INVESTIGATION OF OXYGEN REDUCTION MECHANISMS USING CATHODE MICROELECTRODES PART I: EXPERIMENTAL ANALYSIS OF La$_{1-x}$Sr$_x$MnO$_{3-d}$ AND PLATINUM

Gerardo Jose la O$^a$, Bilge Yildiz$^b$, and Yang Shao-Horn$^a$

$^a$Electrochemical Energy Laboratory
Massachusetts Institute of Technology
Cambridge, MA 02139

$^b$Argonne National Laboratory, Argonne, IL 60439, USA

ABSTRACT

Oxygen reduction reactions (ORR) on La$_{1-x}$Sr$_x$MnO$_{3-d}$ are currently not well understood and no final agreement on the precise oxygen reduction rate-determining step(s) has been made. To investigate ORR, we fabricated thin-film microelectrodes of La$_{1-x}$Sr$_x$MnO$_{3-d}$ and platinum (Pt) by RF-sputtering and patterning via photolithography to obtain precisely defined electrode geometries and features. These were then tested using impedance spectroscopy and under varying conditions such as DC bias, oxygen partial pressure, and current treatment. For the Pt microelectrode, we observed two distinct semicircles and attributed these to processes related to ionic conduction in the electrolyte and an oxygen adsorption at the Pt cathode. For La$_{1-x}$Sr$_x$MnO$_{3-d}$, we found that varying annealing temperatures of the thin films after deposition resulted in different impedance response. Varying oxygen partial pressure, DC bias, and current treatment was also found to affect the electrode impedance response in both Pt and La$_{1-x}$Sr$_x$MnO$_{3-d}$ but had no effect on the electrolyte.

INTRODUCTION

The solid oxide fuel cell (SOFCs) is an all-ceramic energy conversion device that conventionally operates at temperatures above 800°C for enhanced power performance, minimized resistive losses, and high-grade heat byproduct that can be used for heating or other recuperative cycles. Recently, however, there has been aggressive efforts to reduce SOFC operating temperature to lower the overall cost of the system by replacing expensive interconnect materials such as lanthanum chromite with cheaper oxidation resistant steels as well as simplifying gas sealing of SOFC stacks. Lower operating temperatures, however, result in an increase in electrolyte resistive and electrode polarization losses. Therefore understanding the fundamental mechanisms that govern the reactions in these electrochemical devices have taken on great interest. In particular, the oxygen reduction reactions (ORR) that take place along the cathode-electrolyte interface, cathode surface, and three-phase boundaries (tpb) are crucial areas. ORR on the typical SOFC cathode strontium-doped LaMnO$_3$ has been extensively studied for over two decades by numerous research groups, however to date, there is still no agreement on the exact reaction pathway and rate limiting step (rls) (1,2,3,4,5,6,7,8). Moreover, ORR in the cathode is currently the principal contributor to the performance loss in low temperature SOFCs limiting efficient operation to temperatures above 800°C.
The aim of this paper is therefore the investigation of the ORR phenomenon along the cathode, and for this study focusing on platinum (Pt) and La_{0.8}Sr_{0.2}MnO_{3-d} (LSM) materials and utilizing microfabrication techniques to accurately pattern these. This paper is one section of a two-part study, where the focus in the second section is the analytical modeling of AC impedance response from specific oxygen reduction mechanisms on LSM/8YSZ. In the literature, previous thin-film and patterned electrodes have been fabricated for electrochemical characterization and tested (9,10,11,12). This study was performed using thin-film sputtered cathode and electrolytes with single crystalline silicon (Si) as substrate. After patterning the cathodes via photolithography, the films were then either heat treated and/or examined using scanning electron microscopy (SEM) and optical microscopy (OM) to determine surface microstructure. X-ray diffraction (XRD) was used to analyze material crystal structure and phase of the LSM film. Electrochemical impedance spectroscopy (EIS) in conjunction with a microprobe station was then used to examine the electrochemical properties of the sputtered cathodes. EIS tests were performed under varying temperatures, DC bias, current treatment and partial pressure of oxygen (PO₂).

**EXPERIMENTAL**

The microelectrode samples used in this study were prepared by initially depositing 8mol% Y_{2}O_{3}-stabilized ZrO_{2} (8YSZ) (Praxair Specialty Ceramics, Woodinville, WA, USA) using radio-frequency (RF) sputtering (Materials Research Corporation, Orangeburg, NY, USA) on double-side polished Si wafers with (111) orientation and 500µm thickness. The electrolyte 8YSZ was sputtered onto the entire Si wafer surface with plasma power of 1.6 W/cm\(^2\) under argon to oxygen ratio of 7.5:1 for 3 hours in unheated conditions. The deposited film was then annealed in an air furnace at 800°C for 3hrs to crystallize. Cathode microelectrodes of LSM (Praxair Specialty Ceramics, Woodinville, WA, USA) and Pt (Materials Research Corporation, Orangeburg, NY, USA) were deposited then subsequently patterned and tested for this study. The LSM cathode microelectrodes were fabricated by initially sputtering LSM on top of the 8YSZ layer with plasma power of 1.2 W/cm\(^2\) under identical argon to oxygen ratios for 2 hours using a heated substrate with temperatures above 500°C. The LSM film was then patterned by spin-coating positive photoresist (Microposit SC 1287, Shipley Corporation, Marlborough, MA, USA) on the entire surface then exposing under a photomask followed by photoresist developing and finally etching exposed LSM areas with aqua regia (3HCl:1HNO₃) for 5 to 7 minutes. After etching, the Si substrate, with 8YSZ and LSM microelectrodes, was then annealed in an air furnace at 800°C to 900°C for 10 hrs to fully crystallize LSM. The Pt microelectrodes, on the other hand, were patterned using lift-off photolithography. Image-reversal photoresist (AZ5214 Clariant, Basel, Switzerland) was first spin-coated on the 8YSZ layer, exposed under a photomask, and finally developed. A Pt film was then sputtered on top of the photoresist with plasma power of 0.4 W/cm\(^2\) in argon atmosphere for 20 minutes using unheated substrate. Pt microelectrodes were finally obtained by dissolving away the image-reversal photoresist in acetone. All cathode microelectrodes fabricated for this study had dimensions of ~100µm length x ~30µm width and were spaced ~40µm apart.

Atomic force microscopy (AFM) and stylus contact profilometry (both from Veeco, Santa Barbara, CA, USA) measurements were made on the sputtered LSM film and Pt
film, respectively, for microelectrode film thickness determination. XRD analysis (Rigaku RU300, Tokyo, Japan) using glancing angle mode setup for thin films was performed on the LSM sputtered film before and after annealing. The XRD scans were performed from angles 25° to 75° 2-theta using a copper (Cu) X-ray source. In addition, the microelectrodes were also examined using SEM (JEOL 6320FV Field Emission SEM, Peabody, MA) and OM (Mitutoyo FS-70Z, Aurora, IL, USA) to analyze surface quality and morphology. EIS measurements were conducted using a microprobe station (Suss Microtech PM5, Munich, Germany) with temperature controlled stage (Linkam TS1500, Surrey, UK) connected to a frequency response analyzer (FRA) (Solartron 1260, Farnborough UK) and a PC (Dell Dimension, Austin, TX, USA). EIS measurements were conducted using two adjacent cathode microelectrodes spaced ~40µm apart on the 8YSZ film. Tungsten carbide (WC) probe tips with tip radius of 2microns were used to electrically contact each cathode microelectrode for EIS tests. EIS tests were performed from 800°C to 600°C and under ambient atmospheric conditions (PO₂ of 0.21atm) and varied oxygen concentrations (PO₂ of ~1atm, ~10⁻²atm, ~10⁻³atm, and ~10⁻⁴atm). The schematic of microelectrode testing configuration is presented in Figure 1. The EIS measurements were conducted from 10MHz to 1Hz with AC amplitude set at 50mV and DC bias varied from 0mV to 500mV. In addition, current conditioning tests were also performed on the microelectrodes by applying 100mA/cm² for 5 minutes before EIS measurements. A new set of microelectrodes were used for each testing condition to remove any testing history effects.

Figure 1. Schematic of cathode microelectrode and testing configuration used in EIS (not drawn to scale).

RESULTS AND DISCUSSION

Microstructure

The structure and quality of the microelectrodes after sputtering deposition and after LSM annealing were examined by SEM and optical microscopy. Figure 2 presents the surface of the Pt and LSM microelectrodes after photolithography. Both Pt and LSM microelectrodes exhibited smooth surfaces with microelectrodes geometries found to be

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in close agreement with the photomask used in outlining the patterns. The Pt electrodes processed via lift-off photolithography exhibited close to vertical side walls and had good adherence to the 8YSZ film. The LSM electrodes processed by aqua regia etching also had good adherence to the 8YSZ film however this exhibited some undercut etching leading to sloped side walls as seen in the AFM scans presented in Figure 3. Undercutting of the LSM film was found to be controlled by the quality of photoresist adherence on the LSM film. Various photoresists, exposure, and developing conditions were tested and further improvements are required to obtain LSM vertical side walls and better geometric control.

The LSM film after annealing at 800°C or 900°C for 10 hours was observed to have clean and crack-free surfaces. Film thickness was measured to be ~175nm and ~350nm for Pt and LSM, respectively. Previous processing results have shown the 8YSZ film to be ~620nm under these deposition conditions.

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X-Ray Diffraction

XRD analysis of the LSM film after deposition and annealing is presented in Figure 4. Characteristic peaks from 8YSZ and LSM are observed. 8YSZ peak positions are found to be in agreement with the target material and the Joint Committee on Powder Diffraction Standards (JCPDS) card #30-1468. LSM, on the other hand, is found to be in relatively close agreement after deposition with the stoichiometric target material and JCPDS card #40-1100. However, peak shifting to higher 2-theta values is observed after annealing at both 800°C and 900°C for 10 hours. Previous elemental analysis results from these sputtered LSM films have shown La rich and Sr, Mn deficient films. The XRD peak shifting therefore arises from the nonstoichiometry. To resolve this issue, varying target material stoichiometry or changing the deposition technique is required.

Electrochemical Impedance Spectroscopy

Pt microelectrodes Typical EIS data from Pt microelectrodes at 800°C under PO2 of 0.21 atm is presented in Figure 5. Two semicircles were readily apparent in these tests with the polarization observed to increase as testing temperature is decreased. Activation energies were obtained by semicircle fitting the data from 800°C to 740°C in 20°C increments. The activation energies were determined to be 1.01eV and 2.18eV for the high frequency and low frequency semicircles, respectively. Numerous literature studies have reported ~1eV for the high frequency semicircle and have attributed this to the electrolyte ionic conduction (5,7,13,14,15). In addition, a good agreement is found when comparing the high frequency semicircle resistance to literature 8YSZ resistance (16) confirming that this regime is due to the electrolyte contribution.
The low frequency arc on the other hand is attributed to processes at the Pt electrode. As shown in Figure 6a, varying PO2 has no effect on the high frequency impedance response of 8YSZ, however, this has changed the impedance response of the Pt electrode. By observing the effect of Pt electrode polarization as a function of PO2, it was calculated that $1/R_{Pt} \propto PO_2^{1/5}$. According to Takeda and coworkers (1) who studied cathodic polarization phenomena on various perovskite oxides, a relationship where $PO_2^n$ and given $n = \frac{1}{4}$ can be correlated to an oxygen atom adsorption process. The activation energy of 2.18eV observed in this study is also in close agreement with values reported by Takeda for the oxygen adsorption process. Therefore, most probably an oxygen adsorption process dominates the low frequency response. In Figure 6b, changes in the DC bias conditions were made during EIS testing. No significant change in electrolyte response was observed in these tests, however, electrode response was found to increase in as DC bias approached 400mV. Applying DC bias changes the kinetics and possibly the dominating reaction pathways on Pt electrodes. Further tests are required to elucidate what changes are occurring during these tests.

![Figure 5. Typical Nyquist plot of impedance data from Pt microelectrodes obtained at 800°C under PO2 of 0.21 atm. The numbers in the diagram are the frequency logarithms.](image)

![Figure 6. (a) Nyquist plot of impedance data from Pt microelectrodes as a function of PO2 at 800°C. PO2 of ~10^{-2} atm (□), ~10^{-3} atm (○), ~10^{-4} atm(△). (b) Dependence of Pt microelectrode impedance on DC bias at 800°C and PO2 of 0.21 atm. DC bias of 0mV(■), 300mV (○,●), 400mV (△), 500mV (◊). The numbers in the diagram are the frequency logarithms.](image)
In addition, current conditioning tests were also performed prior to EIS measurements and this is presented in Figure 7a. Figure 7b shows the change in electrode morphology after current conditioning of 100mA/cm² for 5 minutes. The high frequency impedance response is again found to be unaffected by current conditioning however the low frequency electrode process is significantly altered by current treatment. Similar types of phenomena using Pt porous electrodes have been observed by Sridhar and coworkers (17,18) and has been attributed to a removal of oxygen containing species at the Pt surface leading to faster oxygen diffusion towards the tpb and eventual transfer into the electrolyte. Similar effects are most likely occurring in these tests. In addition, surface morphological changes are apparent with these microelectrodes which were not observed in studies by Sridhar. Investigations into these surface morphological changes are to be performed to fully understand the enhancement brought about by current conditioning.

**Figure 7.** (a) Impedance spectra of Pt microelectrodes before and after 100mA/cm² for 5 mins current treatment. (b) Optical micrograph of Pt electrodes after current treatment, detailed are locations for oxidation and reduction reactions during current treatment. Microelectrode damage is due to repeated microprobe contacts. The numbers in the diagram are the frequency logarithms.

**LSM microelectrodes** Typical EIS data at a test temperature of 760°C and PO₂ of 0.21 atm from LSM microelectrodes annealed at 800°C and 900°C for 10 hours is presented in Figure 8a and Figure 8b, respectively. Two semicircles are visible in the 800°C annealed sample. Three semicircles, on the other hand, are evident for the 900°C annealed sample. Impedance data at frequencies below 10Hz were found to have significant scatter and were not included here. This scatter was the result of instrument impedance limitation and higher impedance instruments are required to overcome this. Activation energies were calculated from EIS tests performed in the range of 800°C to 600°C using 20°C increments. For the 800°C annealed sample, activation energies were determined to be 1.01eV and 1.12eV for high and low frequency semicircles, respectively. Significant scatter in data was observed in the low frequency semicircle leading to large uncertainty in this measured activation energy. For the 900°C annealed sample, activation energies were determined to be 1.03eV, 0.92eV and 1.35eV for high, middle, and low frequency semicircles, respectively. The high (and middle) frequency impedance responses for both electrodes have activation energy values that are closely correlated with that of 8YSZ.
ionic conduction as previously mentioned. By changing $PO_2$ during EIS tests, as shown in Figure 9a, it can be observed that the high frequency response is not significantly affected in comparison to the low frequency response leading to the probability that this is an electrolyte related process. As $PO_2$ is altered to lower values, the low frequency arc is observed to become more linear. This is characteristic of a mass transfer controlled (19) phenomenon, possibly signifying oxygen diffusion limitations to the surface of the sample due to low $PO_2$ values or surface oxygen diffusion limitation to the tpb. As in the Pt electrode case, changes in DC bias and current treatment also affects the low frequency response more significantly and can be seen in Figures 9b and 10.

Application of DC bias or current treatment and its enhancement to the cathode has been attributed to reduction of LSM material and increased oxygen vacancies allowing for greater current passage as well as removal of passive species on the electrode surface.
leading to more active sites for oxygen reduction (2,20,21,22). Surface morphological changes are also evident, see Figure 10b, after current treatment and further studies are required to fully understand these changes.

![Figure 10. (a) Impedance spectra of LSM microelectrodes before and after 100mA/cm² for 5 mins current treatment. (b) Optical micrograph of LSM electrodes after current treatment, detailed are locations for oxidation and reduction reactions during current treatment. Microelectrode damage is due to repeated microprobe contacts. The numbers in the diagram are the frequency logarithms.](image)

**CONCLUSIONS**

We have demonstrated that cathode microelectrodes with clearly defined microstructure provide a vehicle for analyzing oxygen reduction reactions on various cathode materials. By removing the ambiguity in cathode microstructure it is then possible to test various materials “side-by-side”. In addition, by using microelectrodes it is possible to vary testing parameters with relative ease as well as testing with new sets of electrodes for each testing condition removing any trace of testing history. Pt is found to have much better overall cathodic properties in comparison to LSM under similar microelectrode geometries. Further studies are required to elucidate the exact oxygen reduction processes occurring at these cathodes. Coupling experiments with the analytical modeling in, part two of this study can additionally shed further light into the specific reaction mechanisms that occur during oxygen reduction.

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