A QUANTITATIVE DETERMINATION OF ELECTRODE
KINETICS USING MICROPATTERNED ELECTRODES

A Thesis
Presented to
The Academic Faculty

by

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In Partial Fulfillment
Of the Requirements for the Degree
Doctor of Philosophy in the School of Materials Science and Engineering

Georgia Institute of Technology
May 2006
A QUANTITATIVE DETERMINATION OF ELECTRODE KINETICS USING MICROPATTERNED ELECTRODES

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Any acknowledgements for this work must inevitably start with my father, Larry Koep, for stressing the importance of education. From the bizarre logic of reviewing kindergarten report cards to the unyielding questions about my homework, I have been fortunate to have someone push me so hard to persevere. I would also like to thank my mother, Margaret Andrews, for imploring me to enjoy the journey. Thank you both for helping me to understand my path.

I’d be remiss to think I could have completed this work without the financial and academic support of Dr. Lane Wilson and the Department of Energy. The goals of the DOE, as conveyed by Dr. Wilson, have helped transform this body of work from a purely academic pursuit into a valuable, albeit small, contribution to science.

I’d also like to acknowledge the countless individuals who have directly or indirectly contributed to my personal and professional development. The encouragement and technical support offered by my fellow students and members of the Fuel Cell and Battery Group should not go unnoticed. Additionally, each committee member has added their own distinct mark to this work, and their help is appreciated.

Finally, I’d like to personally thank my advisor, Dr. Meilin Liu, for taking a chance on me and seeing the potential that was buried so far underneath. Without his guidance and support this project would never have taken shape and I would not be the person I am today. I am truly the result of lessons learned from each one of you and I will do my best to make you all very proud.
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<tr>
<td>$R_p$</td>
<td>Interfacial Polarization Resistance</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance, Universal Gas Constant</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity</td>
</tr>
<tr>
<td>$L$</td>
<td>Length</td>
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<tr>
<td>$A$</td>
<td>Area</td>
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<tr>
<td>$Q$</td>
<td>Activation Energy</td>
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<td>$\sigma$</td>
<td>Conductivity</td>
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<tr>
<td>$I$</td>
<td>Current</td>
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<tr>
<td>$\phi$</td>
<td>Electrical Potential</td>
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<tr>
<td>$\Omega$</td>
<td>Ohm</td>
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<tr>
<td>$S$</td>
<td>Siemens</td>
</tr>
<tr>
<td>$\nabla^2$</td>
<td>Laplacian Operator</td>
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<tr>
<td>SOFC</td>
<td>Solid Oxide Electrolyte Fuel Cell</td>
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<tr>
<td>MIEC</td>
<td>Mixed Ionic Electronic Conducting Material</td>
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<tr>
<td>TPB</td>
<td>Three Phase Boundary</td>
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<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
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<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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<tr>
<td>LOR</td>
<td>Lift-Off Resist</td>
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<tr>
<td>YSZ</td>
<td>Yttria Stabilized Zirconia</td>
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<tr>
<td>LSM</td>
<td>Lanthanum Strontium Manganate</td>
</tr>
<tr>
<td>LSC</td>
<td>Lanthanum Strontium Cobaltite</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
</tr>
<tr>
<td>2PB</td>
<td>Two Phase Boundary</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
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<tr>
<td>NIST</td>
<td>National Institute for Standards</td>
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<tr>
<td>PMGI</td>
<td>polydimethylglutarimide</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
</tr>
<tr>
<td>MIBK</td>
<td>Methyl isobutyl ketone</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropanol</td>
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<tr>
<td>PR</td>
<td>Photoresist</td>
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SUMMARY

Interfacial polarization resistances limit the performance of many thin film solid-state devices, especially at low temperatures. To improve performance, a fundamental understanding of the electrode kinetics that govern interfacial reaction rates must be developed. The goal of this work is to determine site-specific reaction mechanisms and the relative significance of various reactions in order to quantify optimum structural parameters within the cathode microstructure. Key parameters include the length of triple phase boundary (TPB), the quantity of exposed electrolyte/electrode surface, and the ratio of electrolyte to electrode material. These parameters, when studied in a specific system, can be incorporated into broader models, which will encompass the specific conductivity of each component to develop an optimized three-dimensional network.

The emphasis of this work is the systematic control and manipulation of potential cathodic reaction sites in order to develop an understanding of the relative importance of specific reaction sites. Since the physical dimensions of reaction sites are relatively small, an approach has been developed that utilizes micro-fabrication (similar to that used in integrated-circuit fabrication) to produce small and highly controlled microstructures. Currently under investigation are electrode patterns with features as small as 2 microns.

Investigations were made into the nature and reactivity of Triple Phase Boundaries (hereafter TPB) through the use of patterned platinum electrodes since only the TPBs are active in these electrodes. After the processing details of micro-fabrication were
established for the platinum electrodes, patterned Mixed-Ionic/Electronic Conducting (MIEC) electrodes were fabricated and studied using impedance spectroscopy to determine the contributions from the MIEC surface versus the TPB. Strontium doped Lanthanum Cobalt Oxide (LSC) and Strontium doped Lanthanum Manganate (LSM) were selected for their vastly different transport properties. Micro-fabrication techniques allowed for tightly controlled variation in TPB and surface area as well as the application of blocking layers to mask specific reaction sites in order to quantify the contribution from each site and to develop a complete map of reaction sites within electrode structures. Further, systematically changing the geometry of the MIEC electrodes (thickness and line width) allowed for the determination of the effect of ambipolar transport within the MIEC on the activity of MIEC surfaces versus the TPB. This information is critical to rational design of functionally graded electrodes (with optimal particle size, shape, porosity and conductivity). In addition to experimental studies, representative patterned electrode samples were made available for collaborative studies with surface scientists at other institutions to provide additional techniques (such as Raman Spectroscopy) on the carefully designed and controlled cathode surfaces.
CHAPTER 1
INTRODUCTION

Due to the ever-increasing human demand for power in a world of limited natural resources, the need for alternative methods of power generation grows increasingly obvious. Continued reliance on fossil fuels indelibly links worldwide economic prosperity to a politically charged region. Only through a move towards energy self-sufficiency can fiscal and political volatility be reduced. Thankfully new technologies present potential solutions to supply our power demands while also reducing or eliminating harmful byproducts.

Among the most promising alternatives, fuel cells demonstrate the potential to alleviate short and long term power shortages through dramatic improvements in the efficiency of power generation. Additional advantages, such as reduced atmospheric pollution, low weight and high power density, are consequences of the improved efficiency of the fuel cell. Despite these considerable advantages, fuel cells must become economically viable in order to become widely used.

In particular, the solid-oxide electrolyte fuel cells (SOFCs) possess some unique advantages and difficulties. SOFCs have the potential to be economically competitive since they do not require the expensive noble metal catalysts of proton exchange membrane (PEM) or direct methanol fuel cells. Furthermore, the SOFCs capability to operate on a multitude of fuels makes it ideal for the upcoming transition to the hydrogen economy.\(^1\) Though conversion to pure hydrogen fuel will make many distinct fuel cells
competitive, in the transition, the improved efficiency of the SOFC will reduce harmful emissions and prolong fossil fuel supplies. While SOFCs sidestep many of these common problems, they do require high operating temperatures. Though the elevated temperatures are necessary to activate the solid electrolytes and internally reform hydrocarbon fuels, these high temperatures also prevent mainstream utilization of the SOFC. Clearly, the high operating temperature is at once the SOFCs greatest source of hope as well as its greatest difficulty.

Potential cost reductions in (SOFC) technology hinge on the ability to reduce operating temperature without sacrificing performance. Gas sealing problems and expensive interconnect materials could be avoided through the use of more moderate operating temperatures. Recently, alternative electrolyte materials (and thin film YSZ technology) have shown sufficient oxygen ion conductivity at 500 - 800°C, sparking renewed interest in low temperature SOFC operation. Specifically, thin GDC (Gd$_{0.1}$Ce$_{0.9}$O$_{2-x}$) and SDC (Sm$_{0.2}$Ce$_{0.8}$O$_{2-x}$) electrolytes have demonstrated sufficient ionic conductivity for good fuel cell performance at 400-600°C. While shifts to lower operating temperatures allow for significant advantages in fabrication and assembly, they also cause substantial increases in the interfacial polarization resistance. Previous studies have shown that at low temperatures the electrode/electrolyte interfaces contribute the majority of the total cell resistance. Furthermore, when hydrogen is used as the fuel, this interfacial resistance can be attributed almost entirely to the cathodic side.
Reduction of oxygen involves a number of elemental steps, such as adsorption of oxygen molecules, dissociation of molecules to atoms, ionization of oxygen molecules and combination of oxygen ions with oxygen vacancies. If either the vacancy or the electrons are unavailable, as would happen far from the TPB, the oxygen reduction will not happen, thus contributing nothing to the fuel cell performance.

For an electrode made from a pure electronic conductor, such as platinum, the electrode reactions can occur only at or near the three phase boundary (TPB), the region where gas phase meets electronic and ionic conducting phases at the electrode-electrolyte interface. For a noble metal electrode all three necessary species -- oxygen vacancies, electrons, and atomic oxygen -- are only available at the TPB. Theoretically, the electrochemical reactions can only proceed along this 1-dimensional interface. However, the TPBs may in fact have a reaction zone that is broader than this linear feature. Even when using precious metal electrodes, the one-dimensional TPBs may in fact have a finite width broader than the linear feature. Surface ion migration or the quantum effect of electron tunneling may serve to expand the TPB to cover a large portion of the surface.

Similarly, the more common use of mixed ionic-electronic conducting (MIEC) materials is intended to dramatically expand the reach of the reaction zone across a larger, two-dimensional surface. Due to the simultaneous transport of both ionic and electronic defects in MIECs, oxygen vacancies are able to migrate extended distances through the MIEC electrode. As a result, the effective reaction sites could be far beyond the TPB. Currently, MIEC reaction rates cannot be definitively attributed to either the
TPB or reactions on the surface of the mixed conducting electrode. Consequently the effective thickness of an MIEC has yet to be determined.

1.1 Problem Statement

Substantial gains in low temperature SOFC performance require reductions in resistance along the cathode/electrolyte interface. This interfacial resistance reflects the nature and performance of small reaction zones along the material boundary. There currently exists no theory or evidence to prove the size of the actual reaction zones using either metallic or MIEC electrodes in fuel cells. The objective of this study is to explore the actual electrode reaction zone through the use of micropatterned electrodes. Standard photolithographic techniques will be used to deposit noble metal electrodes with consistent surface area and varied triple phase boundary lengths. At the same time, the methodology and techniques developed for metallic electrodes will be extended to investigations of MIEC electrodes. Since the performance of SOFCs at low temperatures is determined predominantly by interface reactions, a fundamental understanding of the processes would provide valuable insight to effective improvement in fuel cell performance. Optimization of both electrode material and microstructure should yield an electrode/electrolyte interface in which the entire surface is active.

In fact, interfacial polarization resistances limit the performance of many thin film solid-state devices, especially at low temperatures. A fundamental understanding of the electrode kinetics that govern interfacial reaction rates promises to benefit a wide variety of applications. The goal of this work is to determine site-specific reaction mechanisms and the relative significance of various reactions in order to quantify optimum structural parameters within the cathode microstructure. Key parameters include the length of
triple phase boundary, the quantity of exposed electrolyte/electrode surface, and the thickness of electrode material. These parameters, when studied in a specific system, can be incorporated into broader models, which will encompass the specific conductivity of each component to develop an optimized three-dimensional network.

1.2 Impact

The goal of this work is to determine site-specific reaction mechanisms and relative significance of various reactions in order to quantify optimum structural parameters within the cathode microstructure. While patterned microelectrodes are unlikely to be of industrial significance, they can provide insight into the key parameters for SOFC operation. These parameters, when studied in a specific system, can be incorporated into broader models, which will encompass the specific conductivity of each component to develop an optimized three-dimensional network. In short, this work will provide future scientists with the fundamental understanding necessary to optimize performance of more practical electrodes.
CHAPTER 2
BACKGROUND

2.1 Mixed Ionic-Electronic Conducting Materials

Mixed Ionic-Electronic Conducting (MIEC) materials have recently been investigated due to their unique ability to improve SOFC performance. Since performance of the SOFC ultimately depends on the oxygen incorporation reaction, the reaction can proceed only where ionic and electronic species are present. MIEC materials allow simultaneous transport of both electronic and ionic species, thereby increasing the size of possible reaction sites.

Most recently MIEC materials have been developed as SOFC electrodes. When MIEC materials are employed as electrodes, electrochemical reactions can theoretically proceed along the entire electrode surface. Since both oxygen vacancies and electrons are available anywhere along the electrode surface, reactions are not limited to the TPB, but can proceed along the entire two-phase boundary (2PB), the MIEC surface.

In particular, perovskite materials have been investigated as SOFC electrodes in recent years with considerable promise. MIEC materials typically derive their unique capacity for multi-species conduction from their perovskite structure. The ABO$_3$-type perovskite structure usually has a 2+ valence cation at the A-site with 4+ valence cations at the B-sites. Oxygen anions take octahedral coordination around the B-sites. The key
components of this structure are the 12-fold coordination of the A sites combined with
the 6-fold coordination of the B cation and oxygen anion sites. Since a strong propensity
toward ionic bonding can be inferred from a coordination number greater than 6, A-site
doping largely determines oxygen vacancy concentration. While doping of the B-site
will can also create oxygen vacancies, perovskite stacking leads A-site doping to be the
optimal choice. From this structure, doping of the A-site with a cation of alternative
valence can induce a variety of properties, including piezoelectricity, magnetoresistance
and, most importantly, ionic conductivity.  

Furthermore, A-site doping also leads to improved electronic conduction. Ideal
perovskite compounds are typically insulating or semiconducting materials, but changing
the valence state of the A-site causes ripple effects throughout the compound. A-site
substitution can induce local charge fluctuations that must be balanced according to the
rules of electroneutrality. Local charge compensation is typically accomplished through
a combination of oxygen vacancy creation and valance changes in the B-site cation.
Valance changes of the B-site can alter the band structure, resulting in improved
electrical conduction.

For example, Lanthanum Manganate (LaMnO$_3$) has low intrinsic p-type
cconductivity due to oxygen vacancies. However, doping with Strontium as in Lanthanum
Strontium Manganate (La$_{0.8}$Sr$_{0.2}$MnO$_3$), or LSM, causes both oxygen vacancy initiation
and some partial conversion of Mn 3+ to Mn 4+. The use of Strontium dopant is very
popular since La3+ and Sr 2+ have similar ionic radii. Thus, site exchange does not
introduce significant lattice distortion. However, the Mn valance change assists electrical
conduction by altering the dimensionality of the 3-D framework of the crystal thereby changing the structure of the energy bands. Since LSM conducts through the small polaron hopping conduction mechanism, a slight reduction in the activation energy results in a dramatic increase in electronic conductivity.\textsuperscript{13}

Of the many perovskite materials, LSM has been among the most popular due to its high electronic conductivity and high activity for oxygen reduction. LSM allows oxygen ion conduction and has been shown to be compatible with YSZ electrolytes in terms of stability and CTE match.\textsuperscript{14,15} Since the ionic conductivity of LSM is particularly low, LSM/YSZ composite cathodes have shown better performance by extending the amount of LSM/YSZ interface into a third dimension.

Additionally, doped Lanthanum Cobalt Oxides have been widely studied due to their improved oxygen ion conductivity. In particular La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3} (LSC) perovskites provide superior performance over LSC due to improved conductivity and surface effects.\textsuperscript{16,17} Unfortunately, LSC cathodes have been limited to use with ceria-based electrolytes due to their strong tendency to develop non-conductive La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} or SrZrO\textsubscript{3} films at the interface.\textsuperscript{18,19} Still, the LSC-GDC system provides sufficient performance to warrant further investigation.

Finally, Samarium Cobalt Oxides, in particular Sm\textsubscript{0.5}Sr\textsubscript{0.5}O\textsubscript{3} (SSC), electrodes have shown further improvements in ionic conductivity. While LSM showed sufficient performance for intermediate temperatures (800-1000C), its performance decreased
significantly below 800C. SSC showed good performance at low temperatures (<800C).20,21

Clearly any study of interface reactions should take into account these three materials. Not only are they the most popular materials in the field, but also they provide a wide spectrum of ionic conductivity. Determination of the TPB effect according to cathode ionic conductivity is within the scope of this study.

2.2 Reaction Mechanisms

Though little is known about the relative contributions of reaction sites, general agreement abounds regarding the possible kinetic mechanisms. Specifically, for metallic electrodes, three possible paths are available for electrochemical reduction. In the most obvious case, atmospheric oxygen is directly adsorbed into the electrolyte at the TPB. Another possibility involves dissociative oxygen adsorption on the surface of the electrode. These oxygen ions would then migrate along the electrode surface to the TPB where, in combination with oxygen vacancies, they would be incorporated into the electrolyte sublattice. This possibility is demonstrated in Figure 1a. Another possibility involves electrons tunneling along the surface of the electrolyte. These electrons could then react with atmospheric oxygen and oxygen vacancies far from the TPB. This possibility is demonstrated in Figure 1b.
Figure 1.1  Broadening of reaction area beyond TPB due to (a) transport of oxygen species \((O_s = O_2, O_2^-, O, O^-, O_2^-)\) along the platinum surface and (b) transport of electrons along the surface of the electrolyte.

In either of these two cases, the reaction zone would be extended beyond the theoretical limits of the TPB. While quantum mechanics dictates these possibilities, the actual size of the reaction zone has yet to be determined.

In addition to these three possible reaction paths, MIEC materials offer the added possibility of bulk diffusion. Since MIEC materials tolerate ionic diffusion, all three necessary components -- the electrons, adsorbed oxygen and oxygen vacancies -- are available along the entire surface of the MIEC electrode. Consequently, atmospheric oxygen could be incorporated into the oxygen sublattice at the TPB and anywhere along
the 2PB, as demonstrated in Figure 2. This reaction path can be further broken down into
diffusion through the roof of the electrode or through the sidewall of the electrode.

![Figure 1.2 Broadening of the reaction area for an MIEC due to oxygen diffusion through the bulk of the electrode.](image)

### 2.3 Previous Work

The lack of understanding surrounding the low-temperature behavior of SOFC electrodes has instigated a variety of experiments to help draw out the relationship between geometry and electrode performance. Each method provides unique advantages but somehow fails to fully quantify the association.

**Modeling**

Several models have been developed to determine the actual size of the reaction zone for MIECs. Some of the most prominent have been proposed by LJ Gauckler, J.
Fleig, and M. Liu. Though each of these discusses different systems, they provide the framework for development of a basic model for thin patterned electrodes.

L.J. Gauckler provided a basic model to identify the reaction mechanism associated with platinum electrodes on YSZ. Since ionic conductivity through the bulk does not apply for a noble metal, the process is simplified to three steps. First, atmospheric oxygen molecules were adsorbed dissociatively on the noble metal surface. These adsorbed oxygen species then diffused to the TPB where they were finally incorporated into the oxygen sublattice of the electrolyte. Dissociative adsorption was based on the Langmuir isotherm, while surface diffusion followed a simple derivation of Fick’s Law. Finally the electrochemical reaction was determined via Butler-Volmer. In all, the model matched impedance data poorly, leading to the important conclusion that diffusion kinetics on the platinum surface vary significantly from the model and therefore are not accurately predicted by the Langmuir isotherm.22

Another popular model added the functionality of dealing with MIEC electrodes of well-defined geometries. J. Fleig proposed a model for dense microelectrodes separated with a simple network of gas channels, similar to honeycomb structures. While the surface path may play an important role in the reduction process, in an attempt to simplify, this model only considers the bulk path. Accordingly, Fleig presents a model that serves to quantify only the site-specific contributions for bulk-dominated situations. Fleig found that for MIECs in which only the bulk path was considered, the TPBs heavily dominate the reaction sites for thick electrodes. However, for thin electrodes with good
ionic conductivity, the current should be proportional to $2PB$ area rather than $TPB$ length.\textsuperscript{23} Furthermore, based on material specific properties, models can predict the thickness at which the bulk path contributes to overall cell performance.\textsuperscript{24}

Finally, M. Liu developed some general equations applicable to all MIEC electrodes. While many of these equations are much more complicated than needed here, they can be simplified under some basic assumptions. Specifically, by assuming that only two mobile charge carriers are significant, development of specific equations is straightforward.\textsuperscript{25} These equations will form the basis of the model proposed here.

\textit{Quantification of porous electrodes}

Initial experimental attempts to verify the relationship of TPB with overpotential involved examination of porous electrodes.\textsuperscript{26-28} Mizusaki, et al. first showed cathode overpotential to be related to $3PB$ length by comparing bulk impedance spectra with estimated TPB length. After testing, the porous LSM electrodes were cross-sectioned at the interface with YSZ electrolyte. Electrode pore diameters were measured and length averaged to determine the TPB length. While these methods were accurate enough to show a correspondence between TPB length and cathode overpotential, length averaging is inherently imprecise and fails to quantify the relationship.

Furthermore, porous electrodes made from pastes develop a wide range of pore sizes. Due to the large range of pore size distribution, it is difficult to determine the
performance contribution from specific pore sizes. Recent studies on porous electrodes have concluded that thin dense layers, up to 1µm in thickness, may provide better performance than structures seeking solely to maximize TPB length.²⁹

**Microelectrodes**

While microelectrodes have been in use for quite some time in liquid electrochemistry, they are relatively new to solid-state ionics. Preliminary studies used contact needles as rudimentary microelectrodes in SOFC studies. The contact needles were pressed into the electrolyte, physically deforming the needle tip, thereby creating a roughly circular microelectrode. Unfortunately, this method yielded ill-defined contact areas and an unreliable measurement of the actual TPB length.³⁰

Other studies used photolithography to develop circular microelectrodes. Individual microelectrodes were then contacted with sharp needles to measure impedance of individual grains. Individual microelectrode studies improved upon the previous methods by lithographically producing microelectrodes that now had well-defined contact areas. While they produced good results, limitations in lithographic processing limited these microelectrodes to a smallest feature size of approximately 10µm diameter and a maximum thickness of about 250nm.³¹,³² Furthermore, unusually large impedance values required untested adaptations of the measurement equipment.
Attempts to further quantify the relationship between TPBs and electrode overpotential led to the development of patterned microelectrodes for SOFCs. Working independently, L.J. Gauckler et al. and Mizusaki et al. developed nickel patterned anodes. All methods used photolithographic techniques to develop micropatterned lines of nickel for use as anodes. These patterned microelectrodes allowed for preliminary correlation between the results of bulk impedance spectroscopy with defined amounts of TPB length. All studies found a linear proportionality between overall interfacial resistance and TPB length.\textsuperscript{33-36}

### 2.4 Objectives

The main objective of this work was to gain a basic understanding of the nature and reactivity of different sites for oxygen reduction, including the TPB, electrode surfaces, and the exposed surface of the electrolyte. In particular, the specific technical objectives were to:

- Develop a systematic approach for the microfabrication of patterned electrodes of \textit{well-defined} geometry specific to SOFCs;
- Quantify the relationship between TPB and interfacial resistance for a variety of materials with substantially different transport properties;
- Determine the dominant reaction paths for each material;
- Determine the effective size of the electrochemically active area
for each material;

- Provide insight into the reaction mechanisms occurring at the electrode surface.

A fundamental understanding of these issues is imperative to the development of intelligently designed electrodes of optimized performance.
CHAPTER 3
TECHNICAL APPROACH

3.1 General Technical Approach

Determination of these effects requires small feature sizes and exact control of TPB length. While quantum mechanics dictates a high probability for these paths to exist, the size of the reaction area may be negligible. By placing small electrodes of controlled TPB length very closely together, expanded reaction zones would eventually begin to overlap. Once the active zones overlap, additions of TPB length yield no more reaction area. Consequently, under this possibility, bulk impedance would yield a plateau in interfacial resistance reductions. A strictly linear relationship between TPB length and interfacial resistance would indicate that either the proposed mechanisms did not contribute, or more likely, that the size of the reaction zone due to these mechanisms were less than ½ the smallest feature size (½ the distance between TPBs).

Modeling and Design of Patterned Electrodes

Successful completion of this study requires careful determination of pattern design in order to isolate specific mechanisms. Since the key parameters in this study are the actual TPB length, ratio of electrolyte/electrode area, and the thickness of the electrode, all in reference to the electrode material, pattern selection and generation are critical. Deviations from linear behavior are likely to be discovered only at very small
feature size. Consequently, patterned electrodes with large variations in TPB and very small feature sizes would likely provide the best results. The largest electrolytes that can currently be cast, cut and fired with high yield and good surface uniformity were approximately 1cm diameter circles. Larger electrolytes have a strong tendency to develop excessive defects. Since the smooth surface of the electrolyte is critical to successful deposition of electrodes, surface uniformity limitations have to be considered.

A 1cm diameter circular electrolyte allows for a square microelectrode pattern of approximately 7.07 mm per side. Since allowances should be made for slight misalignments, square microelectrode arrays should be 6mm per side providing a total surface region of 36 mm$^2$.

Square arrays of rectangular microelectrodes were chosen for a variety of reasons. First, rectangles provide more perimeter area per surface area than do circles. Second, rectangular electrodes prove to be more easily fabricated than circular electrodes. The sharp edges of the rectangles provide initiation points for the lift-off procedure. Third, square arrays of rectangular electrodes maximize the available surface area while maintaining structural and electrical integrity.

Since small feature sizes are critical to the success of this study, it follows that the initial working electrode pattern should take full advantage of this capability. Resolution limitations currently dictate that the feature size is at least 2μm. Consequently, a patterned electrode should be made up of rectangular electrodes 2μm in width, 6mm in
length, and approximately 0.6-0.7μm high. These rectangular electrodes were patterned in succession with 2μm spaces between. To complete a square 6mm by 6mm, 1500 line electrodes were patterned in the array. Subsequent patterns will be generated for microelectrode arrays of larger feature sizes.

Next, calculation of sheet resistance for conductors and semiconductors at high temperatures dictated placement of the current collector. The resistance to electronic flow through the electrode can be easily determined through the equations:

\[ R = \rho \left( \frac{L}{A} \right) \]

For Metallic conductors:

\[ \rho = \rho_o \left[ 1 + \alpha_e \Delta T \right] \]

Where: \( \alpha_e (\text{Pt}) = 3.9 \times 10^{-3} /\degree \text{C}, \rho_o = 3.64 \times 10^{-5} \) for Platinum

For Semiconductors:

\[ \rho(T) = \rho_o e^{\left( \frac{-Q}{RT} \right)} \]

Where the activation energy for LSM is 8.7 kJ/mol

Also for an electrode array:
\[
\frac{1}{R_f} = \frac{1}{R_1} + \frac{1}{R_2} + \ldots
\]

Since the cross-sectional area of the smallest electrode is 2\(\mu\text{m} \times 0.1\mu\text{m}\), or \(2 \times 10^{-13} \text{m}^2\), and the largest acceptable sheet resistance should be no more than a few ohms, a current collector should be patterned into the cell. Back calculating from a five ohm resistance dictates that the largest distance from any part of the patterned electrode to the current collector should be no more than 125\(\mu\text{m}\). Current collector lines separated by 250\(\mu\text{m}\) meet this requirement. Theoretical conductivity measurements yielded total resistances of 0.061\(\Omega\) for platinum and 4.76 \(\Omega\)’s for LSM at these dimensions. These values are negligible when compared to the interfacial resistance. Therefore, the processed patterns provided the maximum amount of TPB and the minimum separation between electrodes, all with low sheet resistance and good processing potential.

Another factor of interest is placement of counter and reference electrodes in order to determine the effective impedance contribution from the working electrode. Though symmetric cells allow simple interpretation of data, processing procedures eliminate the possibility of patterned electrodes on both sides of the electrolyte. Use of a porous silver counter electrode ensures that the impedance contribution from the counter electrode would be minimal. The impedance contribution from the patterned electrode can be further separated through judicious use of a reference electrode. Since the reference electrode can be developed with less than 20\(\mu\text{m}\) separation from the working
electrode and the thickness of the tape case electrolytes are more than 250μm, the reference electrode can be used to safely separate contributions from each distinct part of the cell.

*Fabrication of Cells with Patterned Electrodes*

Due to the extensive variation of possible mechanisms proposed for electrochemical reduction of oxygen at the cathode, determination of the active sites requires a systematic study of limiting cases. I propose a series of studies in whose goal will be the isolation of the active regions for a variety of electrochemical and chemical processes. Determination of reaction mechanisms requires the ability to isolate each possible reaction site in order to understand its contribution to the overall interfacial resistance reactions. The study is broken into several parts, beginning with the simplest case of metallic electrodes and then increasing in complexity to determine the impact of ionic transference number in MIECs on the relative importance of various reaction sites.

Previous studies in this area were limited by lithographic capabilities. The best resolution only reduced the smallest feature size to Ni patterned lines of 20μm in width. As predicted in models presented by J. Fleig, the reaction zone for purely electronic conductors may be much smaller than this.

Furthermore, the quality of processing of the microelectrodes was not sufficient to eliminate cracking along the 3TPBs. Uniformity of the patterning technique allows
comparison between samples of different TPB length. Of critical importance to this
study is the actual triple phase boundary length. Since I am proposing that the interfacial
resistance is directly proportional to the TPB length, an accurate measure of the actual
triple phase boundary is imperative. Any roughness, fracture or other anomalies at the
interface can lead to significant extension of the triple phase boundary, often by up to two
orders of magnitude. Consequently, great care was taken to ensure that the surface was
smooth and free of defects. Furthermore, all microfabrication techniques were carefully
monitored to ensure that no structural problems arose. Resolution of increasingly reduced
feature size figures prominently in study of the size of the reaction area. When
necessary, E-beam nano-lithography was incorporated into the study to further reduce
feature size.

While modeling of micropatterned electrodes is straightforward, the difficulty lies
in producing effective microelectrodes for experimental verification of any of these
numerous models. The bulk of models on this subject speak to the importance of having
an in-depth understanding of kinetics at the electrode/electrolyte interface. However,
experimental determination of these parameters is critical to verification of one model
above others.

Fabrication of Platinum Microelectrodes

The initial study sought to determine the effective active size of the reaction zone
for platinum electrodes. This was accomplished through fabrication and impedance
testing of platinum electrodes of constant surface area and varying TPB length. By maintaining a constant electrode height, and altering the number of electrode lines, as demonstrated in Figure 5 (B) and (C), the total surface area of the electrodes and the total electrolyte area are held constant while the effective TPB length can vary by 4 orders of magnitude. Through careful fabrication, electrodes of well-defined geometry can quantitatively link bulk impedance spectroscopy results to TPB length. For a purely electronic conductor, any deviation from linearity can be completely attributed to overlap of the active areas.

Figure 3.1: Schematic of patterned electrode arrays Pattern A has the lowest level of TPB and electrode area. Pattern B has the same amount of TPB as pattern A with double the electrode area. Pattern C has the same electrode area as pattern B with 10 times the TPB of pattern A and B.
Following the process outlined in the previous section, patterned electrodes of MIEC materials were fabricated. Initially the TPB length was varied while Surface Area was held constant to determine the relative importance of the TPB for the mixed conductor. Next, this study continued past the previous method by holding TPB length constant while varying electrode height. In addition to determination of the relative importance any surface diffusion mechanisms, this study should also serve to determine whether there is a thickness at which surface area becomes more important than TPB length. In this case, if this thickness is different than previously resolved, the relative importance of bulk diffusion can be determined as a mechanism.

Studies for MIECs will mirror studies for platinum, but in this case the electrode materials will be Strontium doped Lanthanum cobaltite (LSC) and Strontium doped Lanthanum Manganate (LSM). Comparison of MIEC electrodes of varying ionic/electronic transference numbers should provide insight into optimization of electrode geometry in conjunction with electrode material. This study will determine whether future optimization of electrode geometry for commercial purposes is material dependent.

The final study involved microfabrication of patterned electrodes of LSM. The electrodes were coated on the top surface with titanium dioxide to prohibit ionic transport through the electrode roof. In doing so, we were able to determine the initiating sites for
bulk diffusion through the electrode. Since bulk diffusion of oxygen through the electrode walls is constant, by varying the height of the MIEC electrode, we can determine exactly how far the active region of the electrode surface extends away from the three-phase boundary. Through this study we were able to further clarify the relation between electrode width, transference number and total surface area.

**Determination of Mechanisms**

The most popular model for oxygen reduction at the cathode revolves around the influence of the three-phase boundary (TPB): the two-dimensional intersection of gas with electronically and ionically conducting phases. The first study involved microfabrication of platinum electrodes of constant height and surface area while varying the TPB length. This study helped determine the importance of the TPB in comparison to the surface area of the electrode and the electrolyte.

In addition, through decreasing not only the size of the pattern elements but also the spacing between elements, the actual active area of the TPB was isolated. Specifically, as the TPB region of adjacent electrode elements approached each other, as in the case of smaller, more finely spaced line electrodes, performance benefits would increase linearly up to the point where the overlap of active regions produced no further active sites. Figures 3.2 and 3.3 better elucidate the challenge.
Figure 3.2: Schematic of overlap under oxygen diffusion along the electrolyte surface to the TPB. Here the actual active region of the TPB, shown in red, extends onto the electrolyte. In figure (a) the electrodes are far apart. Figure (b) shows the case of closely spaced electrodes.

Figure 3.3: Schematic of overlap under oxygen diffusion along the electrode surface. Here the active regions of the TPB, shown in red, extend onto the electrode surface. Again, in figure (a) large electrodes would not be able to determine this effect while much smaller metallic electrodes would allow for this determination.

Theoretically, oxygen reduction can occur only at the TPB where all three phases necessary for incorporation of oxygen ions in the YSZ sublattice are available. For metallic electrodes, there is a commonly held view that surface diffusion of oxygen species along either the electrode or electrolyte surfaces may contribute to the reaction pathway, but this may only be discernible with very small feature size. In the case of Figure 1a, the contribution reaction zone is defined by only the amount of TPB within the sample, but Figure 1b shows the limiting case, where the fabrication of additional TPB
onto the electrode can no longer increase the active sites available. Similarly in Figure 2, the traditional and limiting case for oxygen species developing on the electrode surfaces (the 2PB) is presented. Since the active region discernable by micropatterned electrodes would be exactly half the smallest feature size, reducing feature sizes through improved microfabrication techniques may be critical to this study. In the likelihood of a chemical surface reaction, determination of the active area will require both very small electrode feature sizes and very small separation distances.

Clearly, the ability to accurately and precisely control the electrode geometry and spacing will be the defining requisite. Only through careful analysis of well-defined electrodes can accurate TPB lengths be determined. Any fracture or separation of the electrode can increase or decrease (for delamination) the effective TPB length by orders of magnitude, thus compromising the study.

As demonstrated by the above models, the pure electronic conductivity of metallic electrodes provides a natural starting point for this study. Platinum was the obvious choice for a purely electronic conductor since it is the electrode of choice in many SOFC systems and it is the most stable at high temperatures. Platinum electrodes were patterned on tape-cast electrolytes using state of the art photolithographic methods. A combination of Lift-Off lithographic processing in conjunction with deposition via DC sputtering, laser ablation, and e-beam evaporation, was used to fabricate patterned electrodes. Patterns for the desired electrodes will be produced using AutoCAD software and transferred to chrome masks on glass plates. The TPB length of the patterned
electrodes varies from 0.0112 meters to 18.005 meters while keeping the area of the electrodes at 0.36 cm$^2$, yielding electrodes with the ratio of TPB length to area vary over 4 orders of magnitude. Later, e-beam nanolithography was used to reduce the feature size of some patterned electrodes further still.

Having determined the surface mechanisms for metallic electrodes, the next logical step was to continue with the more complex model for MIECs. Expanding this study into electrodes composed of mixed ionic/electronic conductivity (MIEC) adds additional complexity due to the possibility of oxygen diffusion through the bulk electrode material. The second study involved microfabrication of Strontium doped Lanthanum Magnate (LSM) electrodes of constant height and surface area with varying TPB length. In this case, we hoped to determine the relative importance of the triple phase boundary and its relation to surface area for an electrode with a non-zero ionic transference number.

The third study involved holding the TPB length constant while simultaneously varying the electrode height. Due to the large aspect ratio between the electrode width and thickness, the change in surface area was again negligible. This study was performed in order to investigate the relative importance of oxygen diffusion through the electrode bulk. Should the preliminary studies determine a region in which increasing TPB length fails to yield corresponding performance benefits, we will have determined the size of the active region. By varying the size of the electrode, we should then be able to determine which mechanism -- surface diffusion along the electrode or surface diffusion along the
electrolyte -- more significantly impacts electrode performance.

**Impedance Spectroscopy**

Impedance spectroscopy has been shown to provide an accurate insight into the nature of electrode kinetics. From the size and shape of the impedance loop, quantitative estimates of resistances can be determined. Typically, these impedance loops are matched to an idealized model circuit consisting of discrete electrical components.\(^{38}\)

Many proposed impedance curves have been approximated by the equivalent circuit method with great success, but the relative importance of individual reaction mechanisms has been under some dispute.\(^{39-41}\) Since a large part of impedance analysis relies on accurately constructing and interpreting equivalence circuits, the interpretation of data is critical to proper analysis. While the intricacies of impedance interpretation are often vague, determination of the interfacial resistance can be much more straightforward.

Current collectors are designed to overlay each pattern to eliminate excessive resistances from electronic transport. Impedance spectroscopy was then used to isolate the resistance measured for the patterned electrode from that of the other cell components. Two techniques were used to exactly determine the resistance associated with the patterned electrode. The simplistic method was to produce a very low resistance, and highly reproducible counter electrode for the patterned electrodes. This interfacial
resistance of the counter electrode was sufficiently lower than that of the patterned electrodes and could subsequently be neglected or mathematically removed from the pattern electrode test samples.

Concerns about inconsistencies lead to a better solution that relies on the use of a reference electrode in order to clearly isolate the behavior of the patterned electrode from the rest of the cell. Since the position of the reference electrode is critical to determination of intelligible results, the reference electrodes will be developed during microfabrication and patterned within 30µm of the working electrode. It is critical that this distance be sufficiently close to probe the neutral potential of the electrolyte within the electrical field, while not shorting to the working electrode. Since the thickness of our tape-cast electrolytes exceeds 150µm, careful positioning of the reference electrode is required to yield optimal results.

Four-point testing will be performed on both dense film electrodes and also on the micropatterned electrodes themselves to ensure proper conductivity. From further calculations, the size and spacing of the current collector will be fabricated to minimize or compensate for these effects.

*Characterization of Thin Films*

Strontium doped La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) and Strontium doped La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSC) have long been recognized as excellent materials for solid state electronic devices. The mixed ionic and electronic conductivities of these materials make
them ideal choices for electrodes in solid oxide fuel cells\textsuperscript{43,45,46} (SOFC) and oxygen sensors.\textsuperscript{47,48} Recently, alternative electrolyte materials have shown sufficient oxygen ion conductivity at 500 - 800°C, sparking renewed interest in low temperature SOFC operation.\textsuperscript{49-51} Furthermore, in combination with innovative ultra thin film fabrication methods,\textsuperscript{52,4} SOFC operation at 300-500°C may be possible.

Dramatically reduced operating temperatures permit a multitude of possible improvements and potential cost reductions. However, in order to achieve high performance at low temperatures, oxygen reduction kinetics at the cathode must be improved.\textsuperscript{53} One step in improving the rate of oxygen reduction at low temperatures involves the development of a fundamental understanding of the low temperature behavior of LSM and LSC.

Pulsed Laser Deposition (PLD) has emerged as an ideal method for growing complex multi-element films, such as LSC and LSM. Due to its unique method of dislodging atoms from the target, PLD provides some distinct advantages unique among thin film techniques. Paramount among these advantages is the capability for stoichiometric material transfer. For deposition techniques based on ions or electrons, the chamber atmosphere greatly influences the film properties and stoichiometry. However, due to the weak interaction of lasers with gaseous species, ambient atmospheres can be used for PLD with very little contamination. When combined with the high heating rates and plasma-induced ablation, stoichiometric transfer of atoms from the target to the substrate can be achieved.\textsuperscript{54}
PLD has recently demonstrated a unique capability for thin film growth at high or low substrate temperatures.\textsuperscript{55} Recently, perovskite films have been successfully developed by PLD through high temperature deposition or subsequent annealing.\textsuperscript{56-59} While the high temperature behavior is fairly well understood, the low temperature behavior so far has been neglected. In particular, low temperature PLD has been shown to be useful for a variety of novel techniques where a high substrate temperature can be particularly damaging.\textsuperscript{60-63} Here we present the characterization and low temperature behavior of LSM and LSC thin films grown by PLD.

3.2 Experimental

Substrates

Since this study was concerned primarily with interfacial polarization resistance, electrolyte supported cells were chosen for their simplicity in fabrication, low cost and overall durability. While mainstream fabrication of SOFCs has moved to anode supported cells in order to reduce Ohmic losses, in this case, final overall performance can be sacrificed for repeatability and cost concerns. In all, four unique substrates were used in the completion of this body of work. In each case, substrates were chosen with consistency of performance and cost savings in mind.

Quartz
Quartz substrates, purchased from Quartz Scientific (Part #212000), were the first of the three materials (and five substrates) used during completion of this study. Quartz substrates were used primarily during the electrical characterization of thin films. They were chosen because quartz is known to be chemically inert at high temperatures. Since diffusion of species from the substrate into the thin films under consideration would compromise the electrical results, a chemically inert substrate was a priority. Further, electrically insulating properties were critical in this case. Since we were interested in the electrical properties of the thin films, an electrically conductive substrate would fundamentally compromise the study. Additionally, the optically flat polished quartz surface facilitated patterned electrode deposition.

*Silicon*

Silicon wafers (100 orientation) were used during two distinct stages of cell development. First, atomically flat silicon wafers were used during process development since they provided a fast, cheap alternative for development of functional photolithographic and nano-lithographic processes. Since the wafers were significantly flatter and smoother than their zirconia counterparts, a robust process could be developed on silicon first then adapted to the more problematic zirconia substrates. Additionally, the electrical conductivity of silicon significantly simplified nano-lithographic processing by providing an electrical sink for free electrons transmitted by the electron beam. This would prove critical to final resolution of ultra-high resolution electrodes.
Secondly, silicon wafers were also used during the characterization of thin LSM and LSC films. Since many of the X-ray peaks associated with Lanthanum Strontium oxides overlap those associated with Yttria-zirconia oxides, XRD analysis of LSM and LSC on YSZ substrates proved exceedingly difficult. Silicon wafers provided an opportunity for simplified analysis and peak height determination. Specifically, since the (400) silicon peak occurs at approximately 69° 20, X-ray scans can be analyzed by omitting peaks above this. Due to the preferred orientation of the wafer, peaks associated with the thin cathode films could be differentiated against a blank background instead of the necessarily complex background of polycrystalline YSZ.

*Yttria-Stabilized Zirconia*

Yttria-Stabilized Zirconia (YSZ) is currently the most widely used electrolyte for SOFCs for a variety of reasons. It satisfies the many critical electrolyte requirements for any operational SOFC in that it is chemically and morphologically stable in both oxidizing and reducing environments. At operating temperature, YSZ provides adequate ionic conductivity and is thermally and chemically compatible with most electrode materials. Furthermore, it can easily be made sufficiently dense to avoid gas transport and in many cases is robust enough to provide mechanical stability.

Since electrochemical characteristics are fundamentally defined by the materials and geometry of the interfaces, the vast majority of work for this study was
performed on YSZ substrates. For this study, analysis of the substrates can be broken down into two categories: Polycrystalline and Single-crystal YSZ.

Die-pressing

Preliminary attempts to develop polycrystalline YSZ substrates were based on die pressing of YSZ pellets. Pellets were pressed from 99.95% pure 8 mol% Yttria-doped Zirconia powder purchased from Daiichi Corporation, Japan. For die pressed pellets, the YSZ powder was mixed with a 2 weight % Polyvinylalcohol (PVA) solution in acetone. Powder mixture was ground with mortar and pestle to achieve complete mixing. Once mixed, powder was dried and placed in a die press. Powder was isostatically pressed into pellets at a pressure of 10 tons. Green pellets were then fired for 5hrs in air at 1450° in a Carbolite RHF 15/8 box furnace. Pellets were more than 95% dense with no visible pores or cracks on the surface.

Unfortunately, the rough irregular surface of the as-prepared die cast substrates was insufficiently smooth for high resolution photolithographic processing. In order to improve surface smoothness to acceptable levels, die-pressed pellets were polished for 10hrs on Buehler Ecomet 6 sanders. Initial polishing utilized 220 grit sandpaper and progressed incrementally to 0.03µm alumina polish. Due to the extensive polishing times, alternative methods of substrate preparation were prepared.
Tape Casting

Yttria-Stabilized Zirconia (YSZ) pellets prepared by tape casting were used as the substrates for patterned electrode and reference electrode deposition. Daiichi YSZ powder, with a mean particle size of 0.26\( \mu \text{m} \), was suspended in a solvent-based slurry using Menhaden Fish Oil (dispersant) polyvinyl butyrol (binder), poly ethylene glycol (type I plasticizer) and butyl benzyl phthalate (type II plasticizer). The slurry was prepared in a two-stage process and ball-milled for at least 24 hours between stages using 7mm YSZ charge. Prior to casting, the slurry was de-aired by placing the jar in a vacuum chamber for about 5 minutes at -10” Hg.

A stationary blade six-foot tabletop caster from Richard E. Mistler Inc. was used to cast the slurry at a blade height of about 150\( \mu \text{m} \). The tabletop caster was equipped with a DC motor, variable speed control, heated five-foot casting bed, one-foot square granite casting block, and counter directional mass-controlled airflow. The cast tape was then cut into 1.7cm discs and laminated into stacks of three using a uniaxial press. Semi-constrained firing techniques were used in order to minimize warpage while allowing the tape to sinter without cracking. The fired pellets experienced about 22% total shrinkage during firing as determined by dilatometry, were about 400\( \mu \text{m} \) thick according to SEM, and 95% of theoretical density as measured by the Archimedes method. Tape casting was chosen over die pressing since it provided a significantly faster and more viable method for substrate preparation.
Single Crystal

For high resolution photolithography and all nanolithography, single crystal YSZ substrates were needed. The profilometry scan presented in Figure 3.4 demonstrates the difficulties in processing. Digital profilometry of both tape cast and die pressed YSZ pellets yielded local variations up to 2μm in thickness. Consequently, high resolution (2μm and below) photolithography necessitated further improvements in surface flatness and smoothness. When the surface defects were on the order of the electrode features, lithography became impossible as the electrode lines were no longer continuous.

Furthermore, nanolithography processing is significantly different from traditional photolithography, and as such did not allow for a bi-layer resist. By eliminating the bi-layer resist, a considerable amount of process robustness was lost. This further magnified the need for substrates with much improved surface characteristics.
Figure 3.4: Optical profilometry image of a tape cast polycrystalline YSZ substrate. The image displays local variation up to 2μm and global variation of up to 80μm.

Since traditionally prepared substrates would no longer suffice, single crystal YSZ pieces were purchased from MTI corporation. The single crystal zirconia pieces were 99.99% pure with a crystal orientation of <100>. For better processing, one side was polished to a surface roughness of <5Å and a surface flatness of <2μm/cm. This data was again confirmed by digital profilometry, presented in Figure 3.5.
Figure 3.5: Digital profilometer scan of (100) oriented single crystal YSZ. Local variation is less than 200nm while global variation is less than 5μm.

**Deposition Methods**

Critical to the accurate processing of stoichiometrically accurate and geometrically well-defined electrodes are the deposition methods. Several different deposition methods were investigated before DC sputtering, RF sputtering and pulsed laser deposition (PLD) were finally selected for this application. Each technique provides unique advantages and disadvantages, and was structured accordingly.
Sputtering is a physical deposition process where a gas, in this case argon, plasma is induced within the sputtering chamber. Positively charged argon ions are strongly attracted to the negatively charged target. When these high energy ions physically collide with the target surface, they physically knock atoms from the target which settle on the substrate of choice.

**DC Sputtering**

Deposition of all metallic thin films was performed with a CVC products DC sputterer. The CVC Products DC sputterer boasts high vacuum capabilities in addition to the option of 3 inch interchangeable targets of 8 inch stationary one. It is controlled by an electronic stack that contains most of the control devices for the sputterer, including the interface, while the bulk of the sputtering apparatus is contained within the machine housing.

Upon operation, the DC sputterer opens the roughing valve to allow the mechanical pumps to pump the chamber down to 300 milliTorr (mT). Once the chamber pressure reaches this value, the roughing valve is closed and the high vacuum valve is opened. The ion gauge is turned on and the cryo-pump pumps the chamber down to a minimum pressure of $5 \times 10^{-6}$ Torr. Once full pumpdown has been achieved, the high vacuum valve is closed and the chamber is back-filled with Argon to 6mT where it stays for the duration of the process. For each material being deposited, the shutter on the
bottom of the chamber lid moves to the appropriate station for the selected target. The power supply on the instrument rack is turned on and the plasma is ignited, thereby beginning deposition.

Though the DC sputterer provides fast, uniform deposition of thin metallic films, it is a non-directional technique. This means that the sputterer will coat around the edges of any object placed in the chamber, including those at oblique angles. For this reason, a bi-layer resist was necessary for clean resolution of Lift-off processing. The DC sputterer was used for thin film deposition of platinum electrodes in addition to lithographically patterned thin film current collectors for all oxide substrates.

**RF Sputtering**

Deposition of insulating thin films was initially performed with a CVC products RF sputterer. The CVC Products RF sputterer boasts many of the same benefits as the DC sputterer. It is also controlled by an electronic stack that contains most of the control devices for the sputterer, including the interface, while the bulk of the sputtering apparatus is contained within the machine housing.

Upon operation, the RF sputterer works in an identical manner as the DC sputterer with the lone exception of the type of applied current and load. For the RF sputterer, a maximum of 300Watts can be applied. Since the RF sputterer is also a non-directional technique, a bi-layer resist was needed for Lift-off processing. The RF sputterer was
initially tested for thin film deposition of oxides. However, it was found that in order to
achieve a sufficiently high deposition rate of 2 Å/min, a power input of greater than
300 Watts was necessary.

Additionally, a combination of high applied power and highly insulating LSM and
LSC materials caused the targets to crack. After investigation, this was attributed to
electrical arcing across the surface. Local hot spots of sputtering activity were thought to
have caused extreme local temperature and electrical gradients. Under these conditions
the targets cracked.

_Pulsed Laser Deposition_

Given the difficulties associated with sputtering LSM and LSC films, Pulsed laser
deposition (PLD) was investigated as an alternative method for thin film deposition.
Thin films were deposited on a variety to substrates and under several operating
conditions. Silicon (100), single crystal (100) Yttria Stabilized Zirconia (YSZ), and
polycrystalline tape-cast YSZ were used as substrates. Films were deposited both at
room temperature and at 500°C. Each film type was deposited on all three substrates,
yielding a total of six independent samples.

Prior to deposition, the substrates were clamped to the substrate heater and the
chamber was evacuated to the prescribed oxygen partial pressure. If necessary, the
substrates were brought to 500°C under vacuum prior to deposition. For deposition, the
target was encapsulated in a high vacuum chamber pumped to a base pressure of $1 \times 10^{-4}$ Torr. The oxygen partial pressure was held constant at 0.1 mT in order to minimize the film cracking and surface roughness that may occur at high oxygen partial pressure. A COMPex Model 205 laser from Lambda Physik with a 25ns pulse duration was used for ablation. The distance between the substrate and the target was 10 cm. The laser was operated at 10Hz and 353mJ yielding a typical deposition rate around 2 angstroms per second.

The single-phase $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ target was prepared by solid-state sintering method. LSM powder was synthesized from a molar ratio of $\text{La}_2\text{O}_3$, $\text{SrCO}_3$, and $\text{Mn}_2\text{O}_3$. The powder mixture was ball milled, pressed isostatically to a pressure of 11 tons and calcined at 1150°C for 5 hours. The pellet was then ground and ball milled again to a fine powder. The powder was repressed into a pellet and sintered into its final shape at 1300°C for 5 hours.

PLD of Lanthanum containing oxides has been shown to provide stoichiometric thin films under high vacuum conditions with minimal requirements for post-deposition anneal steps. Excess oxygen has been shown to create non-uniform films with significant degrees of surface roughness. Leakage current and fatigue were also found to decrease with oxygen partial pressure. Furthermore, thin layers of LSM deposited via PLD were affected by the crystallographic orientation of the substrate. In order to ensure a smooth and uniform surface, PLD was performed under high vacuum with post-deposition SEM analysis. By depositing the films directly onto a polycrystalline substrate, the preferred tetragonal phase was encouraged.
**Fabrication of patterned electrodes**

In order to minimize the impact of debris particles contaminating the film, all cleaning processes have been performed in a Class 10 cleanroom. Once inside the cleanroom, the YSZ electrolyte was cleaned in subsequent baths of acetone, ethanol, and deionized water, then dried with compressed nitrogen.

A lift-off process utilizing a bi-layer resist was developed prior to film deposition. Following PLD deposition, the negative photoresist pattern was removed leaving only the desired pattern and thickness. Electrode thickness was controlled by deposition time and verified by profilometry.

**Photolithography**

Electrodes were deposited onto the electrolyte surface utilizing standard photolithographic Lift-Off processing. Patterns for the desired electrodes were produced using AutoCAD software and transferred to chrome masks on glass plates. Identical electrodes were produced with electrode line widths of 50µm within a surface area of 36mm² for a total three-phase boundary (TPB) length of 2.05 meters/cm².
Photolithography incorporated a CEE model 100 spinner for spinning a consistent and uniform layer of photoresist onto the substrate. Once the photoresist layer achieved sufficient uniformity and structure, the coated electrolytes were exposed under a Karl Suss MJB-3 Mask Aligner. Configuration of the exposure wavelength was selected to correspond to the optimal exposure range of the chosen photoresist. In this case, the recommended dosage of 150 mJ/cm² was sufficient for optimal processing.

Photoresist was developed through the use of Microchem’s MF-319 Developer yielding good resolution of negative photoresist patterns. Dense LSM electrodes were developed through the use of a CVC Products RF Sputterer. Deposition rates showed very good consistency and SEM analysis of oxides revealed fully dense electrodes. Profilometer measurements confirmed a standard deviation in deposition depth of less than 9%. Fabrication of the titanium layer was accomplished through the use of a CVC Products Electron Beam Evaporator. The E-Beam Evaporator demonstrated good control of deposition rates in addition to completely directional deposition. Standard Lift-off method with a photoresist stripper in conjunction with ultrasonic bath yielded well-defined patterns with uniform thickness. *In-situ* annealing of the patterned electrodes yielded a dense insulating titanium dioxide layer atop the conductive LSM patterned electrode.

In order to ensure that the TiO₂ layer did not approach the edge of the LSM patterned electrode, the TPB, the lithography process was modified by the use of a supplemental polydimethylglutarimide (PMGI) platform. The PMGI created an undercut
platform that facilitated removal of the photoresist layer and ensured reliable definition of the TPB.

LSM electrode thickness was controlled via determination and control of deposition rates. Patterned electrodes were 0.26\(\mu\)m in height and completely dense. Since LSM is a relatively poor ionic conductor, thin LSM electrodes were used to maximize the possibility of bulk diffusion. MIEC electrode patterns consisted of 60 identical rectangular patterned electrode strips (50 \(\mu\)m wide, 0.26 \(\mu\)m thick, and 6 mm long), connected though a lithographically processed current collector (dimension of 50 \(\mu\)m wide, 0.26 \(\mu\)m thick, and 6 mm long), to improve the reproducibility and reliability of the fabrication processes and electrochemical measurements. The smallest feature size of these patterned electrodes has been successfully reduced to about 2 \(\mu\)m.

In order to block the active site on the top surface of the MIEC electrode, an inactive layer of titanium dioxide was deposited on the top of a standard LSM patterned electrode. Density and thickness of TiO\(_2\) layers were controlled in a similar fashion.

The cells consisted of a patterned electrode, covering an area of 6 mm x 6 mm, a reference electrode adjacent to the patterned electrode, and a counter electrode on the other side of the YSZ electrolyte prepared by painting and firing platinum paste (Hereaus LP11-4493). Cells were then placed in a tube furnace for impedance measurement at a constant temperature, ranging from 600 to 800\(^\circ\)C with 50\(^\circ\)C increments. A computer interface, controlling an EG&G 273A potentiostat and 5210 lock-in amplifier, collected
impedance data over a range from 100 kHz to 0.01 Hz using both two and three-electrode configurations.

**Mask Design**

All photolithography is initiated by design and fabrication of a photolithographic mask. While many options are available for design, Computer Aided Design (CAD) software is usually implemented in most cases. Here AutoCAD was used for design of the photolithographic masks. The array capabilities of AutoCAD to deal with large aspect ratios made it a logical choice for mask creation.

**Resist Selection**

Resist selection plays a key role in a complete processing development. Beyond simply being photoreactive, many resist components play an important role. In a functional process, the resist works in harmony with the spin speed, the developer, and the bake and develop times to produce the desired structure. Through careful manipulation of the multitude of resists available many unique structures can be developed.

Lift-off processing typically requires a directional deposition technique, however, it can be adapted to non-directional techniques, such as sputtering through the use of a bi-layer resist. In order for lift-off to be possible with sputtering, an undercut, such as the
one shown in figure 4.1, is necessary to allow a break in the thin film. In this case, two resists are spun and baked onto the substrate in succession. While the first resist is not photoactive, it does have a specific undercut rate. The top layer is photoactive and is patterned by the mask. The second, lower layer undercuts the photoresist to create a three-dimensional structure shown in Figure 4.4.

Microchem’s LOR 10B resist was chosen as the primer layer for lift-off for a variety of reasons. First, it is not photoactive, but rather has a well-defined undercut rate. Furthermore, the undercut rate has a wide range and is determined by the softbake time. Additionally, the LOR 10B resist is somewhat durable after the softbake, thereby providing a solid foundation for spinning the photoresist. The spin speed vs. film thickness curve is presented in Figure 3.6. The undercut rate curve is presented in Figure 3.7, courtesy of Microchem.

Figure 3.6: Film thickness vs. Spin speed for LOR B series resists. Other film thicknesses available upon request.

Figure 3.6: Film thickness vs. Spin speed for LOR resists available from Microchem. LOR 10B resist was chosen since it provided a film thickness of 1.3µm at 1700rpm spin speed. Courtesy of Microchem corporation.
Figure 3.7: Undercut rate vs. Bake temperature for several common resists. When baked at 190°C, the LOR 10B provided an undercut rate of 167 Å, sufficient for clean lift-off resolution with sputtering. Courtesy of Microchem corporation.

For the second layer, Shipley PR-1813 resist was chosen. In addition to being compatible with the LOR 10B resist, PR-1813 provided the desired film thickness without exceeding the maximum spin speed of the spinner. The thickness-spin speed curve is presented in Figure 3.8 courtesy of Shipley corporation. PR-1813 was the photoactive layer and provided robust, precise edges and clean removal.
Spin Coating

A CEE Model 100CB spinner was used for spinning all resists. A spinner is used to uniformly apply a thin film across the surface of the substrate. Since the viscosity of the photoresist is constant, film thickness can be controlled by spin speed and duration. The Model 100CB features a maximum spin speed of 6000 revolutions per minute with 5rpm accuracy. The spinner was leveled prior to initial use.

During process development, a variety of spin parameters were investigated in order to find a process that produced smooth, even films of resist consistently. A primary issue confronted during this process was development of an edge-bead. Specifically, when a liquid with known viscosity is spun onto a surface, surface tension works to keep the fluid from running off the surface. This buildup of surface tension at the edge of the
substrate keeps some extra fluid from being removed and acts to form a characteristic teardrop shape during spinning. If the viscosity of the fluid is low enough, the fluid will resettle into a flat or semispherical upon completion. However, in the case that the fluid is more viscous, as with most types of photoresist, excess fluid will remain near the edge of the substrate causing a characteristic “edge bead.” The edge bead is simply a hardened build-up of resist near the edge of the substrate. It is created by centrifugal forces during the spin step and can disrupt the exposure step by preventing the mask from attaining the proper proximity with the resist.

Edge bead removal is typically performed immediately after the spin coat step. While the substrate is spinning at a relatively low rate (400-600rpm) the edge bead remover is sprayed from a nozzle directly onto the edge of the substrate. The resist buildup that leads to an edge bead is removed by controlling the spin speed and nozzle position of the edge bead remover.

**Softbake**

Once the resist is spun onto the substrate, it needs to partially harden in order to be sufficiently robust to undergo the remaining photolithography steps. For this reason, the resists are all baked on a hotplate prior to exposure. All softbake steps took place on a level pre-heated hotplate. Due to the thermally insulating nature of YSZ, the temperature of the hotplate during softbake was adjusted to approximately 10 degrees higher temperature than for silicon. This adjustment was calculated by measuring
alternately the hotplate surface temperature and the substrate temperature average with a thermocouple.

**Exposure**

Exposure of the photoresist took place on a Karl Suss MJB-3 Mask Aligner. Mask aligners are used in photolithographic processes to transfer a pattern from a mask to a photoresist coating on the substrate. A mask aligner is used to expose a photoresist-coated substrate to ultra-violet light through a photo mask, which casts a shadow on the surface to define the photoresist mask. The MJB-3s was selected because it is most suitable for handling unique substrates not exceeding 3 inches in any direction. Additionally, the right MJB-3 mask aligner was chosen since it is configured for 320nm – 365nm exposure wavelength. Since each photoresist is designed to be sensitive to a particular wavelength of light, it is important to match the output wavelength of the aligner with the resist. In this case, Shipley S1813 resist is sensitive to 350nm light, so the mask aligner was properly configured. In order to identify the optimal exposure time, the film develop process was held constant while the exposure time was altered systematically. Since the develop step involved removal of two distinct resists at once, the develop time was determined entirely by the requirements of the LOR resist. Because of this, optimization of the S-1813 photoresist depended heavily on the exposure time. It was determined that an exposure time of 18 seconds provided optimal resolution of the resist.
For final development of the bi-layer resist structure, Microchem’s MF-319 was chosen since it is chemically compatible with both the S-1813 photoresist and the LOR-10B lift-off resist. The MF-319 is a metal-ion free developer which produces clean edges, sharp corners and sufficient but not overwhelming undercut. Furthermore, since fuel cell components are highly susceptible to metal impurities, a metal-ion free developer is critical to avoiding metal poisoning of the system. By choosing the hardbake temperature of 190°C, and thereby specifying an undercut rate of 167Å/second, a develop time of 45 seconds would cut through a 0.7μm LOR resist. Consequently, the bi-layer resist was dipped in a bath of MF-319 for 45 seconds in order to provide the desired resist microstructure.

The final developed process was then:

Spin Microchem LOR 10B:
Spin Speed: 1700rpm
Ramp Rate: 1000rps
Time: 45 seconds
Softbake at 190°C for 5 minutes

Spin Microchem PR-1813:
Spin Speed: 4000rpm
Ramp Rate: 2000rps ramp rate
Time: 60 seconds
Softbake at 125°C for 90 seconds

Expose in Right MJB-3

Setting: Constant Intensity

Time: 18 seconds

Develop in MF-319

Time: 45 seconds

Lift-off Removal

After the develop step, the substrate structure is then sent to PLD or sputtering processing for thin film deposition which has been covered previously. Following deposition, the portions of unwanted film, along with the resist structure are removed during the actual lift-off step. This is performed by dipping the entire cell into an acetone bath in combination with ultrasound. Care should be taken to agitate the acetone bath with ultrasound prior to inserting the substrate. The substrate is soaked in the acetone bath for a time between 60 seconds and 5 minutes, depending upon the thickness of the films. Thicker films are more difficult to remove and require longer removal times. While acetone will remove the S-1813 photoresist, the LOR resist is relatively impervious to it. The LOR resist can be removed by either Microchem’s PR remover or the MF-319 developer. Since the unwanted film should have been removed with the S-1813, removal of the LOR-10B does not need ultrasound. A 60-90 second soak in either the PR remover or the MF-319 is usually sufficient to remove the LOR-10B. Alternately, the LOR-resist can be burned-off above 300°C in a furnace. It should also be noted that
if the film thickness to LOR resist thickness exceeds 1:1.3, the film will not lift off and the pattern will not be created.

*Nanolithography*

The long illustrious history of traditional photolithography provides some inherent benefits. Due to the rapid development of the semi-conductor industry, photolithography is as well-understood and characterized as any mature technology. Most major technical hurdles have been crossed and the associated cost has been substantially reduced due to commoditization of the technology.

However, recent developments in many areas, including this study, have also brought the inherent disadvantages of photolithography to the forefront. In short, photolithography is inherently limited by itself. Since it depends on visible light to expose the photoresist, feature resolution is then limited by the wavelength of light. Any features below 400nm are intrinsically impossible, though 1μm provides the practical limit for traditional photolithography.

In order to push beyond these limitations, alternate methods of patterning must be incorporated. A few technologies offer alternatives, though all have significant drawbacks. First, dip pen lithography offers the potential for higher resolution than traditional photolithography with a low production cost. In theory, a small film of water between the AFM tip and the substrate acts as a bridge that allows deposition materials to
transfer from the tip to the substrate. Unfortunately the technology is far too slow for large arrays and is not yet well-developed. Alternatively, new methods of lithography have focused on using energy beams of smaller wavelengths to improve resolution capabilities. X-ray lithography, and more recently E-beam lithography have been developed for high resolution patterning. Although these technologies can provide resolution up to 30nm, they are very expensive and difficult to operate. For industrial applications, nano-imprint lithography has been developed to speed up the process and allow rapid replication of standard patterns. Regrettably, this technology is simply a replication process and still requires development of a nano-imprint mask from either E-beam or X-ray lithography.

For research usage where pattern flexibility is at a premium, E-beam lithography is ideal. While it is slow, expensive and cumbersome, E-beam nanolithography provides the unique opportunity to rapidly change and develop patterns with ultra-high resolution (>30nm), and it is easily adaptable to a variety of substrates. For primarily these reasons, a JEOL JBX-9300 E-beam system was purchased for use at Georgia Tech.

Programming

The JEOL E-beam tool is operated through a computer interface. Patterns are again designed in AutoCAD and converted to a GDS-II format through LincCAD software. The JBX filer is then used to convert the .gds file to the proprietary .v30 file recognized by the JBX-9300. Each individual pattern can be incorporated in an array
through the use of the .jdf and .sdf files. The jobdeck (.jdf) and scheduler (.sdf) files are also proprietary JEOL programming language files which provide instructions to the JBX-9300 e-beam tool on how and where to write the patterns to the substrate. For convenience, an operational program is listed in Appendix A.

Several items should be taken into account when developing the magazine file for exposure through the JEOL-9300. Once the necessary dose has been determined, the exposure time, t, can be calculated through the basic current expression:

$$t = \frac{(I \times D)}{A}$$

Where I is the beam current, A the total exposure area, and D the applied dose in \(\mu\text{C/cm}^2\). Since the exposure time for dense arrays, such as this one, can exceed 12 hrs at a time, this information is critical to adjusting the patterns and scheduling accordingly.

*Processing on Silicon*

Processing of substrates for E-beam nano-lithography follows many of the same basic steps as standard photolithographic processing, except that exposure takes place in the JEOL tool instead of the mask aligner. First, resist is spun onto the substrate followed by a hard-bake step. The resist chosen for E-beam lithography provides many of the same features as traditional photoresist, clean edges and high resolution, except that it is not photosensitive, but rather sensitive to an electron beam. In this case, a solution of 2% PMMA in water was chosen as the E-beam resist since it provided superior resolution
with minimal cost. The PMMA was spun at 2000rpm for 60 seconds with a ramp rate of 500 rps. After spincoating resist, the substrate was hardbaked on a hotplate at 180°C for 90 seconds. This process repeatedly produced a film thickness of 75-80nm. The spin speed curve for PMMA is presented in figure 3.9.

Figure 3.9: Spin speed vs. film thickness curve for varying PMMA solutions

It should be noted that due to the extremely small dimensions of the nano-patterns, it is not possible to develop a bi-layer resist to aid the lift-off process. Since no significant undercut could be developed, the lift-off process needed to be altered accordingly. First, the thin film deposition process must be a directional technique. This eliminated all methods of sputtering. In order to proceed with the development of nano-
patterned electrodes, pulsed laser deposition was incorporated as the primary deposition technique. Second, the undercut of the bi-layer resist serves to separate the thin film on the desired portion of the substrate with that on the photoresist. Since the LOR resist, and therefore the undercut, are no longer available, the ratio of photoresist to film thickness must be significantly increased to account for this difference. It is widely accepted that for smooth lift-off of resist coatings in conjunction with a directional technique, an aspect ratio of approximately 3:1 is necessary. The 3:1 resist requirement in combination with the small feature size of the electrodes led to a maximum final electrode thickness of 30nm. The exposure step is performed in the E-beam system immediately prior to development.

The exposure process in the JEOL E-beam tool was developed through several steps. As during development of the photolithographic process, the resist develop process was held constant while the exposure time was altered systematically to find optimal resolution. At first, high-resolution fabrication of 30nm lines was developed on a silicon substrate. This allowed easy optimization of exposure time without complicating the process with the structural and electrical intricacies of a YSZ substrate. As before, current knowledge of silicon processing was leveraged to minimize the time to completion. The PMMA dosage curves developed by the MIRC staff and presented in figure 3.10 provided a rudimentary starting point.
Once a competent process was developed on silicon, the process was further modified to adapt to the unique attributes of YSZ. Though the single crystal YSZ substrates were significantly flatter than their tape cast counterparts, they contained substantially more surface variation than do atomically flat silicon wafers. To complicate matters further, the electrical insulating properties of YSZ contributed to the difficulty of processing. During the initial process development, silicon substrates acted as electron sinks transporting beam electrons away from the resist during exposure. YSZ, on the other hand, accrued the exposure electrons locally, thus causing significant local

Figure 3.10: Dose vs. undeveloped resist for PMMA  Figure Courtesy of Georgia Tech Microelectronics Center

*Processing on YSZ and the Proximity Effect*
charging. This local charging served to reflect much of the e-beam exposure dose, thereby overexposing the PMMA resist.

While the difficulty of producing high resolution features on a rough surface could not be alleviated and minimum feature size was again limited, the disparate difficulties of processing on an insulating substrate were overcome in two ways. First, the exposure dose was significantly reduced from that used with the silicon wafer. While a dose of $225 \mu C/cm^2$ produced 50nm resolution on the silicon substrate, a dose of $125 \mu C/cm^2$ was used to process 50nm resolution on a YSZ substrate. Secondly, prior to exposure, a 70nm thick gold film was deposited directly onto the PMMA photoresist. The gold film was intended to act as an electron sink to limit overexposure and help dissipate charging on the surface.

**Deposition of Gold**

Deposition of the Au film was performed with a Kurt J. Lesker PVD-75 Filament evaporator. The filament evaporator was able to provide thin uniform gold films without exposure of the resist. Like PLD and unlike sputtering, evaporation is considered a directional technique. This means that evaporators only coat the surface facing away from the substrate. Evaporators will provide very little coating to the sides of any features that are perpendicular to the surface of the substrate. The filament evaporator is ordinarily used for gold, nickel, chromium, aluminum, and copper coatings, though it can be used to evaporate most other metals as well. The chamber was pumped down to a pressure of 5 x
10-7 torr to prevent air molecules from interrupting metal atoms as they travel from the evaporation source to the substrate. Then the metal evaporation source was heated to a high temperature by a tungsten filament. This causes the metal to evaporate and be deposited on the substrate. Typical deposition rates ranged from two to five Å/second.

In most cases, metal depositions are performed in the CVC electron beam evaporator or in the CVC DC sputterer. However, the filament evaporator is a good choice for samples that need to be evaporator coated (to avoid coating the sides of rough topologies) or are sensitive to x-ray radiation that may be emitted by the electron beam gun in the e-beam evaporator.

Initial attempts to deposit the gold film using sputtering resulted in complete exposure of the PMMA prior to ever being placed in the JBX-9300. It was speculated that the presence of the sputtering plasma served to expose the PMMA during gold deposition. Use of a sputtering system after pattern development posed no problem since over-exposure of a previously developed film had no consequences. However, if the goal is to produce a thin metallic film without exposure of the underlying resist, the filament evaporator proved unquestionably superior.

*Develop and Removal*

Development of the PMMA E-beam resist consisted of two steps, later expanded to three with the YSZ substrates. The PMMA resist was developed in a 1:1 solution of
MIBK (Methyl isobutyl ketone) and IPA (isopropanol) for 60 seconds. After being
dipped in the 1:1 solution, substrates and the remaining resist pattern were rinsed with
IPA and dried with compressed Nitrogen.

As mentioned previously, thin film deposition for patterns developed on the E-
beam tool require a directional technique. Due to this restraint, pulsed laser deposition
was used for thin film growth and was performed after the develop step but prior to Lift-
off. Similar to standard photolithography, lift-off of the PMMA was performed with
acetone and ultrasound. The entire substrate was soaked in acetone for 5 minutes, then
agitated with ultrasound for another 45 seconds.

Characterization Techniques

SEM Microscopy

For all SEM imaging, a Hitachi S-800 Scanning Electron Microscope was used.
The S-800 features a Field Emission gun for improved resolution, particularly at low
accelerating voltages. Since most of the materials in this study are electrical insulators at
room temperature, modifications were necessary to produce quality images. When
possible, a thin gold film was sputter onto the sample in order to reduce the effects of
electronic charging of the substrate. Due to the some very small feature sizes, and the
desire to perform non-destructive imaging of the electrodes, a gold coating was not
possible in many cases. Consequently, very low accelerating voltages, around 2 kV,
were used to image the electrodes without overwhelming electronic charging of the substrate.

Additionally, the S-800 was used in backscattered mode to perform Energy Dispersive X-ray Spectroscopy (EDS) on some samples. Since atomic number contrast is weakest at high atomic number\textsuperscript{69}, differentiating dopant concentration in the materials, such as yttria in a zirconia background was not to be expected. However, EDS did prove useful in isolating blocking layers, such as titanium dioxide from the active lanthanum-based electrode materials.

\textit{Grazing-Angle X-ray Diffraction}

Since the final accuracy of this body of work depends, at least partially, on the material consistency of each electrode, a thorough investigation of the thin films produced by PLD was undertaken prior to electrochemical testing. A Panalytical X-pert Pro MPD diffractometer with theta-theta geometry was used along with an Anton-Paar HTK1200 high temperature furnace to perform in situ high temperature x-ray diffraction on the as-deposited films. Fixed 1/8 degree incident beam divergence slits were used along with 0.04° incident soller slits and a tube power of 45kV and 40 mA. An Xcelerator linear detector with an acceptance window of 2.127°2θ was used in scanning mode. In situ diffraction measurements were taken from 300°C to 900°C in 50°C temperature intervals. Each measurement was from 20-60°2θ using a 0.216°2θ per second scan rate. The samples were heated at 60°C per minute under static air.
Temperature calibration was performed using the NIST DTA standards KClO4 (Tt 299.5°C) and Ag2SO4 (Tt 430°C).

For electrical measurements, interdigitated arrays of 10 platinum electrodes each were fabricated on insulating quartz substrates. The electrodes were lithographically patterned in order to ensure a constant spacing of 20μm between alternating electrodes. Thin LSM and LSC films were then ablated directly onto the prepared substrate. Electrical contacts were attached to the alternate arrays and impedance spectroscopy was used to analyze the electrical response. Figure 1 presents a schematic of the electrode layout used for impedance measurements.

Each sample was run individually at constant temperature in 100°C increments ranging from 100°C to 700°C. A Solatron 1255 frequency response analyzer connected through a Solatron 1287 electrochemical interface collected impedance data over a range from 100 kHz to 0.01 Hz. A Tencor Alpha Step Profilometer was used to independently verify the thickness of the LSC and LSM films. Impedance results were characterized through a simple model to calculate the conductivity values of the films.

*Impedance Spectroscopy*

Impedance spectroscopy was used to test the electrochemical response of each cell. Due to the complexity and difficulty of producing the patterned electrodes, symmetrical cells were not a possibility. The working electrodes consisted of a patterned
electrode covering an area of 0.6 x 0.6 cm$^2$ with an adjacent reference electrode. The electrode array consisted of patterned rectangular electrodes with widths varying from 100µm to 50nm. In order to keep the surface area consistent, the width of each line was exactly matched by the gap between adjacent lines. A platinum current collector was lithographically patterned and deposited on top of the working electrode. The current collector consisted of 12 identical 50 µm wide platinum strips separated by exactly 490 µm. All 12 platinum strips connected to a platinum pad in order to facilitate wire attach. The adjacent reference electrode was a 0.2 x 0.5 mm$^2$ platinum rectangle separated from the working electrode by less than 20 µm. A painted silver electrode (Hereaus C8800SD) was used on the opposite side of the electrolyte as a counter electrode. Cells were then placed in a tube furnace for impedance measurement. Each sample was run individually at constant temperature in 50 °C increments ranging from 500 to 750 °C. A Solatron 1255 frequency response analyzer connected through a Solatron 1287 electrochemical interface collected impedance data over a range from 100 kHz to 0.01 Hz using both two and three-electrode configurations.
CHAPTER 4

THE PHOTOLITHOGRAPHIC PROCESS AND ITS CAPABILITIES

Abstract

In this study, a photolithographic process was developed that is capable of repeatedly producing patterned electrodes of well-defined geometry on electrolyte substrates. The microfabrication process incorporated Lift-off lithography in order to develop a bi-layer resist structure. This resist structure, when combined with complementary deposition methods, is capable of producing patterned electrodes with creative and precise geometries. SEM and EDS micrographs confirm that a photolithographic process is indeed capable of producing patterned electrodes that satisfy the demands for accurate measurement.

Introduction

In order to successfully develop patterned electrodes of well-defined electrodes, development of a robust accurate lithographic process is crucial. Further, a well-defined geometry implies both accurate translation of the designed pattern and high definition resolution of corners and edges. In contrast to some previous studies, lift-off processing was used in this study. While more involved, lift-off provides the resolution necessary for high definition and small feature sizes. Additionally, lift-off performs well with traditionally difficult to process SOFC cathode materials.
The lift-off process developed for this study proved capable of repeatedly producing electrode arrays with feature sizes down to 50nm. Furthermore, for electrodes of larger feature sizes, it was shown that complex multi-layer electrode structures could be developed off this platform. These multi-layer structures could then also be tested with impedance spectroscopy to draw out the active mechanisms of the oxygen reduction reaction.

The lift-off process can be broken down into a three step process. First, a negative resist pattern is developed through either traditional photolithography or e-beam nanolithography. Next, a thin film is deposited over the entire substrate, both covering the photoresist pattern and filling the gaps between the resist patterns. Finally, the resist is removed, or lifted-off, along with the thin film from unwanted areas. The results of this process are detailed below.

Results and Discussion

The Negative Resist Pattern

Since the final accuracy of the patterned electrode arrays is defined by the accuracy of the developed photoresist, precise control of the lithographic process is critical to this study. A good negative resist pattern allows for thin film deposition in the exact electrode location while simultaneously blocking deposition over unwanted areas. Clean removal of the resist structure, and the unwanted thin film, relies on the
discontinuity of the thin film. The discontinuity is ensured by sufficient undercut of the resist structure.

Shown in Figure 4.1 is a cross-sectional view (SEM micrograph) of an as-processed negative resist structure (dimension of 2.5 μm wide, 3 μm thick, and 6 mm long). It can be easily seen that the PMGI resist is undercut sufficiently back from the surface to avoid contact with the photoresist wall. This undercut allows good resolution of the TPB surface and provides the opportunity for multiple layer deposition.

Figure 4.1: A cross-sectional view (SEM micrograph) of a negative photoresist pattern showing the 3-dimensional structure (Electrode strip width = 1.5μm, gap between two adjacent electrode strips = 2.5μm). Electrode material will be deposited in the gaps allowed between resist lines.

Schematically shown in Figure 4.2 is a desired cross-sectional view of the negative resist with a gap dimension of 5 μm wide and 3 μm thick for deposition of an
electrode with clean resolution of the TPBs. The large PMGI thickness, combined with a non-directional sputtering technique yielded electrodes slightly wider than the open region of the photoresist as determined by the mask.

Figure 4.2: A schematic cross-sectional view of a multi-layer negative photoresist pattern on an YSZ electrolyte. Please note the undercut separation from the edges of the pattern.

All platinum electrodes and most LSM electrodes were fabricated using this process. The undercut allowed for a clean separation of resist with the deposited thin film, thereby allowing uniform TPBs and a precise quantification of TPB length and feature size.

Additionally, since sputtering techniques deposit material from oblique angles, electrode dimensions are finalized slightly larger than mask dimensions. Consequently, subsequent deposition of an insulating layer from a directional source, such as E-beam evaporation, yields a supplemental insulating film completely within the perimeter of the
underlying electrode. This result opens the possibility for fabrication of tiered multi-material structures. One such possibility was studied and will be outlined here.

Deposition and Photoresist Removal

Schematically shown in Figure 4.3 is a cross-sectional view of an MIEC (e.g., LSM) electrode capped with an insulating (e.g., TiO₂) layer after sequential depositions, produced by sputtering of the MIEC electrode (non-directional) followed by e-beam deposition of insulating layer (directional) using a negative resist (with dimension of 50 μm wide and 3 μm thick). Sputtering techniques are well known to cover edges and vertical walls during deposition. During sputtering, electrode material slowly builds up on the vertical walls of the photoresist layer, narrowing the gap for later deposition. This buildup serves to prevent the directional deposition layer from reaching the full outer limit of the pattern, even as defined by the mask.
Figure 4.3: A schematic cross section of a cell with patterned electrodes before removal of photoresist. Notice that the LSM coating slightly covers the interior wall of the photoresist layer, creating a slightly smaller gap for the directional Ti layer.

Once deposition of desired materials has been completed, removal of the photoresist layers yields a patterned electrode of desired dimensions. The Lift-Off process ensures clean edges, necessary for quantifiable TPB length determination, along the entire length of the electrode. Schematically shown in Figure 4.4 is a cross-sectional view of the completed patterned electrode.
Figure 4.4: A schematic cross-sectional view of patterned LSM capped with TiO$_2$ coating after removal of resist layers. The insulating coating effectively blocks ionic diffusion through the roof of the electrode. LSM width is slightly greater than 50µm. TiO$_2$ width is slightly less than 50µm.

Conclusions

In this study, we have successfully developed a microfabrication process capable of producing well-defined three-dimensional geometries. SEM and EDS micrographs confirm that a photolithographic process is indeed capable of producing patterned electrodes that satisfy the demands for accurate measurement.

The process presented here capitalizes on the many advantages of microelectrodes in solid state ionics while simultaneously allowing for easier measurement and interpretation. Averaging over an array of microelectrodes yields performance results that depend on the comprehensive properties of the material rather than the characteristics of individual sites. For many studies this would be a significant improvement as the
information derived is more directly relevant to real systems. The process can be further expanded to determine the relative importance of the active sites for fuel cell reactions.
CHAPTER 5

FABRICATION AND CHARACTERIZATION OF THIN FILMS

Abstract

Dense La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) and La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSC) films were fabricated via pulsed-laser deposition (PLD) on various substrates. The crystal structures of the films were characterized via in-situ X-ray diffraction and the in-plane electrical properties by impedance spectroscopy from room temperature to 700°C. While the ablated films appeared to grow in the perovskite phase with the appropriate electrical properties when the substrate temperature was greater than 500°C, they were amorphous when the substrate temperature was relatively low. Subsequent annealing of amorphous LSM and LSC films in air induced a rapid phase transformation to the perovskite phase at 450°C and 600°C, respectively.

Introduction

Successful fabrication of useful patterned electrodes entails two distinct steps: Lithography and thin film deposition. The lithographic patterning process, described in detail in the proceeding chapter, simply prepares the cell for selective pattern deposition. It is during the deposition step that the patterned electrodes are actually created. Since
the material deposited during thin film deposition eventually makes up the electrodes, the quality of the electrodes is tied directly to the quality of the films.

In order to quantifiably relate cell performance to electrode geometry, it is vital that the actual cell geometry, including TPB length, is identical to the intended cell geometry. Any cracks or pores in the electrodes would unavoidably extend the TPB length and obscure the delicate relationship between TPB length and feature size. Furthermore, variations in film thickness or stoichiometry both within a single array and from one array to another might conceal geometrical effects. Consequently, it is vital to this study to ensure that all films were fully dense, uniform and stoichiometric. SEM, Profilometry and Grazing angle X-ray Diffraction were used to fully characterize the films created by both sputtering and pulsed laser deposition.

Results and Discussion

Figure 5.1 displays an SEM micrograph of the as-tested thin LSM film. All films appeared completely dense and pore-free. Additionally, the films showed good adhesion to the substrate with no instances of delamination. The amorphous films display a unique lack of any distinguishable features and the structures of the underlying electrodes are easily recognized. By contrast, SEM micrographs of LSM and LSC films after annealing in air up to 900°C for 30 minutes show small grain features, readily contrasting the featureless characteristics of the amorphous films.
Figure 5.1: SEM cross-sectional micrograph of a thin dense LSM film approximately 0.6 microns in thickness supported on a quartz substrate. This film was fired up to 800°C and is shown in the final state.

Shown in Figure 5.2 are a series of temperature-dependent XRD diffraction patterns of a thin LSM film deposited on a silicon (100) substrate at room temperature. The low-angle hump apparent in the XRD patterns acquired at low temperatures (300-400°C) is an indication that the LSM film was amorphous. The phase transition from an amorphous state to the orthorhombic phase (PDF #53-57) can be seen to occur between 400°C and 450°C. In direct comparison, the LSM films deposited at a substrate temperature of 500°C were recorded in the orthorhombic phase initially. The initial and final film phases did not depend on the choice of substrate. However, the devitrification temperatures for thin films on both the single crystal YSZ and the polycrystalline YSZ were recorded between 500°C and 550°C, roughly 100°C higher than that for silicon.
Figure 5.2: Temperature-depdendant XRD scan of thin film LSM on (100) Silicon
Intensity is plotted as a function of $2\theta$ on the X-axis and temperature in Celsius on the Y-axis. The phase change from amorphous to the perovskite phase occurs between 400 and 450°C.

Figure 5.3 presents the temperature-dependent XRD patterns of a thin LSC film on a silicon (100) substrate deposited at room temperature. The low-angle hump associated with amorphous film is less apparent in the XRD patterns acquired at low temperatures (300-400°C). Additionally, a minor impurity phase can be seen below the 600°C transition temperature. The phase transition from a predominately amorphous state to the rhombohedral phase (PDF # 48-122) can be clearly seen between 550°C and
600°C for LSC. Again, in direct comparison, the LSC films deposited at 500°C were recorded in the rhombohedral phase initially. For a second time, the initial and final film phases did not depend on the choice of substrate, although the devitrification temperature for thin films on both the single crystal YSZ and the polycrystalline YSZ was recorded roughly 100°C higher than that for silicon. For the YSZ substrates, the phase transition occurred between 650°C and 700°C.

Above 900°C, degradation of the LSC film on silicon becomes evident. A decrease in the peak heights of the rhombohedral La$_{0.5}$Sr$_{0.5}$CoO$_3$ phase in conjunction with the appearance of a second La$_2$CoO$_4$ phase (PDF #34-1296) lead to the conclusion that decomposition was occurring in this instance. This decomposition was not seen with LSC films on either single crystal YSZ or polycrystalline YSZ substrates.

Repeat analysis of the phase change as a function of time reflected the relative time-independence of the phase change. Several temperature-independent scans were performed at 430°C for LSM and 580°C for LSC in hopes of observing the phase change as a function of time. Unfortunately, all phase changes occurred too quickly to be measured with our equipment. In both cases, the phase changes occurred below the 9-second window necessary for time-dependant measurements; as a result, we were unable to obtain any useful information on the kinetics of the phase transformation.
Figure 5.3: Temperature-dependant XRD scan of thin film LSC on (100) Silicon. Intensity is plotted as a function of $2\theta$ on the X-axis and temperature in Celsius on the Y-axis. The phase change between 550°C and 600°C can be clearly discerned.

Shown in Figure 5.4 is a typical impedance spectrum for an LSM film prepared by PLD at low temperatures. The bulk resistance (or the in-plane sheet resistance) of the LSM film was determined from the intercept with the real axis at high frequencies while the interfacial polarization resistance between the LSM film and the Pt electrodes was determined from the diameter of the small impedance loop. All of the amorphous films exhibited this type of behavior. Impedance spectra for the LSC films closely paralleled those for LSM films.
Figure 5.4: A typical impedance spectra of an LSM film measured in air at 400°C and 500°C, respectively. The film was grown via pulsed laser deposition at room temperature.

Impedance Spectroscopy of the thin films yielded temperature-dependant resistance values that were converted to conductivity values with the help of a finite element model developed specifically for the unique geometry of the interdigitated electrodes. Figure 5.5 displays a plot of conductivity as a function of inverse temperature. As expected, the conductivity of LSM displayed a linear trend while that of
LSC displayed a slightly curved shape. The arrows indicate the effective structural transformation temperatures of LSM and LSC respectively. It should be noted that both LSM and LSC performed as expected in both the amorphous and polycrystalline states.

![Graph](image.png)

**Figure 5.5**: Plot of Log Conductivity versus 1/Temperature for both LSM and LSC. The transition points between the amorphous and crystalline phases are 450°C and 600°C and are indicated by arrows. It is important to note that the electronic behavior is consistent throughout both the crystalline and amorphous phases.

**Conclusions**

The developed methodology was used to investigate the temperature-dependant behavior of mixed conducting materials as fabricated by PLD. Films of both LSM and LSC were shown to vary with deposition temperature and substrate material. The films were characterized through SEM microscopy, impedance spectroscopy, and temperature dependant X-ray diffraction.
High temperature deposition, above 500°C, resulted in thin dense films in the orthorhombic and rhombohedral phases respectively. These films were stoichiometrically consistent with the target materials and underwent no phase changes upon annealing. Crystalline films generated by PLD displayed ideal resistive behavior.

Conversely, low temperature deposition yielded stoichiometrically accurate, though amorphous, thin films. Upon annealing, both LSM and LSC amorphous films underwent a phase change to the crystalline phase. In both cases the phase change was rapid. For an amorphous LSM film on a YSZ substrate, the devitrification point was 550°C. For a likewise amorphous LSC film on YSZ, the phase change occurred at 700°C. For thin films on silicon substrates, the phase changes both occurred at roughly 100°C cooler temperatures. Impedance spectra displayed a small impedance loop in addition to the dominant bulk resistance. LSM and LSC films showed resistive behavior, yielding conductivity values at 600°C of 11.5 S/cm and 221 S/cm, respectively.
CHAPTER 6

INTERFACIAL POLARIZATION RESISTANCE

It is well known that the performance of fuel cells as well as hydrogen production and storage systems are often determined by interfacial losses, especially those based on thin-film electrolytes/membranes. To achieve rational design of electrodes, catalysts, and interfaces, we must focus on fundamental investigations into the interfacial processes on the nano- and molecular-scale to gain a profound understanding of reaction mechanisms at different reaction sites and the effect of multi-scale microstructures on these processes. The geometrical complexity of porous electrodes make evaluation of the fundamental parameters extremely difficult. Thus, the study of electrodes with well-defined geometries provides an essential pathway to a more profound understanding of the nature and breadth of reaction sites (TPB or surface) in a porous electrode or structure.

6.1 The TPB Effect

Abstract

Electrode kinetics greatly influence the overall performance of solid oxide fuel cells, especially at low temperatures. Still, little is known about the nature of electrode reactions. In this study, patterned electrodes of well-defined geometry were successfully deposited on electrolyte substrates through microfabrication techniques. The ratio of three-phase boundary (TPB) to surface of electrode can be readily changed by 4 orders of
magnitude, producing electrodes with vastly different characteristics. Impedance measurements reveal a quantifiable relation between the TPB length of a patterned electrode array and the cathodic interfacial resistance, implying that TPBs are the dominating sites for electrode reactions.

**Introduction**

Reduction of oxygen involves a number of elemental steps such as adsorption of oxygen molecules, dissociation of molecules to atoms, ionization of oxygen molecules and combination of oxygen ions with oxygen vacancies. If either the vacancy or the electrons are unavailable, as would happen far from the TPB, the oxygen reduction will not happen, thus contributing nothing to the fuel cell performance. When using precious metal electrodes, the one-dimensional TPBs may in fact have a finite width broader than the linear feature. Surface ion migration or the quantum effect of electron tunneling may serve to expand the triple phase boundary to cover a large portion of the surface.

In this study, patterned electrodes of constant surface area and varying amounts of TPB length were fabricated in order to determine the effective active size of the TPB reaction zone. By maintaining a constant electrode height, and altering the number of electrode lines, as demonstrated in Figure 3.1 (B) and (C), the total surface area of the electrodes and the total electrolyte area are held constant while the effective TPB length can vary by 4 orders of magnitude. Through careful fabrication, electrodes of well-defined geometry can quantitatively link bulk impedance spectroscopy results to TPB
length. As feature size decreases, adjacent reaction zones move steadily closer. Once overlap of reaction zones occurs, the performance benefit from additional TPB length breaks down. For a purely electronic conductor, any deviation from linearity can be completely attributed to overlap of the active areas.

Results and Discussion: Platinum

For an electrode that exhibits pure electronic conduction, such as platinum, the electrode reactions can occur only at or near the three phase boundary (TPB), the region where gas phase meets electronic and ionic conducting phases at the electrode-electrolyte interface. Since the performance of SOFCs at low temperatures is determined predominantly by interface reactions, a fundamental understanding of the processes would provide valuable insight to effectively improve fuel cell performance.

Uniformity of the patterning technique allows comparison between samples of different TPB lengths. Figure 6.1 shows an SEM micrograph of a patterned platinum electrode array. The array, typical of those processed, demonstrates well-defined rectangular electrodes showing remarkable consistency of line depth and accuracy within the pattern. The SEM micrograph of the patterned electrodes also shows that no abnormal boundaries exist at the electrode/electrolyte interface. These micrographs reveal that no significant disruptions exist along the TPB interface. Consequently, the actual TPB lengths closely resemble the theoretical TPB length calculated from mask specifications.
Figure 6.1: SEM micrograph of As-prepared patterned platinum electrodes
Electrodes are 2µm in width with a separation gap of 2µm. The patterned electrodes show good resolution with no cracking or other expansion along the TPB.

Of critical importance to this study is the actual triple phase boundary length. Since we are proposing that the interfacial resistance is directly proportional to the TPB length, an accurate measure of the actual triple phase boundary is imperative. Any roughness, fracture or other anomalies at the interface can lead to significant extension of the triple phase boundary, often by up to two orders of magnitude. Consequently, great care was taken to ensure that the surface was smooth and free of defects. Furthermore, all microfabrication techniques were carefully monitored to ensure that no structural problems arose.
Figure 6.2: Impedance spectra from patterned platinum electrodes taken at 550°C. All electrodes have the same surface area and varying degrees of TPB length. Each curve is labeled with feature size of the electrodes whose array influenced the impedance curve.

Following directly from accurate measurement of the TPB length, impedance data from impedance spectroscopy was analyzed in relation to the TPB length. Shown in Figure 6.2 are the impedance spectra for the interfaces between a YSZ electrolyte and a patterned platinum electrode of the same surface area but different TPB length. The bulk resistance of the YSZ, $R_b$, was removed from the original spectra for clarity. Since other electrolyte and system resistances are incorporated into a bulk resistance measurement before the onset of impedance loops, the impedance loop length along the real axis can be directly attributed to interfacial contributions. A direct relation between the triple phase boundary length and the interfacial resistance is shown in Figure 6.3.
Figure 6.3: Interfacial conductance vs. TPB length for platinum electrodes at 600°C and 650°C. Platinum electrodes showed a linear relationship at large feature sizes, but not small feature sizes. Due to the degradation of electrode arrays during testing, this could not be isolated or quantified.

Looking only at the 650°C plot in Figure 6.3, we can see that the interfacial resistance decreases from values of 200, to 60, and to 41 ohms as the TPB lengths went from 0.384 meters, to 3.606 meters, and to 6.005 meters, respectively. From this plot a direct correlation between increases in TPB length and decreases in interfacial resistance can be drawn. Arrhenius plot’s shown in Figure 6.4 yield activation energies between 2.072 and 2.210 kJ/mol. These values matched well with the published activation energy of 2.411 kJ/mol.
As expected, at low temperatures platinum data proves to be nearly linear all the way to large TPB lengths (small features sizes), indicating a strong dependence on TPB length. However, as the temperature increases, the dependence of performance on TPB length decreases. As temperature goes up, increases in TPB length fail to produce corresponding reductions in interfacial resistance. This result indicates that at elevated temperatures, an overlap of active processes may occur.
Complications with Patterned Platinum Electrodes

At first glance, platinum patterned electrodes seem like a logical point of initiation for a systematic study of the oxygen reduction reaction. The theoretic simplicity of the two or possibly three competing reactions listed in the introduction (reaction paths a&b), offers a more simplistic analysis of impedance results. However, in practice, fabrication of platinum electrodes proved exceedingly difficult. It turns out that the inherent resistance to oxidation and low-reactivity characteristics of platinum also make adhesion to oxide films problematic. While this problem has been occasionally encountered in the semi-conductor industry, the traditional solution is not viable in this case. In the semi-conductor industry a 50-200nm titanium adhesion layer is customarily deposited on the oxide surface immediately prior to platinum deposition. The excellent gripping capability of this thin layer of titanium ensures that the platinum layer will be robustly attached without significantly altering the electronic transport properties critical to integrated circuits.

While a titanium adhesion layer facilitates processing without altering the electronic transport properties, it does inherently disrupt the electrochemical properties. Since it is the platinum/YSZ interface that is of importance to this study, clearly the addition of a titanium layer, even one as thin as 50nm, would fundamentally alter the character of the study. In addition to altering the Pt/YSZ interface, a titanium adhesion layer would alter the TPBs from a Gas/Platinum/YSZ interface to a Gas/Titanium/YSZ interface. Since titanium is not catalytically active, and clearly not the focus of this
study, this processing step would compromise the study. Lacking a functional method for platinum adhesion, high resolution of platinum patterned electrodes proved problematic and a minimum feature size of 2µm was the lowest achieved.

Additionally, platinum electrodes showed significant grain growth at relatively low temperatures. As demonstrated by the SEM micrograph in figure 6.1 the as-prepared platinum electrodes showed good resolution and clean TPBs. These micrographs are typical of the patterned LSM microelectrode surface. While some surface irregularity may exist along the edge of the patterned electrode, the TPB surface is clean nonetheless. Some of the electrode edges are not perfectly straight, but the deviations appear to be simple lumps and ridges along the wall of the electrode. It is important to notice that any roughness along the TPB does not include any cracking that would appreciably increase the TPB length. Although the some of the edges appear wavy at high magnification, no features appear which would indicate significant geometrical expansion of the TPB.

However, after extended time above 750°C, the thin platinum strips beaded under surface tension yielding a discontinuous electrode. Discontinuous platinum electrodes are shown in figure 6.5. At this point, electrode performance degraded considerably to the point where competent electrochemical tests could no longer be performed. Consequently, all platinum electrode studies were performed at temperatures at or below 750°C. Additionally, since the LSM and LSC patterned electrodes employed platinum current collectors, these studies were capped at 750°C as well.
Figure 6.5: SEM micrograph of Platinum electrodes on a YSZ substrate after firing to 800°C for 3 hours. The electrodes no longer display any geometric control. The TPB is dramatically expanded and many parts of the electrode are no longer in electrical contact.

*Results and Discussion: LSM*

For an electrode that exhibits pure electronic conduction, such as platinum, the electrode reactions can occur only at or near the three phase boundary (TPB), the region where gas phase meets electronic and ionic conducting phases at the electrode-electrolyte interface. Similarly, the more common use of mixed ionic-electronic conducting (MIEC) materials, such as LSM is intended to dramatically expand the reach of the reaction zone across a larger, three-dimensional surface. Due to the simultaneous transport of both ionic and electronic defects in MIECs, oxygen vacancies are able to migrate extended distances through the MIEC electrode. As a result, the effective reaction sites could be
far beyond the triple phase boundary. Currently, MIEC reaction rates cannot be
definitively attributed to either the triple phase boundary or reactions on the surface of the
mixed conducting electrode. Consequently the effective width of an MIEC TPB has yet
to be determined. Patterned LSM electrodes were fabricated and tested in order to
understand this phenomenon.

Uniformity of the patterning technique allows comparison between samples of
different TPB length. Figure 6.6 shows a typical SEM micrograph demonstrating well-
defined rectangular LSM electrodes. Each show remarkable consistency of line depth
within the pattern, and both test samples showed total deposition depths well within the
experimental error of the SEM.

Figure 6.6: SEM micrographs demonstrating LSM patterned microelectrodes with well-
defined TPB length. Some surface roughness can be seen, though it does not appreciable
change the amount of TPB length.
Of critical importance to this study is the actual triple phase boundary length. Since we are proposing that the interfacial resistance is directly proportional to the TPB length, an accurate measure of the actual triple phase boundary is imperative. Any roughness, fracture or other anomalies at the interface can lead to significant extension of the triple phase boundary, often by up to two orders of magnitude.\textsuperscript{72} Consequently, great care was taken to ensure that the surface was smooth and free of defects. Furthermore, all microfabrication techniques were carefully monitored to ensure that no structural problems arose.

The SEM micrograph of the patterned electrodes shows that no abnormal boundaries exist at the electrode/electrolyte interface. Figure 6.7 shows deposited micropatterns of LSM, typical of those processed, at increased magnification. These micrographs reveal that no significant disruptions exist along the TPB interface. Consequently, the actual TPB lengths closely resemble the theoretical TPB length calculated from mask specifications.
Figure 6.7: SEM micrograph of the TPB of an LSM electrode on a YSZ substrate. The TPB surface appears smooth and consistent regardless of the locations of grains. Consequently, the actual TPB length can be accurately calculated.

SEM micrographs after testing demonstrate not only the quality of the patterns, but also that impedance testing to 800°C in air had no negative effects on the pattern. Figures 6.6 and 6.7 demonstrate micropatterned electrodes with clearly defined TPB lengths. These micrographs are typical of the patterned LSM microelectrode surface. While some surface irregularity may exist along the edge of the patterned electrode, the TPB surface is clean nonetheless. Some of the electrode edges are not perfectly straight, but the deviations appear to be simple lumps and ridges along the wall of the electrode. It is important to notice that any roughness along the TPB does not include any cracking that
would appreciably increase the TPB length. Although the some of the edges appear wavy at high magnification, no features appear which would indicate significant geometrical expansion of the TPB.

Following directly from accurate measurement of the TPB length, impedance data from impedance spectroscopy was analyzed in relation to the TPB length. Shown in Figure 6.8 are the impedance spectra for the interfaces between a YSZ electrolyte and a patterned LSM electrode of the same surface area but different TPB length. The bulk resistance of the YSZ, $R_b$, was removed from the original spectra for clarity. Since other electrolyte and system resistances are incorporated into a bulk resistance measurement before the onset of impedance loops, the impedance loop length along the real axis can be directly attributed to interfacial contributions. A direct relation between the triple phase boundary length and the interfacial resistance is shown in Figure 6.10.

![Figure 6.8: Impedance spectra for the interfaces between a YSZ electrolyte and patterned electrodes of the same surface area but different TPB length measured at 700°C.](image-url)
Looking at the 700°C plot in Figure 6.8, we can see that the interfacial resistance decreases from values of 147, to 104, and to 50 ohms as the TPB lengths went from 5.142 meters, to 7.206 meters, and to 18.006 meters, respectively. From this plot a direct correlation between increases in TPB length and decreases in interfacial resistance can be drawn. Arrhenius plot’s shown in Figure 4.24 yield activation energies between 1.345 kV and 1.801 kV.

![Arrhenius plots](image)

Figure 6.9: Arrhenius plots for the interfacial polarization resistances of LSM microelectrodes

Impedance Spectroscopy of patterned LSM microelectrode cells yielded well-defined impedance loops. The centers of the experimental impedance arcs were only slightly displaced below the real axis indicating a minor contribution from distributed
elements. Interfacial resistance data was extracted through comparison of multiple configurations of two and three electrode measurements.

LSM interfacial resistance was compiled and compared in relation to TPB length. As shown in Figure 6.10, LSM interfacial resistance displays linear behavior at all TPB lengths. More importantly, though, interfacial resistance has been quantitatively compared with feature size. Since the microfabrication process developed in this study produces electrodes with clean edges and no cracking, the spacing between the TPBs of adjacent electrodes is uniform. Because of this, the interfacial resistance can be compared to feature size and not simply TPB length. Only through comparing feature size can the effective width of the TPB be determined.

Since the active region surrounding the TPB may be very small, it is obvious that deviations from a linear relationship would only arise at very fine feature sizes. Furthermore, LSM is a mixed conducting material and as such has the potential for bulk conduction. Though LSM is a relatively poor ionic conductor, the bulk path should contribute for thin electrodes, especially at high temperatures where the MIEC material would be more active.
As expected, at low temperatures LSM data proves to be nearly linear all the way to large TPB lengths (small features sizes), indicating a strong dependence on TPB length. From this preliminary analysis, the actual width of the LSM TPB cannot be definitively defined. It is only known to be smaller than half the distance between adjacent TPBs, or 1 μm. Since the actual width of the TPB is smaller than half the smallest feature size, fabrication of electrode arrays with yet smaller feature sizes were necessary for completion of the study.

Conclusions

As expected, at low temperatures platinum data proves to be nearly linear all the way to large TPB lengths (small features sizes), indicating a strong dependence on TPB
length. However, the initial findings of platinum patterned electrodes broke down due to complications during testing. The electrodes appeared to bead on the YSZ surface, thereby losing continuity and becoming ineffective as an electrode at elevated temperatures.

For LSM, the triple phase boundary length was found to be inversely proportional to the interfacial resistance for LSM electrodes. Overlap of the reaction zones did not appear to occur, so further study was necessary in order to determine the actual active width of the TPB. While overlap of reaction zones did not occur at 2μm feature size, the importance of the TPB was verified, and methods for further reduction of feature size were developed.

6.2 Selective Blocking of Reaction Paths

Abstract

Electrode kinetics greatly influences the overall performance of solid oxide fuel cells (SOFCs), especially at low temperatures. Yet little is known about the nature of SOFC electrode reactions. In this study, patterned LSM (La0.8Sr0.2MnO3) microelectrodes were capped with a TiO2 insulating layer in order to block the transport of ionic and electronic species across the surface thereby allowing separation of different reaction sites. These microelectrodes verify the concept of selectively blocking certain reaction sites in order to investigate complex electrochemical reaction mechanisms.


Introduction

In addition to patterned electrode arrays in which small feature size is varied, active mechanisms for oxygen reduction can be studied using multi-tiered electrode structures to isolate specific mechanisms. Specifically, the bi-layer lift-off process in conjunction with various deposition methods allows fabrication of patterned electrode arrays in which selective reaction paths are blocked. The cross-sectional schematic of a multi-tiered patterned electrode array displayed in Figure 4.4 is intended to allow oxygen reduction at the TPB while simultaneously blocking oxygen reduction through the bulk electrode.

In order to selectively block reaction paths, the lithographic process described in the previous section was expanded to incorporate alternate deposition methods. Shown schematically in Figure 4.2 is a cross-sectional of the negative resist with dimension of 50 μm wide and 3 μm thick. Sequential deposition of an MIEC electrode by RF sputtering followed by a titanium dioxide blocking layer via PLD or E-beam evaporation yields the structure shown in Figure 4.3. The large PMGI thickness, combined with a non-directional RF sputtering technique yielded MIEC electrodes slightly wider than the open region of the photoresist as determined by the mask. Since sputtering techniques deposit material from oblique angles, MIEC electrode dimensions are finalized slightly larger than mask dimensions. Consequently, subsequent deposition of an insulating layer
from a directional source, in this case E-beam evaporation, yields a supplemental insulating film completely within the perimeter of the underlying electrode.

Schematically shown in Figure 4.3 is a cross-sectional view of an MIEC (e.g., LSM) electrode capped with an insulating (e.g., TiO$_2$) layer after sequential depositions, produced by sputtering of the MIEC electrode (non-directional) followed by e-beam deposition of insulating layer (directional) using a negative resist (with dimension of 50 µm wide and 3 µm thick). Sputtering techniques are well known to cover edges and vertical walls during deposition. During sputtering, electrode material slowly builds up on the vertical walls of the photoresist layer, narrowing the gap for later deposition. This buildup serves to prevent the directional deposition layer from reaching the full outer limit of the pattern, even as defined by the mask. Shown in Figure 6.11 is a cross-sectional view (SEM micrograph) of a patterned LSM electrode capped with a TiO$_2$ layer.

Once deposition of desired materials has been completed, removal of the LOR and photoresist layers yields a patterned electrode of desired dimensions. The Lift-Off process ensures clean edges, necessary for quantifiable TPB length determination, along the entire length of the electrode.

*Results and Discussion*
Shown in Figure 6.11 is an SEM micrograph of the same electrode construction as that demonstrated in Figure 4.4, viewed from above the surface. The edges of the TPB do not show any cracking or surface defects that would lead to increases in the actual TPB length. Furthermore, the edge of the titanium dioxide layer is smooth and uniformly recessed from the edge of the LSM electrode. Figure 6.11 demonstrates good control, thereby selectively blocking only the active sites for oxygen reduction on the top surface of the electrode. This result is further confirmed via the EDS dot-mapping shown in Figure 6.12, indicating that the TiO$_2$ covers the entire surface of the LSM without crossing the TPB. Since the electrochemical activity of the TPB contributes to the overall performance, it is important to ensure that the TPBs are unimpeded by the TiO$_2$ layer. Precise electrode control was achieved through careful processing.
Figure 6.11: Top-down SEM micrograph of Ti coated LSM electrode. The TPB of LSM along YSZ can be clearly seen, as can the edge of the insulating layer.

Figure 6.12: EDS dot mapping for TiO$_2$ capped LSM electrode. Electrode width and height are 50μm and 0.26μm, respectively.
The most successful attempt so far to control bulk transport with blocking layers has been limited to circular disk electrodes. Brichzin et al. demonstrated the effectiveness of an additional alumina layer serving to block ionic transport from the bulk into the electrolyte. In that case, the alumina layer was initially deposited directly onto the electrolyte. Subsequent deposition of the active electrode material yielded a three-dimensional structure with the blocking layer separating the electrode/electrolyte boundary.

Patterned arrays of microelectrodes developed via lift-off retain the electrochemical significance presented by Brichzin while simultaneously providing two distinct advantages. First, photolithography allows easy processing of a large matrix of interconnected patterned electrodes through the application of an overlaid current collector. Simultaneous lithography of the current collector also added a wire bond pad, thereby eliminating the need for an AFM tip for electrical contact. Contact areas for the electrodes were consistently reproducible in addition to being markedly easier to connect. Second, multiple electrodes now cover a significant area of the electrolyte, thereby averaging surface anomalies. Patterned microelectrode arrays measure typical average properties, rather than atypical localized properties, thereby eliminating much of the additional complexity from site-specific microelectrodes. Since many studies seek a relationship between novel materials and overall electrochemical performance, this method may be more useful in some cases. Furthermore, larger amounts of reaction area
lower total polarization resistance thus enhancing signal quality while using standard impedance analyzers.\textsuperscript{74,75}

By applying the insulating layer above the working electrode, as done here, transport across the MIEC top surface is effectively blocked, leaving only the TPB active for oxygen reduction. In this way, we are able to isolate the contribution from the TPB in relation to the bulk and surface effects. While it is unlikely that surface diffusion of adsorbed oxygen ions contributes significantly, by eliminating it from consideration, differentiation about the importance of the TPB can be achieved.

Furthermore, the method developed here may allow for determination of the location of the rate-limiting step. In addition to the ability to deposit blocking layers on the roof of the electrode, the process can also be slightly altered to deposit blocking layers below the electrode. By simply switching the deposition order, an array of patterned electrodes similar to those presented by Brichzin can be produced without interrupting the TPB or surface diffusion. Since the current technique limits both bulk and surface diffusion, a reversal of deposition order would allow surface effects thereby yielding three experimental conditions for the three possible reaction paths.

J. Fleig, among others, has successfully modeled the equipotential lines of a dense MIEC electrode.\textsuperscript{76} These lines vary significantly in shape and breadth according to the location of the blocking layer. By comparing the electrochemical performance of patterned microelectrodes with blocking layers above and below the active electrode
material, the relative importance of the electrode/atmosphere interface can be compared to that of the electrode/electrolyte interface.

*Impedance Spectroscopy of Patterned Electrodes*

Shown in Figure 6.13 are some typical impedance spectra of the interfacial resistance between the electrolyte and the patterned LSM microelectrode with or without a TiO$_2$ layer. In this case, the impedance contribution from the electrolyte/counter electrode interface can be neglected since it accounts for less than 1% of the total interfacial resistance. The interfacial resistances were readily extracted through comparison of multiple configurations of two and three electrode measurements. Due to the use of a reference electrode, the cathode/electrolyte interfacial resistance can be taken from the intercepts of the impedance curve on the real axis. The impedance data clearly indicate that the impedance of the LSM electrode capped with a TiO$_2$ layer is much greater than that of the LSM electrode without a TiO$_2$ layer, implying that the simultaneous transport of electronic and ionic defects through the bulk phase of LSM makes an important contribution to oxygen reduction at the electrode. Both electrodes were patterned with the same thickness and TPB length, the only difference being the TiO$_2$ layer covering the electrode roof in selective cases. In both cases, the TPB region remained active and unimpeded. In the case of the TiO$_2$ capped electrode, surface adsorption on and bulk diffusion through the MIEC electrode was eliminated. Impedance results indicate a direct correlation between the interfacial polarization resistance and the contributions of different reaction path.
Figure 6.13: Impedance spectra for uncapped and TiO$_2$ capped LSM electrode arrays measured at 750°C

Shown in Figure 6.14 is the dependence of the interfacial impedance on temperature at which the impedance spectra were acquired, indicating the increasing importance with temperature of ambipolar transport through the bulk phase of the MIEC. At low temperatures, the bulk path of the electrode does not contribute significantly even for very thin electrodes. However, the increased ambipolar transport through the bulk phase of the MIEC at high temperatures is reflected in the impedance data. Shown in Figure 6.15 are the Arrhenius plots for the interfacial conductance (i.e., the reciprocal of the interfacial resistance). The calculated activation energies for the uncoated and TiO$_2$ coated LSM electrodes were 1.3 KJ/mol and 1.5 KJ/mol, respectively.
Figure 6.14: Dependence of interfacial polarization resistance on temperature of two cells with LSM patterned electrodes (same TPB length and feature size) but with or without a TiO$_2$ coating.
Figure 6.15: Arrhenius plots for interfacial conductance of two LSM patterned electrodes (same TPB length and feature size) with or without a TiO$_2$ coating.

**Conclusions**

In this study, we have successfully developed a microfabrication process capable of producing well-defined three-dimensional geometries. SEM and EDS micrographs confirm that a photolithographic process is indeed capable of producing patterned electrodes that satisfy the demands for accurate measurement. Furthermore, we have developed an improved procedure for selective determination of the relative importance of the MIEC surface in relation to the TPB. This cell provides a proof of concept towards the possibility of selecting particular components for study. By eliminating possible reaction paths, it may be possible to observe each individual path for reductions at an
MIEC electrode, thereby completing a map of the reaction processes including relative contributions from each individual path.

### 6.3 The Characteristic Thickness of LSM

**Abstract**

Dense La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) electrodes were patterned by photolithography and fabricated via pulsed-laser deposition on YSZ electrolytes. The electrode arrays varied in thickness while maintaining a constant electrode area and three-phase boundary length. Impedance analysis shows that the interfacial polarization resistance decreases significantly as electrode thickness drops below a critical value, beyond which the top surface of the LSM becomes active for oxygen reduction. However, when the LSM electrodes become too thin, the in-plane sheet resistance of the LSM starts to limit the utilization of the electrodes along their length. The quantification of the characteristic thickness is important not only to intelligent design of practical mixed-conducting electrodes but also to the design of patterned electrodes for fundamental studies.

**Introduction**

In general, the oxygen reduction reaction may occur via several distinct pathways for an MIEC such as LSM.$^{77}$ (1) Direct electrochemical reduction of oxygen may occur at the three-phase boundary (TPB), where oxygen is available in the gaseous phase. (2) A
surface adsorption step has been proposed in which oxygen may be adsorbed and partially reduced before moving along the electrode or electrolyte surface to the TPB, leading to a finite width of the TPB. (3) Incorporation of oxygen into the electrode through the MIEC surface may occur with subsequent transport of oxygen ions through the electrode bulk to the electrolyte. Clearly, the rate of oxygen reduction through pathway (3) depends critically on the transport properties and thickness of the dense LSM layer. As the LSM electrode becomes thinner, the resistance of pathway (3) drops and, if bulk transport for this mechanism is rate-limiting, the rate of oxygen reduction at the surface will increase.

While there is little argument about the possible pathways, debate abounds regarding the individual contributions of each. Many researchers have found the interfacial polarization resistance to be proportional to the amount of available three-phase boundary \( L_{\text{tpb}} \), whereas others have found that electrode performance depends more on bulk transport phenomena. For instance, the effective catalytic utilization of dense MIEC electrodes is most likely determined by the rate of ionic transport through the MIEC electrode. In general, all possible reaction paths should be considered, although some paths may become more important than others under certain conditions.

In reality, the operating conditions and electrode geometry may very well define the dominant reaction pathway. Specifically, it has been suggested that the highly porous electrodes most common in SOFC fabrication may not take full advantage of the ionic properties of the material. Furthermore, excessive amounts of TPB length may not be
the most effective method for improving interfacial performance.\textsuperscript{91} It becomes clear, then, that the best method for electrochemical analysis of these three competing effects is to compare all three simultaneously in a controlled environment. As limiting cases, studies on porous MIEC electrodes may feature the contributions of the TPB while studies on dense MIEC electrodes, with essentially no TPB length, reflect the effect of bulk transport properties. In order to compare the relative contribution of each pathway, a mixed system of dense electrode regions with a clearly defined, non-zero TPB length should be employed. In such an experiment the competing mechanisms can be quantitatively evaluated.

We completed one such systematic study on the effect of feature thickness in dense patterned electrodes. The results show a definite transition from TPB to bulk-dominated behavior as the geometry of the cell changes. In addition, the study reveals a clear influence of electrical resistance on cell response for the thinnest electrodes.

\textit{Results and Discussion}

SEM analyses confirm that the LSM electrodes are thin, dense and relatively defect-free. Furthermore, the actual thickness and TPB length are as calculated. An SEM micrograph, presented in Figure 6.16, demonstrates close control of the electrode geometry throughout the array.
Figure 6.16: An SEM image of LSM patterned electrodes (with constant TPB length and surface area) on a YSZ substrate. The width of the LSM strip is 40µm and the gap between two adjacent strips is 60µm. Platinum current collector strips run perpendicular to the LSM strips. A schematic of the cell is provided in the top left-hand corner.

Shown in Figure 6.17 are some typical impedance spectra of the interfacial resistance between the electrolyte and the patterned LSM microelectrode. In this case, the impedance contribution from the electrolyte/counter electrode interface can be neglected since it accounts for less than 1% of the total interfacial resistance. The interfacial resistances were readily extracted through comparison of multiple configurations of two and three electrode measurements. Due to the use of a reference electrode, the cathode/electrolyte interfacial resistance can be taken from the intercepts of the impedance curve on the real axis. The impedance data clearly indicate that the thickness of dense electrodes plays a significant role in the overall performance, and shows the
importance of simultaneous transport of electronic and ionic defects through the bulk phase of LSM. Since all electrodes were patterned with approximately the same amount of surface area and TPB length, any significant differences in behavior must be related to the geometric thickness of electrode. Furthermore, since the electrode of lowest interfacial resistance is not the thinnest electrode, it appears that there is a performance-related minimum thickness for dense LSM electrodes.

Figure 6.17: Typical impedance spectra for an interface between the electrolyte and the patterned electrodes (working electrode) of constant TPB length and surface area with varying thickness at 700°C. The insert in the bottom right corner shows a typical impedance spectrum for the counter electrode-electrolyte interface, implying that it is less than 1% of that for the working electrode-electrolyte interface.

Figure 6.18 displays the dependence of the interfacial impedance on the electrode strip thickness at 700 and 750°C. Several unique traits are evident for each temperature range. In particular, note the peak conductance, located between 0.18 and 0.22μm,
followed by a rapid decay with increasing thickness. It should also be noted that the high-thickness decay behavior appears to asymptotically approach a non-zero value. This value, approximately 0.012 Ω⁻¹, has been attributed to the standardized factors within the cell. Among these are the TPB and surface transport contributions of the LSM array as well as the catalytic contributions of the platinum current collector. Since these factors have been systematically controlled through the design and fabrication stages, their contributions should be constant over the entire range of electrode thickness. Consequently, this background value can be subtracted from the overall conductance to yield the contribution merely from a pathway depending upon bulk transport through the dense MIEC.

Figure 6.18: Plot of 1/R_p vs. electrode thickness The horizontal axis has been compressed in some regions to accommodate the scope of all the tested electrodes.
Since only the bulk transport mechanism depends upon electrode thickness, the dramatic reduction in electrode performance with increasing thickness must be due to the increased resistance to bulk transport. In fact, for $700^\circ$C the overall conductance drops below 23% of its peak value by 0.36μm in thickness. Since ionic transport is a thermally activated mechanism, the characteristic bulk-active thickness can be expected to vary with temperature. In order to accurately estimate this thickness for all temperatures, the value at which the total interfacial polarization impedance was twice that of the TPB contribution was defined as the characteristic, or critical, thickness. This critical thickness can be viewed as the thickness below which the overall oxygen reduction rate is predominately determined by oxygen reduction processes depending on bulk transport through the dense MIEC electrode. Further reducing the electrode thickness facilitates transport through the bulk phase of the MIEC, catalytically activating the top surface of the pattern and thus improving electrode performance. The characteristic thickness has been plotted as a function of temperature in Figure 6.20. As expected, a downward linear trend can be discerned with decreasing temperature.

**Conclusions**

This study has demonstrated the effect of electrode thickness on the performance of dense LSM electrodes. Furthermore, the necessary conditions for mixed conducting behavior have been drawn out. It has been shown that the characteristic thickness of a dense LSM electrode varies with temperature and depends heavily on the ionic conductivity. The characteristic thickness at $700^\circ$C for dense LSM was found to be 0.36
\[ \mu m. \] Above 0.36 \( \mu m \), ionic diffusion is sufficiently difficult such that oxygen ion transport through the LSM electrode is essentially negligible. Beyond this point the surface of LSM electrodes cannot be effectively used and the behavior of the electrode is determined largely by the TPBs of the electrodes.

Furthermore, it has been shown that for very thin electrodes, the sheet resistance may dramatically reduce the effective utilization. For the defined geometry of this experiment, electrical effects dominate the performance of the electrode for thicknesses below 0.18\( \mu m \). At this point, the local overpotential drops and the entire surface area can no longer be assumed active. Computational modeling techniques have been used to demonstrate a corresponding drop in the effective utilization of the cathode with decreasing thickness.

This work has implications for the highly porous electrodes more common for industrial applications. Specifically, though much effort has been expended to find materials of greater ionic conductivity, it appears that electrodes with very complex pore networks may be limited not by ionic conductivity, but rather by electronic conductivity very near the electrode/electrolyte interface.
6.4 Current Collection and the Effect of Sheet Resistance

Abstract

It is often erroneously assumed in microelectrode studies that the entire electrode array is at a constant overpotential. In truth, this dramatically oversimplifies the experiment and can lead to substantial errors. In this study, platinum current collectors were lithographically patterned to produce identical arrays that minimized both ohmic losses and the electrochemical impact of the current collector on the patterned electrode array of interest. Further, mathematical models were generated to calculate the sheet resistance and understand the utilization percentage of each array.

Introduction

Unlike many porous electrodes so common in industrial applications, the patterned electrode arrays in this study can be dramatically impacted by ohmic losses due to sheet resistance along the electrodes. While the patterned electrode arrays boast very small, well-defined features, these minute features can also be the source of many complications. Specifically, as the electrode thickness necessarily decreases, the cross-sectional area so important to electronic conduction, also decreases. This reduction in cross-sectional area of the electrodes leads to subsequent increases in sheet resistance.
It is often erroneously assumed in microelectrode studies that the entire electrode array is at a constant overpotential. In truth, this dramatically oversimplifies the experiment and can lead to substantial errors. While the assumption of constant overpotential may be somewhat accurate for thick electrodes of large feature sizes, it is clearly not accurate for the very thin mixed conducting electrode arrays that are of great interest. In fact, ohmic losses due to in-plane sheet resistance can generate dramatic changes in overpotential across the electrode array.

Two alternative approaches were taken to manage the impact of sheet resistance and the resulting change in overpotential for LSM and LSC electrodes. First, lithographically patterned current collectors were developed to improve electrical conduction across the array. Secondly, mathematical models were developed to calculate the impact of sheet resistance on the arrays and to calculate the percent utilization, or in other words, the percentage of the array that can be assumed effective.

**Results and Discussion**

In this study, platinum current collectors were lithographically patterned to produce identical arrays that minimized both ohmic losses and the electrochemical impact of the current collector on the patterned electrode array of interest. Contrary to most applications, traditional methods of current collection, such as application of a porous platinum or porous silver layer, are not possible for this study. While porous metal layers may reduce sheet resistance much more effectively than a dense patterned
current collector array, the also contribute electrochemically in a non-uniform manner. Unfortunately, for this study, the materials available for current collection are also electrochemically active for the oxygen reduction reaction. For this reason, current collectors must be lithographically patterned in this study so that their resulting electrochemical effect can be assured uniform and subsequently removed from the interfacial polarization resistance. The standard current collector array consisted of 12 50μm wide platinum strips 6mm in length. Each strip was 0.25μm in thickness and was separated from each adjacent strip by 490μm. For nanoelectrode arrays, these current collector dimensions were further reduced to 2μm wide strips with a 2μm separation gap. In both cases, the electrochemical contribution of the current collector was experimentally verified by testing the current collector on a clean YSZ substrate.

Since the current collector geometry remains constant throughout the study, the interfacial polarization resistance due to the patterned electrode of interest can be calculated according to:

\[
\frac{1}{R_{PE}} + \frac{1}{R_{CC}} = \frac{1}{R_{Total}}
\]

where \( R_{PE} \) is the interfacial polarization resistance contribution from the patterned electrode, \( R_{CC} \) is the interfacial polarization resistance contribution of the current collector, and \( R_{total} \) is the total interfacial polarization resistance.

Once \( R_{PE} \) has been determined, the area specific resistance was calculated with help from mathematical models. Specifically, the models generated for this study take the exact electrode geometry into account in order to determine the sheet resistance along
each electrode. From the calculated sheet resistance map, the exact amount of active area can be determined, thus yielding a utilization percentage of the actual patterned electrode array.

Sheet Resistance and Current Collection for Interdigitated Patterns

Conductivity values for thin electrode films were calculated via a finite element model developed for the electrode geometry. A schematic of the cross-sectional model is shown in Figure 6.19. A vertical sliced cross-section was taken from the electrode array in order to portray the model domain. The black boundaries were assigned to represent the platinum current collectors. Since the conductivity of the platinum electrodes far exceeds that of LSM or LSC, electric potential drops in the platinum electrodes were neglected. Consequently the boundary values were kept at a uniform potential (1 and 0 volts) at the two Pt electrodes. Similarly, since the quartz substrate used for this experiment has extremely low conductivity relative to both the platinum electrodes and the thin cathode films, current through the substrate can also be neglected. The gray layer, adjacent to the boundaries, was defined as the thin-film cathode material. The height of the film was designated as “d” and chosen in accordance with the actual thickness of the electrode films. The thickness of the LSC and LSM films were measured to be 0.2 and 0.7 microns, respectively, as verified by profilometry.
The Laplace equation, $\nabla^2 \phi = 0$, was solved in the whole domain (LSM or LSC films) as the only constitutive equation. All the boundaries were kept insulated with the obvious exception of the interfaces of the two platinum electrodes with the thin film of LSM or LSC. Ohm’s Law was then used to calculate the effective conductivity of the media.

$$ I = \int_{\text{Area}} - \sigma_{\text{eff}} \frac{\partial \phi}{\partial y} $$

where $I$ is the total current flowing through each model bar (or the interfaces between the platinum electrodes and the LSM or LSC films) and $\frac{\partial \phi}{\partial y}$ is the electrical potential gradient.
on an interface between a platinum electrode and the LSM or LSC film. The surface integration was carried out over the entire interface between the platinum electrode and the LSM or LSC film. For each applied voltage, the total current passing through each model bar was experimentally measured whereas the potential distribution at each point on the interface were calculated using finite element modeling (Femlab version 3.1).

The temperature dependant behavior of both LSM and LSC is displayed in Figure 5.5. For LSM films of 0.7 μm in thickness, the calculated resulting conductivity was approximately 11.5 S/cm at 600°C. The final calculated conductivity for LSC was approximately 221 S/cm at 600°C. For both the LSM and LSC, conductivity values agreed well with published literature.92

Sheet Resistance and Current Collection for Patterned Electrodes

One final point of interest in Figure 6.18 is the dramatic drop in electrode performance at 0.12μm thickness. It is believed that this drop-off in performance is due primarily to limitations of current collection. Below 0.18μm, the sheet resistance within the patterned electrode climbs to values high enough such that the entire surface area of the patterned electrode may no longer be assumed to be at a constant overpotential. At this point, many parts of the electrode array, particularly those locations far from the current collector strips, become less active. The further away that a cathode surface
element is from the current collector, the less it will contribute to the overall electrode performance, leading to larger interfacial resistances.

Figure 6.20: Plot of $1/R_p$ vs. electrode thickness at 700°C. The horizontal axis has been compressed in some regions to accommodate the scope of all the tested electrodes. Points indicate the experimental values while the solid curve is the corrective model. The insert in the top right corner is a plot of Characteristic thickness as a function of temperature for LSM. A downward linear trend can be discerned with decreasing temperature.

For the patterned electrode arrays, ohmic losses within the LSM electrodes were again calculated via a finite element model developed for the specific electrode geometry. A schematic of the cross-sectional model is shown in Figure New. A vertical sliced cross-section was taken from the electrode array in order to portray the model domain. The black boundaries were assigned to represent the platinum current collectors, while the checkered region represents the electrically insulating YSZ substrate. Since the conductivity of the platinum electrodes far exceeds that of LSM or LSC, electric potential drops in the platinum electrodes were neglected. Consequently, the boundary values for the platinum electrodes were kept at a uniform potential of 1 volt. Similarly, since the
YSZ substrate used for this experiment has extremely low electronic conductivity relative to both the platinum electrodes and the thin cathode films, electrical current through the substrate can also be neglected. The gray layer, adjacent to the boundaries, was defined as the thin-film cathode material. The height of the film was designated as “d” and chosen in accordance with the actual thickness of the electrode films. The thickness of each LSM film was uniform across the array and was verified by profilometry. Distinct electrode arrays were produced with film thicknesses ranging from 60 to 3200 nm.

\[
\phi = 0
\]

\[
\phi = 1 \quad \phi = 1
\]

Figure 6.21: Schematic of the cross-sectional utilization model. A vertical sliced-cross-section was taken from the electrode array in order to portray the model domain. The black boundaries were assigned to represent the platinum current collectors, while the checkered boundary represents the electrically insulating electrolyte.

Since the electrode geometry is very well known, a computational model of sheet resistance was developed in order to predict the effect of sheet resistance on electrode performance. From the model, the total percentage of the cathode array utilized, defined
as the percent utilization, was estimated for a given geometry. For the thicker electrodes, the percent utilization was nearly 100% and changed very little. However, when applied to the films of 0.18 μm, 0.12 μm and 0.06 μm in height, the percent utilization dropped dramatically from 76.96% to 52.64%, and 30.64% respectively. The cumulative effect of a drop in utilization is displayed graphically in Figure 6.20. Specifically, in this figure all interfacial conductance values have been normalized to 100% utilization and re-plotted against the original values. From the shape of the corrected value curve further reductions in electrode thickness should yield dramatic increases in electrode performance.

**Conclusions**

The percent utilization figures demonstrate the effect of the overall sheet resistance and explain the interfacial phenomena for very thin films. Although the electrochemical performance of the 0.06 μm thick electrode should be the best due to facile ionic diffusion, with only roughly 30% of the cathode material utilized, the performance fell far short of expectations. Inefficient injection of electrons from the current collector to the LSM electrode strips is the cause of this behavior. Though the relatively high electronic conductivity of LSM is often cited as the materials primary advantage, the results presented here indicate that the electronic conductivity may be the limiting factor in the case of thin films.

The implication of these size limits impacts the rational design of LSM electrodes. On one hand, small grains have the large amounts of surface area necessary
for oxygen reduction. On the other hand, current collection limitations may reduce the effective utilization for very small particles. The critical thickness value of 0.36 µm provides an upper limit to the effective thickness of LSM particles. The lower limit will be determined by the geometry and current collection methods of the system.
CHAPTER 7

NANO-PATTERNED ELECTRODES

Abstract

Dense La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) electrodes were patterned by E-beam nanolithography and fabricated via pulsed-laser deposition on single crystal YSZ electrolytes. The electrode arrays maintained constant surface area and thickness while simultaneously varying TPB length. Patterned electrodes with a minimum feature size approaching 50nm were successfully fabricated and tested. Impedance measurements reveal a quantifiable relation between the TPB length of an LSM electrode and the cathodic interfacial resistance, implying that TPBs are the dominating sites for electrode reactions. Further, this relationship breaks down at very small feature sizes indicating an overlap of active regions and identifying the active TPB width.

Introduction

Recent developments in many areas, including this study, have also brought the inherent disadvantages of photolithography to the forefront. In short, photolithography is inherently limited by itself. Since it depends on visible light to expose the photoresist, feature resolution is then limited by the wavelength of light. Any features below 400nm are intrinsically impossible, though 1μm provides the practical limit for traditional photolithography.
Since the active width of the LSM TPB was found to be smaller than 1µm, new LSM electrode arrays were produced with feature sizes of 500, 100 and 50nm respectively, through E-beam nanolithography.

Results and Discussion

An SEM micrograph of an as-prepared 50nm LSM microelectrode array is displayed in Figure 7.1. While nano-electrode widths ranged from 500 to 50nm, the electrode thickness was held constant at 30nm. Nano-electrodes displayed similar control of feature sizes as their photolithographically produced counterparts. No cracking is evident along the edges of the nano-electrodes and spacing between the electrodes is uniform.
Figure 7.1: SEM image of LSM patterned nano-electrodes on a single crystal YSZ substrate. The electrode array was produced by E-beam nanolithography and pulsed laser deposition. Electrode strips are 50nm wide and 30nm in height.

A 30nm electrode height is clearly below the characteristic thickness for LSM and will therefore activate the electrode bulk path for oxygen reduction. At 30nm thickness, oxygen transport through the bulk of the electrode will be quite facile and will contribute significantly to the overall performance. However, by holding the electrode thickness and surface area constant, the only performance difference should be attributable to the TPB effect alone. A plot of Interfacial Conductance against TPB length is displayed in Figure 7.2.
Figure 7.2: Plot of Interfacial conductivity vs. TPB Length

Electrode feature sizes ranged from 100 μm to 50 nm.

In general, an upward trend is immediately evident at both electrode array indicating that cell performance does indeed improve with further reductions in feature sizes. At each temperature, smaller feature sizes yielded reduced interfacial polarization. However, the preliminary analysis requires modification to more accurately reflect the electrochemical data.

While consistent with each other, due to fabrication restraints, some of the geometrical parameters of the nano-electrodes were nevertheless different from the LSM electrode arrays produced by traditional photolithography. First, the total amount of surface area available for fabrication of nano-electrodes was slightly less than that available for LSM electrodes. Nano-electrodes used a 3mmx3mm square space on the
electrolyte producing a total surface coverage of 9mm$^2$ instead of the 36mm$^2$ surface coverage of the traditional electrode arrays. This change was made to accommodate the constraints of the E-beam equipment and fabricate electrodes in a timely manner. While a 36mm$^2$ array necessitates 300 10μm×6mm rectangular electrodes, a 36mm$^2$ array of 50nm×6mm rectangular electrodes would require more than 60,000 patterned lines. Obviously the time required to produce a pattern of this magnitude was absurd, so the size of the electrode array was reduced.

To account for the differences in surface area, nano-electrodes were normalized to surface area. Due to this transition, the standard method of plotting Interfacial conductance vs. TPB length must also be changed. A plot of Conductance vs. TPB length loses some meaning when an array of 2μm electrodes covering 36mm$^2$ surface area contains approximately the same TPB length as a 500nm electrode array covering 9mm$^2$ surface area. For simplicity, and in an effort to remain consistent with previous work, the TPB length of the nano-electrodes was normalized to the surface area of 36mm$^2$. With this normalization, Feature size and TPB length are again inversely proportional and direct comparisons can again be made.

Secondly, the thickness of the LSM electrodes was reduced from 0.26μm to 30nm to accommodate the difficulties of nanolithography. While the electrochemical surface contribution will change with thickness, the relationship of the electrode with the TPB should be constant since all electrodes are constant in thickness within their subset (traditional and nanolithographic). Furthermore, the electrochemical contribution due to
the electrode bulk should cancel when interfacial resistance is normalized to TPB length and plotted against TPB length. Figure 7.3 demonstrates a plot of interfacial conductance normalized.

![Graph showing log interfacial conductance vs. log TPB length](image)

Figure 7.3: Plot of Log Interfacial Conductance normalized to TPB length vs. Log TPB length. For electrodes of 500, 100 and 50nm, the polarization resistance and TPB length have been normalized to a constant surface area of 36mm².

One complication in the reduction of electrode thickness lies in the additional ohmic losses incorporated in the cell. In order to minimize these effects, two distinct approaches were used. First, the platinum current collector was improved in order to
reduce the spacing between current collecting strips from 490μm to 2μm. This served to significantly improve the percentage of the LSM electrode utilized. Secondly, the model also used to determine the sheet resistance of electrodes of varying thickness was again utilized to determine the losses to ohmic resistance. The details of the model are provided in the previous section. For nano-electrodes, utilization fell to 23.8%, 24.0% and 24.5% for electrodes of 50, 100 and 500nm respectively. Through normalizing to percent utilization, the actual cell performance could be compared with previous LSM data. Figure 7.4 presents a plot of Interfacial conductance against adjusted TPB length normalized to utilization percentage.
When normalized to TPB length, a new trend is evident. While the overall cell performance continues to increase with further reductions in feature size, the performance increases do not continue to scale with feature size. A slight downward trend can now be seen when interfacial conductance is normalized to TPB length.
Conclusions

Patterned electrodes with feature sizes approaching 50nm have been fabricated and tested using impedance spectroscopy. The triple phase boundary length was found to be inversely proportional to the interfacial resistance for LSM electrodes with low TPB length. Though a very slight downward trend can be seen in figure 7.4, increases in TPB length continue to improve cell performance down to very small feature sizes. The performance drop for the 100 and 50nm electrodes is within experimental error and does not clearly indicate any overlap of active regions. These results indicate the any width of the TPB may, in fact, be smaller than half the smallest feature size, or 25nm.
CHAPTER 8

PATTERNED ANODES

Abstract

In this study, patterned nickel anodes were fabricated and exposed to light hydrocarbon fuels. Raman spectroscopy was used to identify carbon species on the anode surface and to map the location of carbon deposition. It can be definitively shown that nickel is the preferred location for hydrocarbon cracking and coking of the electrode.

Introduction

While the progress of patterned electrodes may have reached its logical conclusion with this work, patterned electrodes may be useful in a variety of other studies. The geometric simplicity and precision allow for characterization of complex reaction mechanisms.

Solid oxide fuel cells are fast becoming the fuel cell of choice, as they are capable of internally reforming hydrocarbon fuels and are tolerant to CO as well as minimal levels of sulfur. Liquid hydrocarbon fuels are easy to store and cheap to produce and therefore provide a unique advantage over traditional hydrogen sources. However, for most materials, SOFC power density decreases when the fuel is switched from pure H\textsubscript{2} to
a hydrocarbon species (i.e. methane, propane, etc...) due to carbon deposition and/or decreased kinetics.\textsuperscript{94} It appears that electrode materials that make good reformers and achieve higher power densities are also the ones that suffer most from carbon deposition.\textsuperscript{95} Materials that are not as catalytic have shown the best durability to hydrocarbon fuels, while actually being enhanced by a limited amount of carbon deposition by increasing conductivity.\textsuperscript{96}

Considering that a liquid hydrocarbon fuel can be reformed to a mixture of gaseous $\text{H}_2$, $\text{CO}$, $\text{CO}_2$, $\text{H}_2\text{O}$, and light hydrocarbons, the specific interactions of the light hydrocarbons with the electrode surface need to be studied in-situ to understand and develop rational electrode designs that achieve higher power density.

\textit{Carbon Deposition on SOFC Anodes}

Although considerable efforts have been devoted to the development of electrode materials to deal with hydrocarbon fuels, very little progress has been made because a detailed understanding of the chemistry and electrochemistry on SOFC electrode surfaces is still lacking. The major technical challenge is to develop a set of in-situ characterization techniques capable of probing and mapping interfacial reactions at anode surfaces in an SOFC under practical operating conditions. While this study has successfully developed similar techniques for investigation of oxygen reduction mechanism at the cathode of an SOFC under practical operating conditions, the application of these techniques to the investigation of the anodic reactions in an SOFC is
still a challenge. It requires some significant efforts to overcome the difficulties associated with strong IR absorption of CO$_2$ and water, the inevitable products of fuel oxidation.

FTIR and Raman spectromicroscope with imaging and mapping capabilities will be used not only to determine what molecular processes are occurring on electrode surfaces but also to map where they are happening, identifying active reaction sites.

One of the unique advantages of SOFCs is the possibility of internal reforming or direct oxidation of practical fuels. Questions of particular interest to the SOFC community are how does coking evolve at an anode surface? What are the incipient molecular species formed on pristine anodes as a coking fuel is oxidized? As water is introduced into the feed gas what is the reaction pathway to complete oxidation? In-situ Raman spectroscopy of the anode surface under applied current will be used to follow the chemical evolution of carbon-containing species at the electrode/gas interface. Raman is also very sensitive to sulfur-related reactions at electrode surfaces, and sulfur reaction mechanisms could be studied in future trials. Some preliminary studies on coking and sulfur poisoning are presented here.

With quartz windows instead of KBr windows used in the construction of in-situ Raman-cells, catalysts can be studied at very high temperatures by Raman spectromicroscopy. Especially, when a high frequency excitation laser line is used, black body radiation does not necessarily overwhelm the Raman scattered light. Carbon
deposition and sulfur poisoning are the main causes of severe degradation of anodes in hydrocarbon-fueled SOFCs. Carbon and sulfur on the anodes during the operation of SOFCs can be readily identified. This technique renders possible the determination of structural inhomogeneities in electrode materials, the characterization of structural changes occurring in electrode materials during the reaction, the unravelment of the actual catalytically active species, and the monitoring of catalyst deactivation processes.

**Results and Discussion: Carbon Deposition**

Nickel patterned electrodes have been fabricated and tested. Raman spectroscopy was used to develop a baseline spectrum for a bare nickel anode. This baseline will be used in comparison to cells analyzed after cell tests in hydrocarbon fuels.

Raman Spectroscopy of patterned Ni microelectrode cells yielded the well-defined spectra presented in Figure 8.1. Several distinct peaks are discernible in the spectra, particularly those centered around wavelengths of $220\text{cm}^{-1}$, $494\text{cm}^{-1}$ and $623\text{cm}^{-1}$. These three peaks have previously been attributed to YSZ and independently verified. Since the patterned electrode arrays are fabricated using thin film techniques, the nickel anode layers are particularly thin; between 200 and 600nm in thickness.
Raman spectroscopy analyzes the wavelength and intensity of inelastically scattered light from the object surface. The Raman scattered light is phase shifted in wavelength from the incident light by the exact energies of the molecular vibrations. When incident light from an Argon laser impinges on the sample, some of the light is scattered back to the detector. The vibration of the molecules causes a shift in wavelength, which is recorded by the detector. In this way, Raman spectroscopy is able to determine specific characteristics about the surface.

However, since the laser impacts many more molecules than simply the top layer, the true interaction volume of Raman spectroscopy exceeds the depth of the surface and
can be quite large. Vibrational results from the entire interaction volume are recorded in the spectra, so it is no surprise that the YSZ substrate will “shine” through the thin nickel anodes.

Outside of those associated with YSZ, no other peaks were identified. This indicates that the nickel is likely not Raman active. As with most metals, the free electrons in nickel serve to swamp any Raman shift associated with the material. As a consequence, no Raman peaks will be seen from the anode, thereby leaving a relatively clean background for future studies. In short, Raman mapping of surface adsorbed carbon on nickel anodes due to coking in hydrocarbon fuels is possible.

Once a baseline for the nickel patterned anodes was developed, each cell was exposed to a 50% methane gas stream at 750°C for a specified period of time ranging from 15 minutes to 4 hrs. After exposure, SEM, EDS and Raman spectroscopy were used to analyze the carbon formation upon the Ni anode. Figures 8.2 (a&c) are SEM images of patterned nickel cells exposed to the 50% methane stream for 0.25 and 4 hours respectively. Corresponding EDS maps are shown in Figures 8.2 (b&d). In figure 8.2a, carbon formation is not readily apparent, and the patterned nickel anodes can be seen clearly. In this SEM image the dark regions are the patterned nickel while the light regions reflect the surface of the YSZ substrate. Conversely, in figure 8.2c, graphitic carbon has completely overgrown the cell thereby obscuring the actual nickel electrode. It should be noted that while EDS was able to detect the presence of carbon, mapping
was unable to accurately identify specific high-density locations. For this reason, Raman mapping was undertaken to improve mapping functions.

Figures 8.2 (a-d): Figures a and b are SEM and EDS images respectively of a patterned nickel anode exposed to a 50% methane gas stream at 750°C for 15 minutes. Carbon is not visually apparent in the SEM image, but EDS confirms its existence. Figures c and d are SEM and EDS images of a patterned nickel anode exposed to a 50% methane gas stream at 750°C for 4 hours. Graphitic carbon is readily apparent in the form of long strands enveloping the entire cell. EDS again confirms the existence of carbon formation.
Figure 8.3 is a Raman spectra of carbon deposition on the same patterned Ni cell used for the SEM and EDS in figures 6.2 (a&b). Much like the spectra presented in Figure 8.1, the spectra in Figure 8.3 shows intensity peaks at 220cm\(^{-1}\), 494cm\(^{-1}\) and 623cm\(^{-1}\) corresponding to the YSZ substrate. However, in addition to these peaks, the spectra in Figure 8.3 shows another dominant peak at 1588cm\(^{-1}\). This peak has been attributed to the sp\(^3\)-bonded carbon and appears to be amorphous.

Figure 8.3: Raman spectra of sp\(^3\)-bonded carbon on patterned nickel substrate, 1 micron resolution. The characteristic YSZ peaks seen at wavelengths of 220cm\(^{-1}\), 494cm\(^{-1}\) and 623cm\(^{-1}\) respectively are still evident, while the formation of amorphous sp\(^3\)-bonded carbon arises at 1588cm\(^{-1}\).

Figure 8.4 is a Raman map of carbon on the same patterned Ni cell used in Figures 8.2 (a&b) and 8.3. The Raman map was superimposed over an optical image of the cell for convenience. It is readily evident from the Raman mapping that the vast majority of carbon deposition occurred on the Nickel anodes rather than the YSZ.
substrate. From this we can conclude, as expected, that nickel is the preferred location for hydrocarbon cracking and coking of the electrode. When combined with the eventual coking of the entire cell, as shown in Figures 8.2 (c&d), we can postulate that carbon deposition degrades cell performance by gradually overwhelming the entire nickel surface, thereby steadily eliminating active sites for hydrocarbon reduction.

Figure 8.4 Raman map of sp\(^3\)-bonded carbon, 2 micron resolution, superimposed over an optical image of the patterned Ni electrode after exposure to 50\% methane gas for 15 minutes. Dark regions in the optical image are Nickel while the light regions are the YSZ substrate.

**Conclusions**

Patterned nickel anodes have been successfully fabricated and tested under hydrocarbon gas streams. Raman spectroscopy has been shown to be uniquely sensitive to elemental and graphitic carbon on patterned anodes. Further, Raman mapping has demonstrated that the vast majority of carbon deposition occurs initially on the nickel...
component of the anode, while leaving exposed electrolyte unaffected. From this we can
conclude, as expected, that nickel is the preferred location for hydrocarbon cracking and
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eliminating active sites for hydrocarbon reduction.
CHAPTER 9

CONCLUSIONS

9.1 Photolithographic and Nanolithographic Processing Capabilities

In this study, we have successfully developed a microfabrication process capable of producing well-defined three-dimensional geometries. SEM and EDXS micrographs confirm that a photolithographic process is indeed capable of producing patterned electrodes that satisfy the demands for accurate measurement. Furthermore, we have developed an improved procedure for selective determination of the relative importance of the MIEC surface in relation to the TPB. This cell provides a proof of concept towards the possibility of selecting particular components for study. By eliminating possible reaction paths, it may be possible to observe each individual path for reductions at an MIEC electrode, thereby completing a map of the reaction processes including relative contributions from each individual path.

The process presented here capitalizes on the many advantages of microelectrodes in solid state ionics while simultaneously allowing for easier measurement and interpretation. Averaging over an array of microelectrodes yields performance results that depend on the comprehensive properties of the material rather than the characteristics of individual sites. For many studies this would be a significant improvement as the information derived is more directly relevant to real systems. The process can be further expanded to determine the relative importance of the active sites for fuel cell reactions.
9.2 Characterization of Thin Films

The developed methodology was used to investigate the temperature-dependant behavior of mixed conducting materials as fabricated by PLD. Films of both LSM and LSC were shown to vary with deposition temperature and substrate material. The films were characterized through SEM microscopy, impedance spectroscopy, and temperature dependant X-ray diffraction.

High temperature deposition, above 500°C, resulted in thin dense films in the orthorhombic and rhombohedral phases respectively. These films were stoichiometrically consistent with the target materials and underwent no phase changes upon annealing. Crystalline films generated by PLD displayed ideal resistive behavior.

Conversely, low temperature deposition yielded stoichiometrically accurate, though amorphous, thin films. Upon annealing, both LSM and LSC amorphous films underwent a phase change to the crystalline phase. In both cases the phase change was rapid. For an amorphous LSM film on a YSZ substrate, the devitrification point was 550°C. For a likewise amorphous LSC film on YSZ, the phase change occurred at 700°C. For thin films on silicon substrates, the phase changes both occurred at roughly 100°C cooler temperatures. Impedance spectra displayed a small impedance loop in addition to the dominant bulk resistance. LSM and LSC films showed resistive behavior, yielding conductivity values at 600°C of 11.5 S/cm and 221 S/cm, respectively.
Upon annealing, both films undergo phase changes to the perovskite phase at temperatures significantly below the firing temperatures required for more traditional methods of film preparation. While the high resistance of amorphous films makes them unlikely candidates for low-temperature fuel cells, the low devitrification temperature opens possibilities for unique fabrication methods. Since PLD produced films of useful phases without high-temperature annealing, it holds promise for low-temperature fabrication of SOFCs.

9.3 The TPB Effect: Platinum

The triple phase boundary length was found to be inversely proportional to the interfacial resistance for platinum electrodes with low TPB length in which the width of the electrode strips and the gaps between adjacent strips are greater than the effective width of the TPB. The results attained at electrodes with longer TPB length and elevated temperature indicate that the linear relationship between the TPB length and the interfacial resistance is no longer true, implying that the width of the electrode strips or the gaps between adjacent strips are no longer greater than the effective width of the TPB. While the results confirm the linear relationship of TPB length to interfacial resistance at low ratios of TPB length to surface area, this relationship breaks down as bulk conduction through the MIEC electrode becomes significant.
Furthermore, the effective area of the TPB was found to be much larger than the minimum 2µm feature size at temperatures above 650°C. While it is currently impractical to clearly determine which reaction path is the limiting factor, further work is underway which should elucidate the mechanism. Results of the electrode height study indicate the importance of bulk ionic diffusion in the electrode. Though LSM is a poor ionic conductor, the thin-film nature of the patterned electrodes allowed bulk diffusion at high temperatures.

These initial findings were based solely on the use of dense LSM electrodes, but continued research is underway to expand the reach of this investigation into other mixed conducting electrodes, composites and three-dimensional structures. These further investigations should provide additional insight into active reaction sites, reaction mechanisms and better electrode architecture of mixed conducting electrodes. It is evident that this process can be used to determine the active area for a variety of electrodes leading to direct improvements in electrode design.

9.4 The TPB Effect: LSM

The triple phase boundary length was found to be inversely proportional to the interfacial resistance for LSM electrodes in which the width of the electrode strips and the gaps between adjacent strips are greater than the effective width of the TPB. Though a very slight downward trend can be seen in figure 7.4, increases in TPB length continue to improve cell performance down to very small feature sizes. The
performance drop for the 100 and 50nm electrodes is within experimental error and does not clearly indicate any overlap of active regions. These results indicate the any width of the TPB may, in fact, be smaller than half the smallest feature size, or 25nm.

Results of the electrode height study indicate the importance of bulk ionic diffusion in the electrode. Though LSM is a poor ionic conductor, the thin-film nature of the patterned electrodes allowed bulk diffusion at high temperatures. In spite of the substantial contribution due to bulk diffusion, additional TPB length continued to contribute even at small feature sizes. While the importance of the electrode bulk increases in relative importance, no active width could be determined for the TPB indicating that the TPBs are an excellent method to substantially improve cell performance.

These initial findings were based solely on the use of dense LSM electrodes, but continued research to expand the reach of this investigation into other mixed conducting electrodes, composites and three-dimensional structures could prove beneficial. These further investigations should provide additional insight into active reaction sites, reaction mechanisms of alternative materials. It is evident that this process can be used to determine the active area for a large variety of electrodes leading to direct improvements in electrode design.
9.5 Characteristic Thickness

This study has demonstrated the effect of electrode thickness on the performance of dense LSM electrodes. Furthermore, the necessary conditions for mixed conducting behavior have been drawn out. It has been shown that the characteristic thickness of a dense LSM electrode varies with temperature and depends heavily on the ionic conductivity. The characteristic thickness at 700°C for dense LSM was found to be 0.36 μm. Above 0.36 μm, ionic diffusion is sufficiently difficult such that oxygen ion transport through the LSM electrode is essentially negligible. Beyond this point the surface of LSM electrodes cannot be effectively used and the behavior of the electrode is determined largely by the TPBs of the electrodes.

Furthermore, it has been shown that for very thin electrodes, the sheet resistance may dramatically reduce the effective utilization. For the defined geometry of this experiment, electrical effects dominate the performance of the electrode for thicknesses below 0.18μm. At this point, the local overpotential drops and the entire surface area can no longer be assumed active. Computational modeling techniques have been used to demonstrate a corresponding drop in the effective utilization of the cathode with decreasing thickness.

This work has implications for the highly porous electrodes more common for industrial applications. Specifically, though much effort has been expended to find materials of greater ionic conductivity, it appears that electrodes with very complex pore
networks may be limited not by ionic conductivity, but rather by electronic conductivity very near the electrode/electrolyte interface.

**9.6 Patterned Anodes**

Patterned nickel anodes have been successfully fabricated and tested under hydrocarbon gas streams. Raman spectroscopy has been shown to be uniquely sensitive to elemental and graphitic carbon on patterned anodes. Further, Raman mapping has demonstrated that the vast majority of carbon deposition occurs initially on the nickel component of the anode, while leaving exposed electrolyte unaffected. From this we can conclude, as expected, that nickel is the preferred location for hydrocarbon cracking and coking of the electrode. When combined with the eventual coking of the entire cell we can postulate that carbon deposition degrades cell performance by gradually overwhelming the entire nickel surface, thereby steadily eliminating active sites for hydrocarbon reduction.

**9.7 Final Conclusions**

With current technology, the TPB study has been carried as far as possible. Nano-lithography has hit its practical limitations at 50nm and further reductions in feature size may not be practical. Minor improvements may be made using this method with significantly more time and funding, but the cost seem to far outweigh the benefits of pursuing this study further with these methods. The fabrication process developed
here is capable of producing precisely controlled structures down to 50nm on almost any insulating substrate.

Furthermore, some of the fundamental properties of commonly used cathode materials have been drawn out. In addition to the active width of the TPB, a characteristic thickness has been defined for LSM. The thin films prepared for this work have been thoroughly characterized and the transition temperatures determined.

By understanding the critical dimensions required in the case of metal and mixed conducting electrodes, electrode microstructures can now be optimized to minimize interfacial losses. With patterned electrodes of precisely controlled geometries, active reaction sites, surface characteristics, and the width of triple-phase boundaries (TPBs) were systematically studied and determined. These characteristic values can now be used to verify the prediction of theoretical calculations.
APPENDIX A

DESCRIPTION OF DEFAULT SUBHEADING SCHEME

Inclusive here is the full description of the program file used with the JEOL JBX-9300 E-Beam lithography system. A sample program, Erik11, was used for demonstration, but each program file was adapted to the specific needs of the pattern.

The Jobdeck or .jdf file will now be explained line by line

;--------------------------------
JOB/W 'ERIK10',3 ;piece cassette
;--------------------------------
PATH ERIK
ARRAY (-1600,2, 3200)/(850,2,-1700)
ASSIGN P(1) -> ((*,*),MD1)
AEND
PEND
;--------------------------------
;Layer Definition
;--------------------------------
LAYER1
p(1) ‘EN_500.v30’
SPPRM 4.0,.,1.0,1
MD1: MODULAT ((0,0))
STDCUR 2.0
END
1. ;--------------------------------------------------

   This is a dummy line. “;” Means that the line is a comment.

2. JOB/W 'ERIK10',3

   “JOB” declares the beginning of the jobdeck file.

   “/W” specifies that writing will occur on a wafer or the piece cassette. The piece cassette was ideal for this project since it was able to provide support for substrates as small as 4mm²

   “'ERIK10'” is the name of the jobdeck.

   “3” designates in this case writing will occur using piece cassette. This is reiterated by the comment “;piece cassette.”

3. PATH ERIK

   “ERIK” is the PATH that defines what calibration routines to run before and periodically during pattern writing. The PATH is defined in the file

   /usr/users/eb0/ebtest/eb/prm/calib.men

   In this calib.men file are contained the following statements (there are many of these, this just the calibration file used for this project.):
So for the particular PATH called ERIK, the INITIAL command means that the calibration routines CURRNT,INITBE,PDEFBE,SUBDEFBE will be run before writing the pattern. The CYCLIC command means that the calibration routine CURRNT will be run every 20 minutes, as defined by the CYCLE 20M command, during pattern writing.

INITBE sequences the beam with the stage while PDEFBE and SUBDEFBE sequence the position deflectors and subdeflectors with the stage. These three calibration tests ensure that the position of the stage, and therefore the substrate, is calibrated with the position of the beam. CURRNT calibrates the beam current to ensure accuracy of the applied dose. Since the current can drift during a long exposure, it is recalibrated every 20 minutes to ensure accurate exposure.

4. ARRAY (-1600,2,1600)/(1500,3,-1100)

The ARRAY command allows a pattern to be placed as an array. The ARRAY command has the format

ARRAY ( x, m, p ) / ( y, n, q )

Where:
x = X-coordinate (in microns) of array start point with reference to the coordinate system having its origin at the substrate center

m = Number of array points along the X direction (towards the right)

p = Pitch (in microns) between adjacent array points along the X direction (towards the right)

y = Y-coordinate of array start point with reference to the coordinate system having its origin at the substrate center

n = Number of array points along the Y direction (towards the bottom)

q = Pitch (in microns) between adjacent array points along the Y direction (towards the bottom)

Since a 9mm\(^2\) pattern of 50nm lines would contain 30,000 3mm long lines, the aspect ration problems become severe. AutoCAD is not able to produce arrays of this magnitude, but even if it were, problems during writing would be substantial. In addition to further complications with the proximity effect, the write time of the JEOL-9300 for each pattern would exceed 12 hours further complicating calibration and increasing the risk of a compound problem. For these reasons, the 9mm\(^2\) array was broken down into six 1.5x1mm arrays repeated six times. This yielded the equivalent surface area and nearly equivalent TPB length in an easier to process manner.

5. ASSIGN P(1) -> ((*,*),MD1)
This command assigns \( P(1) \) which is pattern one to all \( x,y \) locations \((*,*)\) in the array (defined by the previous line).

“MD1” defines shot modulation to be applied to the different data types in \( P(1) \).

6. **AEND**

   End of the ARRAY command.

7. **PEND**

   End of the PATH command.

8. **LAYER 1**

   Specifies the beginning of Layer 1. The nominal base dose is later associated with each Layer in the .sdf file. Shot rank modulation percentage is referenced to base dose.

9. **P(1) 'EN_500.v30'**

   Defines pattern one, \( P(1) \), to be “EN_500.v30”.

   This is an array of 500nm

10. **SPPRM 4.0,,,,1.0,1**

    The SPPRM command specifies shot-partition parameters for each writing chip pattern. The SPPRM command has the format:
SPPRM m1, m2, w, p, sc, ss

m1 = defines one side (in microns) of the square area to be written by the sub deflector. default and maximum is 4.
m2 = this parameter is left blank as it is the square of m1
w = this parameter is left blank as it has no application for the JBX-9300FS
p = this parameter is left blank as it has no application for the JBX-9300FS
sc = specifies the magnification or reduction ratio of scaling for pattern writing
ss = Specifies the shift amount for the sub deflector scanning area when shot-shift writing is performed. when ss = 1, no shift occurs. when ss = 2, the initial sub fields are written with half the dose, then the sub fields are shifted by half the scan width and is exposed with half the dose.

11. **STDCUR 2.0**

STDCUR defines the beam current to be used in units of nA.

“2.0” stands for 2.0nA.

12. **MD1: MODULAT (0,0)**

This command defines the shot modulation for the applicable pattern as used in the ARRAY command.

“(0,0)” means that data type = 0, receives the base dose + 0%. For example, if the base dose is 225µC/cm², then data type = 0 would receive a total dose of
225μC/cm². This can be easily changed in order to alter the dosage applied to the pattern. For example, “(0,100)” would mean that data type = 0 (used in every application for this project) would receive the base dose + 100% for a total of 450μC/cm².

13. END

This command ends the job deck file.

;------------------------

The Scheduler, or .sdf, file will now be explained, line by line.

MAGAZIN 'ERIK10'

#1
%3D
JDF 'ERIK10',1
ACC 100
CALPRM '100kv_2nA'
DEFMODE 2 ;2 stage deflection
RESIST 225 ;(Base Dose is 225μC/cm²)
SHOT A, 5 ;(Shot time is automatic with shotpitch set to 5nm)
OFFSET (-1500,0)

END 1

1. MAGAZIN 'ERIK10'

This command defines the beginning of the schedule file. It is convenient to keep the name of the .jdf, .sdf, and MAGAZIN to all be the same.
2. \#1

This command specifies the beginning of a cassette block and the substrates to be used for pattern writing.

3. \%3D

“3” specifies that the piece cassette is to be used.

“D” defines that window D in the piece cassette is to be used. Window D is of a size that best fits the 1cm$^2$ single crystal YSZ substrates.

4. JDF 'ERIK10',1

‘ERIK10’ specifies that the job deck file “ERIK10.jdf” is to be used.

“1” specifies that all subsequent statements refer to Layer 1 of the .jdf file.

5. ACC 100

This specifies that the accelerating voltage is 100kV.

6. CALPRM ’100kv_2nA’

This specifies that the calibration parameters associated with the calibration file “100kv_2nA”. Furthermore, the naming convention of the calibration file lets the user know it is for use with 100kV accelerating voltage and 2nA beam current.

7. DEFMODE 2
This specifies the e-beam deflection stage(s) using a number (1 for single-stage or
2 for double-stage) for pattern writing. The single-stage e-beam deflection can
perform more-accurate pattern writing, while the double-stage e-beam deflection
can perform pattern writing in a shorter time. Since resolution was limited in this
case by the charging and the proximity effect, and not limited by resolution of the
tool, deflection mode 2 could be used to minimize exposure time.

8. **RESIST 225**

Defines the base dose applied to the resist, in this case 225μC/cm².

9. **SHOT A,5**

“A” specifies that the shot time is to be automatically determined from the
sensitivity of the resist and the amount of beam current for writing.

“5” specifies that the shot pitch is 5nm.

The minimum shotpitch is

10. **OFFSET (0,2000)**

This command specifies that all patterns as defined in the Job Deck File will be
offset in the X direction by 0 microns and offset in the Y direction by 2000
microns (towards the top of the wafer.)

11. **END 1**

This command signifies the end of the schedule file.
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