OCV,(b) 500 mV and (c) 50 mV.

Vernoux *et al.* [123] observed that the addition of a small amount of Ru (1 mg/cm²) to a $(La,Sr)(Cr,V)O_3$ -YSZ improved the anode performance in CH₄-H₂O with no coking. They speculated this occurred by initial steam reforming of CH₄ (Eq. 2.26), which generates H₂. H₂ reacts with O²⁻ to form H₂O, which in turn participates in steam reforming of CH₄ again. A benefit of this is that the reaction occurs more gradually compared to Ni-YSZ, thus decreasing the likelihood of carbon deposition. According to their impedance analysis, it was found that R_{pol} decreased significantly due to the increased hydrogen concentration close to the TPBs. It is

possible that methane was processed via a similar route in the case of the cell with LSCrRu2018-GDC. More detailed studies are required to understand how hydrocarbon fuels are processed by these anodes.

4.3 Sulfur Tolerance

The performance of cells with LSCrRu-GDC anode in H₂ with 10 – 100 ppm H₂S were tested to determine the anode sulfur tolerance. The cell was exposed to H₂ with H₂S only after the cell was stabilized in H₂/3% H₂O for > 5 h. Of course, the exact amount of time required to reach stabilization depended upon the Ru doping and current level. After the cell reached a stable voltage, dry H₂ was supplied to the anode until the voltage reached a stable value. Finally, dry H₂ with H₂S was supplied. The reason dry fuel was used was because H₂S dissolves in water to form a weak acid. By flowing H₂ with H₂S through the bubbler before reaching the cell, the amount of H₂S that actually reaches the cell would be reduced.

In all cells with LSCrRu-GDC anodes, the voltage dropped significantly, during the first 30 s of H₂S exposure, then slowly increased. For the cell shown in Fig. 4.11, the voltage dropped from 0.53 V in H₂ to 0.43 V during the initial H₂S exposure (800°C), but a drop to negative voltage has also been observed. This effect was less apparent at higher temperature as seen at 850°C in Fig. 4.11. Kurokawa *et al.* [124] studied the sulfur tolerance of a nanoparticle ceria- and Ru-infiltrated (Sr,Y)TiO₃ anode under similar conditions and did not observe a voltage drop when H₂S was introduced. In addition, this effect was not observed when the sulfur tolerance of Ni-YSZ anode was tested in the Barnett lab (by Dr. Yuanbo Lin). Therefore, it is possible that the initial voltage drop was associated with the presence of LSCr. This phenomenon was not studied in further detail as all cells did recover after the initial voltage drop.

A cell with LSCrRu2005-GDC anode made in the Barnett lab was tested by Dr. Ilwon Kim and Dr. Manoj Pillai at Functional Coating Technology, L.L.C. (FCT, Evanston, IL). The cell performance at 800°C and 850°C, current density = 800 mA/cm² and 50 ppm (denoted S50) and 100 ppm H₂S (S100) in H₂ is shown in Fig. 4.11. Note that between each S50 and S100 exposure, the voltage was allowed to recover in H₂. At 800°C, the recovery was 100% of the original voltage, while at 850°C the voltage reached 97% of its original value. Longer exposure to pure H₂ may have allowed the cell voltage to fully recover.

A stable voltage was never obtained in H_2/H_2S regardless of the sulfur content and temperature. However, the voltage degradation rate was slower at higher temperature and lower sulfur content. The degradation rates (mV/h) based on the linear portions of the voltage drop are summarized in Table 4.1. The large voltage drop immediately following each sulfur exposure was ~ 10%.

The impedance spectra measured at 850°C in H₂ before H₂S exposure, during H₂S exposure and in H₂ again after exposure is shown in Fig. 4.12. The R_{pol} in H₂ increased from 0.25 Ω cm² before sulfur testing to 0.31 Ω cm² after testing. After > 4 h of operation at 850°C in pure H₂ the R_{pol} did not reduce to its original value, which indicates severe damage to the anode. The voltage degradation at 800°C relative to the value prior to sulfur exposure was ~ 12%.

The sulfur tolerance of an anode with higher Ru content, LSCrRu2018-GDC, was also tested. After achieving a stable voltage (660 mV) in H₂, the cell was exposed to 10 ppm H₂S in H₂ for ~ 24 h, then once again exposed to pure H₂. The time-dependence of the cell voltage at 400 mA/cm² and 800°C is shown in Fig. 4.13. The initial voltage drop upon exposure to sulfur



Figure 4.11: Performance of cell with LSCrRu2005-GDC anode in H₂ and

H_2/H_2S at 800°C and 850°C and current density of 800 mA/cm	H	$_{2}/H_{2}$	S	at 8	800°C	and	850°	C	and	current	density	of	800	mA	/cm	2.
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	Temperature					
Гиегтуре	800°C	850°C				
S50	2.76	1.15				
S100	3.96	1.61				

Table 4.1: Summary of voltage degradation rate (mV/h) for cell with

LSCrRu2005-GDC anode at different temperatures and sulfur content.



Figure 4.12: Impedance spectra in H_2 before sulfur exposure, H_2/H_2S and H_2 after sulfur exposure.



Figure 4.13: Time-dependence of voltage in H₂/H₂S and H₂ atmospheres at 800°C.

was large, from 660 mV to < 100 mV. However, the voltage recovered to as high as 509 mV, before steadily decreasing at 4.02 mV/h. The degradation rate is similar to the highest value obtained from the cell with LSCrRu2005-GDC anode. However, in this case, the sulfur content was 10 times lower, the Ru content was 3.6 times higher and the current was only half of the cell with LSCrRu2005-GDC. The lower sulfur content should have resulted in slower, rather than accelerated, voltage degradation, thus the sulfur content does not explain the higher degradation rate.

The exact mechanism of sulfur poisoning of Ru is not known. As with Ni-containing anodes, H₂S may react with the catalyst phase or may adsorb onto the catalyst surface. According to Kurokawa *et al.* [124], at 800°C Ru should not react with H₂S to form RuS₂ at pS₂ $< 6.8 \times 10^{-7}$ atm, while pS₂ for 10 ppm H₂S in H₂ is $\sim 10^{-14}$ atm. However, it is possible that Ru in the anode was poisoned by adsorption of sulfur compounds on the surface. Based on a study

of CO hydrogenation [125], an Al₂O₃-supported Ru catalyst was exposed to a gas mixture containing a very small amount of H₂S (\leq 100 parts per billion), 0.1-4% CO and balanced H₂. It was found that the Ru catalyst was deactivated by surface adsorption of a sulfide, with each sulfur atom blocking two Ru surface atoms. Though the experiment was done at a significantly lower temperature (400°C) than the SOFC operating temperature, it is possible that a similar mechanism is involved in deactivating the Ru nano-particles in the LSCrRu-GDC. This implies that the sulfur contaminant may be removed by treatment at high temperature and/or high pO₂.

For CeO₂, which is also a catalytic material, pS₂ to form Ce₂O₂S is ~ 10^{-15} - 10^{-11} atm for pO₂ ~ 10^{-18} – 10^{-16} atm (pO₂ at the anode) [124]. Therefore, it is possible that sulfur poisoning of the LSCrRu-GDC anode occurred via the formation of Ce₂O₂S. Kim *et al.* [126] have shown that exposing the anode to a high steam content (50 mol% H₂O in N₂ at 700°C) over 3.5 h completely removed the sulfur content and restored the cell performance. The sulfur was possibly removed via the formation of SO₂. Since the poisoning of CeO₂ is more thermodynamically favorable than that of Ru [124, 127], it is likely that the poisoning of CeO₂, rather than Ru, is the major cause for the cell degradation in H₂/H₂S atmosphere. This suggests that the LSCrRu-GDC anode performance may be recoverable by exposure of the anode to a higher pO₂ level, e.g., via steam or oxidation, after H₂/H₂S operation.

Based on the above explanation, the higher Ru content in the LSCrRu2018-GDC anode should not have been the main cause for the higher (or comparable, depending on test conditions) degradation rate in H₂/H₂S, compared to that observed for the cell with LSCrRu2005-GDC. It is possible that the lower operating current may have played a role. With higher current, a higher amount of O^{2-} is forced to the anode/electrolyte surface. If the O^{2-} concentration at the anode is sufficiently high, the formation of SO₂, which is more stable than H_2S , is promoted according to Eq. 2.35.

To determine whether the cell performance could be recovered, the cell with LSCrRu2018-GDC was exposed to two redox cycles following H₂S exposure. The anode was exposed to a total of 21 h in air (no current) during the cycling. The cell voltage at 400 mA/cm² in H₂ after redox cycling is shown in Fig. 4.13 (28-30 h). As predicted, the cell recovered completely, indicated by the final voltage being identical to that observed prior to H₂/H₂S exposure. The impedance spectra at 500 mV (Fig. 4.14) further confirms the cell recovery. The ohmic resistance did not change significantly with sulfur content. However, R_{pol} increased significantly from 0.43 Ω cm² in H₂ prior to H₂S exposure to 1.33 Ω cm² in H₂S. Approximately 1 h after re-introducing pure H₂ to the cell, R_{pol} reduced to 0.64 Ω cm². R_{pol} decreased further to 0.43 Ω cm² after redox cycling, again indicating complete cell recovery.



Figure 4.14: Impedance spectra before, during and after sulfur exposure and after redox cycling.

A cell with LSCrRu2025-GDC anode was shown to have high sulfur tolerance as shown in Fig. 4.15. The cell was tested with 10 ppm H₂S in H₂ at 300 mA/cm² over 14 h. The voltage dropped from 837 mV in H₂ to a maximum of 675 mV in H₂/H₂S, which is 80% of the voltage in H₂. The voltage still appeared to be on the increase at the end of the sulfur exposure. The voltage recovered to 97% of the original value in H₂ within one hour. The I-V curves obtained from this cell (Fig. 4.16) before and after sulfur exposure show that the maximum power density decreased by 17%. The power density in H₂/H₂S increased from 147 mW/cm² after 3 h of sulfur exposure to 209 mW/cm² after 14 h.



Figure 4.15: The time-dependence of cell voltage when a $H_2/10$ ppm H_2S fuel was supplied to the anode for 14 h.



Figure 4.16: I-V curves measured in H_2 before and after H_2S exposure (black solid and dashed lines) and in H_2/H_2S after 3 and 14 h of exposure (gray solid and dashed lines).

The reason for improved stability with higher Ru content is not clearly understood. It is possible that the extent of poisoning of the GDC phase remained the same as was observed in the anodes with lower sulfur content. However, as discussed in Section 3.5.3, cells with higher Ru content exhibit higher overall performance. Thus, the degradation caused by sulfur poisoning may have been offset by the improvement associated with the higher Ru content.

The sulfur tolerance of LSCrRu-GDC anodes should be compared with that of a traditional Ni-YSZ anode. The performance of an anode-supported SOFC with Ni-YSZ anode active layer in $H_2/10$ ppm H_2S at 800°C (tested by Yuanbo Lin) is shown in Fig. 4.17. The initial drop was ~ 8% of the original voltage. The degradation rate after the initial drop was 1.86 mV/h. This degradation rate is higher than that of the cell with LSCrRu2005-GDC anode when measured at 850°C, but lower than the rate at 800°C. Overall, the degradation rate was

comparable to that of the LSCrRu-GDC anodes. However, the performance of Ni-YSZ after reintroduction of H_2 was significantly worse than the initial performance. The overall voltage drop was 8-9%, though most importantly, the voltage continued to degrade with time. The I-V curves (Fig. 4.18) show that the cell performance did not recover even after an additional 45 h of exposure to pure H_2 . The maximum power density in H_2 decreased from 1.05 V prior to sulfur exposure to 0.83 V after exposure.



Figure 4.17: Performance of a Ni-YSZ anode in H₂ with 10 ppm H₂S.

Courtesy of Yuanbo Lin.



Figure 4.18: I-V curves obtained from a Ni-YSZ anode-supported SOFC in H_2 , H_2/H_2S and H_2 again after sulfur exposure. Courtesy of Yuanbo Lin.

The impedance spectra at 500 mV in pure H₂ atmosphere show that R_{pol} remained fairly constant regardless of fuel composition. However, R_{pol} measured at OCV (not shown here) increased from 0.17 to 0.37 Ω cm², before and after sulfur exposure, respectively. Based on a study by Sasaki *et al.* [128], at 800°C the sulfur tolerance of Ni-YSZ was also very low, with a reduction by as much as 400 mV (to 0 V) with 20 ppm H₂S in less than 30 min.

Overall, the performance of LSCrRu-GDC anodes in sulfur-contaminated atmospheres is not significantly better than that of Ni-YSZ when the Ru content is low (5 – 18 mol% Ru in the B site), as indicated by the voltage degradation rate. However, upon re-introducing H₂, the degradation of Ni-YSZ was shown to be more severe and irrecoverable even after long exposures of pure H₂ atmosphere. On the other hand, the performance of LSCrRu-GDC anodes can be fully recovered by exposing the anode to a higher pO_2 atmosphere, which presumably oxidizes the sulfur component and recovers GDC to its original state. Ni-YSZ anodes are not expected to recover completely by this method as microstructural damage is likely to occur from redox cycling. The sulfur tolerance of the anode with highest Ru content, LSCrRu2025-GDC, was superior to that of Ni-YSZ, showing no voltage degradation in H₂/H₂S atmosphere over 14 h. Though the cell voltage was not allowed to recover after H₂ re-introduction, it is likely that this cell would have fully recovered given additional time and/or redox cycling.

4.4 Summary and Conclusions

The following summary and conclusions can be drawn from the studies on the redox stability, performance in hydrocarbon fuel and sulfur tolerance of LSCrRu-GDC anodes.

- The cells with LSCrRu-GDC anode did not degrade significantly with multiple cycles of reduction-oxidation, each cycle was ~ 1 h. The performance in H₂ fuel immediately after redox cycling was worse than the pre-redox performance (maximum power density of ~ 240 mW/cm² compared to ~ 250 mW/cm²). However, upon re-exposure to H₂ for a period of 14 h, the performance improved to above the pre-redox performance (maximum power density ~ 260 mW/cm²).
- 2. When the anode was exposed to oxygen for an extended period of time (24 h) at 800°C, the cell performance permanently degraded after re-exposure to H₂. The time to reach stabilization after the second H₂ start-up was also significantly less than that observed after the initial start-up. This indicated that the Ru electrocatalyst particles did not re-dissolve into the lanthanum chromite. The results were confirmed by XPS measurements of the reduced and re-oxidized Ru 3d peaks, which show that the Ru oxidation state did not change upon re-

oxidation. This should be confirmed via TEM as it has implications on the stability of the Ru particles. Because the Ru particles did appear to grow after 300 h (> 5 nm diameter) (see Section 3.3.2), it would be preferable if the Ru nanoparticles could be re-dissolved and re-precipitated to form small (< 5 nm diameter) particles again.

- 3. The performance of the anode in CH₄ showed that the performance increased over time, though the overall performance was worse than that in H₂. The maximum power density achieved in H₂ was \approx 450 mW/cm² compared to \approx 150 mW/cm² in CH₄. It was speculated that the CH₄ was processed by the slow steam reforming of CH₄, which helps to avoid carbon deposition by methane cracking. The results are encouraging but significant work is required to asses the performance of LSCrRu-GDC in hydrocarbon fuels.
- 4. The sulfur tolerance of LSCrRu-GDC anodes varied among cells, though it is possible that the tolerance improved with Ru content. For cells with LSCrRu2005-GDC and LSCrRu2018-GDC anodes, the voltage slowly reduced over time at a rate of 1 4 mV/h. The performance immediately after re-exposure to pure H₂ fuel was worse than that prior to sulfur exposure. The performance could not be fully recovered even after prolonged exposure to pure H₂. However, it was found that after redox cycling, the performance fully recovered. It was postulated that the poisoning of the anode occurred on GDC, rather than Ru, via the formation of a Ce-O-S compound. Presumably, upon oxidation, this compound reacted with oxygen to form SO₂, which is stable under the operation conditions, thus likely to cause poisoning.
- 5. Overall, the initial results on LSCrRu-GDC anodes showed that it has potential for applications beyond the basic H₂ operation. Several processing and testing factors can be

adjusted to enhance the performance of the anodes. For example, the steam-to-carbon ratio and operation temperature can be adjusted in hydrocarbon operation. For redox cycling, it is suggested that more than three cycles should be tested to fully observe the effects that cycling has one the performance. The microstructure should be studied after cycling (SEM, TEM, XPS, etc.) as this should shed some light on the changes that occur in the anode. In addition, more extended oxidation studies should be carried out with different levels of current running, to determine whether current may accelerate or slow the degradation rate upon re-exposure to hydrogen. Finally, for sulfur testing, more information is needed on the effect of Ru content on the performance. The fuel flow rate, sulfur content, operating current and temperature may be adjusted such that the voltage is stable, or degrades at a negligibly low rate, over time. Methods of recovering the performance should also be studied, as this not only helps to extend the lifetime of the fuel cell, but it also provides information on how the anode is poisoned.

Chapter 5

Alternative Anodes

5.1 Introduction

In addition to the LSCrRu-GDC anode, three other types of anodes were synthesized and tested to determine the applicability of the method of incorporating a nanometer-scale electrocatalyst phase into the anode. The most extensively studied anode presented in this chapter is $La_{0.80}Sr_{0.20}Cr_{1-x}Ni_xO_3$ -GDC (x = 0.18 or 0.31; LSCrNi-GDC), which was fabricated using the same procedures as LSCrRu-GDC. Because Ni is unstable in (La,Sr)(Cr,Ni)O_3 in reducing atmospheres, it was expected to precipitate out similarly to Ru [129]. By decreasing the amount of Ni in the anode (compared to Ni-YSZ) and, assuming Ni does precipitate from the chromite lattice, reducing the Ni particle size, the anode may exhibit high catalytic activity for fuel oxidation without suffering from the many drawbacks of Ni-YSZ anodes. For the purpose of comparison, the Ni contents in the B site of lanthanum chromite, 0.18 and 0.31 mol%, were chosen to match the atomic and weight percentage (5 wt%) of Ru in LSCrRu2018-GDC.

The second alternative anode discussed is a B-site doubly-doped anode: $La_{0.80}Sr_{0.20}Cr_{0.92}Ru_{0.06}Ni_{0.02}$ -GDC (LSCrRuNi-GDC). Several studies on catalysis have shown that the addition of Ru to a Ni-containing catalyst significantly enhances its activity for fuel oxidation, stability and resistance to carbon deposition (see, for example, [130-134]). The general idea is that RuO₂ is reduced by H₂ dissociation. The dissociated H atoms are transferred to Ni from Ru, making Ni less prone to oxidation from steam or local changes in pO₂ [130], thus improving its stability. The improvement in catalytic activity and resistance to coke formation

simply result from the combination of catalytic properties of Ni and Ru. For these reasons, preliminary tests (H_2 operation) were done on LSCrRuNi-GDC anodes to determine its feasibility as an SOFC anode.

The final type of anode discussed in this chapter is a composite of LSCr, Ru and GDC. Note that this anode was different from the three-phase (LSCr-GDC-RuO₂) anode discussed in Section 3.4. The idea was to precipitate the Ru catalyst phase out from GDC, rather than LSCr, which is an electronic conductor. GDC is both electronically- and ionically- conducting at the operation temperature (800°C), therefore, the presence of the catalyst phase on GDC should increase the overall TPB length. In addition, as CeO₂ is also an electrocatalyst, there may be an improvement in catalytic activity from synergistic interactions between the two catalyst phases. To synthesize the anode, RuO₂ and GDC were reacted together at high temperature, then physically mixed with LSCr. This is in contrast with the LSCr-GDC-RuO₂ anode, which was fabricated by physically mixing all three powders at room temperature.

5.2 Experimental Procedures

5.2.1 (La,Sr)(Cr,Ni)O₃-GDC and (La,Sr)(Cr,Ru,Ni)O₃-GDC

The procedures for fabricating the LSCrNi-GDC and LSCrRuNi-GDC anodes were identical to that for LSCrRu-GDC, except NiO starting powder was used instead of (for LSCrNi-GDC) or in addition to RuO₂ starting powder (for LSCrRuNi-GDC). Please refer to Section 3.2 for further details.

<u>5.2.2 (La,Sr)CrO₃-(Ru-GDC)</u>

RuO₂ (99.95%; Alfa Aesar) and GDC (Fuel Cell Materials) were reacted in air at 500°C for 6 h. A relatively low reaction temperature was used in order to avoid RuO₂ evaporation (by

forming gaseous RuO₃ and/or RuO₄), which occurs at temperatures above 800°C [101]. Literature on the solubility of Ru or RuO₂ in CeO₂ is scarce, though based on the information found, there are no Ru-Ce-O compounds [135, 136]. However, the addition of Gd to CeO₂ may alter the solubility limit of Ru, thus the RuO₂-GDC powder was studied regardless of findings from literature. The RuO₂:GDC molar ratio used to fabricate the powder was 1:9, which corresponds to 8:92 weight ratio.

To make LSCr-(Ru-GDC), the RuO₂-GDC powder was mixed with LSCr such that the LSCr:GDC weight ratio was 1:1, as was done in all of the LSCrRu-GDC anodes. This yielded a RuO₂ content of 4 wt% in LSCr-(Ru-GDC), slightly lower than that in LSCrRu2018-GDC (5 wt%). The powder was made into an ink using identical procedures as LSCrRu-GDC. However, since the GDC surface area was high, the loading of powder in the ink was relatively low, ~ 8 vol%, compared to the typical 20 - 25 vol% for LSCrRu-GDC powders.

5.3 (La,Sr)(Cr,Ni)O₃-GDC Anodes

5.3.1 Cell Test Results

The time-dependence of voltage for a cell with LSCrNi2018-GDC anode is shown in Fig. 5.1. Note that the sharp increase in voltage during the initial 3 h of the cell test that was observed in the LSCrRu-GDC anodes, was not observed here. Though several other cells with LSCrNi-GDC anode did show a significant voltage increase in the initial period, the voltage tended to stabilize in less than 3 h.

Based on Fig. 5.1, the cell maintained a relatively stable voltage of 0.8 V (240 mW/cm²) for ≈ 215 h, at which time the voltage dropped by 10 – 20 mV. Based on the impedance spectra for this cell, R_{ohm} measured at 240 and 312 h was $\approx 0.02 \ \Omega \text{cm}^2$ larger than R_{ohm} at earlier times.



Figure 5.1: Voltage versus time measured over 312 h for a cell with LSCrNi2018-GDC at 800°C and 300 mA/cm².



Figure 5.2: Impedance spectra measured from a cell with LSCrNi2018-GDC at OCV (a) and 500 mV (b) at different times.

It is possible that the voltage drop may have been partially caused by degradation of the Ag contacts or wires. However, the low frequency intercept increased by as much as $0.10 \ \Omega \text{cm}^2$, which suggests that the degradation was also an electrode effect.

The smallest R_{pol} measured was 0.38 Ωcm^2 measured at 15 min and 3 h at 500 mV bias. This is approximately twice the minimum R_{pol} achieved from a cell with LSCrRu2018-GDC anode. Note also that the R_{pol} began to increase between 3 – 24 h. In general, for this type of cell, the onset of degradation as indicated by R_{pol} occurred between 3 – 48 h, much earlier than that observed in cell with LSCrRu-GDC anodes, which was generally after ~ 96 h.

The I-V curves obtained from cells with LSCrNi-GDC anode, such as that shown in Fig. 5.3 for a cell with LSCrNi2018-GDC anode, show that maximum improvement in power density



Figure 5.3: The I-V curves obtained from a cell with LSCrNi2018-GDC at 800°C.

was typically only 2 - 6% of the value obtained at 15 min. The degradation in maximum power density between 24 - 312 h was as much as 13%. In addition, the highest power density of this cell, which was the maximum value achieved for cells with LSCrNi-GDC anode, was 364 mW/cm². The power density was significantly lower than that achieved when an LSCrRu-GDC was utilized, i.e., as high as 534 mW/cm².

The maximum power density and minimum R_{pol} obtained from cells with LSCrNi2018-GDC and LSCrNi2031-GDC are shown in Fig. 5.4. For comparison, the results obtained from control cells with (La,Sr)(Cr,V)O₃-GDC-Ni (LSCrV-GDC-Ni) were also included. Note that the Ni weight percentage in the LSCrV-GDC-Ni anode was set to match that of LSCrNi2031-GDC anode ($\approx 5 \text{ wt\%}$). The Ni content in LSCrNi2018-GDC was $\approx 3 \text{ wt\%}$. The plots in Fig. 5.4 show that cells with LSCrNi2018-GDC had the highest performance and those with LSCrV-GDC-Ni anode showed the lowest performance. Since the cell with a separate Ni phase was not expected to consist of nanometer-scale Ni particles due to particle coarsening, the lower performance relative to cells with LSCrNi2031-GDC was expected. On the other hand, unlike cells with LSCrRu-GDC anodes, the higher Ni content in LSCrNi-GDC did not yield a higher performance. In order to explain the difference in performance of these cells, microstructural characterization was carried out using XRD, SEM and TEM (equipment specifications identical to that used to characterize LSCrRu-GDC anodes).



Figure 5.4: The maximum power density (a) and minimum R_{pol} (b) achieved from cells with three different types of anodes.

5.3.2 Microstructural Characterization

X-ray diffraction patterns were obtained from LSCrNi2031 powder as-prepared and annealed in H₂ at 800°C for 3, 45 and 312 h (Fig. 5.5). The dominant phase, presumably $La_{0.8}Sr_{0.2}Cr_{0.69}Ni_{0.31}O_3$, yielded peaks corresponding to that of $La_{0.8}Sr_{0.2}CrO_3$ (JCPDS# 74-1980). However, a peak likely corresponding to that of NiO was also observed in the as-prepared powder. This indicates that 31 mol% of Ni in the B site exceeded the solubility limit. Upon reduction, the NiO peak was no longer visible, while Ni peaks were observed. XRD patterns were not obtained for LSCrNi2018. However, for a powder with lower Ni content, LSCrNi2013, Ni and NiO peaks were not observed.

A shoulder or small peak was observed near some of the lanthanum chromite peaks. This may be due to a shift from a cubic lattice to one with lower symmetry, such as a hexagonal lattice. Note also that small peaks were observed between $2\theta = 25 - 30^{\circ}$. Those peaks may correspond to SrCrO₄, which was thought to be the secondary phase in LSCrRu, and/or Ni-Cr spinel (NiCr₂O₄). The latter has been found in LSCrNi3010 studied by Sauvet *et al.* [65] after operation in CH₄. However, it is possible to form NiCr₂O₄ to form prior to reduction by the reaction of excess NiO with a Cr-containing compound, such as SrCrO₄, excess Cr₂O₃ or (La,Sr)CrO₃ phase. This has been observed by Komatsu *et al.* [137] during the synthesis of La(Ni,Fe)O₃ with excess Cr₂O₃.

Since the Ru-substituted chromite lattice was determined to have a cubic structure, the formation of $SrCrO_4$ was not a likely cause for lattice destabilization. Based on these observations, the change in lattice structure to lower symmetry had two possible causes: Cr deficiency in the lanthanum chromite lattice and/or lattice strain caused by the substitution of a



Figure 5.5: X-ray diffraction pattern of LSCrNi2031 powders as-prepared and reduced for 3, 45 and 312 h at 800°C.

large amount of Ni into the Cr site. Based on literature, $LaCr_{1-x}Ni_xO_3$ has an orthorhombic structure when $x \le 0.6$, and the unit cell volume and specific surface area was found to increase with Ni content indicating that Ni does indeed cause lattice expansion [138-140].

Regardless of the chromite lattice structure, it is clear that the LSCrNi2031 powder was not phase pure. That the values of power density and R_{pol} of cells with LSCrNi2031-GDC was between those with LSCrNi2018-GDC and LSCrV-GDC-Ni agrees well with the findings that Ni existed both inside and outside of the chromite lattice. The presence of NiO outside of the lanthanum chromite lattice was a possible explanation for the lower performance compared to that of LSCrNi2018, as the NiO particles would tend to coarsen over time. However, this does not preclude the possibility that the Ni particles that presumably diffuse out of the chromite lattice did not coarsen as well. The microstructure of LSCrNi was further studied by SEM and TEM. Figure 5.6 shows the microstructure observed by SEM before (Fig. 5.6a) and after testing (Fig. 5.6b) at 800°C. The EDS map of La, Ce and Ni show that the LSCrNi and GDC phases are not thoroughly mixed. There was considerable clustering of GDC (represented by Ce). In addition, there were small areas where the Ni signal was higher than the average background signal. These clusters should not be observed if Ni was distributed within the lanthanum chromite lattice. Therefore, it was concluded that there was at least a small amount of NiO outside of the lattice for LSCrNi2018. Based on this information and the XRD data, the solubility limit of Ni in the B site of La_{0.8}Sr_{0.2}CrO₃ determined from this study is between 13 and 18 mol%.

After the anode was tested for 312 h at 800°C, the lanthanum chromite particles did not grow significantly (~ 1 μ m diameter). However, as was also observed in the LSCrRu-GDC powders, the GDC clusters grew significantly (Fig. 5.6b). EDX maps of the post-test anode did not show large clusters of Ni, though the anode was not thoroughly surveyed.

TEM observations of LSCrNi powders as-prepared and reduced for 3 and 311 h at 800°C are shown in Fig. 5.7. As the focus of the TEM study was on Ni nanoparticles, larger Ni or NiO had not dissolved into the chromite lattice were not examined. The as-prepared powder showed no nanoparticles on the lanthanum chromite surface. After 3 h of reduction, hemispherical Ni particles with 10 - 15 nm diameter were observed. The shell structure seen in the top Ni particle of Fig. 5.7b was determined by the lattice fringes to be NiO, which formed when the anode was exposed to air after reduction. Note that the Gibbs free energy of formation of NiO at room temperature is -212 kJ/mol, thus NiO is more stable than Ni. The NiO shell likely prevented further oxidation of the remaining Ni in each nanoparticle.





Figure 5.6: SEM images obtained from LSCrNi2018-GDC anodes before (a)

and after testing (b).


Figure 5.7: TEM images obtained from LSCrNi powder as-prepared (a), reduced for 3 h (b) and 311 h (c).

The LSCrNi powder after 311 h of reduction shows that the Ni particles had grown significantly. The diameter of the hemispheres were 50 – 60 nm. These findings are in contrast with those of LSCrRu powders, where the diameter of Ru particles did not exceed 10 nm even after 1000 h of reduction. The large disparity in growth rates of Ru and Ni particles can be explained in part by their melting temperatures. The melting temperature of Ru (2334°C) is much higher than that of Ni (1455°C). Therefore, the driving force for particle growth and/or coarsening is higher for Ni. In addition, Ru metal is more stable in reducing atmosphere. At pO₂ = 10^{-18} atm, the temperature above which Ru is more stable than its oxide is 300°C [101]. For Ni, the metal is stable at above 700°C [141]. The implication is that fluctuations in pO₂ at the anode are more likely to cause oxidation of Ni than Ru.

Based on the TEM image after 45 h of reduction, the density of Ni nanoparticles was approximately $1.50 \times 10^{14} \text{ m}^{-2}$, which was over 100 times smaller than the Ru particle density in LSCrRu (~ 4 x 10^{16} m^{-2}). The average LSCrNi and Ni particle diameter were 1 μ m and 25 nm,

respectively. Following the same calculation as for Ru precipitation from LSCrRu (Section 3.3.3), the diffusion coefficient of Ni from LSCrNi was 7 x 10^{-22} m²/s. This value is 10 - 100 times smaller than the value obtained for Ru diffusion out of LSCrRu. According to thermodynamic calculations by Sfeir [129], Ni is unstable in the LaCrO₃ lattice at 800°C and pO₂ $< ~ 10^{-14}$ atm. However, Sfeir observed that a LaCr_{0.5}Ni_{0.5}O₃ exposed to H₂ for 1 week at 780°C showed no demixing. It was therefore suggested that the out-diffusion of Ni is kinetically limited. In the case of LSCrNi, it is possible that the substitution of Sr may have reduced the solubility limit of Ni in the chromite lattice and rendered Ni even less stable in reducing atmospheres.

That the diffusion coefficient of Ni was smaller than that of Ru contradicts the life test results. Generally, for cells with LSCrRu-GDC anode, the voltage increased rapidly at the beginning then slowed until a plateau was reached. The voltage increase of cells with LSCrNi-GDC anode was more rapid, and in the case of the cell shown in Fig. 5.1, appeared to reach a plateau almost immediately upon H₂ exposure. A possible reason for the discrepancy is as follows. The diffusion coefficient was calculated from the Ni particle density seen in the TEM image obtained after 45 h of reduction. Aside from the inaccuracies that may arise from approximations, e.g., particle count, particle size, particle shape, etc., the calculation was also based upon the assumption that the Ni particles are continuously diffusing out. In other words, it is possible that, due to the instability of Ni in the lanthanum chromite lattice, the amount of Ni seen in the image may have diffused out in much less time. Therefore, the calculated diffusion coefficient may have been much larger than the actual value. Future calculations should focus on shorter reduction times, e.g., 15 min, to determine if this is the case.

Another likely explanation for the discrepancy between the diffusion coefficient and life test results is the possible presence of NiO. Note that the TEM images were obtained for LSCrNi2031, which based on the XRD pattern, likely has NiO as a secondary phase. In typical Ni-YSZ anodes, the reduction of NiO occurs within minutes upon exposure to H₂. This would explain the rapid rise in voltage observed in the life test results.

Based on the results from microstructural characterization, the following conclusions were drawn regarding LSCrNi-GDC anodes:

1. The Ni in LSCrNi2018-GDC and LSCrNi2031-GDC existed as a dopant in the B site of lanthanum chromite and also as a separate phase, i.e., NiO prior to reduction. The solubility limit of Ni in the B site was between 13 and 18 mol%. LSCrNi2031-GDC was expected to consist of a higher NiO content than LSCrNi2018-GDC. The lower performance of cells with LSCrNi2031-GDC compared to those with LSCrNi2018-GDC was unexpected. The catalytic activity of the anode should increase with increasing catalyst content, as observed for the LSCrRu-GDC anodes. A possible explanation for the lower performance is that variations in pO_2 during SOFC operation may have caused some of the Ni to oxidize to NiO, which would lower the overall catalytic activity of the anode. The higher Ni content in LSCrNi2031-GDC caused this anode to be more susceptible to oxidation. A second possible explanation is the higher NiO content in LSCrNi2031 lead to a higher concentration of NiCr₂O₄. Though NiCr₂O₄ has relatively high conductivity (62.5 S/cm at 750°C in air), the formation of this compound also causes a decrease in the amount of Ni catalyst (outside of the chromite lattice). It is unlikely that the catalytic activity of NiCr₂O₄ is as high as that of Ni. The results (lower performance with higher Ni content) agree with that found in literature. According to Sauvet *et al.* [65], the catalytic activity for methane reforming was higher for LSCrNi3005 than LSCrNi3010 and the lower performance was attributed to the formation of the Ni-Cr spinel.

2. Relative to cells with LSCrRu-GDC anode, the performance of those with LSCrNi-GDC was significantly worse. As discussed above, the possible presence of NiCr₂O₄ likely played a role in lowering the catalytic activity of the anode. No secondary phase consisting of the catalyst phase was discovered in LSCrRu-GDC anodes. Despite the smaller Ni content compared to Ni-YSZ anodes, the LSCrNi-GDC anodes also had poor stability over 312 h. TEM images reveal that Ni nanoparticles grow significantly over time. The average particle diameter increased by as much as six times over 309 h. It was determined that the difference in nanoparticle size between Ni and Ru is due to the more refractory nature of Ru and its higher stability in reducing atmosphere.

5.3.3 (La,Sr)(Cr,Ni)O₃-GDC Anode Extended Applications

5.3.3.1 Hydrocarbon Operation

The performance of the LSCrNi-GDC anode in hydrocarbon fuel was tested by supplying 50 sccm humidified CH₄ to a cell with LSCrNi2018-GDC anode. The I-V curves obtained from this cell in CH₄ and H₂ before and after CH₄ operation are shown in Fig. 5.8. Prior to CH₄ operation (96 h), the power density was 275 mW/cm². The performance in CH₄ was very low, only achieving ≈ 25 mW/cm². The cell voltage in CH₄ and decreased rapidly, so the fuel was switched back to H₂ after only 1 h of CH₄ operation. Suprisingly, 1 h after switching back to H₂ (104 h), the power density had increased from the initial value in H₂ to ≈ 320 mW/cm². However, after 24 additional hours of exposure to H₂, the performance was only slightly better



Figure 5.8: I-V characteristics obtained from a cell with LSCrNi2018-GDC anode before, during and after CH_4 operation at 800°C.

than that observed prior to CH₄ operation. The impedance spectra at 500 mV (not shown here) also show that the R_{pol} decreased from $\approx 0.95 \ \Omega \text{cm}^2$ prior to CH₄ operation to $\approx 0.80 \ \Omega \text{cm}^2$ 1 h after CH₄ operation and $\approx 0.92 \ \Omega \text{cm}^2$ after 24 more hours. The performance enhancement after hydrocarbon deposition has been observed after direct oxidation of hydrocarbon fuels on SOFCs with Cu-YSZ anode by McIntosh *et al.* [142]. It was concluded that the improvement was due to the increased connectivity between the metallic particles, i.e., Cu, which allowed for more conduction paths for electrons and ions. In other words, the carbon deposits bridged the gaps between the conductive phases. This initial performance (prior to hydrocarbon operation) was reversed by oxidation of the anode followed by normal H₂ operation. In the LSCrNi2018-GDC

anode, it is possible that the carbon deposits may have enhanced the contact between the lanthanum chromite and GDC phases. This behavior was not observed in LSCrRu2018-GDC anodes operating on CH_4 due to the minimal carbon deposition.

Though the performance enhancement after hydrocarbon deposition is interesting, the fact remains that carbon deposition still occurs on these LSCrNi-GDC anodes, despite the lower Ni content compared to Ni-YSZ anodes. In addition, the carbon deposition did not provide a long term benefit to the anode. Finally, the cell could not tolerate more than 1 h of CH4 operation, which is unsatisfactory. However, these are only initial experiments and the fuel flow rate and operation temperature had not been studied. It is possible that there are suitable operation temperatures and steam-to-methane ratios that would allow for stable operation of the cell in CH₄.

5.3.3.2 Reduction-Oxidation Stability

A cell with LSCrNi2031-GDC anode was tested for its redox stability by subjecting the cell to two cycles of reduction-oxidation atmospheres. Each cycle varied in duration, as shown in Fig. 5.9. Prior to redox cycling, the cell voltage was ≈ 0.54 V (300 mA/cm² operating current). The voltage was slightly higher, though not allowed to stabilize (as shown between 1 – 1.5 h), after the first redox cycle. The second oxidation period was longer, slightly over 20 h. Hydrogen operation after the long oxidation showed a stable voltage of ≈ 0.6 V. The increase in voltage after the redox cycling may be partially due to the fact that the cell voltage was still increasing when it was subjected to redox cycling. However, that the voltage improved at all indicates that there was not significant damage to the anode due to the oxidation. Unlike the LSCrRu-GDC anodes, the rapid rise in voltage after the long period of oxidation does not

indicate that the Ni did not re-dissolve into the chromite lattice. As discussed in Section 5.3.1, the voltage of cells with LSCrNi-GDC anode increased rapidly upon initial exposure to hydrogen, unlike cells with LSCrRu-GDC anode.

The I-V characteristics were obtained from this cell (in H₂) before and after redox cycling (Fig. 5.10). The results confirm that the performance of the cell did indeed improve after cycling, though the improvement was not significant. Based on these results, the LSCrNi-GDC anodes could have high stability towards redox cycling. This anode is expected to be more stable than Ni-YSZ as the Ni nanoparticles are not part of the core structure of the anode.



Figure 5.9: Redox cycling of a cell with LSCrNi2031-GDC anode at 750°C.



Figure 5.10: I-V characteristics of a cell with LSCrNi2031-GDC anode before and after redox cycling.

5.3.3.3 Sulfur Tolerance

A cell with LSCrNi2018-GDC anode was tested in H₂/H₂S at 800°C. The I-V curves (Fig. 5.11) show that the maximum power density degraded slightly (from 255 mW/cm² to 250 mW/cm²) during the 24 h, yielding a degradation rate of ~ 0.7 mV/h. This is significantly lower than the rate observed for the degradation of the cell with LSCrRu2018-GDC anode (~ 4 mV/h; Section 4.3). This was the only cell with LSCrNi-GDC anode tested, so it is not certain whether this low degradation rate was typical behavior for this type of cell. After re-introduction of H₂ for 2 h, the maximum power density reached 97% of the value prior to sulfur exposure. Further experiments may be performed to determined whether oxidation, redox cycling or prolonged exposure of the anode to H₂ will allow the cell performance to fully recover.



Figure 5.11: I-V curves obtained from a cell with LSCrNi-GDC anode before, during and after sulfur exposure.

5.4 (La,Sr)(Cr,Ru,Ni)O₃-GDC Anodes

The life test results obtained from a cell with $La_{0.80}Sr_{0.20}Cr_{0.94}Ru_{0.06}Ni_{0.02}O_3$ -GDC anode is shown in Fig. 5.12. The cell was tested at 800°C and current density of 300 mA/cm² for 96 h. The cell had a time-dependence behavior similar to that observed from cells with LSCrRu-GDC anode. During the first 3 h of testing, the voltage increased by 75% (Region I). A stable voltage of 0.80 V was reached after 30 h (Region III). The voltage trend after 30 h showed a slight increase to nearly 0.81 V at 96 h. The time to reach stabilization was relatively small, compared to most cells with LSCrRu2018-GDC (on average, ~ 50 – 75 h). Based on the results for cells with LSCrNi-GDC anode, the small amount of Ni may have been the cause for the enhanced rate of voltage stabilization.



Figure 5.12: The life test results of a cell with LSCrRuNi-GDC anode measured at 800°C and 300 mA/cm².



Figure 5.13: I-V curves measured from a cell with LSCrRuNi-GDC anode over time at 800°C.

The I-V curves measured from this cell (Fig. 5.13) also resembles that of cells with LSCrRu-GDC anode. The maximum power density improved by nearly 320% between 15 min (maximum power density = 84 mW/cm²) and 96 h (350 mW/cm²). The overall performance was inferior to that of cells with LSCrRu-GDC, but comparable to those with LSCrNi-GDC anode. The minimum R_{pol} obtained from the impedance spectra (Fig. 5.14) was 0.4 Ω cm², measured at 500 mV and 96 h. This value is twice as large as that achieved by LSCrRu-GDC anodes. However, R_{pol} did decrease significantly over time, by as much as 86% of the value measured at 15 min.

The SEM images obtained from the LSCrRuNi-GDC anode before and after testing are shown in Fig. 5.15. Both before and after testing, the anode had a wide particle size distribution, though it was slightly wider for the pre-test sample. The GDC particles had also grown significantly as was expected based on observations from other anodes.

TEM images were not obtained for this type of anode, thus it was difficult to determine the cause of the lower performance compared to LSCrRu-GDC anodes. Overall, the cell performance was most similar, but inferior, to those with LSCrRu2008-GDC anodes. Considering the total atomic percentage of dopant in the chromite B site were identical between the two anodes (8 mol%), the results are reasonable. The reason for the lower performance may be explained by the significant coarsening of Ni particles over time and the possible presence of a phase with low catalytic activity (relative to Ni), NiCr₂O₄.



Figure 5.14: Impedance spectra from a cell with LSCrRuNi-GDC

anode at OCV (a) and 500 mV (b).



Figure 5.15: SEM images of LSCrRuNi-GDC anode before (a) and after testing (b) at 800°C for 96 h.

5.5 (La,Sr)CrO₃-(Ru-GDC) Anode

Since phase diagrams from literature [135, 136] indicated that there was no solubility of RuO_2 in CeO₂, the first step in studying the LSCr-(Ru-GDC) anode was to test whether RuO_2 could be dissolved into the GDC lattice. The XRD pattern obtained from an as-reacted RuO_2 -GDC powder (500°C for 6 h) (not shown here) correspond to that of cubic fluorite structured GDC (JCPDS #75-0161). No peaks corresponding to RuO_2 or any other secondary phases were observed. If RuO_2 existed as a separate phase in the powder, the peaks should have been visible, considering the RuO_2 content in the mixture was 10 mol%. It was determined that most, if not all, of the RuO_2 was dissolved in the GDC lattice after solid-state reaction.

Figure 5.16 shows TEM images obtained from the as-reacted powder and after reduction for 3 h at 800°C. The particle diameters ranged between 5 - 10 nm, which agrees with the

manufacturer specification for both GDC (Fuel Cell Materials) and RuO_2 (Alfa Aesar). To confirm that the mixture was a solid solution, rather than a mixture, of RuO_2 and GDC, EDS spectra were obtained from several single particles as well as a group of particles in the powder (see, for example, Fig. 5.16). The spectra from single particles and groups of particles were nearly identical. None showed a high concentration of Ru, which is an indication that the RuO_2 particles were not separated from the GDC particles.

After the RuO₂-GDC powder was reduced for 3 h at 800°C, the GDC particles had grown significantly to as large as 50 nm in diameter and particle faceting was observed (Fig. 5.16b). Ru nanoparticles, identified by EDS, were observed on the surface of GDC, with diameters \leq 5 nm. When the pure RuO₂ powder (no GDC) was reduced under the same conditions, the resulting Ru particles were \approx 500 nm in diameter. This was an indication that the presence of GDC prevented the growth of Ru particles. Based on the aforementioned XRD and TEM evidence, it was determined that this occurred not by mere physical separation of Ru particles (i.e, GDC as a diffusion barrier), but by the precipitation of Ru from GDC.

Once it was established that Ru nanoparticles can be precipitated from GDC, an anode made of LSCr-(Ru-GDC) was prepared and tested. Figure 5.18 shows the life test results from a cell with LSCr-(Ru-GDC) anode at 800°C and 300 mA/cm². Unfortunately, the cell showed poor performance. The voltage rose from 0.60 V to 0.66 V in 10 h, then slowly, but steadily, degraded thereafter. The voltage degradation between 10 - 192 h was 3%. The quick rise to a maximum voltage, compared to cells with LSCrRu-GDC, was expected. Since the starting particle size of GDC (5 – 10 nm diameter) was much smaller than that of LSCr (~ 1 µm diameter), the distance that Ru had to diffuse to reach the surface was much smaller. In addition,



Figure 5.16: TEM images of an as-reacted RuO₂-GDC powder (a) and the powder reduced at 800°C for 24 h. Courtesy of Dr. Yingmin Wang.



Figure 5.17: An example of the EDS spectra measured from several locations in the RuO_2 -GDC powder. The spectrum shown in (b) was measured from the particle shown in (a) (small circle). The spectrum measured from the area in bound by the large circle was practically identical to that shown in (b). Courtesy of Dr. Yingmin Wang.

the diffusion coefficient of Ru through GDC and LSCr are presumably different, due to the different crystal structures and levels of stability of Ru in each lattice.

The I-V curves measured over time (Fig. 5.19) reveal a maximum power density of only 214 mW/cm² measured at 24 h. At 120 h, the maximum power density decreased to 210 mW/cm², and at the end of the test (192 h), the power density only reached 205 mW/cm². The impedance spectra show that R_{ohm} was $\approx 0.60 - 0.66 \ \Omega cm^2$. The LSGM electrolyte was $\approx 400 \ \mu m$ thick, which should yield $R_{ohm} = 0.4 \ \Omega cm^2$. The cause for the high ohmic resistance and poor overall cell performance was discovered when SEM images were obtained from the cell after testing. An image of the anode is shown in Fig. 5.20. The thickness LSGM was confirmed to be 400 μm . However, the anode layer was very thin, $\leq 10 \ \mu m$, compared to the typical 25 – 50 μm anode thickness. This explained the high R_{ohm} observed by impedance spectroscopy. The low solids loading in the ink (see Section 5.2.2) was most likely the reason for the thin anode. In addition, the particles in the anode were only loosely connected. This was an indication that the sintering step (1200°C for 3 h) was not sufficient for the anode to form a highly networked structure, resulting in low performance.

On the upside, SEM images before and after testing (Fig. 5.21) reveal that GDC had not grown into large (i.e., 5 μ m diameter) clusters, in contrast with most of the anodes tested in this work, with the exception of the attrition-milled LSCrRu-GDC anode. Though the phases were not distinguished by EDS mapping, the particles were generally 0.5 – 1 μ m in diameter. Based on previous observations of LSCr-GDC anodes, the LSCr particle diameter was ~ 1 μ m, so it is possible that the 0.5 μ m-diameter particles were GDC.



Figure 5.18: Life test results from a cell with LSCr-(Ru-GDC) anode.



Figure 5.19: I-V curves measured over time for a cell with LSCr-(Ru-GDC) anode.



Figure 5.20: SEM image obtained from a cell with LSCr-(Ru-GDC) anode after testing at 800°C for 192 h.



Figure 5.21: SEM images of LSCr-(Ru-GDC) anode before and after testing at 800°C for 192 h.

In comparison with the attrition-milled LSCrRu-GDC anode microstructure (Fig. 3.39), the overall particle sizes are similar. These were the only two anodes which were made without pre-calcining the GDC. It is apparent that the advantage of starting with a smaller GDC particle size was the higher surface area. However, the disadvantage is the difficulty in integrating the powder into the vehicle to form a 20 - 25 vol% solids loading ink. Despite the higher GDC surface area, the performance of both types of anodes were relatively low compared to LSCrRu-GDC anodes, which had large GDC particles. This indicated that the disadvantage outweighed the advantage for these anodes. Further work should be done on the anodes that contain nanometer-scale GDC particles to optimize the microstructure. The GDC surface area should remain relatively high while the solids loading in the ink is increased to at least 20 vol%. The sintering temperature of the anode must also be optimized to yield an interconnected structure.

5.6 Summary and Conclusions

Three types of alternative anodes were tested to determined whether the behavior would be similar to that of LSCrRu-GDC anodes. The following conclusions were drawn from the experimental results:

1. Cells with LSCrNi-GDC anodes showed fair performance, though not as high as cells with LSCrRu-GDC anodes. The maximum power density achieved was only slightly above 350 mW/cm² and $R_{pol} \approx 0.42 \ \Omega cm^2$. The time-dependent behavior of these anodes was also drastically different from the Ru-doped anodes. The voltage increased very rapidly upon exposure to hydrogen, while the increase in voltage for cells with LSCrRu-GDC was relatively slower. This behavior contradicts with the calculated diffusion coefficient of Ni in LSCrNi. The diffusion coefficient, based on the particle density after 45 h of reduction, was

on the order of 10^{-22} m²/s compared to ~ 10^{-21} m²/s for Ru diffusion in LSCrRu. The discrepancy may have been caused by a) the overestimation of diffusion time and b) the possible presence of NiO, which reduces to Ni rapidly upon exposure to H₂. TEM images obtained from LSCrNi powders as-prepared and after reduction reveal that the Ni nanoparticles grow significantly over time, from 10 - 15 nm in diameter after 3 h to 50 – 60 nm after > 300 h. This was thought to be the cause for the degradation over time, in addition to the coarsening of GDC particles.

2. The cells with LSCrNi-GDC anodes were also tested for redox stability, sulfur tolerance and resistance to carbon deposition. The redox cycling test reveals improved performance after two reduction-oxidation cycles. The cell performed well even after a long-term exposure (> 20 h) of oxidation, which is in contrast with cells with LSCrRu-GDC anodes. Though the results are promising, further work needs to be done to determine whether the redox stability of LSCrNi-GDC anodes are higher than that of tradition Ni-YSZ anodes. Regarding the sulfur tolerance of the anode, testing shows that the performance degraded slightly after sulfur exposure. However, the cell was not allowed to recover further, whether by prolong exposure to H₂, redox cycling or oxidation, thus it was not determined whether the cell performance can be completely recovered as was shown for a cell with LSCrRu-GDC anode. Finally, it was shown that the performance of a cell with LSCrNi-GDC anode improved after hydrocarbon operation. It was speculated that this was due to the enhanced connectivity between conducting phases via carbon deposition. The original performance was nearly recovered over time indicating that this was not a permanent effect. It was likely that oxidation of the cell would have recovered the original performance completely. Though the performance improved temporarily, it also implied that there was carbon deposition. Further studies must be done to determine the extent of carbon deposition. It was expected that the smaller Ni content and the nanoscale Ni particles would improve the anode resistance towards carbon deposition.

- 3. The results obtained from cells with LSCrRuNi0602-GDC anodes show that the performance was most similar to that of cells with LSCrRu2008-GDC anode. This was thought to be due to the similar atomic percentage of the catalyst phase (8 mol% in the B site of lanthanum chromite). The lower performance compared to the LSCrRu-GDC anode may be due to the a) Ni particle coarsening over time (for both Ni nanoparticles and possible secondary phase Ni) and b) the possible existence of a Ni-Cr-O phase, which has low catalytic activity compared to Ni. The latter explanation was drawn from the results from LSCrNi-GDC anode results. The LSCrRuNi-GDC anode was not studied extensively and, based on the initial results, the performance may be improved by adjusting the Ru and Ni contents. The idea is to combine the advantages of Ru (high resistance towards sintering and coking) with that of Ni (high catalytic activity). However, the Ni content should be kept relatively low to prevent the formation of a NiO/Ni secondary phase.
- 4. An attempt to improve upon the properties of the LSCrRu-GDC anodes was carried out by doping the GDC, rather than LSCr, with Ru. TEM observations show that Ru can be dissolved into the GDC lattice, despite thermodynamic calculations found in literature, which indicate otherwise. TEM results also reveal that Ru indeed precipitated from GDC particles upon reduction. Unfortunately, the results from cells with LSCr-(Ru-GDC) anode show low performance. Impedance spectra reveal a high ohmic resistance of 0.60 0.66 Ωcm²,

significantly higher than the value calculated from LSGM conductivity, 0.40 Ω cm². SEM observations reveal that the major cause for the low performance was due to the extremely thin anode. This was caused by the low solids loading in the anode ink. The GDC nanoparticles had extremely high surface area (nearly 200 m²/g), thus the amount of vehicle required to coat the GDC particles was very high. In other words, for the same amount of powder as, for example, LSCrRu-GDC (in which GDC was typically pre-calcined), more vehicle was needed, yielding a low solids loading. Because of the extremely thin anode, the performance of the anode material could not be assessed with certainty.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

The primary goal of this work was to thoroughly examine the behavior of (La,Sr)(Cr,Ru)O₃-GDC anodes to determine its feasibility as an alternative anode material. As this is a novel anode material, most of the experimental work carried out in this study was focused on basic characterization of the material, i.e., electrochemical behavior and performance during hydrogen operation, microstructure and the relationship between the microstructure and It was determined through electrochemical measurements of cells with performance. (La,Sr)(Cr,Ru)O₃-GDC anodes that this anode material has high performance, and with further microstructural optimization, even better results are likely to be achieved. By characterizing the microstructure of the anode using various techniques, it was determined that the time-dependent improvement in performance observed in all cells with (La,Sr)(Cr,Ru)O₃-GDC anodes were due to the precipitation of Ru from the lanthanum chromite particles, forming nanometer-scale particles. Due to the high surface area of the electrocatalyst phase, the anode yielded cells with high power density. Control experiments using cells with (La,Sr)CrO₃-GDC, i.e, no Ru, and (La,Sr)CrO₃-GDC-RuO₂ anodes yielded significantly less satisfactory results. The results indicated that, not only was the presence of a catalyst phase essential in the improvement of the anode performance, but also the high catalyst surface area. More specific experiments were done to evaluate the role of Ru content, the anode current collection layer, operation temperature and current on the anode performance. It was concluded that, overall, the performance was higher

with increasing Ru content, current collection layer thickness, operation temperature and current. The rate at which the anode performance improved was also higher with higher Ru content, operation temperature and current. However, higher Ru content and temperature also generally lead to an earlier onset of performance degradation. Therefore, to optimize the performance and lifespan of the anode, the aforementioned factors must be adjusted accordingly. Results from tests on reduction-oxidation cycling, sulfur tolerance and hydrocarbon fuel operation show that the anode material has potential in these respects, but substantial work is still required to accurately assess its performance under those conditions.

Overall, the (La,Sr)(Cr,Ru)O₃-GDC anode showed very good potential as an alternative to the traditional Ni-YSZ anode. Ideally, the technique of precipitating a nanometer-scale electrocatalyst phase can be applied to several other material combinations. The major advantage of this technique is that the fabrication process is simple, especially compared to infiltration, which is another common method of adding nanometer-scale catalyst particles into an SOFC electrode. The anode material can also simply be added onto a support as an anode active layer, which limits the amount of expensive precious metal required in the SOFC. This is in contrast with the infiltration technique where there the placement of the catalyst phase cannot be easily controlled. In addition, the catalyst phase is not a core structural component, thus any structural changes in the catalyst particles, e.g., due to reduction and oxidation, should not undermine the structural integrity of the anode.

To determine whether the technique of nano-catalyst precipitation can be used with other materials, experimental work was carried out on three other types of anodes. Though the performance of these anodes did not match that of the (La,Sr)(Cr,Ru)O₃-GDC anodes,

nanometer-scale catalyst particles were observed in at least two of the anode powders, namely $(La,Sr)(Cr,Ni)O_3$ -GDC and $(La,Sr)CrO_3$ -(Ru-GDC). Electrochemical characterization results also revealed similar time-dependent behavior compared to $(La,Sr)(Cr,Ru)O_3$ -GDC anodes, with the exception of $(La,Sr)(Cr,Ni)O_3$ -GDC. Less effort was put into improving the performance of these anodes by adjustment of factors such as catalyst content and starting particle sizes as they were not the main focus of this research work. Therefore, it is likely that several processing factors and testing conditions can be adjusted such that these anodes yield higher performance. In summary, it was demonstrated that the technique of nanoscale catalyst precipitation can be applied to other material combinations.

6.2 Future Work

Though much of the experiments done in this research work aimed towards gaining a better understanding of the relationship between the microstructure and the time-dependent behavior and performance of the anode, several key questions regarding the nature of the anode remain unanswered. Though the high melting point of Ru explains the relative stability of the Ru nanoparticles to some degree, the nucleation, growth and possible coarsening mechanisms are not well understood. It is clear from the diffusion calculations that the growth of the Ru particles is limited by different processes at different times. Currently, modeling work is being done (primarily by Megna Shah in the Voorhees group) using the phase field method, where the growth of Ru particles is allowed to occur via bulk diffusion and coarsening via both bulk and surface diffusion. A more accurate method of Ru particle density, distribution and particle size (than by TEM observations) is needed in order to develop a realistic model. It is not yet clear how this information can be obtained, but future work may be done using a combination of

methods such as x-ray diffraction, small angle x-ray scattering and XANES/EXAFS. Results from the latter two techniques should also provide information regarding the oxidation state and the environment surrounding Ru atoms. Using an inductively coupled plasma (ICP) to analyze the Ru content of a reduced and as-prepared powder should also help in providing information regarding the amount of Ru that precipitates out from the lanthanum chromite particle. A three-dimensional reconstruction of FIB-SEM images obtained from a portion of the anode would also be extremely helpful in characterizing the anode microstructure. Quantitative analysis of the reconstruction can yield valuable information, such as the TPB length, structure and tortuosity.

The performance of (La,Sr)(Cr,Ru)O₃-GDC with regards to reduction-oxidation cycling, sulfur tolerance and hydrocarbon operation should also be further investigated. It is not understood why the anode does not degrade significantly with redox cycling while long-term oxidation caused significant damage. This may also be indirectly linked to the effect of current on the performance of the anode, as the anode appeared to fair well when it was exposed to oxidizing atmospheres for a short amount of time while current is applied. Ideally, the anode microstructure should be studied by TEM after testing to determine whether the effect is related to the Ru nanoparticle rate, distribution or precipitation rate. Recent attempts to find Ru particles by TEM in post-test anodes have proved that this is not a trivial task, as the chromite particle sizes were thick and the powder also consisted of GDC and (La,Sr)CrO₃, which made it more difficult to find (La,Sr)(Cr,Ru)O₃ particles. The chromite particle sizes were larger than typically used in previous TEM observations as the powder was not ground in order to avoid any alterations in the post-test microstructure. The effect of current on the Ru nanoparticles may be tested indirectly by fabricating cells with (La,Sr)(Cr,Ru)O₃ anode (no GDC, (La,Sr)CrO₃) and a

typical cathode and operating each cell at different current levels. The post-test anode powder may be crushed if the particles are too thick, though this is not recommended for the reason mentioned earlier. Regarding the sulfur tolerance and hydrocarbon fuel operation, more tests simply need to be carried out to fully assess the anode performance.

Finally, as mentioned in the previous section, the technique of nanoscale catalyst precipitation presented in this work has several advantages. If the technique can be applied to other combinations of materials, this could prove to be a useful technique in enhancing the performance of SOFCs without substantially increasing the fabrication cost. The alternative anodes discussed in chapter 5 do have potential and further optimization of the microstructure and testing conditions may be performed to improve their performance. This technique of nanoscale catalyst precipitation may also be applied to SOFC cathode materials. The requirement for cathode is that the catalyst phase must be stable in the host lattice at room temperature and have a low driving force for oxide formation at high temperature (SOFC operating temperature) and pressure up to ~ 1 atm (pO₂ at SOFC cathode).

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Appendix A

Equivalent Circuit Fitting of Cathode Symmetric Cells

A.1 Experimental Procedures

In order to account for the cathode contribution in the impedance spectra measured on the SOFCs presented in this dissertation, a cathode symmetric cell was tested. The symmetric cell was fabricated by screen printing LSCF-GDC cathode and LSCF cathode current collector on both sides of a sintered LSGM pellet (6 h at 1450°C). The cathode, materials and methods used were identical to that used in the SOFCs. The cathode and current collector layers were co-sintered at 1000°C for 3 h. An Au current collection grid was screen printed on top of the LSCF layer. The cell was connected to the impedance analyzer (BAS-Zahner IM-6) via Ag wires connected to the Au grid. The electrode active area was ≈ 0.5 cm² and the electrolyte thickness was 320 µm. Impedance spectra of the symmetric cell were measured between 600 – 800°C. The frequency range was 0.1 Hz – 1 MHz. All measurements were done in air at OCV and using 20 mV excitation amplitude.

The measured impedance spectra were fitted using the EQUIVCRT software, which utilizes a non-linear least squares (NLLS) fitting method. The quality of each fit was determined by the chi-squared value (χ^2), which is a measure of the deviation between the experimental and fitted values. In all cases presented here, the resulting χ^2 were on the order of $10^{-4} - 10^{-5}$ depending on the level of fluctuations in the experimental results, especially at low frequencies. Note that the χ^2 value was calculated by EQUIVCRT according to [Boukamp, 1986]:

$$\chi^{2} = \sum_{i=1}^{N} w_{i} [y_{i} - Y(x_{i}, a_{1} \dots a_{M})]^{2}$$
(A.1)

N is the number of measured data points in each spectrum, and M is the number of adjustable parameters (a_i to a_M). w_i corresponds to the weight (significance) of the *i*th data point, which is determined during impedance measurement. The value of the *i*th data point is y_i , and Y is the fitted value for that point. Note that when χ^2 is normalized by the degrees of freedom of the system (N-M-1), the value should be approximately equal to unity. For further details on the calculations involved in EQUIVCRT, the reader is referred to refs. [Boukamp, 1986; Boukamp, 1989].

A.2 Impedance Fitting Results

The impedance spectra were fitted to an $LR_{ohm}(R_{LF}Q_{LF})(R_{HF}Q_{HF})$ model circuit. The measured and fitted curves (for 600°C, 700°C and 800°C) are plotted in Fig. A.1. The fit results are shown in Table A.1. Note that LF and HF correspond to low frequency and high frequency, respectively.

The activation energy (E_A) based on R_{ohm} was calculated to be 0.733 eV (Fig. A.2). This is in good agreement with literature values for the conduction of LSGM electrolyte, which range between 0.723 – 0.892 eV [Kim and Yoo, 2001; Cong *et al.*, 2003; Gorelov *et al.*, 2001]. The activation energy for the polarization resistance ($R_{pol} = R_{HF} + R_{LF}$) was 1.272 eV (Fig. A.3). Based on literature, the activation energy for LSCF-GDC ranges between 0.95 – 1.65 eV [Madsen, 2005; Dusastre and Kilner, 1999; Murray *et al.*, 2002]. The low frequency arc is typically associated with diffusion of oxygen species, while the high frequency arc is attributed to charge transfer processes [Madsen, 2005 and references cited therein].



Figure A.1: Measured and fitted results for LSCF/LSCF-GDC/LSGM/LSCF-GDC/LSCF symmetric cells between 600 – 800°C.

Temp (°C)	L (H)	R _{ohm} (Ωcm²)	R _{LF} (Ωcm²)	n _{LF}	f _{LF} (Hz)	С _{нғ} (F/cm²)	R _{HF} (Ωcm²)	n _{HF}	f _{HF} (Hz)	С _{нғ} (F/cm²)
600	2.47E-07	1.519	1.310	0.89	14.73	8.12E-03	0.266	0.5	309.87	1.37E-03
650	2.62E-07	0.930	0.505	0.84	37.80	8.08E-03	0.088	0.5	989.62	1.29E-03
700	2.70E-07	0.596	0.203	0.79	84.01	8.82E-03	0.048	0.41	2315.71	8.48E-04
750	2.74E-07	0.407	0.126	0.70	145.53	7.73E-03	0.022	0.5	6.58E+05	7.82E-06
800	2.73E-07	0.310	0.019	1	196.52	2.21E-02	0.062	0.5	302.44	3.00E-03

 Table A.1: Equivalent circuit fitting results for a LSCF/LSCF-GDC symmetric cell on

 LSGM between 600 – 800°C.

At 800°C, which was the operation temperature for most of the SOFCs presented in this dissertation, the polarization resistance for the LSCF/LSCF-GDC cathode was determined to be 0.0405 eV. Note that the values shown in Table A.1 take into account the cathode on both sides of the electrolyte. The peak frequencies were \approx 196 and 302 Hz for the low and high frequency arcs, respectively. These peak frequencies were closer to each other than that reported by Murray *et al.* [2002] for LSCF-GDC at 750°C (~ 10 and 1000 Hz). The low frequency arc was fairly similar to that measured by Dr. Madsen for LSCF-GDC on GDC (165 Hz) [Madsen, 2005]. It is possible that the addition of an LSCF current collection layer played a role in decreasing the peak frequency of the high frequency arc. In addition, the two arcs were highly overlapped at higher temperature, which made the fitting procedure more difficult.



Figure A.2: Plot of $\ln(\sigma T)$ versus 1000/T for the ohmic resistance between 600 – 800°C. The slope yielded $E_A = 0.733$ eV.



Figure A.3: Plot of $\ln(\sigma T)$ versus 1000/T for the polarization resistance between $600 - 800^{\circ}$ C. The slope yielded $E_A = 1.272 \text{ eV}$.

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Appendix B

Diffusion Calculations

B.1 Initial Calculation

Assuming 30 vol% porosity in the anode, and a 1:1 weight ratio of LSCrRu2018:GDC, the volume percentage of LSCrRu2018 in the anode is 35 vol%. The typical anode dimensions are 50 μ m thick and 0.5 cm² active area, yielding an anode volume of 2.5 x 10⁻⁹ m³. Therefore, the LSCrRu2018 volume per anode is:

$$V_{LSCrRu} = 35\% \times 2.5 \times 10^{-9} \, m^3 = 8.75 \times 10^{-10} \, m^3 \tag{B.1}$$

The mass of LSCrRu2018 per anode, assuming LSCrRu2018 density (ρ_{LSCrRu}) of 6.77 g/cm³, is equal to:

$$M_{LSCrRu} = \rho_{LSCrRu} \times V_{LSCrRu} = 6.77 \times 10^{6} \, g \,/\, m^{3} \times 8.75 \times 10^{-10} \, m^{3} = 5.92 \times 10^{-3} \, g \tag{B.2}$$

The number of LSCrRu2018 particles, assuming spherical particles of 1 µm diameter, is:

$$n_{LSCrRu} = \frac{V_{LSCrRu}}{V_{particle}} = \frac{8.75 \times 10^{-10} \, m^3}{\frac{4}{3} \pi (0.5 \, \mu m)^3} = 1.67 \times 10^9$$
(B.3)

The total mass of Ru in LSCrRu2018 per anode is given by:

$$M_{Ru} = M_{LSCrR_{u}} \times mass \ fraction \ Ru \ in \ LSCrRu \ 2018 = 5.92 \times 10^{-3} \ g \times 0.0766 = 4.54 \times 10^{-4} \ g \ (B.4)$$

The total mass of Ru per 1 LSCrRu2018 particle is therefore:

$$m_{Ru} = \frac{M_{Ru}}{n_{LSCrRu}} = \frac{4.54 \times 10^{-4} g}{1.67 \times 10^{9}} = 2.72 \times 10^{-13} g$$
(B.5)

Based on the TEM image obtained after 45 h of reduction, the Ru hemispheres had an average diameter of 5 nm, and the hemisphere density (ρ_{hemi}) was ~ 4 x 10¹⁶ m⁻². The volume of the Ru hemispheres per surface area LSCrRu is:

$$V_{hemi} = 4 \times 10^{16} \, m^{-2} \times \frac{2}{3} \, \pi (2.5 \times 10^{-9} \, m)^3 = 1.31 \times 10^{-9} \, m^3 \, Ru \, / \, m^2 \, LSCrRu \tag{B.6}$$

The mass of precipitated Ru per LSCrRu particle is given by:

$$m_{precip,Ru} = \rho_{Ru} \times (V_{hemi} \times a_{LSCrRu}) = 5.1 \times 10^{-14} g$$
(B.7)

Note that ρ_{Ru} is the density of Ru (12.37 g/cm³) and a_{LSCrRu} is the surface area per LSCrRu particle given by $4\pi (0.5 \mu m)^2 = 3.14 \times 10^{-12} m^2$. Finally, the mass fraction of precipitated Ru over total Ru in an LSCrRu2018 particle is:

$$x_{Ru} = m_{precip,Ru} / m_{Ru} = 5.1 \times 10^{-14} g / 2.72 \times 10^{-13} g = 12.5\%$$
(B.8)

Ideally, Ru is homogeneously distributed within the LSCrRu particle. Therefore, the depth (L = 0.5-r µm) from the surface of LSCrRu (Fig. B.1) from which 12.5% of Ru precipitates can be calculated using simple geometry.



Figure. B.1: Ideal (spherical) LSCrRu particle with 0.5 μ m radius. The shaded area corresponds to the area (or volume in three dimensions) of depth L from which 12.5% of Ru precipitates.

The radius r can be calculated by:

$$\frac{4}{3}\pi (0.5\mu m)^3 - \frac{4}{3}\pi r^3 = 12.5\% \times \frac{4}{3}\pi (0.5\mu m)^3$$
(B.9)

Solving this equation yields $r = 0.478 \ \mu m$. Therefore, the depth L is equal to 22 nm. The diffusion coefficient is therefore:

$$D \sim L^2 / t = (22 \times 10^{-9} m)^2 / (45 h \times 3600 s / h) = 2.99 \times 10^{-21} m^2 / s$$
(B.10)

B.1 Calculation for Short Times

The following calculation, courtesy of Megna Shah, is based on the diffusion through a semi-infinite rod, as illustrated in Fig. B.2. The surface is defined as x = 0 and the bulk is $x = \infty$.



Figure B.2: Semi-infinite rod geometry

The following equation must be solved:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{B.11}$$

where C is the Ru concentration in the (La,Sr)(Cr,Ru)O solid solution, t is the time and D is the diffusion coefficient. The boundary conditions are as follows:

$$C = C_o at x = 0, t > 0 (B.12)$$

$$C = C_1 at x > 0, t = 0$$
(B.13)

The solution to Eq. B.11 using the boundary conditions (B.12 - B.13) is:

$$C = (C_1 - C_o) erf\left(\frac{x}{2\sqrt{Dt}}\right) + C_o$$
(B.14)

The flux of Ru through the surface (x = 0) is given by:

$$J(x=0) = -D\frac{\partial C}{\partial x}|x=0$$
(B.15)

where

$$\frac{\partial C}{\partial x} = \frac{(C_1 - C_o)}{\sqrt{Dt\pi}} \exp\left(\frac{-x^2}{4Dt}\right)$$
(B.16)

By integrating the Ru flux over time, the total amount of Ru atoms at the surface is obtained:

$$n_{Ru} = \int_0^t J(x=0)dt = 2\sqrt{\frac{Dt}{\pi}}(C_1 - C_o)$$
(B.17)

By dividing the total number of Ru atoms, n_{Ru} (atoms/m²) by the number of Ru hemispheres (hemispheres/m²), the number of Ru atoms per hemisphere is calculated. The hemisphere volume can then be calculated by assuming a Ru atom radius of 0.13 nm. Finally the hemisphere radius is calculated by:

$$r_{hemi} = \left(\frac{3V_{hemi}}{2\pi}\right)^{\frac{1}{3}}$$
(B.18)

Using the above equations, r_{hemi} can be calculated for any given time. The diffusion coefficient was determined by varying the diffusion coefficient until the radius of the average Ru hemispheres approximately matched the value observed by TEM at 45 h (2.5 nm radius with 4 x 10^{16} m⁻² surface coverage). The values of C_o and C₁ were 4 x 10^{24} m⁻³ and 4 x 10^{27} m⁻³, respectively. Though the concentration values were approximate, it was determined that the

solutions did not change significantly with the absolute values of C_0 and C_1 as long as $C_1 >> C_0$. Using this method, the diffusion coefficient was calculated to be on the order of 10^{-20} m²/s.

Appendix C

Relevant Phase Stability Diagrams

Exact phase diagrams for (La,Sr)(Cr,Ru)O₃ have not been determined in this study, nor in literature. The following are phase diagrams of similar materials found in literature.



Figure C.1: The solubility limit of $La_{1-x}M_xCrO_3$ where M is Sr or Ca. The solubility of Mg in the B site is shown as well (triangular symbols) to illustrate that the solubility does not follow the same trend for A and B site substitution. Open symbols refer to results obtained in air, while solid symbols are for measurements made at $pO_2 \sim 10^{-8}$ atm [Sfeir, 2003].



Figure C.2: Stability of $La_{1-x}M_xCrO_3$ (M = Sr, Ca) as a function of x at 800°C (a) and temperature (b) [Sfeir, 2003].



Figure C.3: Volatility diagrams for La_{0.93}Sr_{0.07}CrO₃ at 800°C [Sfeir, 2003].

Based on the x-ray diffraction pattern of LSCrRu2018, the secondary phase, SrCrO₄, was expected to form based on thermodynamic calculations and experimental results in literature.



Figure C.4: Single and multi-phase regions for $La_{0.8}Sr_{0.2}CrO_3$. In the multi-phase region, the secondary phase is $SrCrO_4$ and possibly other unknown phases [Miyoshi *et al.*, 2004].

The Ellingham diagram for Ru/RuO₂ is shown below. Based on thermodynamics, Ru was expected to oxidize upon cooling down after the LSCrRu powder was reduced and after cell testing. However, Ru did not appear to oxidize, which implies that the oxidation of Ru was kinetically-limited.



Figure C.5: Ellingham diagram for the Ru/RuO₂ [Kaga *et al.*, 1999].

As mentioned earlier, $SrCrO_4$ was identified as a possible secondary phase in LSCrRu and LSCrNi. Though a phase diagram was not available for 800°C, the following phase diagram (at 977°C) should provide the reader some idea regarding the phase boundaries.



Figure C.6: Phase diagram for Sr-Cr-O system measured at 977°C in air [Jacob and Abraham, 2000].

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Appendix D

Detailed Results on Ru Content Effect

The cell test results shown in Section 3.5.3 were obtained from representative cells, which had the most average performance among cells with the same type of anode, i.e., identical Ru content. Shown below are the results for all cells for more detailed comparison. For each Ru content, 3 - 4 cells were tested.



Figure D.1: Plots of cell area specific resistance versus time for cells with LSCrRu2005-GDC (a), LSCrRu2008-GDC (b), LSCrRu2018-GDC (c) and LSCrRu2025-GDC (d) anodes.