2014

Preparation of solid oxide fuel cell cathodes and analysis by impedance spectroscopy

Juwana Hennadige Lalanthi Kaushalya de Silva

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**PREPARATION OF SOLID OXIDE FUEL CELL CATHODES
AND ANALYSIS BY IMPEDANCE SPECTROSCOPY**

Juwana Hennadige Lalanthi Kaushalya de Silva

**Dissertation submitted to the Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Chemistry**

**Harry Finklea, Ph.D., Chair
Fabien Goulay, Ph.D.
Justin Legleiter, Ph.D.
Alan Stolzenberg, Ph.D.
Nianqiang Wu, Ph.D.**

C. Eugene Bennett Department of Chemistry

**Morgantown, West Virginia
2014**

**Keywords: Solid Oxide Fuel Cell, Impedance Spectroscopy, Deconvolution,
Infiltration, Current collector**

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Abstract

Preparation of Solid Oxide Fuel Cell Cathodes and Analysis by Impedance Spectroscopy

Juwana Hennadige Lalanthi Kaushalya de Silva

The solid oxide fuel cell (SOFC) is a promising energy conversion device with high efficiency, fuel flexibility and less pollution. The requirement for high operating temperatures limits its applications due to high cost and the need for compatible cell components. Therefore, it is important to design SOFCs that operate in intermediate temperatures; which have cathodes with improved microstructures to enhance the oxygen reduction reaction. However, designing novel cathode structures needs a fundamental understanding of cell processes. Impedance spectroscopy is a very powerful tool for studying SOFCs which yields useful yet complex data due to overlapping impedance related processes. Therefore, we used a deconvolution method to analyze the impedance data and extract information about individual processes through equivalent circuit fitting.

Current collectors play a vital role in SOFC characterization. Platinum (Pt), Gold (Au), Silver (Ag) and Lanthanum Strontium Manganite (LSM) are some commonly used cathode current collectors. We carried out a preliminary study in order to investigate the current collection properties of these materials and to choose the most suitable current collectors for our symmetrical cell characterizations. Based on the results (good adhesion properties and reproducible performance), it was decided continue to using Ag and LSM as the current collectors for our characterizations.

Cathode microstructure can be improved by increasing the triple phase boundary (TPB) area of a cathode. This can be done by developing composite cathode structures which consist of both electron and ion conducting phases. Traditionally, composited cathodes are formed by mixing powders of LSM and Ytria Stabilized Zirconia (YSZ) with high temperature sintering. More recently, the infiltration technique (infiltrating a pre-sintered YSZ scaffold with a LSM solution followed by low temperature sintering) has been used to prepare LSM-YSZ composite cathodes. A previous study has reported the performance comparison of LSM infiltrated YSZ nanofiber cathode with LSM-YSZ powder composite cathode. However, this work does not provide the deconvolution analysis of impedance data. In our work, the properties of LSM infiltrated YSZ nanofiber cathodes and LSM infiltrated YSZ powder cathodes were compared. LSM infiltrated YSZ nanofiber cathodes showed better performance compared to LSM infiltrated YSZ powder cathodes and deconvoluted impedance data for both types of cells showed “Gerischer” like behavior which arises due to the thickness of the cathode. Based on this knowledge, an attempt was made to prepare improved LSM infiltrated YSZ cathodes with thin YSZ scaffolds.

LSM cathodes are usually prepared using the pastes of commercial LSM powders. Despite the extensive studies carried out on LSM infiltrated YSZ cathodes, to the best of our knowledge, no attempt has been made to study the activity of the infiltrant LSM alone as a cathode. In this work, symmetrical cells with cathodes prepared by evaporating and

sintering LSM infiltrant solution directly on YSZ electrolytes were characterized using Ag, Au and Pt current collectors. Impedance studies of solution-based LSM cathodes with Ag current collectors resulted in very low polarization resistances (resistance associated with the oxygen reduction reaction) and 2-3 orders of magnitude higher peak frequencies compared to powder based LSM cathodes. Properties of these solution based LSM cathodes vary with different current collectors, which suggests that the current collector participates in the oxygen reduction reaction of the solution based LSM cathodes. Nonetheless, it would be possible to further investigate and develop these “solution-based LSM cathodes with Ag current collectors” as a composite cathode for intermediate temperature SOFCs.

The significant difference of peak frequencies between the powder based and solution based LSM cathodes led to an investigation of LSM-YSZ hybrid cells (powder based LSM cathode as the working electrode and solution based LSM cathode with Ag current collector as counter electrode) in order to isolate and study the properties of powder based LSM cathode with minimal overlapping impedance processes. According to our knowledge, this direct method that we have used to study a single electrode under applied DC bias has not been reported before.

Also, using the measurements at open circuit voltage (OCV) and with applied DC bias, we have demonstrated that the properties of the powder based LSM cathode change with time and applied potential/current, at unexpectedly low overvoltages. This observation suggests that the use of Butler-Volmer equation to represent current-potential behavior in simulations may be inappropriate.

Dedicated to my father J. H. Ranjith Jayantha and my mother Hemavo Wijetunge.

Acknowledgements

First and foremost I would like to express my sincere gratitude to my Ph.D. advisor Dr. Harry Finklea for the tremendous support given to me during last five years. Dr. Finklea was always available and willing to help me with all kinds of questions and concerns I had and spent many hours helping me with experiments, discussing my results and editing my dissertation. I am so grateful to Dr. Finklea for his helpfulness, friendliness and patience and I consider myself very lucky to have worked with such a great teacher, a renowned scientist and a wonderful person.

I am very grateful to Dr. Fabien Goulay, Dr. Justin Legleiter, Dr. Alan Stolzenberg and Dr. Nick Wu for serving in my graduate committee and for helping me in numerous ways despite their busy schedules. Also, their advice and suggestions are greatly appreciated.

I am thankful to Dr. Nick Wu and Dr. Mingjia Zhi (MAE-WVU) for providing me with YSZ nanofibers, Dr. Edward Sabolsky (MAE-WVU) for providing me with the ink vehicle and Dr. Alan Stolzenberg (Chemistry-WVU) for allowing me to borrow the WIG-L-BUG. I would also like to acknowledge Dr. Lisa Holland and Tyler Davis (Chemistry -WVU) for the support given to me during HF-etching experiments; Dr. Jonathan Boyd, Julie Vrana and Alice Han (Chemistry-WVU) for helping me with freeze-drying experiments; Dr. Peter Gannett and Katherine Hickey (HSC-WVU) for facilitating the contact angle goniometry measurements; Dr. Jingxin Wang and Dr. Xingeng Xie (Forestry-WVU) for their help with the TGA experiments; Dr. Kirk Gerdes and Dr. Harry Abernathy (NETL-Morgantown) for the support given to me to conduct pO_2 experiments; James Poston (NETL-Morgantown) for providing me with the XRD data for LSM; and Sherman Adams, Allen Burns and Randall Eaglen for helping me to develop experimental set ups without any delays.

I would also like to thank the NETL-RUA for funding and the Solid Oxide Fuel Cell research team at NETL-Morgantown for helping me in numerous ways.

It was a pleasure to work with my group members Dr. Oktay Demircan, Dr. Yun Chen, Dr. Xiaoke Chen, Dr. Wei Zhang and Mahfuzur Jony. I would especially like to thank Mahfuzur Jony for providing me with all the SEM images and EDS spectra which were

very important for my dissertation. I would also like to thank my friends at WVU and my Sri Lankan friends in Morgantown for all their support and for the great times we had.

I am very grateful to my wonderful parents (J.H. Ranjith Jayantha and Hemavo Wijetunge), awesome siblings (Madhubhani, Sankha and Ludilu) and lovely grandparents (Edwin Silva, Aceda Mallika, Ranjani Wijetunge and late Dairas Wijetunge) for their unconditional love and constant support. They always believed in me and encouraged me to do my best.

Last but not least, I would like to take this opportunity to thank my amazing husband (Oshadha Ranasingha) for always being there for me and supporting me to achieve the best in life.

As part of the National Energy Technology Laboratory's Regional University Alliance (NETL-RUA), a collaborative initiative of the NETL, this technical effort was performed under the RES contract DE-FE0004000.

Table of Contents

Abstract	ii
Acknowledgments.....	v
Table of Contents.....	vii
List of figures.....	xi
List of tables	xviii
Abbreviations.....	xxi
Chapter 01: Introduction.....	1
1.1 Background.....	1
1.2 Solid Oxide Fuel Cells.....	1
1.3 Oxygen Reduction Reaction.....	4
1.4 Symmetrical Cells	6
1.5 Current Collectors.....	7
1.6 Electrochemical Characterization	7
1.7 Equivalent Circuit Elements and Electrochemical Processes	9
1.8 Challenges for Solid Oxide Fuel Cells.....	14
1.9 Objectives and the Structure of the Dissertation	15
1.10 References	16
Chapter 02: (Section I) Metal And LSM Current Collectors	18
2.1 Introduction	18
2.2 Experimental.....	19
2.2.1 Cyclic Voltammetry Measurements.....	20
2.2.2 Electrochemical Impedance Spectroscopy Measurements.....	20
2.3 Platinum (Pt).....	22
2.3.1 Introduction	22
2.3.2 Sample Preparation	22
2.3.3 Electrochemical Characterization	22
2.3.4 Results and Discussion.....	23
2.3.5 Summary	26
2.4 Gold (Au)	26
2.4.1 Introduction	26

2.4.2 Sample Preparation	26
2.4.3 Electrochemical Characterization	27
2.4.4 Results and Discussion.....	27
2.4.5 Summary	28
2.5 Silver (Ag)	28
2.5.1 Introduction	28
2.5.2 Sample Preparation	29
2.5.3 Electrochemical Characterization	29
2.5.4 Results and Discussion.....	29
2.5.5 Summary	31
2.6 Lanthanum Strontium Manganite (LSM).....	32
2.6.1 Introduction	32
2.6.2 Sample Preparation	32
2.6.3 Electrochemical Characterization	32
2.6.4 Results and Discussion.....	32
2.6.5 Summary	33
2.6 Conclusion.....	33
Chapter 02: (Section II) YSZ Nanofiber Cathodes (PAR System)	35
2.8 Introduction	35
2.9 Experimental.....	36
2.9.1 Sintering Study.....	38
2.9.2 Electrochemical Characterization	38
2.10 Results and Discussion.....	38
2.10.1 Sintering Study.....	38
2.10.2 Pt current collectors on YSZ nanofiber cathodes	40
2.10.3 Au current collectors on YSZ nanofiber cathodes	42
2.10.4 Ag current collectors on YSZ nanofiber cathodes	43
2.10.5 Ag current collectors on YSZ powder cathodes.....	47
2.10.6 Ag current collectors on LSM infiltrated YSZ cathodes.....	49
2.11 Summary.....	51
2.12 Conclusion.....	51

2.13 References	52
Chapter 03: LSM current collectors and LSM infiltrated YSZ	
Scaffolds.....	54
3.1 Introduction	54
3.2 Experimental.....	56
3.3 Results and Discussion.....	59
3.4 Summary	72
3.5 Conclusion.....	72
3.6 References	74
Chapter 04: Solid Oxide Fuel Cell Cathodes and Deconvolution	
Studies.....	76
4.1 Introduction	76
4.2 Powder based LSM cathodes	77
4.2.1 Sintering Study of LSM powder cathodes.....	78
4.2.2 Aging Study of LSM powder/YSZ symmetrical cells.....	79
4.2.3 Deconvolution studies of LSM powder/YSZ symmetrical Cells.....	81
4.3 Solution based LSM cathodes	83
4.3.1 Contact Angle Measurements	84
4.3.2 XRD analysis	86
4.3.3 Thermogravimetric Analysis.....	87
4.3.4 Sintering study of LSM solution based cathodes.....	88
4.3.5 Aging Study of LSM solution/YSZ symmetrical cells with Ag current collectors.....	92
4.3.6 Deconvolution studies of LSM solution/YSZ symmetrical cells Ag current collectors.....	95
4.3.7 LSM solution/YSZ symmetrical cells with different metal current collectors.....	96
4.3.8 “Mixed” Performance of solution based LSM cathodes with Ag current collectors.....	102
4.3.9 LSM solution/HIONIC® symmetrical cells.....	106

4.3.10 Ag/organic LSM/YSZ symmetrical cells with different oxygen partial pressures	108
4.4 Deconvolution study of LSM infiltrated YSZ cathodes	110
4.5 Summary	114
4.6 Conclusion	115
4.7 References	116
Chapter 05: LSM/YSZ Hybrid Cells	119
5.1 Introduction	119
5.2 Experimental	121
5.2.1 Temperature Study	121
5.2.2 LSM/YSZ Hybrid Cell Characterization under Polarization	123
5.3 Summary	139
5.4 Conclusion	139
5.5 References	141
Appendix A	143

List of Figures

Figure 1.1: Schematic diagram of a Solid Oxide Fuel Cell	2
Figure 1.2: Orthorhombic lattice structure of LaMnO_3	3
Figure 1.3: Triple Phase Boundary of LSM cathode on YSZ electrolyte.....	4
Figure 1.4: Cathodic reaction paths on electron conducting perovskite materials	5
Figure 1.5: Schematic diagram of a LSM/YSZ/LSM symmetrical cell operating in air	7
Figure 1.6: Nyquist plot with EIS data	8
Figure 1.7: The polarization curve (black) and the power curve (red) for a single SOFC.....	9
Figure 1.8: A Bode plot (a) and the corresponding deconvoluted spectrum (b) which reveals the peaks/shoulders for three possible impedance processes	10
Figure 1.9: Bode plots ($-Z''$ vs $\log f$): (RC) and (RQ) elements with varying exponent U values shown. The arc is symmetrical in the left plot. In the double log plot, the magnitudes of the slopes of the lines away from the peak frequency are equal to the U value	12
Figure 1.10: Representing a porous electrode as a series of cylindrical pores.	13
Figure 1.11: Fractal Gerischer element with varying P values. The Bode plot is asymmetrical with a long tail on the high frequency side. The double log plot shows that the slope on the low frequency side is 1 and the magnitude of the slope on the high frequency side is P	13
Figure 1.12: HN element with $P = 0.5$ and varying U values. The Bode plot is again asymmetrical with a long tail on the high frequency side. The magnitude of the slope of the log log plot approaches U on the low frequency side and $P*U$ on the high frequency side.....	14
Figure 2.1 Cross section of the tube furnace when the cell is mounted	19

Figure 2.2: Voltammogram for a Pt/YSZ nanofiber/YSZ symmetrical cell (d = 4 mm) at 700 ⁰ C. The total resistance calculated by the reciprocal slope of the line is 4.36 kOhms	20
Figure 2.3: A plot of EIS data for a Pt/Roughened YSZ/Pt symmetric cell at 700 ⁰ C. The series resistance obtained by the high frequency intercept is 11.2 Ohms	21
Figure 2.4: Arrhenius plot for the series resistance (R_s) and the deduced activation energy for the oxide ion conductivity across the cell. Slope = 11565+/- 453, Intercept = -9.5 +/- 0.4, $R^2 = 0.997$, $E_a = 1.00\pm 0.04$ eV	21
Figure 2.5: Arrhenius plot for the polarization resistance (R_p) and the deduced activation energy for the oxygen reduction reaction at the cathode. Slope = 32300+/-1173, Intercept = -24 +/- 1, $R^2 = 0.997$, $E_a = 2.8\pm 0.1$ eV.....	21
Figure 2.6: SEM images of a (a) YSZ nanofiber cathode sintered at 1300 ⁰ C (3000 X) and (b) YSZ powder cathode sintered at 1500 ⁰ C (5000 X) on YSZ electrolyte.....	35
Figure 2.7: The Electrospinning apparatus	37
Figure 2.8: Schematic diagram of a Solid Oxide Fuel Cell.....	37
Figure 2.9: SEM images of YSZ nanofibers sintered at (a) 850 ⁰ C (3500X), (b) 1100 ⁰ C (6000X), (c) 1150 ⁰ C (7000X), (d) 1200 ⁰ C (7000X), (e) 1250 ⁰ C (8000 X), (f) 1300 ⁰ C (12000X), (g) 1350 ⁰ C (3000 X), (h) 1400 ⁰ C (10000X) and (i) 1450 ⁰ C (5000 X).....	39
Figure 2.10: YSZ nanofibers sintered with Bi (NO ₃) ₃ at 850 ⁰ C, nanofibers are melted.....	42
Figure 3.1: Multi step infiltration process.....	55
Figure 3.2: Discrete particles (c) or continuous thin film (d) on the cathode backbone	55
Figure 3.3: Cross section SEM image of YSZ nanofiber electrode prepared using the paste that was not ball-milled. Red squares highlight the gaps.....	64

Figure 3.4: Cross section SEM image of YSZ nanofiber electrode prepared using the ball milled paste. Blue square shows the uniform electrode and the electrolyte	64
Figure 3.5: SEM images of 30% LSM infiltrated (a) YSZ nanofiber cathode (b) YSZ powder cathode	70
Figure 3.6: EDS spectrum for the LSM infiltrated YSZ nanofiber cathode	70
Figure 4.1: SEM image of an LSM cathode sintered at 1200 °C for 1 hour	79
Figure 4.2: Polarization resistances recorded over time during the aging experiment for LSM powder cathode sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time over the entire experiment	80
Figure 4.3: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of LSM powder cathode sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time from the temperature change. At the beginning of Day 2 and Day 4, the cell temperature was dropped from 800 °C to 700 °C. At the beginning of Day 3 and Day 5, the cell temperature was raised from 700 °C to 800 °C	80
Figure 4.4: Deconvoluted and simulated data for LSM powder/YSZ symmetrical cells at 800 °C with (a) Ag (b) Pt and (c) Au current collectors (d) negative out of phase impedance vs log frequency plot with equivalent circuit fitting (3 RQ elements) of impedance data collected for (c).....	82
Figure 4.5: A telescope goniometer.....	84
Figure 4.6: Different contact angle measurements	85
Figure 4.7: Contact angle measurements for aqueous LSM solution on as received YSZ (a) and hydrophilic YSZ (b) and organic LSM solution on as received YSZ (c) and hydrophilic YSZ (d)	85
Figure 4.8: XRD data for aqueous LSM (a) and organic LSM (b)	86
Figure 4.9: Thermograms for organic (blue) and aqueous (red) LSM	

precursor solutions.....	88
Figure 4.10: ESEM image of an organic LSM cathode sintered at 800 °C for 1 hour, 5000 X magnification, 900 °C imaging temperature	91
Figure 4.11: Polarization resistances recorded over time during the aging experiment for organic LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ at (a) 700 °C and (b) 800 °C. This figure shows the cathode behavior vs. time over the entire experiment	93
Figure 4.12: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of organic LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ. This figure shows the cathode behavior vs. time from the temperature change. At the beginning of Day 2 and Day 4, the cell temperature was dropped from 800 °C to 700 °C. At the beginning of Day 3 and Day 5, the cell temperature was raised from 700 °C to 800 °C	93
Figure 4.13: Polarization resistances recorded over time during the aging experiment for organic LSM solution cathode (with Ag current collector) sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time over the entire experiment.....	94
Figure 4.14: Figure 4.14: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of organic LSM solution cathode (with Ag current collector) sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time from the temperature change. At the beginning of Day 2 and Day 4, the cell temperature was dropped from 800 °C to 700 °C. At the beginning of Day 3 and Day 5, the cell temperature was raised from 700 °C to 800 °C	94
Figure 4.15: Deconvoluted (blue) and simulated (red) data at 800 °C for Ag/organic LSM/YSZ symmetrical cell sintered at 900 °C.....	95

Figure 4.16: Deconvoluted (blue) and simulated (red) data at 800 ⁰ C for (i) Ag (thick)/YSZ (ii) Ag (thin)/YSZ (iii) Ag powder/YSZ and (iv) Pt/YSZ symmetrical cells.....	97
Figure 4.17: Deconvoluted (blue) and simulated (red) data at 800 ⁰ C for (v) Pt/organic LSM/YSZ (vi) Au/organic LSM/YSZ symmetrical cells.....	100
Figure 4.18: Deconvoluted (blue) and simulated (red) data at 800 ⁰ C for Ag/organic LSM/YSZ symmetrical cell sintered at 1200 ⁰ C....	103
Figure 4.19: Deconvoluted and simulated data for Ag-LSM/YSZ symmetrical cells at 800 ⁰ C.....	105
Figure 4.20: Deconvoluted and simulated data for Ag/ organic LSM/HIONIC symmetrical cells at 800 ⁰ C.....	107
Figure 4.21: Relationship between the oxygen partial pressure and the polarization resistance of a Ag/ organic LSM/YSZ symmetrical cell. Polarization resistances recorded from 0.2 atm to 0.002 atm (down) and from 0.002 atm to 0.2 atm (up) at 750 ⁰ C and 800 ⁰ C are shown.....	109
Figure 4.22: Deconvoluted and simulated data for LSM infiltrated YSZ nanofiber scaffold (a) and powder scaffold (b) with LSM current collectors at 800 ⁰ C.....	111
Figure 4.23: Deconvoluted and simulated data for LSM infiltrated improved YSZ scaffolds (types i and ii) with Ag current collectors at 800 ⁰ C.....	112
Figure 5.1: Cole-Cole plot (a) and Negative out of phase impedance vs log frequency plot with equivalent circuit fitting (b) for a LSM/YSZ hybrid cell with Ag current collectors at 800 ⁰ C.....	119
Figure 5.2: Surface and bulk paths for oxygen reduction reaction on a porous cathode	121
Figure 5.3: Cole-Cole plot (a) and Negative out of phase impedance vs log frequency plot with equivalent circuit fitting (b) for a LSM/YSZ hybrid cell under 2.5 mA applied current at 800 ⁰ C. The solid	

lines in (b) show the contributions of the three elements (RQ1, RQ2 & RC) in the equivalent circuit	125
Figure 5.4: Negative out of phase impedance vs log frequency plots for different applied positive voltages at 800 °C for (a) powder based LSM/YSZ symmetrical cell and (b) solution based LSM/YSZ symmetrical cell.....	126
Figure 5.5: (a) Current vs. time plots for Cell A (potentiostatic experiment). (b) Potential vs. time plots for Cell B (galvanostatic experiment). at 800 °C.....	126
Figure 5.6: Fitting parameters of equivalent circuit elements used for impedance data collected for Cell A ((a)-(f)) and Cell B ((g)-(l)) under anodic polarization (LSM paste electrode anode, LSM solution electrode cathode) at 800 °C. Note the sign change on the voltage axes for R3 and Q2	126
Figure 5.7: Variation of resistance (R4) associated with low frequency (gas diffusion arc) with applied voltage for Cell A (a) and Cell B (b). The values are based on an assumed RC equivalent circuit for the gas diffusion process	130
Figure 5.8: (a) Current vs. time plots for Cell A (potentiostatic experiment). (b) Potential vs. time plots for Cell B (galvanostatic experiment). at 800 °C.....	131
Figure 5.9: Fitting parameters of equivalent circuit elements used for impedance data collected for Cell A ((a)-(f)) and Cell B ((g)-(l)) under cathodic polarization at 800 °C. Note the positive voltages for R3 and Q2 plots	132
Figure 5.10: Cole-Cole plot (a) and Negative out of phase impedance vs log frequency plot (b) for a LSM/YSZ hybrid cell under -3.6 mA applied current at 800 °C.....	134
Figure 5.11: Cole-Cole plot (a) and Bode plots (b) and (c) showing the slight drift in impedance spectra at low frequencies for Cell A at 0.01 V, 800 °C	135

Figure 5.12: Current-over voltage plots for series resistance (R_1), resistance for powder based LSM cathode (R_2) and resistance for solution based LSM cathode (R_3) of Cell A ((a), (c), (e)) and Cell B ((b), (d), (f)), respectively 136

Figure 5.13: Resistance of the powder based LSM cathode as a function of the applied voltage for Cell A (a) and Cell B (b) respectively. Resistance values at open circuit voltages OCV 1 (red), OCV 2 (orange), OCV 3 (purple), OCV 4 (black), OCV 5 (blue) and OCV 6 (green) are shown in different colors 138

List of Tables

Table 2.1: Series resistances, polarization resistances and activation energies for Pt containing cells	23
Table 2.2: Summary of average series resistances and activation energies for conductivity across the cell of Pt containing cells	24
Table 2.3: Series resistances, polarization resistances and activation energies of Au containing cells	27
Table 2.4: Summary of average series resistances and activation energies for conductivity across the cell of Au containing cells.....	28
Table 2.5: Series resistances, polarization resistances and activation energies of Ag containing cells	30
Table 2.6: Summary of average series resistances and activation energies for conductivity across the cell of Ag containing cells.....	31
Table 2.7: Series resistances, polarization resistances and activation energies of LSM/YSZ symmetric cells	33
Table 2.8: Series resistances, polarization resistances and activation energies of YSZ nanofiber cathodes with Pt current collectors	41
Table 2.9: Series resistances, polarization resistances and activation energies of YSZ nanofiber cathodes with Au current collectors.....	43
Table 2.10: Series resistances, polarization resistances and activation energies of YSZ nanofiber cathodes with Ag current collectors...	45
Table 2.11: Series and Polarization resistances of YSZ powder cathodes with Ag current collectors.....	48
Table 2.12: Series resistances, polarization resistances and activation energies of LSM infiltrated YSZ cathodes with Ag current collectors.....	50
Table 3.1: Series resistances, polarization resistances and activation energies for LSM/YSZ symmetrical cells	60
Table 3.2: Series resistances, polarization resistances and activation energies for LSM/YSZ scaffold/YSZ symmetrical cells	62

Table 3.3: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ nanofiber symmetrical cells with 10% C-LSM current collector	63
Table 3.4: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ powder symmetrical cells with 10% C-LSM current collector	65
Table 3.5: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ nanofiber symmetrical cells with pure LSM current collector	66
Table 3.6: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ powder symmetrical cells with pure LSM current collector	68
Table 4.1: Summary of results for the sintering study of LSM powder/YSZ symmetrical cells.....	78
Table 4.2: Normalized fitting parameters for at 800 °C with (a) Ag (b) Pt and (c) Au current collectors for LSM powder/YSZ symmetrical cells	83
Table 4.3: Summary of results for the sintering study of organic LSM solution/YSZ symmetrical cells	89
Table 4.4: Summary of results for the sintering study of aqueous LSM solution/YSZ symmetrical cells	89
Table 4.5: Normalized fitting parameters at 800 °C for Ag/organic LSM/YSZ symmetrical cell sintered at 900 °C	96
Table 4.6: Normalized fitting parameters for Ag/YSZ and Pt/YSZ symmetrical cells at 800 °C.....	99
Table 4.7: Normalized fitting parameters for Pt/organic LSM/YSZ and Au/organic LSM/YSZ symmetrical cells at 800 °C.....	101
Table 4.8: Normalized fitting parameters at 800 °C for Ag/organic LSM/YSZ symmetrical cell sintered at 1200 °C	103
Table 4.9: Normalized fitting parameters for Ag-LSM/YSZ symmetrical cell at 800 °C.....	105
Table 4.10: Normalized fitting parameters for Ag/ organic LSM/HIONIC	

symmetrical cell at 800 °C	107
Table 4.11: Normalized fitting parameters for LSM infiltrated YSZ scaffolds with LSM current collectors at 800 °C.....	112
Table 4.12: Normalized fitting parameters for LSM infiltrated improved YSZ scaffolds with Ag current collectors at 800 °C	113
Table 5.1: Summary of results obtained for the temperature study of LSM/YSZ hybrid cells.....	122
Table 5.2: Experimental protocol used for impedance analysis of LSM/YSZ hybrid cells under applied DC voltages (Cell A) and DC currents (Cell B).....	123
Table 5.3: Parameters recorded for Cell A and Cell B at open circuit voltage (800 °C)	137

Abbreviations

CV – Cyclic Voltammetry
ECR – Electrochemical Conductivity Relaxation
EDS – Energy Dispersive Spectroscopy
EIS – Electrochemical Impedance Spectroscopy
ESEM – Environmental Scanning Electron Microscope
FFT – Fast Fourier Transform
FIB-SEM - Focused Ion Beam Scanning Electron Microscope
LSM – Lanthanum Strontium Manganite
OCV – Open Circuit Voltage
ORR – Oxygen Reduction Reaction
PAR – Princeton Applied Research
 pO_2 – partial pressure of oxygen
SEM - Scanning Electron Microscope
SOFC - Solid Oxide Fuel Cell
TEC - Thermal Expansion Coefficient
TGA – Thermo Gravimetric Analysis
TPB – Triple Phase Boundary
YSZ – Yttria Stabilized Zirconia
WE – Working Electrode
XRD – X-Ray Diffractometry
8YSZ - 8 mol% Yttria Stabilized Zirconia

Chapter 01

Introduction

1.1 Background

According to the *International Energy Outlook 2013 (IEO2013)* report released by The Energy Information Administration (EIA), world energy demand will increase by 56% between 2010 and 2040 and ~80% of this demand will still need to be fulfilled by fossil fuels [1]. Excessive usage of fossil fuels over years makes the demand vulnerable to scarcity [2]. Furthermore, burning fossil fuels to generate energy result in greenhouse gas emissions which results in global warming [3]. Therefore, it is imperative to construct and use alternative energy sources such as solid oxide fuel cells that efficiently convert simple fuels into electricity without emitting CO₂ to the environment.

1.2 Solid Oxide Fuel Cells

The solid oxide fuel cell (SOFC) is a device that can be used to directly convert the chemical energy of fuels into electricity with high efficiency and less pollution, in comparison to combustion-based methods [4]. It consists of a porous cathode and a porous anode with a dense solid electrolyte separating the two electrodes. At the cathode (reaction 1.1), oxygen molecules get reduced to oxide (O²⁻) ions using electrons from the external circuit. The solid electrolyte (typically zirconia doped with yttria) conducts O²⁻ ions at higher temperatures but does not conduct electrons. At the anode (reaction 1.2), H₂ fuel gets oxidized to water, forming electrons which flow through the external circuit as the current [4] (Figure 1.1).

Figure 1.1: Schematic diagram of a Solid Oxide Fuel Cell.

Doped lanthanum gallate, rare earth doped ceria and rare earth doped bismuth oxide are some of the SOFC electrolytes that have been well studied. These SOFC electrolytes are usually oxide ion conductors and the oxide ion conduction is thermally activated. The state of the art electrolyte for high temperature and intermediate temperature SOFCs is Yttria Stabilized Zirconia (YSZ) [5]. Requirements for a suitable SOFC electrolyte are [6]:

- i. excellent ionic conductivity and negligible electronic conductivity
- ii. stability over a range of temperatures and oxygen partial pressures
- iii. compatibility of thermal expansion coefficient with the other cell components
- iv. negligible chemical reactions with electrode materials
- v. high abundance and low cost

The fuel oxidation takes place on the anode of SOFC. Pt and Ni are some of the anode materials that have been studied over a long time. However, Ni was chosen as the best candidate due to its chemical stability, low cost and catalytic activity towards fuel oxidation. However, Ni alone cannot be used as the anode due to the thermal coefficient mismatch between Ni and YSZ, which results in anode delamination. Therefore, Ni-YSZ

cermet is used as the state of the art anode in SOFCs. The YSZ phase not only mitigates the thermal expansion mismatch but also prevents the Ni agglomeration and acts as an oxide ion conductor for the catalytic reaction on Ni. Following are the general requirements for a SOFC anode [6]:

- i. chemical and thermal stability
- ii. good electronic and ionic conductivity
- iii. catalytic activity for fuel oxidation
- iv. thermal expansion compatibility with other cell components
- v. tolerance to carbon deposition and sulfur poisoning

The most commonly used SOFC cathode material is Strontium doped Lanthanum Manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) (LSM). LSM is an ABO_3 type perovskite material (orthorhombic phase when $x = 0.2$) with high electronic conductivity and low ionic conductivity. Figure 1.2 shows the orthorhombic lattice structure of Lanthanum Manganite (LaMnO_3) [7]. The electrical conductivity and the catalytic activity of Lanthanum Manganite (LaMnO_3) increase when it is doped with Sr [8].

Figure 1.2: Orthorhombic lattice structure of LaMnO_3 [3].

The oxygen reduction reaction of SOFC cathode takes place when oxygen gas, oxide ion vacancies and electrons are present. In other words, the oxygen reduction reaction (Kroger – Vink notation shown in reaction 1.3) occurs only at places where the gas phase, an oxide ion conductor and an electronic conductor meet together. These reaction sites are called Triple phase Boundaries (TPB) (Figure 1.3).

$\text{V}_{\text{O}}^{\bullet\bullet}$ = vacant oxygen site, $\text{O}_{\text{O}}^{\times}$ = oxygen ion in YSZ lattice [6].

Figure 1.3: Triple Phase Boundary of LSM cathode on YSZ electrolyte [9].

1.3 Oxygen Reduction Reaction

Oxygen reduction reaction (ORR) kinetics of SOFC cathodes is widely studied and researchers have proposed different mechanisms with different rate determining steps. However, a well understood exact mechanism for this reaction has yet to be identified [10]. According to Sun et al.'s [9] review paper, the overall oxygen reduction reaction of the SOFC cathode which is (reaction 1.4):

consists of several elementary steps:

- i. adsorption of the O_2 molecules
- ii. dissociation of O_2 molecules
- iii. reduction into O^{2-} anions and incorporation into the cathode material
- iv. O^{2-} ion transport through the cathode to the electrolyte
- v. O^{2-} ion hopping into the electrolyte lattice

Jurgen Fleig [11] has proposed three possible paths (electrode surface path, bulk path and electrolyte surface path (Figure 1.4)) for the cathodic reaction on electron conducting perovskite materials such as LSM. According to Fleig [11], the cathodic reaction of SOFC can simultaneously take place through all three paths.

Figure 1.4: Cathodic reaction paths on electron conducting perovskite materials [11].

In the electrode surface path, oxygen gas gets adsorbed on to the cathode and diffuses along the cathode surface to the TPB where the ionization and the oxide ion hopping to the electrolyte occur. In the bulk path, oxygen gas gets adsorbed on to the cathode followed by dissociation and ionization. Then, the oxide ions are transported through the cathode and transferred in to the electrolyte. In the electrolyte surface path, oxygen gas gets adsorbed to the electrolyte surface followed by the ionization using electrons (from the electrolyte). Then, the oxide ions get incorporated into the electrolyte. However, since most electrolytes (eg: YSZ) are poor electron conductors, this reaction takes place in the vicinity of the TPB, making it very similar to the above mentioned electrode surface path [11].

The oxygen reduction reaction of a SOFC has a typical activation energy higher than 1.5 eV and is the main contributor to the total cell resistance [9], [11]. The rate of the oxygen reduction reaction exponentially decreases with the lower operating temperatures [12].

An experimentally accessible quantity, the polarization resistance, is used to characterize the performance of a cathode. The inverse of the polarization resistance is proportional to the rate of the cathode processes. There are various mechanistic contributions to the cathodic polarization resistance (R_{cathode}) [12].

$$R_{\text{cathode}} = R_{\text{gas diffusion}} + R_{\text{surface adsorption}} + R_{\text{charge transfer}} + R_{\text{ohmic}} \quad (1.5)$$

Resistance due to gas diffusion ($R_{\text{gas diffusion}}$) can be overcome by optimizing the microstructure in order to increase the porosity of the cathode. Resistance due to surface adsorption ($R_{\text{surface adsorption}}$) can be overcome by optimizing the microstructure of the cathode in order to increase the surface area and by increasing the surface diffusivity of the material to increase the kinetics of the oxygen reduction reaction. By increasing the surface area and having continuous charge transfer pathways in the optimized microstructure, and by increasing the kinetics of the oxygen reduction reaction, the resistance due to charge transfer ($R_{\text{charge transfer}}$) can be minimized. Also, the Ohmic resistance (R_{ohmic}) can be reduced by using a compound with high conductivity and by improving the connectivity of the microstructure [12].

Therefore, there are two approaches to reduce the polarization losses of the cathodes [12]

- i. using a compound with high conductivity and improved kinetics for oxygen exchange, diffusion and reduction
- ii. optimizing the microstructure of the cathode in order to increase the porosity and to extend the Triple Phase Boundary (TPB) length, or the surface area of the cathode

1.4 Symmetrical Cells

Symmetrical cells have the same material on both sides of the electrolyte as overlapping electrodes (Figure 1.5). These cells allow assigning impedance data explicitly to the cathode or anode. However, the impedance data collected for symmetrical cells are only valid at OCV [13]. With applied current, the electrode impedances are no longer identical since one electrode becomes the cathode and the other electrode the anode.

Figure 1.5: Schematic diagram of a LSM/YSZ/LSM symmetrical cell operating in air.

1.5 Current Collectors

The current collector is a vital component in SOFCs. It should evenly distribute the current into the cathode and efficiently draw out current from the anode in order to minimize the contact resistance [14]. Also, the current collector should not be involved in any chemical or electrochemical reactions during cell operation [15]. Most commonly used current collectors are metal paste current collectors and metal mesh current collectors.

1.6 Electrochemical Characterization

Electrochemical Impedance Spectra (EIS), open circuit voltage (OCV), the power curve (IP curve) and the polarization curve (IV curve) are the main indicators that are used to evaluate the performance of SOFCs [13].

In Electrochemical Impedance Spectroscopy (EIS), an AC voltage is applied to the cell at different frequencies and the resulting AC current is measured. The impedance of the system (Z) can be calculated using an expression analogous to Ohm's law (equation 1.6) [13],[16].

$$Z = \frac{\Delta E_{AC}}{I_{AC}} \quad (1.6)$$

The impedance is usually expressed as a complex number with a real part (Z') and an imaginary part (Z''). Impedance data can be plotted in a Nyquist plot (Figure 1.6) in which the X – axis is real/ in-phase component of impedance (Z') and the Y-axis is the negative

imaginary/out-of-phase component of impedance ($-Z''$). Each data point of the Nyquist plot represents impedance at a single frequency.

Figure 1.6: Nyquist plot with EIS data.

The high frequency intercept of the plot represents the series resistance R_s (the resistance for O^{2-} ion conductivity across the cell) and the diameter of the arc represents the polarization resistance R_p (resistance for the oxygen reduction reaction at the cathode). The low frequency intercept represents the total resistance ($R_s + R_p$) of the cell. Furthermore, the impedance of SOFC electrodes can be modeled using equivalent circuits with parameters that have chemical and physical interpretations [16].

The electrical potential difference between two terminals of a device (when there is no external current flow between the terminals) is called the Open Circuit Voltage (OCV) [13] or open circuit potential. The OCV of a typical SOFC operating at 800 $^{\circ}\text{C}$ is ~ 1.1 V [15] and OCV for a symmetrical cell is 0 V.

In the polarization curve (Figure 1.7), the Y- axis represents the cell voltage while the X- axis represents the current. Cell voltage decreases with the increasing current. In the power curve, the Y- axis represents the power (voltage*current) while the X- axis represents the current. The peak power density of the SOFC according to this plot is ~ 0.8 Wcm^{-2} .

Figure 1.7: The polarization curve (black) and the power curve (red) for a single SOFC [13].

1.7 Equivalent circuit elements and electrochemical processes

Characterization of SOFCs using impedance spectroscopy yields useful yet complex data due to overlapping impedance related processes. Ivers-Tiffée [17] developed a method called “deconvolution” (distribution of relaxation times) in order to identify important relaxation times that are relevant to cell processes, using the impedance data. A well detailed discussion on deconvolution method is presented in Xiaoke Chen’s [13] Ph.D. dissertation. In order to perform the deconvolution, impedance data are fitted to a mathematical expression that is derived from the Voigt’s circuit (equation 1.7).

$$Z_{(\omega)} = R_0 + R_p \sum g_k / (1 + j\omega\tau_k) \quad (1.7)$$

Where “ $Z_{(\omega)}$ ” is impedance data, “ R_0 ” is series resistance, “ R_p ” is polarization resistance, “ g_k ” is fraction of R_p in an element at a particular frequency, “ τ_k ” is the time constant for the process.

If the data obey Karamers –Kronig transformation, only the out of phase impedance (Z'') can be used for data fitting. The first step is the removal of the inductance from the impedance data. Then, Fast Fourier Transform (FFT) will be applied to the Z'' vs. frequency data in order to get the Z_n (fourier transform of Z'') and S_n (fourier transform of hyperbolic secant function. Dividing each Z_n by the corresponding S_n results in fourier

coefficients of G_n . After that, a filter function will be applied to remove noise and inverse FFT on G_n coefficients will be performed in order to get the deconvoluted spectrum [13] (Figure 1.8 (b)).

Deconvolution process sharpens the impedance features and hence reveals the processes that are not readily visible in a Bode plot (Figure 1.8).

Figure 1.8: A Bode plot (a) and the corresponding deconvoluted spectrum (b) which reveals the peaks/shoulders for three possible impedance processes.

The information obtained through deconvolution of impedance data is very important for proposing suitable equivalent circuit models (which usually consist of a series of arc forming elements shown below [18]), which in turn helps to calculate the polarization resistances at each electrode.

i. Parallel RC element (RC)

This element represents charge transfer at the electrode/electrolyte interface. The R value is inversely related to the rate of the process which determines the current. The capacitance C can either be the interfacial capacitance of the electrode/ electrolyte interface (often called the double layer capacitance) or the chemical capacitance associated with the mechanism for charge transfer.

The chemical capacitance can be interpreted as proportional to the moles of species undergoing an oxidation state change in the mechanism. Chemical capacitances can be much larger than double layer capacitances in SOFCs.

The chemical capacitance C is related to the charge available at the electrode/electrolyte interface. If Q_{total} = charge available in C/cm^2 , then

$$C = Q_{\text{total}}/(4RT/F) \quad (1.8)$$

Where R = Ideal Gas Constant, T = temperature in K, and F = Faraday's constant.

For surface species with coverage Γ in mol/cm²,

$$Q_{\text{total}} = F\Gamma \quad (1.9)$$

For bulk species, let A be the moles of redox active species per cm³, and let f be the volume of species in cm³ covering the electrolyte area in cm² ($f = \text{cm}^3/\text{cm}^2$). Then

$$\Gamma = Af \quad (1.10)$$

This simple equivalent circuit implies that the electrode/electrolyte interface occupies a single well defined plane with identical electrolyte resistance to all parts of the electrode and identical rates of reaction and capacitances.

$$Z = R/(1 + T(j\omega)) \quad (1.11)$$

R = polarization resistance

T = time constant = R*C

And $\omega = 2\pi f$ = radial frequency

ii. Parallel RQ element (RQ)

This element is similar to the (RC) element except that the properties or rates associated with R and C are now distributed. Q is called a constant phase element since it exhibits a constant phase angle at all frequencies. The admittance for the Q element is:

$$Y = Q(j\omega)^U \quad (1.12)$$

Hence,

$$Z = R/(1 + T(j\omega)^U) \quad (1.13)$$

$$T = RQ \quad (1.14)$$

This element collapses to the parallel RC element when the exponent $U = 1$. Typically U is less than 1. Then Q is no longer a capacitance, and T is no longer a time constant.

Figure 1.9: Bode plots ($-Z''$ vs $\log f$): (RC) and (RQ) elements with varying exponent U values shown. The arc is symmetrical in the left plot. In the double log plot, the magnitudes of the slopes of the lines away from the peak frequency are equal to the U value [18].

iii. Gerischer element (Ge)

The Gerischer element arises for two situations. For a SOFC electrode composed of a mixed ionic electronic conductor, this element appears in the impedance spectrum as the result of two simultaneous processes, the reaction of the gas with the electrode throughout the electrode structure, and mass transfer of the reaction products to the electrode/electrolyte interface. The Gerischer element also describes the impedance response of a porous electrode with the pores filled with electrolyte (Figure 1.9 [19]). The de Levie analysis [20] represents the porous structure as a series of cylindrical pores perpendicular to the electrode/electrolyte plane. The system behaves like a transmission line. In the limit of infinitely long pores, Gerischer behavior is obtained.

$$Z = R/(1 + T(j\omega))^P \quad (1.15)$$

$P = 0.5$ for a Gerischer element. A single fractal Gerischer element allows P to deviate from 0.5. The interpretation of T depends on the mechanism.

Figure 1.10: Representing a porous electrode as a series of cylindrical pores [19].

Figure 1.11: Fractal Gerischer element with varying P values. The Bode plot is asymmetrical with a long tail on the high frequency side. The double log plot shows that the slope on the low frequency side is 1 and the magnitude of the slope on the high frequency side is P [18].

iv. Havriliak-Negami element (HN)

Because many properties are distributed, a real SOFC electrode exhibits behavior that does not fit the true Gerischer element or the single fractal Gerischer element. The Havriliak-Negami element (aka the double fractal Gerischer element) allows both exponents to adopt a range of values.

$$Z = R/(1 + T(j\omega)^U)^P \quad (1.16)$$

Figure 1.12: HN element with $P = 0.5$ and varying U values. The Bode plot is again asymmetrical with a long tail on the high frequency side. The magnitude of the slope of the log log plot approaches U on the low frequency side and $P*U$ on the high frequency side [18].

v. Warburg impedance (W)

The Warburg impedance appears when mass transfer by diffusion is controlling the impedance. For a SOFC, the presence of convective gas flow outside the electrodes usually means that diffusion is the dominant form of mass transfer only inside the porous electrode. Diffusion over a fixed length leads to the finite length Warburg element.

$$Z = R \cdot \tanh(u) / u \quad (1.17)$$

$$u = (j\omega T)^n \quad (1.18)$$

R is the diffusion resistance. Ideally, the exponent $n = 0.5$, but a generalized finite length Warburg (FLW) allows deviation of the exponent from $1/2$. The T parameter equals l^2/D , where l is the finite diffusion length, and D is the diffusion coefficient of the reactant.

1.8 Challenges for Solid Oxide Fuel Cells

The high operating temperature (800 °C -1000 °C) is the major disadvantage of SOFCs since it results in slow start up time, fast cell degradation and requirement for more expensive materials such as ceramic interconnects [8]. Therefore, there is a high interest to reduce the operating temperature of SOFCs. However, when the operating temperature of SOFC is decreased, rates of electrochemical reactions drop exponentially; especially the cathode reactions which have high activation energies and low reaction kinetics compared to the anode reactions. This in turn decreases the overall cell performance [8]. Therefore, it

is imperative to develop SOFC cathodes that are best performing in intermediate temperatures (600 °C -800 °C) either by improving the microstructure and/or by developing high performance materials.

On the other hand, improvement of microstructure needs fundamental understanding of the reaction processes associated with the cathode that can be learned using impedance spectroscopy [17]. However, in order to extract useful information, it is important to use methods that can separate different processes associated with different cell components, especially under applied DC voltages/currents.

1.9 Objectives and the Structure of the Dissertation

As mentioned above, development of better performing cathodes are very important for the advancement of intermediate temperature solid oxide fuel cells. Therefore, one objective of this research is to develop SOFC cathodes with improved microstructures which in turn would result in better performance at intermediate temperatures. The other objective is to study different processes associated with different cell components (with minimal effect from each other) in order to better understand the processes associated with cell reactions.

Choosing a suitable current collector is very important for SOFC characterization. Therefore, current collection properties of noble metals (Pt, Au and Ag) and LSM were investigated using the Princeton Applied Research (PAR) system and the results are discussed in Chapter 02 – Section I. Preliminary studies carried out on YSZ nanofiber cathodes using the PAR system are discussed in Chapter 02 – Section II. Chapter 03 discusses the results obtained using the Solartron system for LSM infiltrated YSZ cathodes with LSM current collectors. Impedance spectroscopy data of different SOFC cathodes (LSM, Ag-LSM, LSM-YSZ) and their deconvolution analysis are discussed in Chapter 04. Chapter 05 discusses the possibility of studying a single electrode with DC current flow using LSM/YSZ “hybrid” cells.

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Chapter 02

Section I

Metal and LSM Current Collectors

2.1 Introduction

Current collector properties are vital for the solid oxide fuel cell (SOFC) performance since the resistance due to contact materials results in Ohmic losses. Noble metals (Pt, Pd, Au, Ag) and some ceramic materials (CaCoO_3 , LaCrO_3) are commonly used as current collectors in high temperature SOFCs. High costs associated with noble metal current collectors (Pt, Au, Pd) make them less desirable to be used in large scale even though they are very stable at high operating temperatures. Ceramic current collectors have higher stability in oxidizing conditions which makes them good candidates for cathode current collection but the low electrical conductivity limits their desirability [1].

The main goal of this study was to compare the current collection properties of platinum (Pt), gold (Au), silver (Ag) and Lanthanum Strontium Manganite (LSM) on Yttria Stabilized Zirconia (YSZ) electrolyte. Moreover, their performance as SOFC cathodes was also studied by measuring the polarization resistances.

Commercially bought YSZ disks (8 mol% yttria) from Fuel Cell Materials (diameter = 20 mm, thickness = 0.3 mm) were used as the electrolytes for our experiments. As reported in literature [2], the activation energy for conductivity across 8YSZ (8 mol% yttria stabilized zirconia) is around 0.91 eV at 850 °C-1000 °C and 1.10 eV at 400 °C-500 °C.

The main problem we had to face was the delamination of metal current collectors (especially Pt and Au) from the YSZ electrolyte. Therefore, we tried roughening the electrolyte surface by sand papering or by screen printing an additional YSZ layer. Furthermore, we used Bi_2O_3 , a well-known sintering aid in order to improve the adhesion of metal current collectors to YSZ electrolyte. In order to do this, a thin layer (~0.05 mL) of $\text{Bi}(\text{NO}_3)_3$ solution (0.27 M) was deposited on YSZ and sintered at 800 °C to get the Bi_2O_3 -

modified YSZ surface. Also, a Bi_2O_3 powder was prepared by thermal oxidation of $\text{Bi}(\text{NO}_3)_3$ at 700°C , and this powder was mixed with the metal pastes to achieve good adhesion to the YSZ electrolyte.

2.2 Experimental

Current collection properties of the chosen metals and LSM were studied by the electrochemical characterization of symmetrical cells. The symmetrical cells (preparation methods will be discussed later) were characterized using the Princeton Applied Research (PAR) system from 850°C (or 800°C) to 700°C in air by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). For CV measurements, a Potentiostat (EG & G instruments- Model 283) with a Digitizing Oscilloscope (Tektronix-TDS 430 A) and a Universal Programmer (EG& G instruments- Model 175) was used while the Potentiostat (EG & G instruments- Model 283) and a Lock-in Amplifier (EG & G instruments- 7220 DSP) was used for EIS measurements.

Figure 2.1 shows how the symmetrical cell was mounted for the electrochemical characterization. The cell was kept inside the tube furnace with the aid of a quartz cell holder. One of the Ag/Au wires coming out of the furnace were connected to the working and sense leads while the other wire was connected to the reference and counter leads of the potentiostat.

Figure 2.1: Cross section of the tube furnace when the cell is mounted.

The total resistance of the cell can be obtained using CV data. EIS data provide the series resistance (the resistance for oxide ion conductivity across the cell plus the resistance of the wires and current collector contacts). From the difference between the total resistance and the series resistance, the polarization resistance (resistance for the oxygen reduction reaction at the cathode) can be obtained.

2.2.1 Cyclic Voltammetry Measurements

In order to do CV measurements, the symmetric cell was connected to the potentiostat and the voltage was swept from 0 V to a negative cell voltage, then to a positive cell voltage and back to 0 V; while recording the current. Then, the reciprocal slope of the voltammogram (Figure 2.2) was used to obtain the total cell resistance.

Figure 2.2: Voltammogram for a Pt/YSZ nanofiber/YSZ symmetrical cell ($d = 4$ mm) at 700°C . The total resistance calculated by the reciprocal slope of the line is 4.36 kOhms.

2.2.2 Electrochemical Impedance Spectroscopy Measurements

In our EIS experiments, a Potentiostat (EG & G instruments- Model 283) and a Lock –in Amplifier (EG & G instruments- 7220 DSP) was used to make the measurements at frequencies 10, 20 50 and 100 kHz. Due to instrument limitations, only four measurements at four different frequencies were manually collected and a straight line was obtained in the high frequency region instead of an arc. This high frequency intercept was recorded as our series resistance R_s . Figure 2.3 is an example of a plot that was obtained for EIS data.

Figure 2.3: A plot of EIS data for a Pt/Roughened YSZ/Pt symmetric cell at 700°C. The series resistance obtained by the high frequency intercept is 11.2 Ohms.

By repeating the CV and EIS measurements in a range of temperatures, the activation energy for the oxygen reduction reaction of the cathode and the activation energy for the conductivity across the cell can be found by the Arrhenius plots. The slope of the Arrhenius plot can be multiplied by the gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$) and divided by Faraday's constant (96485 Cmol^{-1}) to achieve the activation energy in electron volts (eV). Figures 2.4 and 2.5 show an example of the Arrhenius plots for a Pt/roughened YSZ symmetrical cell characterized at 700 °C, 750 °C, 800 °C and 850 °C.

Figure 2.4: Arrhenius plot for the series resistance (R_s) and the deduced activation energy for the oxide ion conductivity across the cell. Slope = 11565 ± 453 , Intercept = -9.5 ± 0.4 , $R^2 = 0.997$, $E_a = 1.00 \pm 0.04 \text{ eV}$.

Figure 2.5: Arrhenius plot for the polarization resistance (R_p) and the deduced activation energy for the oxygen reduction reaction at the cathode. Slope = 32300 ± 1173 , Intercept = -24 ± 1 , $R^2 = 0.997$, $E_a = 2.8 \pm 0.1 \text{ eV}$.

2.3 Platinum (Pt)

2.3.1 Introduction

Platinum is a pure electronic conductor [1] and the oxygen reduction on Pt is a reaction that has been well studied over a long time [3]. Also, because of its stability at temperatures up to 1000 °C, Pt mesh is a commonly used current collector in SOFCs [4].

2.3.2 Sample Preparation

Different symmetrical cells (5) listed below were prepared using pure Pt paste (SPI-CHEM) on bare/roughened/ Bi_2O_3 -modified YSZ electrolytes, Pt and YSZ mixture (0.4 g Pt paste with 0.1 g YSZ powder (Fuel Cell Materials YSZ8-TC)) on bare YSZ electrolyte and Pt paste and Bi_2O_3 powder mixture (1:1 by weight) on bare YSZ electrolytes.

- i. Pt/bare YSZ: Pt electrodes were painted on bare YSZ electrolyte surface and sintered at 1100 °C or 850 °C.
- ii. Pt/roughened YSZ: The YSZ electrolyte surface was modified by screen-printing a thin, additional YSZ layer followed by sintering at 1300 °C (in order to enhance the adhesion of the Pt layer). Then, Pt electrodes were painted on roughened YSZ surface and sintered at 900 °C.
- iii. Pt - YSZ/YSZ: Pt paint and YSZ powder was mixed together to form a paste which was painted on bare YSZ and sintered at 1100 °C.
- iv. Pt / Bi_2O_3 – YSZ: Pt electrodes were painted on Bi_2O_3 -deposited YSZ substrates and sintered at 1100 °C or 850 °C.
- v. Pt - Bi_2O_3 /YSZ: Pt paint and Bi_2O_3 powder was mixed together to form a paste which was painted on bare YSZ and sintered at 850 °C.

2.3.3 Electrochemical Characterization

These symmetrical cells were electrochemically characterized by CV and EIS at 850 °C, 800 °C, 750 °C and 700 °C using Au wires and Au paste. Some cells were aged at 700 °C for a certain time period and the electrochemical characterization was repeated at the above mentioned temperatures.

2.3.4 Results and Discussion

Note: When the same cell was re-characterized/aged, it is shown with a prime ('). Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated.

Table 2.1: Series resistances, polarization resistances and activation energies for Pt containing cells.

Sample	Description	R_s (Ωcm^2) at 800°C	E_a (eV) for R_s	R_p (Ωcm^2) at 800°C	E_a (eV) for R_p
i (a)	Pt/bare YSZ sintered at 1100 °C	1.21	0.6 (+/-0.0)	18.27	2.6 (+/-0.1)
i (a)'	Pt/bare YSZ sintered at 1100 °C (~48hrs aged)/Au current collector	1.22	0.6 (+/-0.0)	255.5	1.9 (+/-0.1)
i (b)	Pt/bare YSZ (sintered at 850 °C)	1.03	1.0 (+/-0.0)	2.41	2.3 (+/-0.2)
ii (a)	Pt/roughened YSZ, sintered at 900 °C	1.06	1.1 (+/-0.0)	19.9	2.3 (+/-0.1)
ii (b)	Pt/roughened YSZ, sintered at 900 °C	0.74	1.0 (+/-0.1)	9.4	1.9 (+/-0.1)
ii (c)	Pt/roughened YSZ, sintered at 900 °C	1.12	1.0 (+/-0.0)	45.7	2.8 (+/-0.1)
ii (c)'	Pt/roughened YSZ, sintered at 900 °C (~96 hrs aged)	1.00	0.6 (+/-0.1)	20.09	2.5 (+/-0.0)
iii	Pt-YSZ/YSZ, sintered at 1100 °C/Au current collector	1.79	0.7 (+/-0.0)	3.97	1.3 (+/-0.0)
iv (a)	Pt /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ sintered at 850 °C, Pt sintered at 850 °C	0.71	0.8 (+/-0.0)	0.41	2.1 (+/-0.1)
iv (b)	Pt /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ sintered at 850 °C, Pt sintered at 850 °C	0.91	1.03 (+/-0.0)	1.31	2.9 (+/-0.1)
iv(c)	Pt /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ sintered at 850 °C, Pt sintered at 1100 °C	0.98	0.98 (+/-0.0)	4.93	2.3 (+/-0.2)
v (a)	Pt - Bi ₂ O ₃ /YSZ , sintered at 850 °C	1.24	1.2 (+/-0.0)	1.13	2.4 (+/-0.1)
v (a)'	Pt - Bi ₂ O ₃ /YSZ , sintered at 850 °C, re-characterization of v(a)	0.88	0.9 (+/-0.0)	0.81	1.8 (+/-0.2)
v (b)	Pt - Bi ₂ O ₃ /YSZ , sintered at 850 °C	2.47	1.0 (+/-0.0)	5.72	2.3 (+/-0.1)
v (b)'	Pt - Bi ₂ O ₃ /YSZ , sintered at 850 °C, re-characterization of v(b)	1.51	0.9 (+/-0.0)	3.59	2.2 (+/-0.1)

Table 2.1 present the series and polarization resistances measured at 800 °C and the corresponding activation energies for Pt containing cells. A summary of average series resistances and corresponding activation energies for Pt containing cells are presented in

Table 2.2. When Student's t-test was used for statistical analysis [5], there was no statistically significant difference between the average R_s values for samples (i) and (ii) which suggests that the adhesion of Pt to YSZ substrate was similar in both cases. Furthermore, since their average R_s values are higher than expected ($> 0.7 \text{ Ohmcm}^2$ at 800°C), it can be concluded that the bare or roughened YSZ surfaces did not promote the adhesion of the Pt layer. There is a 95% confident significant difference between the average R_s values for samples (i) and (iv) due to Bi_2O_3 . Sample (iv) yielded the most consistent R_s values and consequently appears to be the best method for obtaining a good bond between YSZ and Pt paint. There is no significant difference between the average activation energies (E_a) for samples (i) and (ii) or (i) and (iv).

Barbucci et al. [6] reports the R_s value at 900°C for their Pt/YSZ system as $\sim 1.0 \text{ Ohmcm}^2$ which is slightly higher than our results. However, this is a property that depends on the thickness of the YSZ substrate and differs from one batch/manufacturer to another.

Table 2.2: Summary of average series resistances and activation energies for conductivity across the cell of Pt containing cells.

Sample	Average R_s at 800°C (Ohmcm^2)	Standard deviation	Average E_a for R_s (eV)	Standard deviation
(i)	1.15	+/- 0.1	0.73	+/- 0.2
(ii)	0.98	+/- 0.2	0.93	+/- 0.2
(iii)	1.79	-	0.70	+/- 0.0
(iv)	0.87	+/- 0.1	0.94	+/- 0.1
(v)	1.53	+/- 0.7	1.01	+/- 0.1

Badwal [7] has reported resistivity values ranging from $\sim 25 - 36 \text{ Ohmcm}$ for 8YSZ at 800°C , while the resistivity value calculated for our 8YSZ electrolytes is also $\sim 25 \text{ Ohmcm}$ at 800°C .

The polarization resistances of Pt electrodes drastically decreased when bismuth oxide was used as a sintering aid. However, sample iv(c) has a comparatively high R_p value. Furthermore, it can be seen that the performance of Pt electrodes was comparatively

enhanced when they were sintered at 850 °C, compared to the electrodes sintered at 1100 °C. Possibly high temperature sintering causes agglomeration of the Pt particles which would reduce the porosity and the oxygen availability for the oxygen reduction reaction which in turn results in higher R_p values. Also, it is known that Pt tends to volatilize at higher temperatures and to be deposited at the cathode/electrolyte surface which decrease the cell performance [4]. Furthermore, when a gold current collector was used on Pt, the R_p values increased drastically.

Barbucci et al. [6] performed a similar experiment with a 3-electrode system where the working electrodes (WE) was sintered at 1100 °C for 2 hours and then characterized at 900 °C. They reported a R_p value of 4.76 Ohmcm² for pure Pt WE and 1.5 Ohmcm² for a WE that consists of a mixture of Pt and YSZ. These results are comparable to some values that we have obtained for pure Pt (eg: samples (i)a, (ii)a and (ii)b) and also it was observed that the R_p values decrease when a mixture of Pt and YSZ is used as the WE (sample iii). The lowest R_p values were obtained when Bi₂O₃ was used in Pt electrodes. Verkerk et al. [8] have reported their results of a similar study where they characterized sputtered Pt electrodes on YSZ and Bi₂O₃- Er₂O₃. They observed that both the R_s and R_p values significantly decreased when Bi modified electrolytes were used. This is not surprising as Bi₂O₃ is a very good oxide ion conductor at high temperatures with a conductivity that is ~2 times higher than YSZ [2]. Due to high ionic conductivity of Bi₂O₃ and its ability to sinter Pt well onto the YSZ electrolyte, R_s values become smaller (e.g., Sample iv (a)). Also, having Pt (pure electronic conductor) and Bi₂O₃ (oxide ion conductor) together with the gas phase increases the triple phase boundary (TPB) length; resulting in lower R_p values (e.g., Sample iv (a)).

Vladikova et al.[9] have reported the activation energy for oxygen reduction reaction on Pt/YSZ electrodes (for temperatures above 600 °C) as 1.6 eV. However, the activation energy values that we have observed for the oxygen reduction reaction are relatively higher than this value.

2.3.5 Summary

Pt electrodes delaminating from the YSZ electrolyte was the most significant issue while characterizing Pt containing symmetrical cells. Typical R_s value for these YSZ electrolytes at 800 °C is $\sim 0.7 \text{ Ohmcm}^2$. However, according to Table 2.1, only 2 cells (ii (b) and iv (a)) showed R_s values in this range and one of them had Bi_2O_3 as a sintering aid. Some compositions (eg: iv (a)) exhibited both very low R_p and R_s values which suggest that these compositions would be good candidates as a SOFC cathode material.

2.4 Gold (Au)

2.4.1 Introduction

Gold (Au) is known to be a better current collector than Pt due to its lower mobility and inertness [4]. However, it is reported to be a poor SOFC cathode due to its low catalytic activity for oxygen reduction [10], [11]. Similar to Pt, the oxygen reduction reaction is limited to triple phase boundaries in Au cathodes [4], [12].

2.4.2 Sample Preparation

Different symmetrical cells (4) listed below were prepared using pure Au paste (Heraeus) on bare/roughened/ Bi_2O_3 -modified YSZ electrolytes and Au paste and Bi_2O_3 powder mixture (1:1 by weight) on bare YSZ electrolytes.

- i. Au/bare YSZ: Au electrodes were painted on bare YSZ electrolyte surface and sintered at 900 °C or 850 °C.
- ii. Au/roughened YSZ: YSZ electrolyte surface was modified by screen printing a thin, additional YSZ layer followed by sintering at 1300 °C (in order to enhance the adhesion of the (Au layer). Then, Au electrodes were painted on roughened YSZ surface and sintered at 900 °C.
- iii. Au / Bi_2O_3 – YSZ: Au electrodes were painted on Bi_2O_3 deposited YSZ substrates and sintered at 700 °C or 850 °C.
- iv. Au - Bi_2O_3 /YSZ: Au paint and Bi_2O_3 powder was mixed together to form a paste which was painted on bare YSZ and sintered at 850 °C.

2.4.3 Electrochemical Characterization

These symmetrical cells were electrochemically characterized by CV and EIS at 850 °C, 800 °C, 750 °C and 700 °C using Au wires and Au paste.

2.4.4 Results and Discussion

Note: When the same cell was re-characterized/aged, it is shown with a (‘) or (’’) or (’’’), and further details are given in the table. Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated.

Table 2.3: Series resistances, polarization resistances and activation energies of Au containing cells.

Sample	Description	R_s (Ωcm^2) at 800 °C	E_a (eV) for R_s	R_p (Ωcm^2) at 800 °C	E_a (eV) for R_p
i (a)	Au/bare YSZ sintered at 900 °C	0.66	0.8 (+/-0.0)	414	1.6 (+/-0.1)
i (b)	Au/bare YSZ sintered at 850 °C	0.72	0.8 (+/-0.1)	8.2	1.3 (+/-0.2)
ii (a)	Au/roughened YSZ, sintered at 900 °C	1.47	1.0 (+/-0.0)	519	1.2 (+/-0.1)
ii (b)	Au/roughened YSZ, sintered at 900 °C	4.22	0.9 (+/-0.1)	2203	1.7 (+/-0.0)
iii (a)	Au /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ sintered at 850 °C, Au sintered at 850 °C	0.62	0.9 (+/-0.0)	2.2	1.7 (+/-0.1)
iii (b)	Au /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ sintered at 850 °C, Au sintered at 850 °C	0.77	0.8 (+/-0.1)	3.6	1.2 (+/-0.0)
iii (c)	Au /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ and Au sintered at 850 °C	0.64	0.9 (+/-0.1)	5.5	1.6 (+/-0.1)
iii (d)	Au /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ and Au sintered at 700 °C	1.14	0.8 (+/-0.0)	3.9	1.3 (+/-0.1)
iii (e)	Au /Bi ₂ O ₃ – YSZ, Bi (NO ₃) ₃ sintered at 1100 °C, Au sintered at 850 °C	1.02	1.1 (+/-0.0)	4.5	1.8 (+/-0.0)
iv	Au - Bi ₂ O ₃ /YSZ, sintered at 850 °C	0.72	0.8 (+/-0.1)	0.46	1.1 (+/-0.0)

Table 2.4: Summary of average series resistances and activation energies for conductivity across the cell of Au containing cells.

Sample	Average R_s at 800 $^{\circ}\text{C}$ (Ohmcm^2)	Standard deviation	Average E_a for R_s (eV)	Standard deviation
(i)	0.7	+/- 0.0	0.8	+/- 0.0
(ii)	2.9	+/- 2.0	1.0	+/- 0.1
(iii)	0.9	+/- 0.2	0.9	+/- 0.1
(iv)	0.7	-	0.8	-

According to Tables 2.3 and 2.4, very high R_s values for sample (ii) suggest that Au was not completely sintered on roughened YSZ electrolytes. Similar to Pt, the lowest R_s and R_p values were observed when Bi_2O_3 was incorporated into Au electrodes. Samples (i) and (iv) show the typical series resistance for these YSZ electrolytes at 800 $^{\circ}\text{C}$ ($\sim 0.7 \text{ Ohmcm}^2$), which confirms that there was no electrode delamination while the electrochemical characterization was carried out. Furthermore, Vladikova et al. [9] have reported the activation energy for oxygen reduction reaction on Au/YSZ (for temperatures below 450 $^{\circ}\text{C}$) as 1.0 eV. Since our measurements were carried out in 700 $^{\circ}\text{C}$ – 850 $^{\circ}\text{C}$ temperature range, it limits the direct comparison of activation energy values.

2.4.5 Summary

As same as with Pt, delamination of Au electrodes from the YSZ electrolytes was the major obstacle. However, when Bi_2O_3 was used as a sintering aid, low R_s values were achieved (most of the time), which suggests good adhesion. Also, very low R_p and R_s values for sample (iv) suggest that a mixture of Au and Bi_2O_3 sintered on YSZ is a good candidate for SOFC cathodes.

2.5 Silver (Ag)

2.5.1 Introduction

There are contradictory ideas on the current collection ability of Silver (Ag). Some state that it is a poor current collector due to its high volatility at high temperatures which makes it less inert [4]. However, some people show that lowest resistances were always achieved

when Ag current collectors were used [11]. Also, Ag is reported to be a good catalyst for oxygen reduction reaction which makes it a suitable candidate for SOFC cathodes [11].

2.5.2 Sample Preparation

Different symmetrical cells (3) listed below were prepared using pure Ag paste (Fuel Cell Materials) on bare/ Bi₂O₃-modified YSZ electrolytes.

- i. Ag (thin)/bare YSZ: A thin layer of Ag paste was painted on bare YSZ electrolyte surface and sintered at 700 °C or 800 °C.
- ii. Ag (1 tape thick)/bare YSZ: A thick layer of Ag paste (thickness of the tape used to define the electrode area) was painted on bare YSZ electrolyte surface and sintered at 800 °C.
- iii. Ag /Bi₂O₃ – YSZ: Ag electrodes were painted on Bi₂O₃ deposited YSZ substrates and sintered at 800 °C.

2.5.3 Electrochemical Characterization

These symmetrical cells were electrochemically characterized by CV and EIS at 800 °C, 750 °C and 700 °C using Ag wires and Ag paste. Some cells were aged at 700 °C for a certain time period and the electrochemical characterization was repeated at the above mentioned temperatures.

2.5.4 Results and Discussion

Note: When the same cell was re-characterized/aged, it is shown with a (‘) or (’’) or (’’’), and further details are given in the table. Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated.

Unlike Au and Pt containing cells, Ag containing cells showed low series and polarization resistances that were reproducible (Table 2.5). Compared to Au and Pt, Ag was well sintered on bare YSZ electrolytes as confirmed by the R_s values which are around 0.7- 0.8 Ohmcm² (Table 2.6).

When thick Ag electrodes were compared with thin Ag electrodes, both showed the same R_s values but different activation energies for conductivity across the cell. Also, the R_p values increased when thicker Ag electrodes were used. This may occur due to limited oxygen transport to the Ag/YSZ interface in thicker silver layers, which results in increased polarization and total resistances.

Table 2.5: Series resistances, polarization resistances and activation energies of Ag containing cells.

Sample	Description	R_s (Ωcm^2) at 800 °C	E_a (eV) for R_s	R_p (Ωcm^2) at 800 °C	E_a (eV) for R_p
i (a)	Ag (thin)/bare YSZ sintered at 700 °C	1.08	1.1 (+/-0.0)	0.38	1.3 (+/-0.2)
i (b)	Ag (thin)/bare YSZ sintered at 800 °C	0.72	0.9 (+/-0.0)	0.75	1.0 (+/-0.0)
i (c)	Ag (thin)/bare YSZ sintered at 800 °C	0.65	0.9 (+/-0.0)	0.64	1.0 (+/-0.0)
i (c)'	Ag (thin)/bare YSZ sintered at 800 °C, aged ~24 hrs	0.68	0.9 (+/-0.0)	0.7	1.0 (+/-0.0)
ii (a)	Ag (1 tape thick)/bare YSZ sintered at 800 °C, heating	0.75	0.7 (+/-0.0)	4.45	1.0 (+/-0.0)
ii (a)'	Ag (1 tape thick)/bare YSZ sintered at 800 °C, cooling	0.76	0.7 (+/-0.0)	4.59	1.1 (+/-0.1)
ii (a)''	Ag (1 tape thick)/bare YSZ sintered at 800 °C, aged ~48 hrs, heating	0.75	0.7 (+/-0.0)	4.40	1.0 (+/-0.1)
ii (a)'''	Ag (1 tape thick)/bare YSZ sintered at 800 °C, aged ~48 hrs, cooling	0.75	0.7 (+/-0.0)	4.52	1.1 (+/-0.1)
ii (b)	Ag (1 tape thick)/bare YSZ sintered at 800 °C, heating	0.77	0.7 (+/-0.0)	3.97	0.9 (+/-0.1)
ii (b)'	Ag (1 tape thick)/bare YSZ sintered at 800 °C, cooling	0.78	0.7 (+/-0.0)	4.01	1.2 (+/-0.1)
ii (c)	Ag (1 tape thick)/bare YSZ sintered at 800 °C, heating	0.77	0.7 (+/-0.0)	3.44	1.0 (+/-0.1)
ii (c)'	Ag (1 tape thick)/bare YSZ sintered at 800 °C, cooling	0.77	0.7 (+/-0.0)	3.54	1.2 (+/-0.1)
iii	Ag /Bi ₂ O ₃ – YSZ , Bi (NO ₃) ₃ sintered at 850 °C, Ag sintered at 800 °C	0.88	1.1 (+/-0.0)	0.77	1.2 (+/-0.0)

Table 2.6: Summary of average series resistances and activation energies for conductivity across the cell of Ag containing cells.

Sample	Average R_s at 800 °C (Ohmcm ²)	Standard deviation	Average E_a for R_s (eV)	Standard deviation
(i)	0.8	+/- 0.2	0.9	+/- 0.1
(ii)	0.8	+/- 0.0	0.7	+/- 0.0
(iii)	0.9	-	1.1	+/- 0.0

Due to high oxygen solubility in silver [1], it acts as a better SOFC cathode compared to Pt and Au which show very low oxygen solubility. Sarikaya et al. [1] have reported 1.85 Ohmcm² as the R_p value at 800 °C for their Ag/YSZ symmetric cells. However we have observed very low R_p values (~0.7 Ohmcm²) for thin Ag electrodes and much higher R_p values (~4.0 Ohmcm²) for thick Ag electrodes, at 800 °C.

Similar to the Pt and Au systems, very low R_s and R_p values were obtained when Ag electrodes were painted on Bi₂O₃ modified YSZ, which is attributed to the high ionic conductivity of Bi₂O₃ and its ability to act as a sintering aid.

Short term aging study of Ag/YSZ symmetric cells (Samples 1(d), ii(c) and ii(d)) show that Ag electrodes did not significantly deteriorate with time when aged at 700 °C. However, when operated at 800 °C for a long time, Ag particles tend to agglomerate and sinter together which reduces its porosity, resulting in deterioration of its collection properties [1] and its ability to act as a cathode in SOFCs.

2.5.5 Summary

Ag showed good adhesion to YSZ electrolytes even in the absence of a sintering aid. Therefore, we have decided to continue using Ag paste as one of the current collectors in our future studies. Also, Ag current collectors were extensively studied using the Solartron system and the results will be discussed in Chapter 04.

2.6 Lanthanum Strontium Manganite (LSM)

2.6.1 Introduction

Lanthanum Strontium Manganite (LSM) is the most investigated, widely used cathode material in high temperature SOFCs [13]. Also, LSM is used as a current collector in SOFC cathodes [14]. We have characterized only one LSM/YSZ symmetric cell using the PAR system as a preliminary study.

2.6.2 Sample Preparation

Commercial LSM powder ($(\text{La}_{0.8}\text{Sr}_{0.2})\text{MnO}_{3-\delta}$) bought from Fuel Cell Materials was mixed with α -terpineol (2:1 by weight) to make a thick LSM paste which was painted on both sides of a YSZ electrolyte and sintered at 1200°C.

2.6.3 Electrochemical Characterization

This LSM/YSZ symmetrical cell was electrochemically characterized by CV and EIS at 800 °C, 750 °C and 700 °C using Ag wires. No metal current collectors were used and a small amount of Ag paste was used to attach the Ag wires on to the LSM electrode. Then, this cell was aged for ~24 hours at 700 °C and the electrochemical characterization was repeated at the above mentioned temperatures.

2.6.4 Results and Discussion

Note: When the same cell was re-characterized/aged, it is shown with a (‘) or (’’) or (’’’), and further details are given in the table. Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated.

Only one LSM/YSZ symmetric cell was characterized using PAR system (Table 2.7). $R_s \sim 0.8 \text{ Ohmcm}^2$ suggests that the LSM electrodes were properly sintered on YSZ electrolyte. Also, R_p drastically increased when the cell was aged at 700 °C for ~24 hrs.

Table 2.7: Series resistances, polarization resistances and activation energies of LSM/YSZ symmetric cells.

Sample	Description	R_s (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_s	R_p (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_p
i (a)	LSM/ YSZ sintered at 1200 $^{\circ}\text{C}$, heating	0.8	0.6 (± 0.0)	10.1	0.7 (± 0.0)
i (a)'	LSM/ YSZ sintered at 1200 $^{\circ}\text{C}$, cooling	0.8	0.7 (± 0.1)	10.4	1.1 (± 0.1)
i (a)''	LSM/ YSZ sintered at 1200 $^{\circ}\text{C}$, aged ~24 hrs, heating	0.8	0.7 (± 0.0)	23.9	1.0 (± 0.0)

We have extensively studied LSM/YSZ symmetrical cells using the Solartron system and the results of those studies will be discussed in detail in Chapter 04.

2.6.5 Summary

The symmetrical cell (LSM/YSZ) that was characterized using the PAR system looked promising since it showed good adhesion and low R_s values. However, its major disadvantage is the requirement of a high sintering temperature compared to the metal current collectors. LSM was further studied as a current collector using the Solartron system.

2.7 Conclusion

Pt, Au, Ag and LSM are already in use as current collectors for SOFCs. The purpose of this study was to choose the most suitable current collector for the electrochemical characterization of our symmetrical cells. Since it was difficult to overcome the delamination of Pt and Au electrodes from YSZ; we have decided to continue using Ag and LSM as the current collectors for YSZ based electrodes since they exhibit good adhesion properties and reproducible performance. Detailed analysis of LSM and Ag current collectors (using the Solartron system) will be presented in Chapter 03 and Chapter 04. Adding an oxide ion conductor (eg: Bi_2O_3 , YSZ) to a noble metal that is a pure electronic conductor (eg: Pt, Au) lowered the R_p and R_s values of the cathodes in some cases.

However, most of them did not show good adhesion to the YSZ electrolyte which can be further proven by high R_s values.

Section II

YSZ nanofiber cathodes (PAR system)

2.8 Introduction

As discussed in Chapter 1, performance of SOFC highly depends on its cathode. Optimizing the microstructure to increase the porosity and to extend the Triple Phase Boundary (TPB) length [15] or the surface area is one approach to reduce the polarization losses at the cathode.

Oxygen reduction in a porous SOFC cathode is known to be a surface reaction. Therefore, it is important to have increased gas/solid interfacial area. 1-D nanofibers have high surface/volume ratio which increases the number of active reaction sites and the catalytic activity [3], [16]. Also, having a continuous charge transfer pathway within the microstructure increases the charge mobility and decreases the overpotential [16] (“overpotential is the additional potential beyond the thermodynamic requirement) that is needed to drive a reaction at a certain rate” [17]). Furthermore, the nanofiber cathode structure is more porous than the conventional powder cathode (Figure 2.6) which facilitates the gas transport through the cathode.

Figure 2.6: SEM images of a (a) YSZ nanofiber cathode sintered at 1300 °C (3000 X) and (b) YSZ powder cathode sintered at 1500 °C (5000 X) on YSZ electrolyte.

As we have discussed before, a higher density of TPBs increases the SOFC cathode performance. The conventional method of achieving this is mixing ionic conductor (YSZ) and electronic conductor (LSM) powders together and sintering at a higher temperature to create a composite cathode. The major difficulty is finding an optimum sintering temperature for both powders while avoiding degradation reactions. However, the infiltration technique appears to produce SOFC cathodes that have better performance while avoiding the issue of an optimum sintering temperature for two materials. In this technique, the porous cathode backbone (YSZ) is sintered at a higher temperature to ensure proper connectivity between the electrolyte and the cathode. Then, the porous scaffold is infiltrated with a solution to form the second phase (LSM) and sintered at a relatively low temperature. This approach minimizes unfavorable side reactions between the two phases and also delaminating issues due to mismatch of Thermal Expansion Coefficients (TECs) [18].

In this study, we will compare the preliminary results of the performance of non-infiltrated YSZ cathodes with the infiltrated YSZ cathodes and also the difference between powder-based and nanofiber-based YSZ cathodes. Infiltration methods used and the results obtained using the Solartron system will be discussed in detail in Chapter 03.

2.9 Experimental

We received YSZ nanofiber samples from Dr. Nick Wu and Dr. Mingjia Zhi (Department of Mechanical and Aerospace Engineering, WVU). They have used the “electrospinning” technique to synthesize YSZ nanofibers [19].

Electrospinning technique is less expensive and simpler than the template-derived method. As shown in Figure 2.7, an electrospinning apparatus usually consists of a high voltage supply, a syringe with a metallic needle and a ground collector. In a typical spinning process, the syringe is filled with the viscous precursors and a high voltage is applied between the needle and the ground collector. At a critical voltage, the repulsion between the charged polymer molecules of the precursor solution overcomes the surface tension and the liquid droplet at the needle tip stretches as a liquid jet towards the low potential [20]. When it reaches the ground collector, the liquid jet dries into solid

nanofibers [16]. Subsequent firing converts the dried blend of polymer and metal salts to the desired oxide material without loss of the nanofiber morphology (Figure 2.8).

Figure 2.7: The Electrospinning apparatus.

Figure 2.8: YSZ nanofibers sintered at 400 °C on an YSZ electrolyte.

Our goal was to create a porous YSZ nanofiber cathode that sinters well to the YSZ electrolyte, while retaining the structure of the nanofibers. However, delamination of nanofibers from the YSZ electrolyte was observed after sintering at lower temperatures. In order to overcome delamination, we tried using roughened YSZ surfaces (by HF etching) and also a well known sintering aid Bi_2O_3 . Using Bi_2O_3 to sinter YSZ at lower temperatures has been extensively studied and it is reported that the sintered YSZ has a dense structure with smaller grains when Bi_2O_3 is present [21]. Furthermore, a study was carried out to find the suitable sintering temperature for YSZ nanofibers.

2.9.1 Sintering Study

YSZ nanofibers were mixed with α -terpineol (1:10 by weight YSZ nanofiber : α -terpineol) to make a paste which was painted on YSZ electrolyte substrates. Then, these samples were sintered at 850 °C, 1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C, 1350 °C, 1400 °C and 1450 °C for 1 hour. Then, they were observed under a Scanning Electron Microscope (SEM) to study the porous YSZ structure (Figure 2.9).

2.9.2 Electrochemical Characterization

Different symmetrical cells and half cells were prepared using YSZ nanofiber paste (1:10 by weight YSZ nanofiber : α -terpineol) and/or YSZ powder paste (1:1:2 by weight YSZ powder: graphite powder : α -terpineol) on bare/roughened/ Bi₂O₃-modified YSZ electrolytes. A double sided tape was used to define the area and the thickness of the electrode before sintering. Sometimes, two tapes were used on top of each other in order to prepare thicker electrodes. After drying the electrode at ~ 150 °C, the tapes were carefully removed before the cells were sintered at higher temperatures. Pt, Au or Ag current collectors were used and the cells were electrochemically characterized by CV and EIS at 800 °C, 750 °C and 700 °C (while heating from 700 °C to 800 °C and/or cooling from 800 °C to 700 °C) using Au or Ag wires. Some cells were aged at 700 °C for a certain time period and the electrochemical characterization was repeated at the above mentioned temperatures. A set of initial measurements were made on LSM infiltrated YSZ scaffolds as well. However, since this work was continued using the Solartron system, the results of infiltrated cathodes will be discussed in detail in Chapter 3.

2.10 Results and Discussion

2.10.1 Sintering Study

The “sintering study” (Figure 2.9) showed that at temperatures lower than 1300 °C, YSZ nanofibers did not sinter well. At temperatures above 1350 °C, the nanofiber structures were melted. However at 1300 °C and 1350 °C, nanofibers sintered well while retaining their structure.

Figure 2.9: SEM images of YSZ nanofibers sintered at (a) 850 °C (3500X), (b) 1100 °C (6000X), (c) 1150 °C (7000X), (d) 1200 °C (7000X), (e) 1250 °C (8000 X), (f) 1300 °C (12000X), (g) 1350 °C (3000 X), (h) 1400 °C (10000X) and (i) 1450 °C (5000 X).

2.10.2 Pt current collectors on YSZ nanofiber cathodes

Cells characterized:

- i. Pt/YSZ nanofiber/YSZ: YSZ nanofiber electrodes were painted on bare YSZ electrolyte surface and sintered at 1100 °C. Then, Pt paint was applied on top of the YSZ nanofiber electrodes and sintered again at 1100 °C.
- ii. Pt/YSZ nanofiber/ Bi₂O₃ – YSZ: YSZ nanofiber electrodes were painted on Bi₂O₃ deposited YSZ substrates and sintered at 1100 °C or 850 °C. Then, Pt paint was applied on top of the YSZ nanofiber electrodes and sintered again at 1100 °C or 850 °C.

Note: When the same cell was re-characterized/aged, it is shown with a (‘) and further details are given in the table. Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated.

Table 2.8: Series resistances, polarization resistances and activation energies of YSZ nanofiber cathodes with Pt current collectors.

Sample	Description	R_s (Ωcm^2) at 800 °C	E_a (eV) for R_s	R_p (Ωcm^2) at 800 °C	E_a (eV) for R_p
i (a)	Pt/YSZ nanofiber/YSZ , nanofiber sintered at 1100 °C, Pt sintered at 1100 °C	5.67	1.5 (+/-0.1)	22.42	2.0 (+/-0.1)
i (a)'	Pt/YSZ nanofiber/YSZ , nanofiber sintered at 1100 °C, Pt sintered at 1100 °C (~48hrs aged)	4.07	1.6 (+/-0.1)	17.67	1.5 (+/-0.1)
ii (a)	Pt/YSZ nanofiber/ Bi_2O_3 – YSZ, $\text{Bi}(\text{NO}_3)_3$ sintered at 850 °C, nanofiber sintered at 850 °C, Pt sintered at 850 °C	1.15	1.1 (+/-0.0)	0.51	2.7 (+/-0.2)
ii (b)	Pt/YSZ nanofiber/ Bi_2O_3 – YSZ, $\text{Bi}(\text{NO}_3)_3$ sintered at 850 °C, nanofiber sintered at 850 °C, Pt sintered at 850 °C	0.80	0.9 (+/-0.0)	0.32	2.4 (+/-0.2)
ii(c)	Pt/YSZ nanofiber/ Bi_2O_3 – YSZ, $\text{Bi}(\text{NO}_3)_3$ sintered at 850 °C, nanofiber sintered at 1100 °C, Pt sintered at 1100 °C	0.87	1.0 (+/-0.0)	6.21	2.8 (+/-0.1)

When Student’s t-test was used for statistical analysis [5], there is a significant difference in average R_s and E_a values of samples (i) and (ii). However, the comparison of sample (ii) and sample (iv) of Section 2.3 (Pt / Bi_2O_3 – YSZ) shows that there is no significant difference between their average R_s or E_a values. The significant difference between samples (i) and (ii), and the similarity between samples (ii) and (iv) of Section 2.3 can be attributed to the following observations. The only difference between samples (i) and (ii) was that the YSZ substrate of sample (ii) was modified with Bi_2O_3 . The SEM images (Figure 2.10) of this sample showed that Bi_2O_3 caused the YSZ nanofibers to “melt down” which resulted in a “ Bi_2O_3 modified roughened YSZ surface”. Therefore, this sample (ii) behaved more similar to sample (iv) of Section 2.3, than sample (i). According to Keizr et al. [22], Bi_2O_3 promotes low temperature sintering of YSZ by reacting with the fluorite

phase of ZrO_2 . This reaction yields a reactive (which might be a liquid) medium that aid the sintering reaction. This might be the reason for our observation of “melted” YSZ nanofibers in the presence of Bi_2O_3 .

Figure 2.10: YSZ nanofibers sintered with $\text{Bi}(\text{NO}_3)_3$ at $850\text{ }^\circ\text{C}$, nanofibers are melted.

R_p values drastically decreased when Bi_2O_3 was incorporated in to symmetric cells. However, sample ii (c) showed a comparatively high R_p value may be because Pt was sintered at a higher temperature ($1100\text{ }^\circ\text{C}$).

Furthermore, SEM images of sample (i) clearly showed poor sintering of YSZ nanofibers at $1100\text{ }^\circ\text{C}$ (Figure 2.9 (b)). This results in a poorly defined pathway for oxide ion conduction from the electrolyte to current collector which results in comparatively higher R_p , R_s and E_a values.

2.10.3 Au current collectors on YSZ nanofiber cathodes

Cells characterized:

- i. Au/ Bi_2O_3 -YSZ nanofiber/YSZ: YSZ nanofiber and Bi_2O_3 powder was mixed together to form a paste which was painted on bare YSZ and sintered at $850\text{ }^\circ\text{C}$. Then, Au paste was applied on top of those electrodes and sintered at $850\text{ }^\circ\text{C}$.
- ii. Au/YSZ nanofiber/ Bi_2O_3 -YSZ: YSZ nanofiber electrodes were painted on Bi_2O_3 deposited YSZ substrates and sintered at $850\text{ }^\circ\text{C}$ or $1100\text{ }^\circ\text{C}$. Then, Au paint was applied on top of the YSZ nanofiber electrodes and sintered again at $700\text{ }^\circ\text{C}$ or $850\text{ }^\circ\text{C}$.

Table 2.9: Series resistances, polarization resistances and activation energies of YSZ nanofiber cathodes with Au current collectors.

Sample	Description	R_s (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_s	R_p (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_p
iii	Au/ Bi_2O_3 -YSZ nanofiber/YSZ, mixture sintered at 850 $^{\circ}\text{C}$, Au sintered at 850 $^{\circ}\text{C}$	0.85	0.9 (± 0.0)	1.0	1.6 (± 0.1)
iv (a)	Au/YSZ nanofiber/ Bi_2O_3 -YSZ, $\text{Bi}(\text{NO}_3)_3$ sintered at 850 $^{\circ}\text{C}$, YSZ nanofibers sintered at 850 $^{\circ}\text{C}$, Au sintered at 700 $^{\circ}\text{C}$	2.81	0.7 (± 0.1)	3.4	1.8 (± 0.0)
iv (b)	Au/YSZ nanofiber/ Bi_2O_3 -YSZ, $\text{Bi}(\text{NO}_3)_3$, YSZ nanofibers, Au sintered at 850 $^{\circ}\text{C}$	1.03	0.7 (± 0.0)	1.3	1.4 (± 0.2)
iv(c)	Au/YSZ nanofiber/ Bi_2O_3 -YSZ, $\text{Bi}(\text{NO}_3)_3$ and YSZ nanofibers sintered at 1100 $^{\circ}\text{C}$, Au sintered at 850 $^{\circ}\text{C}$	1.97	0.9 (± 0.1)	18.2	1.7 (± 0.1)

Sample (iii) which has a mixture of Bi_2O_3 and YSZ nanofibers shows the lowest R_s value for these samples (Table 2.9). As discussed above, melting of YSZ nanofibers in the presence of Bi_2O_3 which results in a “roughened YSZ surface” might be the reason for this relatively low R_s value. R_s value for sample iv (a) is higher than for samples iv (b) and iv(c). Possibly, the Au current collector did not sinter well onto the YSZ nanofiber cathode at 700 $^{\circ}\text{C}$. As same as for the series resistance, sample (iii) shows the lowest R_p value at 800 $^{\circ}\text{C}$. Sample iv (c) shows an unusually high R_p value compared to samples iv (a) and iv (b).

2.10.4 Ag current collectors on YSZ nanofiber cathodes

Cells characterized:

- v. Ag/YSZ nanofiber/ Bi_2O_3 -YSZ: YSZ nanofiber electrodes were painted on Bi_2O_3 deposited YSZ substrates and sintered at 850 $^{\circ}\text{C}$. Then, Ag paint was applied on top of the YSZ nanofiber electrodes and sintered again at 800 $^{\circ}\text{C}$.
- vi. Ag/YSZ nanofiber (thin)/ HF etched YSZ: A YSZ pellet was etched with Hydrofluoric acid to roughen the surface and thin YSZ nanofiber electrodes were

- painted on this etched region and sintered at 800 °C. Then, Ag paint was applied on top of the YSZ nanofiber electrodes and sintered again at 700 °C.
- vii. Ag/YSZ nanofiber (thin) /YSZ: Thin YSZ nanofiber electrodes were painted on bare YSZ electrolyte surfaces and sintered at 1300 °C. Then, Ag paint was applied on top of the YSZ nanofiber electrodes and sintered again at 700 °C.
 - viii. Ag/YSZ nanofiber (1 tape thick) /YSZ: YSZ nanofiber electrodes (thickness of the tape which was used to define the electrode area) were painted on bare YSZ electrolyte surfaces and sintered at 1300 °C. Then, Ag paint was applied on top of the YSZ nanofiber electrodes and sintered again at 800 °C.
 - ix. Ag/ YSZ nanofiber (1 tape thick) /YSZ-half cell: YSZ nanofiber electrodes (thickness of the tape used to define the electrode area) were painted on one side of bare YSZ electrolyte surfaces and sintered at 1300 °C. Then, Ag paint was applied on top of the YSZ nanofiber electrode and on the opposite side of the electrode and sintered again at 800 °C.
 - x. Ag/ YSZ nanofiber (2 tapes thick) /YSZ-half cell: Thick YSZ nanofiber electrodes (thickness of 2 tapes used to define the electrode area) were painted on one side of bare YSZ electrolyte surfaces and sintered at 1300 °C. Then, Ag paint was applied on top of the YSZ nanofiber electrode and on the opposite side of the electrode and sintered again at 800 °C.

Note: When the same cell was re-characterized/aged, it is shown with a (‘) or (’’) or (’’) or (‘’) and further details are given in the table. Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated. Also, it should be noted that the R_p values presented for half cells consist of the polarization resistances for both YSZ powder electrode and Ag (counter) electrode.

As we have discussed before, “Sample v” which has $\text{Bi}(\text{NO}_3)_3$ in it shows a comparatively low R_s value (Table 2.10). However, “Sample vii” which has a thin layer of YSZ nanofibers sintered at 1300 °C shows the lowest R_s value. According to the sintering study, YSZ nanofibers sinter well at this temperature without melting down. However, since we

used a thin nanofiber layer, maybe the Ag current collector was directly in contact with the electrolyte at some places which resulted in a relatively low series resistance.

Table 2.10: Series resistances, polarization resistances and activation energies of YSZ nanofiber cathodes with Ag current collectors.

Sample	Description	R_s (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_s	R_p (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_p
v	Ag/YSZ nanofiber/ Bi_2O_3 -YSZ, Bi (NO_3) ₃ sintered at 850 $^{\circ}\text{C}$, YSZ nanofibers sintered at 850 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$	1.82	1.3 (+/-0.1)	0.22	1.9 (+/-0.1)
vi	Ag/YSZ nanofiber (thin)/ HF etched YSZ, YSZ nanofibers sintered at 800 $^{\circ}\text{C}$, Ag sintered at 700 $^{\circ}\text{C}$	3.17	0.9 (+/-0.1)	3.19	1.1 (+/-0.1)
vii	Ag/thin YSZ nanofiber/YSZ, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 700 $^{\circ}\text{C}$	0.61	1.0 (+/-0.0)	0.34	1.2 (+/-0.0)
viii(a)	Ag/YSZ nanofiber (1 tape thick) /YSZ, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, heating	2.61	1.0 (+/-0.0)	6.56	0.7 (+/-0.1)
viii(a)'	Ag/YSZ nanofiber (1 tape thick) /YSZ, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, cooling	2.6	1.0 (+/-0.0)	6.88	0.9 (+/-0.0)
viii(a)''	Ag/YSZ nanofiber (1 tape thick) /YSZ, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~24 hrs, heating	2.62	1.0 (+/-0.0)	6.91	0.6 (+/-0.1)
viii(a)'''	Ag/YSZ nanofiber (1 tape thick) /YSZ, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~24 hrs, cooling	2.64	1.0 (+/-0.1)	7.18	0.8 (+/-0.0)
viii(a)''''	Ag/YSZ nanofiber (1 tape thick) /YSZ, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged another ~24 hrs, heating	2.76	0.9 (+/-0.0)	7.15	0.6 (+/-0.1)
ix(a)	Ag/ YSZ nanofiber (1 tape thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, heating	1.28	0.8 (+/-0.0)	6.86	-
ix(a)'	Ag/ YSZ nanofiber (1 tape thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, cooling	1.29	0.8 (+/-0.0)	7.24	-

ix(a)''	Ag/ YSZ nanofiber (1 tape thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 °C, Ag sintered at 800 °C, aged ~24 hrs, heating	1.31	0.8 (+/-0.0)	6.53	-
ix(a)'''	Ag/ YSZ nanofiber (1 tape thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 °C, Ag sintered at 800 °C, aged ~24 hrs, cooling	1.31	0.9 (+/-0.0)	6.8	-
x(a)	Ag/ YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 °C, Ag sintered at 800 °C, heating	2.57	0.8 (+/-0.0)	15.49	-
x(a)'	Ag/ YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 °C, Ag sintered at 800 °C, cooling	2.57	0.8 (+/-0.0)	13.92	-
x(a)''	Ag/ YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 °C, Ag sintered at 800 °C, aged ~24 hrs, heating	2.57	0.8 (+/-0.0)	10.59	-
x(a)'''	Ag/ YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 °C, Ag sintered at 800 °C, aged ~24 hrs, cooling	2.57	0.8 (+/-0.1)	10.67	-

In “Sample vi”, we tried to sinter the YSZ nanofibers at a lower temperature (800 °C) by creating a roughened YSZ electrolyte surface by HF etching. However, the high R_s value at 800 °C suggests that the nanofibers did not sinter well. Sample viii (YSZ nanofiber symmetrical cell) was characterized after aging it at 700 °C. Since the R_s values did not drastically change with aging, the electrodes and the current collectors show good adhesion.

In “Samples ix and x”, YSZ nanofiber half cells were used instead of symmetrical cells. It should be noted that the R_p values presented for half cells consist of the polarization resistances for both YSZ nanofiber electrode and Ag (counter) electrode. Since we were not able to record impedance spectra using PAR system, we did not have any means of separating the resistances for the nanofiber cathode and the Ag cathode. “Sample x” had a YSZ nanofiber layer which is as twice as thick as the nanofiber layer in “Sample ix”. Therefore, the R_s value (at 800 °C) for “Sample x” is ~2 times higher than the value for “Sample ix”. Aging study of these samples also shows that the cathodes were very stable over the tested time period.

As we have observed before, “Sample v” which has $\text{Bi}(\text{NO}_3)_3$ in it shows the lowest R_p value. “Sample vii” also shows a very low R_p value and a comparatively high activation energy which might be a result of the reasons discussed before for R_s values. Aging study of “Samples viii, ix and x” shows the cathodes were very stable over time. Also, when “Samples ix and x” are compared, it can be seen that as same as R_s values, R_p values also increase with the thickness of the cathode.

2.10.5 Ag current collectors on YSZ powder cathodes

Cells characterized:

- xi. Ag/ YSZ powder (1 tape thick) /YSZ: YSZ powder (paste of YSZ powder and graphite) electrodes (thickness of a tape used to define the electrode area) were painted on bare YSZ electrolyte surfaces and sintered at 1300°C . Then, Ag paint was applied on top of the YSZ powder electrodes and sintered again at 800°C .
- xii. Ag/ YSZ powder (1 tape thick) /YSZ-half cell: YSZ powder (paste of YSZ powder and graphite) electrodes (thickness of a tape used to define the electrode area) were painted on one side of bare YSZ electrolyte surfaces and sintered at 1300°C . Then, Ag paint was applied on top of the YSZ powder electrode and on the opposite side of the electrode and sintered again at 800°C .

Note: When the same cell was re-characterized/aged, it is shown with a (‘) or (’’) or (’’) and further details are given in the table. Calculated activation energies and only the resistances measured at 800°C are presented in tables so that the resistances at the other temperatures can be calculated. Also, it should be noted that the R_p values presented for half cells consist of the polarization resistances for both YSZ powder electrode and Ag (counter) electrode.

When “Samples ix, x (Table 2.10), xi and xii (Table 2.11)” are compared, it can be seen that the activation energies for conductivity across the cell (0.7- 0.9 eV) are in the same range for both the YSZ powder cathode and the YSZ nanofiber cathode. Aging study shows that the YSZ powder cathodes also are stable over time.

When the R_s values of “Samples viii and xi” are compared, it can be seen that “Sample xi” has a higher R_s value than the “Sample viii”, even though both of them had “1 tape thick” YSZ powder and nanofibers respectively. However, the SEM images of the cross sections of these cells showed that the YSZ nanofibers form a comparatively thin electrode (~30 μm) than the YSZ powder electrode (~60 μm), after sintering at 1300 $^{\circ}\text{C}$. In both structures, it is clear that the porous YSZ structure exhibits a substantial Ohmic resistance in the absence of a percolating electrode network inside the porous structure.

Table 2.11: Series and Polarization resistances of YSZ powder cathodes with Ag current collectors.

Sample	Description	R_s (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_s	R_p (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_p
xi(a)	Ag/ YSZ powder (1 tape thick) /YSZ, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, heating	5.94	0.7 (+/-0.1)	6.25	0.9 (+/-0.0)
xi(a)'	Ag/ YSZ powder (1 tape thick) /YSZ, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, cooling	6.09	0.7 (+/-0.1)	6.32	1.1 (+/-0.0)
xi(a)''	Ag/ YSZ powder (1 tape thick) /YSZ, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~72 hrs, heating	6.35	0.9 (+/-0.0)	5.72	1.0 (+/-0.0)
xi(a)'''	Ag/ YSZ powder (1 tape thick) /YSZ, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~72 hrs, cooling	7.29	0.9 (+/-0.0)	5.31	1.1 (+/-0.0)
xii(a)	Ag/ YSZ powder (1 tape thick) /YSZ-half-cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, heating	2.03	0.8 (+/-0.0)	8.43	-
xii(a)'	Ag/ YSZ powder (1 tape thick) /YSZ-half-cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, cooling	2.03	0.9 (+/-0.0)	8.51	-
xii(a)''	Ag/ YSZ powder (1 tape thick) /YSZ-half-cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~24 hrs, heating	2.11	0.8 (+/-0.0)	8.24	-
xii(a)'''	Ag/ YSZ powder (1 tape thick) /YSZ-half-cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~24 hrs, cooling	2.11	0.8 (+/-0.0)	8.28	-

2.10.6 Ag current collectors on LSM infiltrated YSZ cathodes

Here we have tested only 2 half cells using the PAR system as a preliminary study. Note that the R_p values presented for these half cells consist of the polarization resistances for both LSM infiltrated YSZ electrode and Ag (counter) electrode. The infiltration work will be continued using the Solartron system and symmetrical cells which will be discussed in greater detail in Chapter 03.

Cells characterized:

- xiii. Ag/LSM infiltrated YSZ nanofiber (2 tapes thick) /YSZ-half cell: YSZ nanofiber electrodes (thickness of 2 tapes used to define the electrode area) were painted on one side of bare YSZ electrolyte surfaces and sintered at 1300 °C. Then, organic LSM (30%) was infiltrated through the porous YSZ electrode and sintered at 900 °C. Finally, Ag paint was applied on top of the YSZ nanofiber electrode and on the opposite side of the electrode and sintered again at 800 °C.
- xiv. Ag/LSM infiltrated YSZ powder (1 tape thick)/YSZ-half cell: YSZ powder electrodes (thickness of a tape used to define the electrode area) were painted on one side of bare YSZ electrolyte surfaces and sintered at 1300 °C. Then, organic LSM (30%) was infiltrated through the porous YSZ electrode and sintered at 900 °C. Finally, Ag paint was applied on top of the YSZ powder electrode and on the opposite side of the electrode and sintered again at 800 °C.

Note: When the same cell was re-characterized/aged, it is shown with a (‘) or (’’) or (’’) and further details are given in the table. Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated.

In this section we have compared an LSM infiltrated YSZ nanofiber cathode with an LSM infiltrated YSZ cathode. Since the SEM images showed that the sintered YSZ nanofiber cathodes have a lesser thickness (~ 30 μm) than the sintered powder cathodes (~ 60 μm), we used a “2 tapes thick” YSZ nanofiber layer so that we can directly compare the performances of the 2 cells.

Table 2.12: Series resistances, polarization resistances and activation energies of LSM infiltrated YSZ cathodes with Ag current collectors.

Sample	Description	R_s (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_s	R_p (Ωcm^2) at 800 $^{\circ}\text{C}$
xiii(a)	Ag/LSM infiltrated YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, heating	0.64	0.5 (+/-0.0)	1.3
xiii(a)'	Ag/LSM infiltrated YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, cooling	0.63	0.6 (+/-0.0)	1.3
xiii(a)''	Ag/LSM infiltrated YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~24 hrs, heating	0.64	0.6 (+/-0.0)	1.35
xiii(a)'''	Ag/LSM infiltrated YSZ nanofiber (2 tapes thick) /YSZ-half cell, YSZ nanofibers sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~24 hrs, cooling	0.64	0.6 (+/-0.0)	1.35
xiv(a)	Ag/LSM infiltrated YSZ powder (1 tape thick)/YSZ-half cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, heating	0.8	0.7 (+/-0.1)	1.78
xiv(a)'	Ag/LSM infiltrated YSZ powder (1 tape thick)/YSZ-half cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, cooling	0.8	0.6 (+/-0.0)	1.8
xiv(a)''	Ag/LSM infiltrated YSZ powder (1 tape thick)/YSZ-half cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~ 72 hrs, heating	0.8	0.6 (+/-0.0)	1.49
xiv(a)'''	Ag/LSM infiltrated YSZ powder (1 tape thick)/YSZ-half cell, YSZ powder sintered at 1300 $^{\circ}\text{C}$, LSM sintered at 900 $^{\circ}\text{C}$, Ag sintered at 800 $^{\circ}\text{C}$, aged ~ 72 hrs, cooling	0.8	0.6 (+/-0.0)	1.48

When the porous YSZ nanofiber or YSZ powder scaffold was infiltrated with LSM, R_s and R_p values drastically decreased as expected (Table 2.12). When YSZ ionic conductor and LSM electronic conductor together are in contact with air (inside the porous cathode), the number of triple phase boundaries increase resulting in lower R_p values. R_s values ~0.7

Ohmcm^2 suggest that there is good connectivity from the YSZ electrolyte through the LSM infiltrated YSZ electrode to the current collecting Ag layer. For both cells, activation energies for conductivity across the cell (0.5- 0.7 eV) are in the same range. However, both R_s and R_p values measured at 800 $^{\circ}\text{C}$ are slightly lower for LSM infiltrated nanofiber cathodes. Also, the short aging study shows that these cells performed stably over time.

2.11 Summary

The sintering study showed how the YSZ nanofiber morphology changes with the sintering temperature. Sintering starts at 1300 $^{\circ}\text{C}$ and melting of the nanoparticles occurs at higher temperatures. Compared to Pt and Au, Ag acted as a better current collector for porous YSZ cathodes. As expected, infiltrating the YSZ cathodes with LSM improved their performance.

2.12 Conclusion

Based on the SEM images of the “sintering study”, we can conclude that Bi_2O_3 is not a suitable sintering aid for YSZ nanofibers since this composition destroys the YSZ nanofibers and results in a dense YSZ scaffold. Therefore, we chose 1300 $^{\circ}\text{C}$ as the sintering temperature for YSZ nanofibers without any sintering aid. Since the preliminary results achieved for these LSM infiltrated YSZ cathodes look promising, continuation of this work on the symmetrical LSM infiltrated YSZ scaffolds will be presented and discussed in detail in Chapter 03.

2.13 References

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Chapter 03

LSM current collectors and LSM infiltrated YSZ scaffolds

3.1 Introduction

The objective of this project is to create a high performing cathode based on a porous YSZ scaffold on a YSZ electrolyte infiltrated with LSM nanoparticles and with a current collector based on larger LSM particles. The polarization resistances and series resistances extracted using impedance data are presented in this chapter. Deconvolution analysis of the impedance spectra for these LSM infiltrated YSZ scaffolds and equivalent circuit fitting is discussed in Chapter 04 – Section 4.4.

As we have discussed before, the electrocatalytic activity of the cathode plays a major role in the overall performance of the SOFC. “Infiltration/impregnation” is a widely investigated technique used for the surface modification of SOFC cathodes [1], [2]. Infiltration technique requires two different sintering steps. First, the porous cathode backbone is sintered at a higher temperature to ensure structural stability and good connectivity between the cathode and the electrolyte, which facilitates the ionic and electronic conductivity [1]. Then, the infiltration solution containing nanoparticles or stoichiometric amounts of metal salt precursors is infiltrated through the cathode backbone and sintered at a much lower temperature. As a result of this lower sintering temperature, nano sized catalyst particles (which results in high active surface area) can be formed inside the porous cathode. Furthermore, the low temperature sintering minimizes unfavorable reactions which lead to undesirable secondary phases and also eliminates delaminating issues due to TEC (thermal expansion coefficient) mismatch [1], [2]. Infiltration is also a cost effective technique since it utilizes a limited amount of the catalyst as opposed to conventional composite cathodes [2].

In order to coat the cathode backbone with sufficient infiltrated material, a multiple number of infiltration steps have to be repeated as shown in Figure 3.1. After the final sintering step, the infiltrated material can either form a continuous thin film or discrete particles on the cathode backbone (Figure 3.2).

Figure 3.1: Multi step infiltration process [2].

Figure 3.2: Discrete particles (c) or continuous thin film (d) on the cathode backbone [1].

Properties of both the cathode backbone and the infiltration solution are important for a better performing infiltrated cathode. Less viscous infiltration solutions with surfactants/complexing agents have been reported to result in uniform catalyst layers. Porosity, morphology, dimensions and the wetting properties of the cathode backbone also affects the infiltration process and the properties of the resulting SOFC [1], [2].

The small particles generated by the infiltration method present a challenge for current collection. In many SOFC cathodes, larger LSM particles are used to create an effective current collector for the active part of the cathode [3]. Since infiltration was performed with the LSM current collector layer in place, experiments with LSM-graphite powder mixtures were included with the goal of increasing the porosity of the LSM layer. Since long term stability is one of the requirements of practical SOFCs, aging studies were performed on some of the fabricated cells.

3.2 Experimental

This study was carried out in 3 steps. Step 1 was performed to observe the cathode and current collection properties of pure LSM and “mixtures of LSM and graphite”. These control experiments provided a baseline of ohmic and polarization resistances for the porous scaffold systems. We used a thin layer of Ag paste on top of the LSM current collector to reduce further the ohmic resistance and to ensure complete current collection using a silver wire contact. In Step 2, we compared the performance of Ag/LSM/YSZ scaffold/YSZ symmetric cells where the YSZ scaffold is based on either YSZ nanofibers or YSZ powder. From these measurements, the ohmic ionic resistance of the scaffold is obtained. In Step 3, we infiltrated the YSZ scaffolds with an organic LSM solution prepared using a method published by Choi et al. [4] and studied the electrochemical performance of Ag/LSM/LSM infiltrated YSZ/YSZ symmetric cells. The organic LSM (0.1 M) solution was prepared by dissolving proper amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.82 g), $\text{Sr}(\text{NO}_3)_2$ (0.10 g) and $\text{Mn}(\text{NO}_3)_2$ (412 μL) in a mixture of glacial acetic acid (8.3 mL) and 2-methoxy ethanol (16.7 mL) (1:2) [4].

Commercial LSM powder ($(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-\delta}$) and YSZ powder (YSZ8-TC, surface area: 7.4 m^2/g , and YSZ8-N, surface area: 144 m^2/g) were obtained from Fuel Cell Materials. Graphite powder (~ 325 mesh) was purchased from Alfa Aesar.

A Solartron SI 1287 electrochemical interface and 1252A frequency response analyzer were used to perform the electrochemical characterization at 800 $^\circ\text{C}$, 750 $^\circ\text{C}$ and 700 $^\circ\text{C}$. Some cells were aged at 700 $^\circ\text{C}$ for a certain time period and re-characterized. Impedances were measured using 10 log linear frequencies per decade, starting at 100 kHz and ending at 0.1 Hz or 0.02 Hz, using a 10 mV AC amplitude.

Step 1:

The LSM pastes used for current collectors were prepared as follows.

- a) Commercial LSM powder (2 g) was mixed with α -terpineol (1 g) (2:1 by weight) to make the pure LSM paste.

- b) Commercial LSM powder (0.5 g) was mixed with graphite powder (0.05 g) (Alfa Aesar, ~325 mesh) (10:1 by weight) and α -terpineol (1 g) to make the 10% C-LSM paste.
- c) Commercial LSM powder (0.3 g) was mixed with graphite powder (0.3 g) (Alfa Aesar, ~325 mesh) (1:1 by weight) and α -terpineol (1 g) to make the 50% C-LSM paste.

All these pastes were “ball-milled” using a WIG-L-BUG (borrowed from Dr. Alan Stolzenberg’s laboratory). Then, they were painted on YSZ (tape was used to define the thickness of the electrode) electrolytes and sintered at 1200 °C for 1 hour to create LSM/YSZ symmetric cells which were electrochemically characterized.

Step 2:

A YSZ nanofiber paste was prepared by mixing the nanofibers (0.4 g) (received from Dr. Nick Wu’s group) with α -terpineol (4 g) (1:10 by weight). A YSZ powder paste was prepared by ball-milling (using WIG-L-BUG) YSZ powder (1 g) (YSZ8-TC) with graphite powder (1 g) and α -terpineol (2 g) (1:1:2 by weight). Then, these YSZ pastes were painted on YSZ electrolytes and sintered at 1300 °C or 1400 °C for 2 hours. A double sided tape was used to define the area of the electrodes. Therefore, the thickness of the tape (~100 μ m) defined the thickness of the electrode before sintering. After the cells cool down, pure LSM or “LSM- graphite mixture” current collectors were painted on YSZ electrodes and sintered again at 1200 °C for 1 hour. Then, these cells were characterized using Ag paste current collectors and Ag wires.

Step 3:

In addition to the YSZ pastes mentioned in Step 2, the following YSZ pastes were prepared.

- a) A different YSZ powder paste was prepared by ball-milling (using WIG-L-BUG) YSZ powder (0.7 g) (YSZ8-N) with graphite powder (0.7 g) (Alfa Aesar, ~325 mesh) and α -terpineol (1.4 g) (1:1:2 by weight)

- b) A ball-milled YSZ nanofiber paste was prepared by using the WIG-L-BUG to grind the nanofiber paste prepared in Step 2.

Then, as mentioned in Step 2, these YSZ pastes were painted on both sides of YSZ electrolytes (a double sided tape was used to define the area and the thickness of the electrodes before sintering) and sintered at 1300 °C, 1400 °C or 1500 °C. After cooling, pure LSM or “LSM-graphite mixture” current collectors were painted on YSZ electrodes and sintered again at 1200 °C for 1 hour. Then, these YSZ scaffolds were infiltrated (through the LSM current collector) with the organic LSM solution [4]. Multiple infiltrations had to be carried out in order to achieve 30 % by weight LSM in each YSZ electrode. In the example shown below, 20 µL was infiltrated in 10 infiltration steps (2 * 1 µL infiltrated at each step). After each infiltration, the cell was dried at ~150 °C to evaporate the solvents. After ~3 infiltration steps, the cell was heated at ~450 °C to decompose the nitrates [5], [6]. Finally, the cell was sintered at 800 °C and characterized using Ag paste and Ag wires as contact to the LSM paste layer.

Shown below is an example which shows the weights measured for a ~45% LSM infiltrated YSZ scaffold.

$$\text{Weight of the YSZ electrolyte} = 466.6 \text{ mg}$$

$$\begin{array}{l} \text{Weight of the YSZ electrolyte and YSZ scaffolds on} \\ \text{both sides} \end{array} = 468.4 \text{ mg}$$

$$\begin{array}{l} \text{Approximate weight of one YSZ scaffold} \\ \\ \end{array} = \begin{array}{l} (468.4 \text{ mg} - 466.6 \text{ mg})/2 \\ \\ = 0.9 \text{ mg} \end{array}$$

$$\begin{array}{l} \text{Weight of the cell after infiltrating one YSZ scaffold} \\ \text{with 20 } \mu\text{L of LSM solution followed by sintering at} \\ \text{800 } ^\circ\text{C for 1 hour} \end{array} = 468.8 \text{ mg}$$

$$\begin{array}{l} \text{Approximate weight of infiltrated LSM on one YSZ} \\ \text{scaffold} \end{array} = (468.8 \text{ mg} - 468.4 \text{ mg})$$

$$\begin{aligned}
&= 0.4 \text{ mg} \\
\% \text{ LSM infiltrated on 1 YSZ scaffold} &= (0.4 \text{ mg}/0.9 \text{ mg}) * 100 \\
&= \sim 44\%
\end{aligned}$$

3.3 Results and Discussion

Note: When the same cell has been characterized after aging at 700 °C, it is shown as ('), (')') or (')')'). Calculated activation energies and only the resistances measured at 800 °C are presented in tables so that the resistances at the other temperatures can be calculated.

Step 1:

Following are the samples prepared using the LSM pastes. In all these cells, pure LSM or 10%C-LSM or 50%C-LSM mixtures were painted on both sides of the bare YSZ electrolyte surface and sintered at 1200 °C.

- i. LSM/YSZ
- ii. 10%C-LSM/YSZ
- iii. 50%C-LSM/YSZ

When the series resistances (R_s) measured at 800 °C are considered (Table 3.1), it can be seen that the Samples i and ii have the typical series resistance of $\sim 0.7 \text{ Ohm cm}^2$ which is assigned to the solid YSZ electrolyte. However, Sample iii shows a higher series resistance which suggests that the LSM was not sintered well to the YSZ electrolyte when 50% graphite powder was used. This result also supports our observation of LSM electrode delamination in Sample iii.

Polarization resistances (R_p) of Samples i and iii are in the same range ($\sim 10 \text{ Ohmcm}^2$). However, R_p values for Sample ii are much lower than for the other samples. When the electrode with LSM/graphite paste sinters at a high temperature, graphite particles burn off and leave pores inside the LSM cathode. These pores facilitate gas transfer inside the LSM cathode and may increase the number of TPBs, which reduces the polarization resistances.

This might be the reason for lower R_p values measured in Sample ii. However, this cannot be observed in sample iii since the electrode did not make a good connection with the electrolyte due to poor sintering.

Table 3.1: Series resistances, polarization resistances and activation energies for LSM/YSZ symmetrical cells.

Sample	Description	R_s (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_s	R_p (Ωcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_p
i (a)	LSM/ YSZ sintered at 1200 $^{\circ}\text{C}$	0.71	0.7 (+/-0.0)	8.90	1.3 (+/-0.1)
i (a)'	LSM/ YSZ sintered at 1200 $^{\circ}\text{C}$, aged ~24 hrs	0.71	0.7 (+/-0.0)	10.71	1.3 (+/-0.1)
ii (a)	10%C-LSM/ YSZ sintered at 1200 $^{\circ}\text{C}$	0.67	0.7 (+/-0.0)	5.42	1.4 (+/-0.1)
ii (a)'	10%C-LSM / YSZ sintered at 1200 $^{\circ}\text{C}$, aged ~24 hrs	0.67	0.7 (+/-0.0)	4.11	1.5 (+/-0.1)
iii (a)	50%C-LSM / YSZ sintered at 1200 $^{\circ}\text{C}$	1.51	0.7 (+/-0.0)	14.01	1.4 (+/-0.1)
iii(a)'	50%C-LSM / YSZ sintered at 1200 $^{\circ}\text{C}$, aged ~24 hrs	1.52	0.7 (+/-0.0)	10.01	1.7 (+/-0.2)

Jogensen and Mogensen [7] have reported a R_p value of $\sim 1.6 \Omega\text{cm}^2$ (at 1000 $^{\circ}\text{C}$) for an LSM ($(\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_{3\pm\delta}$) pointed electrode in contact with YSZ (contact area between the LSM electrode and YSZ electrolyte $\sim 10^{-5} \text{ cm}^2$). Also, Murray and Barnett [8] have reported a R_p value of $3.5 \Omega\text{cm}^2$ at 750 $^{\circ}\text{C}$ and an activation energy of 1.6 eV for the LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$) electrode (corresponding to $1.5 \Omega\text{cm}^2$ at 800 $^{\circ}\text{C}$) in an LSM/YSZ symmetrical cell. Furthermore, Jiang's [2] review paper reports that R_p values for LSM electrodes at 700 $^{\circ}\text{C}$ range from 9-54 Ωcm^2 . The R_p values we observed for LSM electrodes in this study are somewhat higher and the activation energies are somewhat lower than these values reported in literature. However, the composition of the LSM paste, the sintering temperature and the A-site deficiency of LSM plays a major role in reducing the polarization resistance of LSM cathodes.

Step 2:

Below are the YSZ nanofiber and powder scaffold samples with different LSM current collectors. In all these cells, a thick layer of YSZ nanofiber mixture (thickness of the tape which was used to define the electrode area) was painted on both sides of the YSZ electrolyte and sintered at 1300 °C or 1400 °C. Then, pure LSM or 10% C-LSM or 50% C-LSM mixtures were painted on these YSZ electrodes and sintered at 1200 °C.

- iv. LSM/YSZ nanofiber (1 tape thick)/YSZ
- v. 10% C-LSM/YSZ nanofiber (1 tape thick)/YSZ
- vi. 10% C-LSM/YSZ nanofiber1400 (1 tape thick)/YSZ
- vii. 50% C-LSM/YSZ nanofiber (1 tape thick)/YSZ
- viii. 10% C-LSM/YSZ powder (1 tape thick)/YSZ
- ix. 10% C-LSM/YSZ powder1400 (1 tape thick)/YSZ

Note: LSM/YSZ powder/YSZ and 50% C-LSM/YSZ powder/YSZ symmetrical cells were prepared but the results are not presented since they had delamination issues.

The series resistances with the YSZ scaffolds are greater than in the absence of the scaffolds (Table 3.2), as expected. When the series resistances of YSZ scaffolds are compared, it can be seen that both the YSZ nanofiber and powder scaffolds which were sintered at 1400 °C showed lower resistances. Higher sintering temperature assures good connectivity between the porous YSZ scaffold and the YSZ electrolyte, which lowers the resistances. Also, these YSZ scaffolds sintered at 1400 °C showed better stability with aging. The SEM images (section 2.10.1) show that at 1400 °C, YSZ nanofibers melt to form a less porous, dense structure. This thinner YSZ structure accounts for the lower series resistance of the YSZ nanofibers fired at the higher temperature. Activation energies of the series resistances are slightly larger than for the solid YSZ electrolyte.

Polarization resistances for these structures are significantly smaller than for LSM paste structures in direct contact with the solid YSZ electrolyte. The rougher YSZ scaffold probably provides more TPB contact length per unit area, thus lowering the polarization resistance. Activation energies are consistent with the values for the LSM/YSZ electrodes

Pure LSM and 10% C-LSM were chosen to use as the current collectors for Step 3 since they are more mechanically stable than the 50% C-LSM current collector.

Table 3.2: Series resistances, polarization resistances and activation energies for LSM/YSZ scaffold/YSZ symmetrical cells.

Sample	Description	R_s (Ohmcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_s	R_p (Ohmcm^2) at 800 $^{\circ}\text{C}$	E_a (eV) for R_p
i (a)	LSM/YSZ nanofiber (1 tape thick) /YSZ	2.53	1.0 (+/-0.0)	1.95	1.3 (+/-0.0)
i (a)'	LSM/YSZ nanofiber (1 tape thick) /YSZ, aged ~24 hrs	2.92	1.0 (+/-0.0)	3.23	1.3 (+/-0.0)
ii (a)	10% C-LSM/YSZ nanofiber (1 tape thick)/YSZ	3.04	0.9 (+/-0.0)	2.68	1.4 (+/-0.0)
ii (a)'	10% C-LSM/YSZ nanofiber (1 tape thick)/YSZ, aged ~24 hrs	3.05	0.9 (+/-0.0)	3.00	1.3 (+/-0.0)
iii (a)	10% C-LSM/YSZ nanofiber1400 (1 tape thick)/YSZ	1.17	0.7 (+/-0.0)	1.97	1.5 (+/-0.0)
iii(a)'	10% C-LSM/YSZ nanofiber1400 (1 tape thick)/YSZ, aged ~24 hrs	1.18	0.7 (+/-0.0)	1.76	1.2 (+/-0.0)
iv (a)	50% C-LSM/YSZ nanofiber (1 tape thick)/YSZ	2.05	1.0 (+/-0.0)	2.06	1.4 (+/-0.0)
iv (a)'	50% C-LSM/YSZ nanofiber (1 tape thick)/YSZ, aged ~24 hrs	2.06	1.0 (+/-0.0)	2.56	1.5 (+/-0.1)
v (a)	10% C-LSM/YSZ powder (1 tape thick)/YSZ	4.28	0.8 (+/-0.0)	4.00	1.3 (+/-0.1)
v (a)'	10% C-LSM/YSZ powder (1 tape thick)/YSZ, aged ~24 hrs	4.08	0.8 (+/-0.0)	4.50	1.2 (+/-0.0)
vi (a)	10% C-LSM/YSZ powder1400 (1 tape thick)/YSZ	1.61	0.8 (+/-0.0)	3.07	1.4 (+/-0.0)
vi (a)'	10% C-LSM/YSZ powder1400 (1 tape thick)/YSZ, aged ~24 hrs	1.68	0.7 (+/-0.0)	3.11	1.2 (+/-0.0)

Step 3:

Below are the LSM infiltrated YSZ nanofiber samples with 10% C-LSM current collectors. A thick layer of ball milled/ not ball milled YSZ nanofiber mixture (thickness of the tape which was used to define the electrode area) was painted on both sides of the YSZ electrolyte and sintered at 1300 $^{\circ}\text{C}$ or 1400 $^{\circ}\text{C}$. Then, 10% C-LSM paste was painted on these YSZ electrodes and sintered at 1200 $^{\circ}\text{C}$. Then, the YSZ scaffolds were infiltrated (through the LSM current collector) with the organic LSM solution (multiple infiltration steps were carried out to achieve 30% by weight LSM) and sintered at 800 $^{\circ}\text{C}$ for 1 hour.

- i. 10% C-LSM/30% LSM infiltrated YSZ nanofiber/YSZ
- ii. 10% C-LSM/30% LSM infiltrated YSZ nanofiber1400/YSZ
- iii. 10% C-LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ

Table 3.3: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ nanofiber symmetrical cells with 10% C-LSM current collector.

Sample	Description	R_s (Ohmcm^2) at 800°C	E_a (eV) for R_s	R_p (Ohmcm^2) at 800°C	E_a (eV) for R_p
i (a)	10% C-LSM/30% LSM infiltrated YSZ nanofiber/YSZ	0.72	0.6 (+/-0.0)	0.21	1.5 (+/-0.0)
i (a)'	10% C-LSM/30% LSM infiltrated YSZ nanofiber /YSZ, aged ~24 hrs	0.73	0.6 (+/-0.0)	0.23	1.5 (+/-0.1)
i (b)	10% C-LSM/30% LSM infiltrated YSZ nanofiber /YSZ	0.78	0.7 (+/-0.0)	0.20	1.5 (+/-0.0)
i (b)'	10% C-LSM/30% LSM infiltrated YSZ nanofiber/YSZ, aged ~24 hrs	0.84	0.7 (+/-0.0)	0.21	1.5 (+/-0.1)
i (c)	10% C-LSM/30% LSM infiltrated YSZ nanofiber/YSZ	0.92	0.7 (+/-0.0)	0.29	1.6 (+/-0.1)
i (c)'	10% C-LSM/30% LSM infiltrated YSZ nanofiber/YSZ, aged ~24 hrs	0.97	0.7 (+/-0.0)	0.35	1.5 (+/-0.0)
ii (a)	10% C-LSM/30% LSM infiltrated YSZ nanofiber1400/YSZ	0.82	0.7 (+/-0.0)	0.15	1.3 (+/-0.0)
ii (a)'	10% C-LSM/30% LSM infiltrated YSZ nanofiber1400/YSZ, aged ~24 hrs	0.84	0.6 (+/-0.1)	0.19	1.3 (+/-0.0)
ii (a)''	10% C-LSM/30% LSM infiltrated YSZ nanofiber1400/YSZ, aged for another 3 days	0.84	0.7 (+/-0.1)	0.22	1.4 (+/-0.0)
iii (a)	10% C-LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ	1.25	0.7 (+/-0.0)	0.23	1.5 (+/-0.1)
iii (a)'	10% C-LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ, aged ~24 hrs	1.29	0.6 (+/-0.0)	0.28	1.5 (+/-0.1)
Average values and standard deviations		0.91 (+/-0.19)	0.7 (+/-0.0)	0.23 (+/-0.05)	1.5 (+/-0.1)

In Table 3.3, most of the cells show the typical R_s value for YSZ at 800°C , which is ~0.7-0.8 Ohmcm^2 with some exceptions (Sample i(c) and Sample iii). Consequently, the infiltrated LSM must be contacting the solid YSZ electrolyte over the area of the scaffold and must exhibit a low resistance current path through the YSZ scaffold.

YSZ nanofibers which were sintered at 1400 °C show the best performance compared to other compositions with lower R_p values and lower activation energy for the oxygen reduction reaction. Also, most of the cells did not show a drastic increase in R_p values with aging.

When the symmetrical cells were prepared with the YSZ nanofiber paste that was not ball-milled, wide gaps were seen in the cross section SEM images of the electrode (Figure 3.3). Since we wanted to investigate how this affects the cell performance, the paste was ball milled to prepare an electrode with no gaps (Figure 3.4). The R_p values are the same for both cell compositions. However, R_s values are slightly higher for the ball milled YSZ nanofiber electrode, suggesting that the true active area was smaller than the geometric area.

Figure 3.3: Cross section SEM image of YSZ nanofiber electrode prepared using the paste that was not ball-milled. Red squares highlight the gaps.

Figure 3.4: Cross section SEM image of YSZ nanofiber electrode prepared using the ball milled paste. Blue square shows the uniform electrode and the electrolyte.

Below are the LSM infiltrated YSZ powder samples with 10% C-LSM current collectors. A thick layer of YSZ powder paste (thickness of the tape which was used to define the electrode area) was painted on both sides of the YSZ electrolyte and sintered at 1300 °C or 1500 °C. Then, 10% C-LSM paste was painted on these YSZ electrodes and sintered at 1200 °C. Then, the YSZ scaffolds were infiltrated (through the LSM current collector) with

the organic LSM solution (multiple infiltration steps were carried out to achieve 30% by weight LSM) and the structure sintered at 800 °C for 1 hour.

- i. 10% C-LSM/30% LSM infiltrated YSZ powder/YSZ
- ii. 10% C-LSM/30% LSM infiltrated YSZ powder1500/YSZ

Table 3.4: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ powder symmetrical cells with 10% C-LSM current collector.

Sample	Description	R_s (Ohmcm^2) at 800°C	E_a (eV) for R_s	R_p (Ohmcm^2) at 800°C	E_a (eV) for R_p
i (a)	10% C-LSM/30% LSM infiltrated YSZ powder/YSZ	0.81	0.6 (+/-0.1)	0.13	1.8 (+/-0.2)
i (a)'	10% C-LSM/30% LSM infiltrated YSZ powder/YSZ, aged ~24 hrs	0.76	0.7 (+/-0.0)	0.45	1.9 (+/-0.0)
i (b)	10% C-LSM/30% LSM infiltrated YSZ powder/YSZ	0.98	0.6 (+/-0.0)	0.29	1.5 (+/-0.0)
i (b)'	10% C-LSM/30% LSM infiltrated YSZ powder/YSZ, aged ~24 hrs	0.99	0.6 (+/-0.0)	0.26	1.6 (+/-0.1)
i (b)''	10% C-LSM/30% LSM infiltrated YSZ powder/YSZ, aged for another 3 days	0.99	0.7 (+/-0.0)	0.29	1.5 (+/-0.1)
ii (a)	10% C-LSM/30% LSM infiltrated YSZ powder1500/YSZ	1.29	0.6 (+/-0.0)	0.27	1.5 (+/-0.0)
ii (a)'	10% C-LSM/30% LSM infiltrated YSZ powder1500/YSZ, aged ~24 hrs	1.21	0.6 (+/-0.0)	0.34	1.5 (+/-0.1)
ii (a)''	10% C-LSM/30% LSM infiltrated YSZ powder1500/YSZ, aged for another 3 days	1.18	0.7 (+/-0.0)	0.35	1.5 (+/-0.0)
Average values and standard deviations		1.03 (+/-0.19)	0.6 (+/-0.0)	0.30 (+/-0.09)	1.6 (+/-0.2)

All the cells in Table 3.4 (except for Sample i) show higher R_s values at 800 °C. The YSZ scaffolds which were sintered at a higher temperature (1500 °C) show high R_s values. Possibly the high sintering temperature created a dense non-porous YSZ layer, resulting in a longer ionically conducting path through the cell. The average R_p values measured at 800 °C (0.3 Ohmcm^2) and the average activation energy (1.6 eV) for the oxygen reduction reaction on these YSZ powder electrodes are slightly higher than the values for YSZ

nanofiber electrodes (0.23 Ohmcm^2 , 1.5 eV respectively) with 10% C-LSM current collectors. Also, except for Sample i, the cells did not show drastic aging effects.

Below are the LSM infiltrated YSZ nanofiber samples with pure LSM current collectors. A thick layer of (ball milled/ not ball milled) YSZ nanofiber mixture (thickness of the tape which was used to define the electrode area) was painted on both sides of the YSZ electrolyte and sintered at 1300°C or 1400°C . Then, pure LSM paste was painted on these YSZ electrodes and sintered at 1200°C . Then, the YSZ scaffolds were infiltrated (through the LSM current collector) with the organic LSM solution (multiple infiltration steps were carried out to achieve 30% by weight LSM) and sintered at 800°C for 1 hour.

- i. LSM/30% LSM infiltrated YSZ nanofiber/YSZ
- ii. LSM/30% LSM infiltrated YSZ nanofiber1400/YSZ
- iii. LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ

Table 3.5: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ nanofiber symmetrical cells with pure LSM current collector.

Sample	Description	R_s (Ohmcm^2) at 800°C	E_a (eV) for R_s	R_p (Ohmcm^2) at 800°C	E_a (eV) for R_p
i (a)	LSM/30% LSM infiltrated YSZ nanofiber/YSZ	1.01	0.7 (+/-0.0)	0.32	1.4 (+/-0.0)
i (a)'	LSM/30% LSM infiltrated YSZ nanofiber /YSZ, aged ~24 hrs	1.01	0.7 (+/-0.0)	0.32	1.4 (+/-0.0)
i (a)''	LSM/30% LSM infiltrated YSZ nanofiber /YSZ, aged for another 3 days	1.01	0.7 (+/-0.0)	0.32	1.5 (+/-0.0)
i (b)	LSM/30% LSM infiltrated YSZ nanofiber/YSZ	1.22	0.6 (+/-0.0)	0.36	1.4 (+/-0.0)
i (b)'	LSM/30% LSM infiltrated YSZ nanofiber /YSZ, aged for 3 days	1.18	0.7 (+/-0.0)	0.39	1.5 (+/-0.0)
ii (a)	LSM/30% LSM infiltrated YSZ nanofiber1400/YSZ	0.87	0.7 (+/-0.0)	0.21	1.4 (+/-0.0)
ii (a)'	LSM/30% LSM infiltrated YSZ nanofiber 1400/YSZ, aged ~24 hrs	0.89	0.7 (+/-0.0)	0.25	1.4 (+/-0.0)
ii (a)''	LSM/30% LSM infiltrated YSZ nanofiber 1400/YSZ, aged for another ~24 hrs	0.90	0.7 (+/-0.0)	0.25	1.5 (+/-0.0)
iii (a)	LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ	1.17	0.6 (+/-0.0)	0.18	1.4 (+/-0.0)

iii (a)'	LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ, aged ~24 hrs	1.08	0.7 (+/-0.0)	0.19	1.6 (+/-0.0)
iii (a)''	LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ, aged for another 24 hrs	1.12	0.6 (+/-0.0)	0.21	1.5 (+/-0.0)
iv (a)	LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ	0.95	0.7 (+/-0.0)	0.18	1.7 (+/-0.2)
iv (a)'	LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ, aged ~24 hrs	1.01	0.6 (+/-0.1)	0.23	1.5 (+/-0.0)
iv (a)''	LSM/30% LSM infiltrated ball-milled YSZ nanofiber/YSZ, aged for another 24 hrs	0.95	0.7 (+/-0.1)	0.23	1.5 (+/-0.1)
Average values and standard deviations		1.03 (+/-0.11)	0.7 (+/-0.0)	0.26 (+/-0.07)	1.5 (+/-0.1)

In Table 3.5, the series resistances are slightly higher than before, suggesting some discrepancy between the true active area and the electrode geometric area. As we have seen before, YSZ nanofiber electrodes sintered at 1400 °C showed the lowest R_s values at 800 °C. LSM infiltrated ball-milled YSZ nanofiber electrodes show the lowest R_p values. Aging studies show that these infiltrated cells are very stable over time. There are no significant differences in polarization resistances with respect to the cell structures with graphite/LSM current collectors.

Below are the LSM infiltrated YSZ powder samples with pure LSM current collectors. A thick layer of YSZ powder (large particles/small particle) paste (thickness of the tape which was used to define the electrode area) was painted on both sides of the YSZ electrolyte and sintered at 1300 °C or 1500 °C. Then, LSM paste was painted on these YSZ electrodes and sintered at 1200 °C. Then, the YSZ scaffolds were infiltrated (through the LSM current collector) with the organic LSM solution (multiple infiltration steps were carried out to achieve 30% by weight LSM) and sintered at 800 °C for 1 hour.

- i. LSM/30% LSM infiltrated YSZ powder/YSZ
- ii. LSM/30% LSM infiltrated YSZ powder 1500/YSZ
- iii. LSM/30% LSM infiltrated YSZ powder (SP)/YSZ

The R_s values for LSM infiltrated YSZ powder electrodes (prepared using smaller particles) are lower than for the other YSZ powder electrodes (Table 3.6). However, the R_p

values are comparatively high for these electrodes. Possibly, these smaller YSZ particles sinter together to form a less porous YSZ scaffold with lower number of TPBs, hence a higher polarization resistance. Also, the average R_p value at 800°C (0.45 Ohm cm²) for LSM infiltrated YSZ powder electrodes with LSM current collectors, is as twice as higher than the average R_p value for LSM infiltrated YSZ nanofiber electrodes with LSM current collectors (0.26 Ohm cm²). However, the average R_s values and the activation energies for conductivity across the cell and the oxygen reduction reaction are similar for both LSM infiltrated YSZ scaffolds with LSM current collectors.

Table 3.6: Series resistances, polarization resistances and activation energies for LSM infiltrated YSZ powder symmetrical cells with pure LSM current collector.

Sample	Description	R_s (Ohmcm ²) at 800°C	E_a (eV) for R_s	R_p (Ohmcm ²) at 800°C	E_a (eV) for R_p
i (a)	LSM/30% LSM infiltrated YSZ powder/YSZ	1.10	0.6 (+/-0.0)	0.35	1.5 (+/-0.1)
i (a)'	LSM/30% LSM infiltrated YSZ powder/YSZ, aged ~24 hrs	1.07	0.6 (+/-0.0)	0.34	1.5 (+/-0.1)
ii (a)	LSM/30% LSM infiltrated YSZ powder1500/YSZ	1.16	0.7 (+/-0.0)	0.40	1.3 (+/-0.1)
ii (a)'	LSM/30% LSM infiltrated YSZ powder1500/YSZ, aged for ~24 hrs	1.13	0.7 (+/-0.0)	0.39	1.4 (+/-0.1)
ii (a)''	LSM/30% LSM infiltrated YSZ powder1500/YSZ , aged for another ~24 hrs	1.11	0.7 (+/-0.0)	0.40	1.3 (+/-0.1)
iii (a)	LSM/30% LSM infiltrated YSZ powder (SP)/YSZ	0.82	0.7 (+/-0.0)	0.49	1.5 (+/-0.0)
iii (a)'	LSM/30% LSM infiltrated YSZ powder (SP)/YSZ, aged ~24 hrs	0.83	0.7 (+/-0.0)	0.58	1.5 (+/-0.0)
iii (a)''	LSM/30% LSM infiltrated YSZ powder (SP)/YSZ, aged for another ~24 hrs	0.83	0.7 (+/-0.0)	0.64	1.4 (+/-0.0)
Average values and standard deviations		1.01 (+/-0.15)	0.7 (+/-0.0)	0.45 (+/-0.11)	1.4 (+/-0.1)

The best performances (lowest R_s and R_p values) were obtained using nanofiber YSZ electrodes. However, the R_p values are not significantly better than the literature values obtained using YSZ powders (see below for discussion). The high cost of YSZ nanofibers

would prohibit their use in commercial SOFCs. Activation energies are quite consistent, 0.7 eV for YSZ conductivity and 1.4 eV for LSM polarization resistance. In some instances, stable polarization resistances were obtained over short (days) aging periods.

Nevertheless, there are a number of recent reports on ceramic nanofiber cathodes that have shown improved performance. Chang et al. [9] have prepared $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC)/CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) symmetrical cells using SSC nanofibers and reports a polarization resistance of 0.01 Ohmcm^2 at 700°C , which is lower than the resistance for the powder based SSC/CGO symmetrical cells (0.08 Ohmcm^2 at 700°C). Also, Qiang et al. [10] have prepared $\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_4$ (LSN)/CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) symmetrical cells using LSN nanofibers and have reported a polarization resistance of 0.40 Ohmcm^2 at 700°C . Liquan et al. [11] have prepared a $\text{Sr}_{0.7}\text{Y}_{0.3}\text{CoO}_{2.65-\delta}$ (SYCO) nanofiber scaffold which has been infiltrated with $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (GDC). They reports a 0.01 Ohmcm^2 polarization resistance at 750°C . They have also tested the stability of these SYCO-GDC composite cathodes by a 108 hour constant current test. Furthermore, Liquan et al. [12] have developed a $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SSC-GDC) composite cathode by infiltrating GDC into a SSC nanofiber cathode. They have reported a 0.038 Ohmcm^2 polarization resistance at 650°C and states that this value is 2.6 times smaller than the polarization resistance of a GDC infiltrated SSC scaffold prepared using nanoparticles. Erqing et al. [13] have prepared $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) scaffolds which were infiltrated with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) and have reported a 0.07 Ohmcm^2 polarization resistance at 650°C . Xuening et al. [14] have carried out a comparison study on nanofiber based $\text{GdBaCo}_2\text{O}_{5+\delta}$ (GBCO)/ $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) symmetrical cells and powder based GBCO/GDC symmetrical cells. At 750°C , they have measured a 0.04 Ohmcm^2 polarization resistance for the nanofiber based cathode and a 0.08 Ohmcm^2 polarization resistance for the powder based cathode. Also, Li-Ping et al. [15] have prepared $\text{Nd}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ /CGO symmetrical cells and reports a polarization resistance of 0.26 Ohmcm^2 at 700°C . They also state that this value is two times smaller than the resistance obtained for a powder cathode with the same composition.

As we have discussed before, the infiltrated materials can either form discrete particles or a continuous thin film on a cathode backbone. According to Jiang [2], an “ionic conducting” scaffold (eg: YSZ) requires a continuous network of infiltrated particles for good electron

conduction. The SEM images (Figure 3.5) show the LSM distribution in our YSZ nanofiber and YSZ powder cathodes. The distribution appears to be a continuous network of LSM nanoparticles. Also, Figure 3.6 is the EDS spectrum for the LSM infiltrated YSZ nanofiber cathode which shows the signals for each element present.

Figure 3.5: SEM images of 30% LSM infiltrated (a) YSZ nanofiber cathode (b) YSZ powder cathode.

Figure 3.6: EDS spectrum for the LSM infiltrated YSZ nanofiber cathode.

In Chapter 02 – Section II, we have reported the results of a preliminary study on LSM infiltrated YSZ scaffolds, where we used a PAR system to do the electrochemical measurements. However, using proper infiltration techniques and the Solartron system for characterization, we were able to achieve better results for infiltrated YSZ electrodes. Zhi et al.[16] have reported a R_p value of 0.27 Ohmcm² (at 800 °C) for their 50% LSM infiltrated

YSZ nanofiber cathode. We were able to achieve average R_p values of 0.23 - 0.27 Ohmcm^2 at 800 $^{\circ}\text{C}$, for 30% LSM infiltrated YSZ nanofiber cathodes.

Shah et al. [17] have carried out a similar experiment using symmetrical cells. They sintered YSZ powder scaffolds at 1400 $^{\circ}\text{C}$, and again sintered them at 1125 $^{\circ}\text{C}$ after applying an LSM current collector. Then, these scaffolds were infiltrated with an LSM nitrate solution and sintered at 800 $^{\circ}\text{C}$. Then, they have recorded EIS data while aging at 800 $^{\circ}\text{C}$. They report that the R_p value increased from 0.2 Ohmcm^2 to 0.5 Ohmcm^2 after 300 hours. With the LSM infiltrated YSZ nanofibers, we were able to achieve R_p values in this range. However, most of the R_p values we observed for LSM infiltrated YSZ powder electrodes are higher than this reported value.

Buyukaksoy et al.[6] have characterized LSM infiltrated YSZ powder symmetrical cells using Pt current collectors and they reported an amazing R_p value of 0.022 Ohmcm^2 (at 800 $^{\circ}\text{C}$) for their cells and an activation energy of 1.35 eV for the oxygen reduction reaction.

Chen et al. [18] have carried out an experiment to study the effect of sintering temperature on 40% LSM infiltrated YSZ cathodes. Pt current collectors have been used and they sintered the infiltrated cathodes at 900 $^{\circ}\text{C}$ and 1100 $^{\circ}\text{C}$. The symmetrical cell sintered at 900 $^{\circ}\text{C}$ exhibited a R_p value of 0.21 Ohmcm^2 at 800 $^{\circ}\text{C}$ while the other cell showed a R_p value of 0.74 Ohmcm^2 . Also, the activation energies for the oxygen reduction reaction on the cells sintered at 900 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$ are 1.39 eV and 1.40 eV respectively. The average activation values that we observed for the oxygen reduction reaction ranges from 1.42 eV - 1.60 eV.

In a study performed by Huang et al.[5], the optimum temperature for sintering an LSM infiltrated YSZ scaffold is reported as 1050 $^{\circ}\text{C}$. Furthermore, they state that sintering temperatures lower than 1050 $^{\circ}\text{C}$ form porous LSM while the temperatures higher than 1050 $^{\circ}\text{C}$ results in dense LSM layers. For a 40% LSM infiltrated YSZ symmetrical cell sintered at 850 $^{\circ}\text{C}$, they have achieved a R_p value of 0.5 Ohmcm^2 at 700 $^{\circ}\text{C}$.

3.4 Summary

Even though the porosity is imperative for a better performing cathode current collector, adding 50% or more graphite to the LSM paste results in delamination. Therefore, pure LSM or LSM with 10% graphite was used as a current collector. Also, for all the cells that were characterized, a thin Ag paste was applied on top of the LSM to ensure good current collection.

LSM infiltrated YSZ nanofiber scaffolds yielded slightly lower R_p values compared to the LSM infiltrated YSZ powder cathodes. However, the decrease in polarization resistance was not dramatic, suggesting that the high surface area of the nanofibers did not result in a large increase in TPB length in the cathode. The high cost of producing YSZ nanofibers would consequently prohibit their use in commercial SOFCs. Both types of cathodes showed similar E_a values for oxygen reduction reaction which suggests that the oxygen reduction reaction mechanism on both cathodes is the same.

LSM infiltrated cathodes prepared using YSZ nanofibers sintered at 1400 °C showed relatively lower R_p values at 800 °C. The high temperature sintering is known to melt the nanofibers, creating a highly roughened surface structure. Ball-milling the YSZ nanofibers resulted in better electrodes with less gaps but it did not significantly affect the performance of the electrode.

Also, the LSM infiltrated YSZ powder cathodes prepared using smaller particles results in slightly higher R_p values at 800 °C.

3.5 Conclusion

The conventional method to prepare composite cathodes is via mixing ionic conductor and electronic conductor powders together followed by high temperature sintering. Infiltration is a modern technique where the powder based ionic conductor is sintered at a higher temperature to make the scaffold and then it is infiltrated (multiple times) with a precursor solution of electronic conductor before sintering at a lower temperature. For the first time, Zhi et al [9] have prepared a YSZ scaffold using YSZ nanofibers and compared the

performance of the LSM infiltrated YSZ nanofiber cathode with a composite cathode prepared using LSM and YSZ powders. In this study, we have compared the performance of LSM infiltrated YSZ nanofiber cathodes with LSM infiltrated YSZ powder cathodes. Furthermore, we have carried out the deconvolution analysis on the impedance data collected for these cells and the results are presented in chapter 04.

Based on our results, both pure LSM and 10% C-LSM current collectors resulted in similar cell performance which suggests that either current collector can be used without any significant effects. The R_p values we obtained at 800 °C are comparable to most of the reported values in literature. However the E_a value we obtained for the oxygen reduction reaction is slightly higher than the reported values. Also, according to our results, YSZ cathodes prepared using a powder with larger particles results in better performing electrodes. It would be worthwhile to modify the YSZ scaffold in order to achieve a better performing cathode, which will be discussed in Chapter 04.

3.6 References

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Chapter 04

Solid Oxide Fuel Cell Cathodes and Deconvolution Studies

4.1 Introduction

The cathode provides the reaction sites for the oxygen reduction reaction (ORR) in a solid oxide fuel cell. Therefore, a cathode must be stable in an oxidizing environment, compatible with other cell components, possess sufficient electronic conductivity and porosity and also needs to have good catalytic activity for oxygen reduction reaction. Lanthanum Strontium Manganite (LSM) is the most widely used SOFC cathode material due to its high electronic conductivity and the compatibility with other cell components including the YSZ electrolyte [1]. LSM by itself can be used as a SOFC cathode while LSM-YSZ composite cathodes prepared by mixing powders or infiltration results in better cell performance.

While operating solid oxide fuel cells at high temperatures, cell performance decreases over time due to degradation of the cell components. Cathode degradation takes place mainly due to changes in the microstructure (e.g., coarsening), cation migration resulting in a poor cathode material, insulating secondary phase formation (e.g., Lanthanum and Strontium Zirconates) and delamination [2], [3]. Therefore, it is important to carry out aging studies in order to investigate the stability of SOFCs over time.

Impedance spectroscopy is a very powerful tool to study SOFCs. Analyzing impedance data is very useful to gain the knowledge needed to design improved microstructures and materials for SOFC cathodes. However, the impedance data collected for SOFCs are very complex since there are overlapping impedance related cell processes taking place. “Deconvolution” (distribution of relaxation times) is a method developed by Ivers-Tiffée [4] in order to identify relaxation times that are relevant to cell processes, using the impedance data. In simple terms, when the impedance data are subjected to deconvolution, the resulting graph shows peaks with different frequencies for different cell processes. This information is very important for proposing a suitable equivalent circuit model, which in turn helps to calculate the polarization resistances at each electrode [3],[4]. A well detailed

discussion on the deconvolution method is presented in Xiaoke Chen's [3] Ph.D. dissertation. Chapter 1 – Section 1.7 of this dissertation discusses impedance elements and their interpretation in terms of processes.

In this chapter, the experiments carried out with conventional LSM powder cathodes will be discussed in detail first. SOFC researchers around the world have studied composite LSM-YSZ cathodes prepared by infiltrating a pre-sintered porous YSZ backbone with an LSM solution. However, according to our knowledge, no one has studied the catalytic activity of the infiltrating LSM solution alone on the YSZ electrolyte. Therefore, we prepared LSM/YSZ symmetrical cells simply by evaporating the LSM solution on YSZ electrolyte followed by sintering; in order to study the LSM solution-based cathodes using impedance spectroscopy. Finally, the deconvolution studies of impedance data collected for LSM infiltrated YSZ cathodes (described in Chapter 03) and the data for LSM infiltrated YSZ cathodes with improved microstructures will be presented.

4.2 Powder based LSM cathodes

Commercial LSM ($(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-\delta}$) powder (2.4 g) (LSM 20-P, $d_{50} \sim 1 \mu\text{m}$, Fuel Cell Materials) and the ink vehicle (0.8 g) (3:1 by weight) received from Dr. Edward Sabolsky's (MAE - WVU) laboratory (which contains α -terpineol and other additives) were “ball-milled” using a WIG-L-BUG, to produce the paste. The paste was painted on YSZ electrolytes (the thickness was defined by tape) and sintered at a higher temperature to produce LSM powder/YSZ symmetrical cells. The thickness of the LSM electrode after sintering at 1200°C for 1 hour is $\sim 10 \mu\text{m}$.

Initially, a sintering study was carried out to find the optimum sintering temperature for LSM cathodes. Then, the aging studies were carried out on LSM powder/YSZ symmetrical cells.

A Solartron SI 1287 electrochemical interface and 1252A frequency response analyzer were used to perform the electrochemical characterization using Ag current collectors and Ag wires. For comparison, two LSM powder/YSZ symmetrical cells were characterized using Au and Pt current collectors as well. Impedances were measured using 10 log linear

frequencies per decade, starting at 100 kHz and ending at 0.1 Hz or 0.02 Hz. Typically, impedances were collected at 800 °C, 750 °C and 700 °C to obtain the activation energies of processes.

4.2.1 Sintering Study of LSM powder cathodes

Experimental:

The LSM powder/YSZ symmetrical cells were prepared as mentioned above and sintered at 1050 °C, 1100 °C, 1150 °C or 1200 °C for 1 hour. Then, these cells were characterized by impedance spectroscopy.

Table 4.1: Summary of results for the sintering study of LSM powder/YSZ symmetrical cells.

Sintering Temperature (°C)	Average normalized R_s (Ohmcm ²) at 800 °C	Average normalized R_p (Ohmcm ²) at 800 °C	Peak frequency range (Hz) at 800 °C	E_a (eV) for R_p
1200	0.77 (+/-0.01)	6.37 (+/-0.19)	1	1.4 (+/-0.1)
1150	0.78 (+/-0.01)	9.65 (+/-0.54)	1-4	1.4 (+/-0.2)
1100	0.81	14.88	6	1.4
1050	0.79 (+/-0.04)	11.21 (+/-2.88)	4-10	1.5 (+/-0.0)

Results and Discussion:

The average series resistances at 800 °C range from 0.77 to 0.81 Ohmcm² while the lowest resistance is obtained for the cell sintered at 1200 °C. This series resistance range is consistent with previous measured series resistances on the commercial YSZ plates. The lowest polarization resistance was also obtained for the cell sintered at 1200 °C. The activation energy values obtained for the oxygen reduction reaction are in the same range for these LSM cathodes sintered at different temperatures, except for the cells sintered at 1050 °C. Furthermore, these activation energy values are in the same range (1.5-1.7 eV) as reported in literature [3].

As Cronin et al. [5] have reported for LSM-YSZ composite cathodes, the peak frequency of the impedance spectra of these LSM cathodes show a decreasing trend with the increasing sintering temperature. Since the LSM powder/YSZ symmetrical cell sintered

at 1200 °C showed the lowest and reproducible resistances which are comparable to previously reported values [3], [6], 1200 °C was chosen as the sintering temperature for our LSM powder cathodes. The SEM image of the top surface of an LSM powder cathode sintered at 1200 °C for 1 hour (Figure 4.1) shows a well-connected network of LSM particles with dimensions on the order of 1 micron and also sufficient porosity.

Figure 4.1: SEM image of an LSM cathode sintered at 1200 °C for 1 hour.

4.2.2 Aging Study of LSM powder/YSZ symmetrical cells

Experimental:

As mentioned in Section 4.2.1, a LSM powder/YSZ symmetrical cell was prepared and characterized as follows:

Day 1: Electrochemical characterization at 800 °C, 750 °C, 700 °C and aging overnight at 800 °C

Days 2 & 4: Record an initial reading at 800 °C; change the temperature to 700 °C and after 1 hour, record readings at each hour and age overnight at 700 °C.

Days 3 & 5: Record an initial reading at 700 °C; change the temperature to 800 °C and after 1 hour, record readings at each hour and age overnight at 800 °C.

Results and Discussion:

Figure 4.2: Polarization resistances recorded over time during the aging experiment for LSM powder cathode sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time over the entire experiment.

Figure 4.3: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of LSM powder cathode sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time from the temperature change. At the beginning of Day 2 and Day 4, the cell temperature was dropped from 800 °C to 700 °C. At the beginning of Day 3 and Day 5, the cell temperature was raised from 700 °C to 800 °C.

When the cell aging over the course of time of complete experiment (Figure 4.2) is considered, polarization resistances and series resistances generally showed an increasing trend at both temperatures. However, after aging at Day 3 cell polarization decreased considerably and increased again at Day 5.

When the polarization resistances were recorded at each hour (Figure 4.3), the resistances at 700 °C showed a reproducible increasing trend (on both Day 2 and Day 4) while one set of resistances at 800 °C showed a decreasing trend (Day 3) and the resistances recorded in Day 5 showed an increasing trend. The pattern observed for polarization resistances at 700

$^{\circ}\text{C}$ is similar to the reversible cathode aging trend reported by Abernathy et al. [6] for LSM/YSZ symmetrical cells when the temperature was cycled between 700°C and 800°C . Unlike our data, they have observed the reproducible decreasing pattern for polarization resistances recorded at 800°C as well. However, their experimental approach is different since their symmetrical cells were initially aged at 800°C for 500 hours in order to remove the effects of irreversible cell aging, before the cell was thermally cycled [6]. Therefore, the reason for not observing the reversible pattern (at 800°C) in our data may be because our cell was still undergoing the irreversible thermal aging which results in increased polarization resistances.

Abernathy et al. [6] propose the “cation segregation” as a possible cause for the reversible aging behavior they observed at 700°C and 800°C . Cation migration can take place due to the changes in cathode microstructure, redistribution of cations throughout the lattice or secondary phase formation [6]. Jiang and Love [7] have reported that LSM cathodes tend to form passive surface layers such as SrO and MnO_x which results in lower cell performance. Also, there are several studies [8], [9] showing that the degree of Sr enrichment (passive SrO formation) on LSM increase with decreasing temperature, which might be the reason for increasing R_p values observed at 700°C . However, Caillol et al. [10] have reported contradictory results where they observed Sr segregation on LSM surface at 1200°C and desegregation at 800°C , which means the cation segregation increase with increasing temperature. The cause of the slow reversible aging remains uncertain.

4.2.3 Deconvolution studies of LSM powder/YSZ symmetrical cells

Deconvolution of the impedance data obtained for LSM powder cathodes resulted in a complex spectrum with several overlapping peaks indicating multiple processes. Figure 4.3 (d) shows a negative out of phase impedance vs log frequency plot with individual RQ elements for impedance data of LSM/YSZ symmetrical cell with Au current collectors at 800°C . Therefore, an equivalent circuit of $\text{LR}(\text{RQ})_3$ and the Zview® software were used to fit the impedance data and obtain the polarization resistances (Table 4.2). Notice that the peak frequencies lie around 1.5-5 Hz for these LSM powder cathodes.

Figure 4.4 shows the deconvoluted data (blue) and the simulation result obtained using the equivalent circuit fitting (red) for LSM powder/YSZ symmetrical cells with different current collectors. These deconvoluted and simulated spectra show a reasonable agreement except for the discrepancies at lower frequencies especially with the Ag current collector.

Figure 4.4: Deconvoluted and simulated data for LSM powder/YSZ symmetrical cells at 800 °C with (a) Ag (b) Pt and (c) Au current collectors; (d) negative out of phase impedance vs log frequency plot with equivalent circuit fitting (3 RQ elements) of impedance data collected for (c).

Xiaoke Chen [3] has also performed a deconvolution analysis on commercial LSM powder/YSZ symmetrical cells (sintered at 1200 °C for 4 hours and characterized using Au current collectors) and used an equivalent circuit consist of 5RQ elements in order to fit the impedance data. The peak frequency of her reported data lies around 63 Hz.

Polarization resistances and the activation energies for the oxygen reduction reaction (presented in Table 4.2), of these LSM powder/YSZ symmetrical cells are comparable to the typical values of LSM powder cathodes that have been reported previously [3]. For silver and platinum current collectors, one RQ element dominates the impedance. As will be shown in chapter 5, typical equivalent circuit values for the LSM paste electrodes are around $R = 10 \text{ Ohmcm}^2$, $Q = 0.01$, $n = 0.7$, and the peak frequency is near 1 Hz.

Table 4.2: Normalized fitting parameters for at 800 °C with (a) Ag (b) Pt and (c) Au current collectors for LSM powder/YSZ symmetrical cells.

		Ag Current Collector	Pt Current Collector	Au Current Collector	
Element	Parameter	Value	Value	Value	Units
Series R	R1	0.61	0.86	0.86	Ohmcm ²
Inductance	L	2.74E-07	2.86E-07	3.14E-07	Hcm ²
RQ1	R2	8.9 E-03	0.08	0.09	Ohmcm ²
RQ2	R3	0.14	0.81	7.17	Ohmcm ²
RQ3	R4	12.13	14.62	1.18	Ohmcm ²
RQ1	n1	1	1	1	
RQ2	n2	0.879	0.921	0.765	
RQ3	n3	0.692	0.698	0.479	
RQ1	f1	39000	92	123	Hz
RQ2	f2	79	4	4	Hz
RQ3	f3	1	1	2	Hz
RQ1	Q1	4.57E-04	2.29E-02	1.46E-02	
RQ2	Q2	3.03E-02	6.53E-02	8.51E-02	
RQ3	Q3	2.36E-02	1.52E-02	3.83E-03	
Polarization R	R _p	6.14	7.75	4.22	Ohmcm ²
Activation Energy for ORR	E _a	1.5 (+/- 0.0)	1.7 (+/- 0.0)	1.7 (+/- 0.0)	eV

4.3 Solution based LSM cathodes

The conventional LSM cathodes are prepared using powders that are pre-sintered to higher temperatures during processing steps. According to Sasaki et al [11], processing parameters including calcination temperature, characteristics including particle size of the LSM powder and the cathode sintering temperature greatly influence the cathode microstructure and hence the cathode performance. Therefore, we have tried to prepare and characterize LSM solution based cathodes that were not pre-sintered at very high temperatures.

An organic LSM precursor solution (0.1 M) was prepared as mentioned in Section 3.2 [12]. An aqueous LSM precursor solution (0.03M) was prepared following the procedure

published by Zhu et al. [13]. In order to prepare the aqueous LSM solution, proper amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.3 g), $\text{Sr}(\text{NO}_3)_2$ (31.7 mg) and $\text{Mn}(\text{NO}_3)_2$ (120 μL) were dissolved in a mixture of water (12.5 mL) and ethanol (12.5 mL) (1:1) with glycine (142 mg) (molar ratio LSM : Glycine: = 1:2.53) and polyvinyl pyrrolidone powder (12.5 mg) (0.05 weight % of LSM solution). Concentrated nitric acid was added to adjust the pH of the solution to ~ 3 . The wetting properties of these solutions were characterized using contact angle goniometry. Furthermore, the resulting powders were characterized by X-ray diffractometry (XRD) and Thermogravimetric Analysis (TGA).

Then, LSM solution/YSZ symmetrical cells were prepared by evaporating LSM precursor solutions on YSZ and firing at 800 $^{\circ}\text{C}$, 900 $^{\circ}\text{C}$, 1000 $^{\circ}\text{C}$ or 1200 $^{\circ}\text{C}$ for 1 hour. Initially, Ag current collectors were used for electrochemical characterization. However, Pt and Au current collectors were also used later for comparison. Aging studies of these cathodes were carried out as well. Furthermore, a symmetrical cell based on LSM solution electrodes was prepared on HIOINIC® electrolyte as well in order to study the effect of the electrolyte. Finally, how the organic solution based LSM cathode (with Ag current collector) behaves with different oxygen partial pressures was studied.

4.3.1 Contact Angle Measurements

A telescope goniometer (Dr. Peter Gannett's laboratory, Health Sciences Campus, WVU) (Figure 4.5) was used to measure the contact angle between the LSM solution droplet and the YSZ surface. A contact angle smaller than 90 $^{\circ}$ means the solution tends to wet the surface well while a contact angle larger than 90 $^{\circ}$ means the solution has a less tendency to spread over the surface (Figure 4.6) [13].

Figure 4.5: A telescope goniometer [14].

Figure 4.6: Different contact angle measurements [14].

Experimental:

As received YSZ electrolytes and YSZ electrolytes pre-heated at 500 °C for ~30 minutes and cooled to room temperature (to make the surfaces hydrophilic) were used as substrates in order to investigate the wetting properties of organic and aqueous LSM solutions using a telescope goniometer.

Results and Discussion

Figure 4.7: Contact angle measurements for aqueous LSM solution on as received YSZ (a) and hydrophilic YSZ (b) and organic LSM solution on as received YSZ (c) and hydrophilic YSZ (d).

The average contact angle measurement for aqueous LSM solution on as received YSZ is 35.2° while it is 4.3° on hydrophilic YSZ. Also, the average contact angle measurement for organic LSM solution on as received YSZ is 15.9° and 6.7° on hydrophilic YSZ. This shows that both aqueous and organic LSM solutions readily spread on the hydrophilic YSZ surfaces (Figure 4.7).

4.3.2 XRD analysis

In order to ensure that our precursor solutions result in crystalline LSM upon sintering, XRD analysis of the powders were carried out at the NETL-Morgantown site.

Experimental:

Aqueous and organic LSM precursor solutions were placed in two different crucibles and sintered at 800°C for 1 hour. Then, the resulting powders were characterized by XRD.

Results and Discussion:

XRD data shown in figure 4.8 show that LSM phase is formed since the characteristic peaks for LSM in an XRD spectrum can be seen at $2\theta \sim 23, 33, 42, 47, 53, 59$ and 69° [12].

Figure 4.8: XRD data for aqueous LSM (a) and organic LSM (b).

4.3.3 Thermogravimetric Analysis

In thermogravimetric analysis (Dr. Jingxing Wang's laboratory, Division of Forestry and Natural Resources, WVU), the mass of a sample (which is in a controlled atmosphere) is continuously recorded (as a function of time) while the temperature of the sample is linearly increased. TGA can provide information about decomposition reactions, oxidation reactions, vaporization, sublimation and desorption processes of the sample [15].

Experimental:

Both organic and aqueous LSM precursor solutions were evaporated on YSZ electrolyte pieces while heating to a temperature $\sim 80^{\circ}\text{C}$ in order to obtain dry samples. Since these samples were highly hygroscopic, they were stored in a desiccator until the analysis was done. TGA of the samples were carried out (in atmospheric conditions without any gas purging) while heating the sample to 900°C using a $20^{\circ}\text{C}/\text{min}$ ramp rate and held at 900°C for another 30 minutes.

Results and Discussion:

Thermograms recorded during the TGA experiment are shown in Figure 4.9. According to previously published data [16]-[18], the initial weight loss from the start to around 150°C - 200°C is due to evaporation of water and loss of surface adsorbed gas molecules. The weight change around 200°C - $\sim 400^{\circ}\text{C}$ is assigned to decomposition of nitrates and organic matter. The final weight changes occur with the oxide formation which results in the LSM phase. No weight change was observed when the TGA was continued for 30 minutes at 900°C which ensures the complete LSM formation had already taken place. Also, there is no significant weight change between 800°C and 900°C which means the LSM phase is already formed at 800°C .

Figure 4.9: Thermograms for organic (blue) and aqueous (red) LSM precursor

4.3.4 Sintering study of LSM solution based cathodes

Experimental:

Organic and aqueous LSM solutions were deposited on both sides of YSZ electrolytes (~ 10-20 uL total volume in multiple depositions of ~5 uL aliquots) and dried at ~100 °C. A dried layer of varnish was used to define the area of the electrodes. Then these LSM solution/YSZ symmetrical cells were sintered at 800 °C, 900 °C, 1000 °C or 1200 °C for 1 hour. Electrochemical characterizations of the cells were done using Ag wires and Ag current collectors.

Results and Discussion:

Note that in samples shown in tables 4.3 and 4.4, only the solution based LSM cathodes were sintered at different temperatures (800 °C, 900 °C, 1000 °C or 1200 °C). After that, all the cathodes were characterized in the same way after applying Ag paste as the current collector followed by heating to 800 °C. Therefore, it would be assumed that the differences in the cathode performance are due to the different sintering temperatures of the LSM phase.

Table 4.3: Summary of results for the sintering study of organic LSM solution/YSZ symmetrical cells.

Sintering Temperature ($^{\circ}\text{C}$)	Average normalized R_s (Ohm cm^2) at 800°C	Average normalized R_p (Ohm cm^2) at 800°C	Peak frequency range (Hz) at 800°C	E_a (eV) for R_p
800	0.97 (+/-0.08)	0.73 (+/-0.20)	710-1780	1.5 (+/-0.1)
900	0.64 (+/-0.04)	0.50 (+/-0.25)	630-2820	1.3 (+/-0.1)
1200	0.86	1.03	100	1.0

Table 4.4: Summary of results for the sintering study of aqueous LSM solution/YSZ symmetrical cells.

Sintering Temperature ($^{\circ}\text{C}$)	Average normalized R_s (Ohm cm^2) at 800°C	Average normalized R_p (Ohm cm^2) at 800°C	Peak frequency range (Hz) at 800°C	E_a (eV) for R_p
800	0.96 (+/-0.06)	0.44 (+/-0.01)	4000-10000	1.1 (+/-0.1)
900	0.78 (+/-0.13)	0.27 (+/-0.14)	3550-10000	1.1 (+/-0.1)
1000	0.82	0.66	890	0.9

For both aqueous and organic solution based LSM cathodes sintered at 800°C , the R_s values obtained at 800°C were relatively high compared to the other sintering temperatures. This may be because 800°C is not enough to well sinter the LSM on to YSZ electrolytes. Also, the R_p values obtained for cathodes sintered at 800°C are noticeably higher than the values obtained for cathodes sintered at 900°C . This again might be due to poor sintering of LSM particles at 800°C which results in a comparatively poor cathode. For both LSM solutions, the cells sintered at 900°C resulted in lower R_p values compared to other sintering temperatures. However, when the solution based cathodes were sintered at a higher temperature (1000°C or 1200°C), the R_p values increased and the peak frequencies decreased noticeably as reported by Cronin et al. [5]. In their study, Cronin et al. [5] used 3D-FIB SEM tomography to study the cathode structures obtained after different sintering temperatures. Their LSM-YSZ composite powder cathodes sintered between 1075°C - 1175°C showed the lowest R_p values (0.35 - 1.0 Ohmcm^2) and highest impedance peak frequencies (1000 - 100 Hz) at 800°C . Their tomography images show a

well sintered percolated network of LSM particles at the optimum firing temperatures (1075 °C-1175 °C). Furthermore, values calculated from the 3D reconstructed electrodes show that the active TPB density was at a maximum ($\sim 8 \mu\text{m}^{-2}$) when the sintering temperatures were between 1075 °C-1175 °C. Cathodes sintered at higher temperatures showed higher R_p values and lower peak frequencies. 3D tomography image of the cathode sintered at 1325 °C shows particle coarsening and densification which reduces the calculated active TPB to $\sim 3 \mu\text{m}^{-2}$ [5]. This study clearly shows that the higher sintering temperature results in particles coarsening which leads to reduced TPB density, increased R_p values and low impedance peak frequencies. In other words, particle size is a very important contributor to the cathode performance. Sarikaya et al. [19] have studied how the microstructural evolution affects the SOFC performance using LSM paste/YSZ symmetrical cells. When they tested two LSM cathodes prepared using powders with different particle sizes ($d_{50} = 1 \mu\text{m}$ and $d_{50} = 0.3 \mu\text{m}$), the latter cathode showed better performance with lower R_p values; which further proves that small particles result in better performing cathode material.

Organic LSM solution based cathode sintered at 1200 °C and all the cathodes prepared using the aqueous LSM solution exhibited activation energy values ~ 1 eV for the oxygen reduction reaction, which is different to the activation energy values associated with LSM (1.5 eV-1.7 eV or 1.3 eV) [3]. However, the activation energy values obtained for organic LSM solution based cathodes sintered at 800 °C and 900 °C are comparable to the reported activation energy values for LSM. The possible reasons for these observations will be discussed in Section 4.3.8 of this chapter.

R_p values obtained for all these solution based cathodes are around an order of magnitude lower compared to the powder based LSM cathodes. Also, the peak frequencies obtained for these cathodes are 2 to 3 orders magnitude higher than the peak frequencies obtained for LSM powder cathodes. As reported by Cronin et al. [5] and Sarikaya et al. [19], these observations might be related to particle size differences between the powder based and solution based LSM cathodes.

SEM image of the LSM powder cathode sintered at 1200 °C (Figure 4.1) show a crystalline phase with grains in the μm range. However, the microstructure of the LSM solution cathode (Figure 4.10) is completely different from the structure of the LSM powder cathode (Figure 4.1). Instead of a crystalline phase, it shows an “amorphous sponge-like” structure at 5000 X magnification. Also, there appear to be pores which might be continuous from the air/LSM interface to the YSZ electrolyte since these cathodes are extremely thin. We were not able to image these cathodes at higher magnifications due to instrumental limitations. However, Shiwoo Lee [20] at NETL-Morgantown have done a similar study where he deposited a solution of La-Sr-Co nitrates on different substrates followed by sintering at ~ 900 °C and carried out SEM imaging. He observed similar amorphous structures on his material at low magnification SEM images. However, very high magnification (30000 X-100000 X) SEM images showed well defined grains in nm range. Therefore, we can assume that our solution based cathodes also consist of LSM particles that are in the nm range and hence results in lower R_p values and higher impedance peak frequencies compared to the LSM powder cathodes with particles in μm range. A cathode with smaller LSM particles have comparatively high TPB area and hence a higher number of active sites for oxygen reduction reaction to occur, which results in a cathode with high performance.

Figure 4.10: ESEM image of an organic LSM cathode sintered at 800 °C for 1 hour, 5000 X magnification, 900 °C imaging temperature.

Summary:

Note that this summary is for solution based LSM cathodes with Ag current collectors.

- Lowest R_p values were obtained for both solution based LSM cathodes sintered at 900 °C.

- Solution based cathodes sintered at higher temperatures (1000 °C or 1200 °C) resulted in relatively high R_p values and low peak frequencies.
- Organic solution based LSM cathodes sintered at 800 °C and 900 °C yielded activation energies around 1.5 (+/- 0.1) eV and 1.3 (+/- 0.1) eV respectively.
- Organic solution based LSM cathodes sintered at 1200 °C yielded activation energies around 1.0 eV.
- Aqueous solution based LSM cathodes sintered at both 800 °C and 900 °C yielded activation energies around 1.1 (+/- 0.1) eV.
- Aqueous solution based LSM cathodes sintered at 1000 °C yielded activation energies around 0.9 eV.
- Microstructure of powder based LSM cathode shows a crystalline phase with grains in the μm range while the solution based LSM cathodes show an amorphous like phase (with nm range grains hypothesized).

4.3.5 Aging Study of LSM solution/YSZ symmetrical cells with Ag current collectors

Experimental:

As mentioned in Section 4.3.4, LSM solution/YSZ symmetrical cells were prepared and characterized using the aging protocol mentioned in section 4.2.2.

Results and Discussion:

The aging studies of all the aqueous and organic LSM solution cathodes (with Ag current collectors) sintered at 800 °C and 900 °C showed similar aging patterns. Therefore, only the data obtained for organic LSM solution sintered at 900 °C cathode is shown in Figures 4.11 and 4.12. The data obtained for the other cells are presented in the Appendix A.

Figure 4.11: Polarization resistances recorded over time during the aging experiment for organic LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ at (a) 700 °C and (b) 800 °C. This figure shows the cathode behavior vs. time over the entire experiment.

Figure 4.12: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of organic LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ. This figure shows the cathode behavior vs. time from the temperature change. At the beginning of Day 2 and Day 4, the cell temperature was dropped from 800 °C to 700 °C. At the beginning of Day 3 and Day 5, the cell temperature was raised from 700 °C to 800 °C.

With aging, the R_p values recorded both at 700 °C and 800 °C increased slightly (or stayed constant). We did not observe reproducible R_p values or reversible thermal aging patterns as reported for LSM powder cathodes [6]. The R_p values measured at 800 °C on Day 5 eventually reached a constant value which might be because the cell has stopped undergoing the initial irreversible thermal aging. An interesting feature observed in all these data is the following. After aging the cell overnight at 700 °C (at the end of Day 2 and Day 4), the next R_p value measured was smaller than the preceding R_p value. However, when the cell was aged overnight at 800 °C, the measured R_p values increased. Assuming that LSM is the active cathode material, this might occur if the cation desegregation is

favored at the lower temperature (700 °C) which results in an active cathode surface and hence lower polarization resistance as Caillol et al. [10] have reported.

Figure 4.13: Polarization resistances recorded over time during the aging experiment for organic LSM solution cathode (with Ag current collector) sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time over the entire experiment.

Figure 4.14: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of organic LSM solution cathode (with Ag current collector) sintered at 1200 °C on YSZ. This figure shows the cathode behavior vs. time from the temperature change. At the beginning of Day 2 and Day 4, the cell temperature was dropped from 800 °C to 700 °C. At the beginning of Day 3 and Day 5, the cell temperature was raised from 700 °C to 800 °C.

The aging patterns observed for organic LSM solution cathode (with Ag current collector) sintered at 1200 °C (Figures 4.13 and 4.14) are completely different from the aging patterns observed for other solution based cathodes. The R_p values measured at both temperatures were approximately reproducible and constant. However, we did not observe the decreasing trend of R_p values at 800 °C, as reported by Abernathy et al.[6]. Since this cathode was sintered at a higher temperature (1200 °C), it must have already undergone irreversible aging, which results in constant R_p values during the aging study.

4.3.6 Deconvolution studies of LSM solution/YSZ symmetrical cells with Ag current collectors

Deconvolution of impedance data collected for all solution based LSM cathodes with Ag current collectors resulted in a well-defined sharp peak at higher frequencies (kHz range) which could be well fitted with a LR(RQ) circuit which has one or two elements. Figure 4.15 shows the deconvoluted data and the simulated data fit for an organic LSM solution based cathode sintered on YSZ at 900 °C for 1 hour. The cell was characterized using Ag current collectors and Ag wires. Deconvoluted data (blue) and the simulation result obtained using the equivalent circuit (red) fitting show a very good agreement and the fitting parameters are shown in table 4.5.

Figure 4.15: Deconvoluted (blue) and simulated (red) data at 800 °C for Ag/organic LSM/YSZ symmetrical cell sintered at 900 °C.

A typical LSM powder cathode yields impedance data that has to be fitted using multiple equivalent circuit elements and also yields peak frequencies around 1-10 Hz range. However, the LSM solution based cathodes not only resulted in high peak frequencies but also less complex deconvoluted spectra that can be fitted using one/two equivalent circuit elements.

These solution based electrodes that are in contact with YSZ electrolyte are very thin (~ 2-D) structures. Therefore, there might be a possibility for the metal current collector to penetrate the LSM layer and come into direct contact with the electrolyte and behave as a cathode. Due to this reason, it was decided to further investigate these solution based LSM cathodes with different current collectors and to study the effect of current collector on their performance.

Table 4.5: Normalized fitting parameters at 800 °C for Ag/organic LSM/YSZ symmetrical cell sintered at 900 °C.

Element	Parameter	Value	Units
Series R	R1	0.64	Ohmcm ²
Inductance	L	3.14E-07	Hcm ²
RQ1	R2	1.22	Ohmcm ²
RQ2	R3	0.24	Ohmcm ²
RQ1	n1	0.793	
RQ2	n2	0.966	
RQ1	f1	779	Hz
RQ2	f2	423	Hz
RQ1	Q1	9.72E-04	
RQ2	Q2	2.05E-03	
Polarization R	R _p	0.73	Ohmcm ²
Activation Energy for ORR	E _a	1.3 (+/- 0.1)	eV

4.3.7 LSM solution/YSZ symmetrical cells with different metal current collectors

An ideal current collector should not take part in the reactions taking place at the SOFC electrodes [21]. However, the current collection method and the material used as the current collector have a significant impact on the cell performance [22].

First, we prepared and characterized Ag/YSZ and Pt/YSZ symmetrical cells in order to study their impedance behavior. We attempted to prepare Au/YSZ symmetrical cells as well; however, Au showed very poor adhesion to the YSZ substrate during sintering. After that, we studied the impedance behavior of LSM solution electrodes with Pt and Au current collectors. The results in Chapter 02 - Sections 2.3 (Pt/YSZ cells) and 2.5 (Ag/YSZ) cells are limited to just Rs and Rp values. This study includes the full impedance spectra for these metal/YSZ symmetrical cells.

Experimental:

The symmetrical cells that were electrochemically characterized at 800 °C, 750 °C and 700 °C using impedance spectroscopy were prepared as follows. After soaking the cell at 800 °C for ~ 1 hour, measurements were taken at each temperature.

- (i) Ag (thick)/YSZ symmetrical cell: As received Ag paste (Fuel Cell Materials) was used to paint thin Ag electrodes on YSZ electrolytes and dried at 450 °C. Then, Ag wires were attached and the cell was heated to 800 °C to start collecting data at each temperature.
- (ii) Ag (thin)/YSZ symmetrical cell: The commercial Ag paste (~0.1 mL) was diluted with a thinner (~0.2 mL) (SPI Pt paint thinner – butyl acetate) to make a less viscous diluted Ag paste which was used to paint very thin Ag electrodes on YSZ electrolytes and dried at 450 °C. Then, Ag wires were attached and the cell was heated to 800 °C to start collecting data at each temperature.
- (iii) Ag (powder)/YSZ symmetrical cell: A Ag paste was prepared by mixing a Ag powder (~1 g) (Alfa Aesar, 0.7-1.3 micron) and the ink vehicle (~1 g) (from Dr. Sabolsky's laboratory) in order to obtain a Ag paste which was used to paint very thin Ag electrodes on YSZ electrolytes and sintered at 800 °C for 1 hour. Then, Ag wires were attached and the cell was heated to 800 °C to start collecting data at each temperature.
- (iv) Pt/YSZ symmetrical cell: As received Pt paste (SPI-CHEM) was used to paint thin Pt electrodes on YSZ electrolytes and sintered at 900 °C for 1 hour. Then, Au wires were attached and the cell was heated to 800 °C to start collecting data at each temperature.

Results and Discussion:

Figure 4.16: Deconvoluted (blue) and simulated (red) data at 800⁰C for (i) Ag (thick)/YSZ (ii) Ag (thin)/YSZ (iii) Ag powder/YSZ and (iv) Pt/YSZ symmetrical cells.

Based on the deconvolution spectra in Figure 4.16, an equivalent circuit which consists of a double fractal Gerischer element paired with an RQ element (parameters shown in Table 4.6) had to be used in order to fit the deconvoluted impedance data obtained for all three Ag/YSZ symmetrical cells. Gerischer impedance arises when a chemical reaction is coupled with a diffusion step [23]. According to Boukamp and Bouwmeester [23], a slow dissociative adsorption step or a distributed charge transfer step coupled with surface diffusion would result in Gerischer impedance [23].

The peak frequencies for these spectra lie between 125-500 Hz, values which are noticeably lower than the kHz peak frequencies observed for solution-deposited LSM with silver paste current collectors.

Sarikaya et al. [24] characterized a Ag/YSZ symmetrical cell prepared using a Ag paste (by mixing Ag powder with alpha-terpineol) and they reported 1.85 Ohmcm² as the measured R_p value at 800 ⁰C. Furthermore, they have used an equivalent circuit consist of a resistor and a finite length Warburg element to fit their data.

The impedance data obtained for the Pt/YSZ symmetrical cell was very different from the Ag/YSZ cells since the data fitting was achieved using a LR (RQ)² equivalent circuit and the peak frequency lies around 3 kHz.

Table 4.6: Normalized fitting parameters for Ag/YSZ and Pt/YSZ symmetrical cells at 800 °C.

Symmetrical Cells		Ag (thick) /YSZ	Ag(thin) /YSZ	Ag(powder) /YSZ	Pt/YSZ	
Element	Parameter	Value	Value	Value	Value	Units
Series R	R1	0.72	0.83	0.90	1.17	Ohmcm ²
Inductance	L	3.26E-07	4.18E-07	4.20E-07	4.32E-07	Hcm ²
Ge	R	0.84	0.50	1.43	-	Ohmcm ²
RQ1	R2	0.11	0.08	0.73	14.23	Ohmcm ²
RQ2	R3	-	-	-	0.61	Ohmcm ²
RQ1	n1	-	-	-	0.854	
RQ2	n2	0.684	0.727	0.730	0.569	
RQ1	f1	-	-	-	2325	Hz
RQ2	f2	764	1666	1532	156	Hz
Ge	f	150	155	471	-	Hz
Ge	T	5.72E-04	7.15E-04	1.77E-04	-	Ohmcm ²
Ge	U	0.934	0.931	0.890	-	
Ge	P	0.514	0.595	0.717	-	
RQ1	Q1	-	-	-	1.95E-05	
RQ2	Q2	2.73E-02	1.47E-02	1.69E-03	3.23E-02	
Total Polarization R	R _p	0.48	0.29	1.08	7.43	Ohmcm ²
Activation Energy for ORR	E _a	0.9 (+/- 0.0)	0.9 (+/- 0.0)	1.0 (+/- 0.0)	1.9 (+/- 0.1)	eV

The higher R_s value obtained for Pt/YSZ symmetrical cell suggests that the Pt did not sinter well onto the YSZ substrate (as we have reported before in Chapter 02). Also, Pt cathode shows a higher R_p value as well as a higher E_a value for oxygen reduction reaction. The lowest R_p value was obtained for the thin Ag cathode prepared using the diluted Ag paste and all the Ag cathodes resulted in an activation energy ~ 0.9 - 1.0 eV for the oxygen reduction reaction. However, Vladikova et al. [25] have reported the activation energy for the oxygen reduction reaction above 450 °C as 1.4 eV for Ag cathodes.

Experimental:

In order to further investigate this phenomenon, the following cells were prepared and characterized using impedance spectroscopy.

- (v) Pt/organic LSM/YSZ symmetrical cell: Organic LSM solution was deposited on both sides of the YSZ electrolyte (~ 10 - 20 uL total volume in multiple depositions of ~ 5 uL aliquots) and dried at ~ 100 $^{\circ}\text{C}$, followed by sintering at 900 $^{\circ}\text{C}$ for 1 hour. Then, Pt paste (NETL) was painted on the LSM solution electrodes and sintered at 900 $^{\circ}\text{C}$ for 1 hour. The cell was characterized using Au wires connected to the Pt paste.
- (vi) Au/organic LSM/YSZ symmetrical cell: Organic LSM solution was deposited on both sides of the YSZ electrolyte (~ 10 - 20 uL total volume in multiple depositions of ~ 5 uL aliquots) and dried at ~ 100 $^{\circ}\text{C}$, followed by sintering at 900 $^{\circ}\text{C}$ for 1 hour. Then, Au paste (Heraeus) was painted on the LSM solution electrodes and sintered at 800 $^{\circ}\text{C}$ for 1 hour. The cell was characterized using Au wires connected to the Pt paste.

Results and Discussion:

Figure 4.17: Deconvoluted (blue) and simulated (red) data at 800 $^{\circ}\text{C}$ for (v) Pt/organic LSM/YSZ (vi) Au/organic LSM/YSZ symmetrical cells.

Table 4.7: Normalized fitting parameters for Pt/organic LSM/YSZ and Au/organic LSM/YSZ symmetrical cells at 800 °C.

Symmetrical Cells		Pt/organic LSM/YSZ	Au/organic LSM/YSZ	
Element	Parameter	Value	Value	Units
Series R	R1	0.99	0.82	Ohmcm ²
Inductance	L	4.40E-07	4.13E-07	Hcm ²
RQ1	R2	5.17	0.06	Ohmcm ²
RQ2	R3	-	1.38	Ohmcm ²
RQ1	n1	0.757	0.866	
RQ2	n2	-	0.687	
RQ1	f1	532	3912	Hz
RQ2	f2	-	98	Hz
RQ1	Q1	4.16E-04	2.47E-03	
RQ2	Q2	-	8.80E-03	
Total Polarization R	R _p	2.59	0.72	Ohmcm ²
Activation Energy for ORR	E _a	1.7 (+/- 0.0)	1.1 (+/- 0.0)	eV

The deconvolution spectra and fitting parameters used for Pt/organic LSM/YSZ and Au/organic LSM/YSZ symmetrical cells are presented in Figure 4.17 and Table 4.7. For both cells, an LR (RQ)2 equivalent circuit has to be used to obtain a reasonable fit to the data. The average activation energy for the oxygen reduction reaction on organic LSM cathode (sintered at 900 °C) with Ag current collector was 1.3 (+/- 0.1) eV. However, it was 1.1 eV with Au current collector and 1.7 eV with Pt current collector while latter being more consistent with the reported values [3] for ORR on LSM. The peak frequencies for Pt/organic LSM/YSZ and Au/organic LSM/YSZ cells lie in the ranges of 500 Hz and 100 Hz respectively while it was in the kHz range for most Ag/organic LSM/YSZ symmetrical cells. However, the deconvolution spectrum of the Au/organic LSM/YSZ cell clearly shows that there is a small peak at around ~3 kHz which corresponds to a very small resistance. Furthermore, the Pt/organic LSM/YSZ symmetrical cell showed a significantly higher R_p value compared to the other solution based LSM cathodes with Ag or Au current collectors.

This study clearly shows that the performance of the LSM solution based cathodes vary with different current collectors. Therefore, the superior performance of the LSM solution based cathodes cannot be exclusively due to LSM but maybe due to a mixed performance between the LSM and the metal current collectors.

4.3.8 “Mixed” Performance of solution based LSM cathodes with Ag current collectors

For all the Ag cathodes prepared using different methods, we achieved activation energy ~ 1 eV for the oxygen reduction reaction (Table 4.6). In Section 4.3.4, table 4.4 reports ~ 1 eV activation energy for the oxygen reduction reaction on all the aqueous LSM solution based cathodes. We have stated that this value does not agree with typical LSM cathodes. The concentration of the aqueous LSM solution is ~ 0.03 M (compared to 0.1 M of organic LSM solution) and only ~ 15 - 20 μ L of the LSM solution is used to prepare the cathode, which means the amount of LSM on these (aqueous solution based) cathodes are significantly low. Then, a Ag paste layer is applied as the current collector on top of these pre-sintered LSM cathodes. According to these observed activation energies, there is a possibility that the Ag was acting as the cathode material while LSM must have assisted its performance as another catalyst as well as an aid to resist the agglomeration and retain the porosity of the cathode.

The organic LSM solution based cathode sintered at 1200°C with Ag current collector also showed activation energy ~ 1 eV for the oxygen reduction reaction. Unlike the other solution based LSM/YSZ symmetrical cells, the impedance deconvolution spectrum for this cell showed two well defined peaks that are well apart, suggesting that there can be two different processes governing the oxygen reduction reaction (Figure 4.18).

Figure 4.18: Deconvoluted (blue) and simulated (red) data at 800 °C for Ag/organic LSM/YSZ symmetrical cell sintered at 1200 °C.

Table 4.8: Normalized fitting parameters at 800 °C for Ag/organic LSM/YSZ symmetrical cell sintered at 1200 °C.

Symmetrical Cell		Ag/Organic LSM 1200/YSZ	
Element	Parameter	Value	Units
Series R	R1	0.86	Ohmcm ²
Inductance	L	5.68E-07	Hcm ²
RQ1	R2	0.20	Ohmcm ²
RQ2	R3	1.87	Ohmcm ²
RQ1	n1	0.715	
RQ2	n2	0.790	
RQ1	f1	10495	Hz
RQ2	f2	98	Hz
RQ1	Q1	1.76E-03	
RQ2	Q2	3.36E-03	
Total Polarization R	R _p	1.03	Ohmcm ²
Activation Energy for R2	E _{a, R2}	1.2 (+/- 0.0)	eV
Activation Energy for R3	E _{a, R3}	1.0 (+/- 0.0)	eV
Activation Energy for ORR	E _a	1.0 (+/- 0.0)	eV

The fitting parameters (listed in Table 4.8) can be used to calculate the activation energies associated with different processes as 1.0 eV for the main process (which defines the total activation energy for the ORR as ~ 1.0 eV) and 1.2 eV for the process which shows a lower contribution to the overall cathode reaction. We can suggest that the RQ1 element with the 1.2 eV activation energy is associated with the LSM particles. The 1200 °C sintering temperature must have resulted in very active particles of a crystalline LSM phase (evident by high peak frequency). However, when the Ag current collector is applied, a large number of Ag particles would be directly in contact with YSZ and may take part in the cathodic reaction as the main contributor (RQ2) while LSM particles also participate in the reaction. At the same time, LSM particles would inhibit the Ag agglomeration and maintain a continuous distribution of Ag particle network to assure better cathode performance over time, as observed by the aging study (Figure 4.12).

Sholklapper et al. [26] have carried out a research to study the Ag and Ag-LSM infiltrated Scandia Stabilized Zirconia (SSZ) cathodes. They observed that the Ag-LSM infiltrated cathode performed better than the Ag infiltrated cathode. Also, their SEM images clearly showed how the nano scale LSM particles were separating the nanoscale Ag particles. Furthermore, they have identified the length of the oxygen diffusion path (in a thick Ag layer) as the limiting factor for ORR. Therefore, they infiltrated a nm thick Ag layer in order to have short oxygen diffusion paths and hence higher cathode activity.

Sarikaya et al. [24] have reported a study where they mixed Ag and LSM powders to prepare a better performing current collector. Their purpose of mixing LSM with Ag was to prevent the densification of Ag layer and to maintain sufficient porosity over time. We have reproduced their experiment in order to investigate how this Ag-LSM mixture would behave as a cathode.

Experimental:

LSM powder (LSM 20-P, $d_{50} \sim 1$ μm , Fuel Cell Materials) (0.25 mL), Ag powder (0.7-1.3 micron, Alfa Aesar) (1 mL) and ink vehicle (~ 1 g) [24] (from Dr. Sabolsky's laboratory) were "ball milled" together using the WIG-L-BUG. Then, the resulting paste was used to paint very thin electrodes on both sides of an YSZ electrolyte which was sintered at 800 °C

for 1 hr. Then, this symmetrical cell was characterized by impedance spectroscopy (at 800 °C, 750 °C and 700 °C) using Ag wires.

Results and Discussion:

Figure 4.19: Deconvoluted and simulated data for Ag-LSM/YSZ symmetrical cells at 800 °C.

Table 4.9: Normalized fitting parameters for Ag-LSM/YSZ symmetrical cell at 800 °C.

Symmetrical Cells		Ag-LSM/YSZ	
Element	Parameter	Value	Units
Series R	R1	0.75	Ohmcm ²
Inductance	L	3.21E-07	Hcm ²
RQ1	R2	1.31	Ohmcm ²
RQ2	R3	0.19	Ohmcm ²
RQ1	n1	0.693	
RQ2	n2	0.954	
RQ1	f1	7289	Hz
RQ2	f2	969	Hz
RQ1	Q1	4.50E-04	
RQ2	Q2	1.30E-03	
Total Polarization R	R _p	0.75	Ohmcm ²
Activation Energy for ORR	E _a	1.0 (+/- 0.0)	eV

Deconvoluted data and simulated data fit (Figure 4.19) for the impedance of Ag-LSM cathode was achieved using a LR(RQ)2 equivalent circuit. The peak frequency for this data lies in the kHz region as well. The activation energy value (Table 4.9) for the oxygen reduction reaction is 1.0 eV, which is as same as the activation energy for oxygen reduction reaction on pure Ag cathode prepared using Ag powder and some of the solution based LSM cathodes with Ag current collectors.

Guo et al. [22] have conducted a very interesting study where they investigated the “electrochemical contribution of Ag current collector to the oxygen reduction reaction of BSCF”. They report in their literature survey that the lowest R_p values have always been achieved when Ag current collectors were used. Also, they report that the Ag alone did not perform well as a cathode in comparison to $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). However the BSCF cathode with Ag current collectors performed significantly better than the cathode with the Au current collectors. Therefore, they suspected that Ag particles migrate into the BSCF cathode structure and enhance its performance. However, their detailed characterization using EDX did not show any signs of such migrations.

4.3.9 LSM solution/HIONIC® symmetrical cells

To study whether the electrolyte has an effect on the performance of LSM solution cathodes, an experiment was carried out using a HIONIC electrolyte (Fuel Cell Materials). This is a patent pending electrolyte that is a mixture of Scandium oxide and Zirconium oxide. The vendor claims that this electrolyte has higher conductivity and strength than YSZ [27], [28].

Experimental:

Ag/organic LSM/HIONIC symmetrical cell: Organic LSM solution was deposited on both sides of the HIONIC electrolyte (~ 10-20 uL total volume in multiple depositions of ~5 uL aliquots) and dried at ~100 °C, followed by sintering at 900 °C for 1 hour. Then, the cell was characterized using Ag paste current collectors and Ag wires.

Results and Discussion:

Figure 4.20: Deconvoluted and simulated data for Ag/ organic LSM/HIONIC symmetrical cells at 800 °C.

Table 4.10: Normalized fitting parameters for Ag/ organic LSM/HIONIC symmetrical cell at 800 °C.

Symmetrical Cells		Ag/organic LSM/HIONIC	
Element	Parameter	Value	Units
Series R	R1	0.43	Ohmcm ²
Inductance	L	4.29E-07	Hcm ²
RQ1	R2	1.02	Ohmcm ²
RQ2	R3	0.49	Ohmcm ²
RQ1	n1	0.738	
RQ2	n2	0.821	
RQ1	f1	362	Hz
RQ2	f2	2154	Hz
RQ1	Q1	3.28E-03	
RQ2	Q2	8.36E-04	
Total Polarization R	R _p	0.75	Ohmcm ²
Activation Energy for ORR	E _a	1.3 (+/- 0.0)	eV

As shown in Figure 4.20 and Table 4.10, impedance data obtained for the Ag/ organic LSM/HIONIC symmetrical cell was fitted using a LR(RQ)2 equivalent circuit. As claimed by the manufacturer, this electrolyte is more conductive than the YSZ electrolyte since it produced a R_s value of 0.43 Ohmcm² at 800 °C, compared to ~0.7- 0.8 Ohm cm² for YSZ.

Other than that, the R_p values, peak frequencies and activation energy value for the oxygen reduction reaction are comparable to the other Ag/ organic LSM/YSZ symmetrical cells sintered at 900⁰C, which means that the performance of the solution based LSM cathodes are independent of the electrolyte.

4.3.10 Ag/organic LSM/YSZ symmetrical cells with different oxygen partial pressures

The original objective of this study was to investigate the performance of solution based LSM cathodes in different oxygen partial pressures in order to propose an oxygen reduction mechanism on solution based LSM cathodes. However, since it is apparent that the Ag current collector participates in the oxygen reduction reaction of the LSM solution cathode, these results are presented as a preliminary study of Ag-LSM “composite” cathodes that needs to be investigated further.

Experimental:

Organic LSM solution was deposited on both sides of the YSZ electrolyte (~10-20 uL total volume in multiple depositions of ~5 uL aliquots) and dried at ~100 ⁰C, followed by sintering at 900 ⁰C for 1 hour. Then, Ag paste was painted on the LSM solution electrodes and sintered at 800 ⁰C for 1 hour. The cell was mounted using Au wires in the Electrochemical Conductivity Relaxation (ECR) apparatus at NETL and the impedance data were collected as a function of oxygen partial pressures (pO_2) (from 0.2 atm to 0.002 atm (down) and from 0.002 atm to 0.2 atm (up)) at both 750 ⁰C and 800 ⁰C. N₂ was used to control the required oxygen partial pressures.

Results and Discussion:

An equivalent circuit consists of two RQ elements were needed to fit the impedance data. The polarization resistances increased with the decreasing pO_2 levels (Figure 4.21). This trend is consistent with pure LSM cathode studies in the literature [30] and the dependence of the polarization resistance on pO_2 level is often used as a parameter in the discussion of oxygen reduction kinetics. Given a mechanism, one can derive the predicted exponent and the measured value allows elimination of possible mechanisms.

The $\log R_p$ vs $\log p_{O_2}$ plot (Figure 4.21) yielded an average slope ~ -0.3 to -0.4 . Given the changes in slope in the plot for decreasing and increasing p_{O_2} , the average slope has a large uncertainty and it is difficult to compare this value to slopes predicted by mechanisms. The activation energy value calculated using resistance values measured at 800°C and 750°C (for $0.2\text{ atm } p_{O_2}$) is $1.8 \pm 0.3\text{ eV}$. Siebert et al. [30] have reported a 1.8 eV activation energy and a slope ~ -0.5 for their study on pin-shaped LSM cathodes with different oxygen partial pressures. Van Herle et al.'s [31] study on porous LSM cathodes report a slope of -0.53 and an activation energy of 2.11 eV for a p_{O_2} range of $10^{-4}\text{ atm} - 1\text{ atm}$ at $700^\circ\text{C} - 900^\circ\text{C}$. Also, Co and Birss [32] report a slope of -0.5 for porous LSM-YSZ cathodes ($p_{O_2} = 0.01 - 1\text{ atm}$, $T = 600^\circ\text{C}$) and a slope of ~ 1 for dense LSM cathodes ($p_{O_2} = 0.03 - 1\text{ atm}$, $T = 800^\circ\text{C}$). Murray et al. [33] reports a slope of -0.16 and an activation energy of 1.6 eV ($p_{O_2} = 10^{-3} - 1\text{ atm}$, $T = 550^\circ\text{C} - 850^\circ\text{C}$) for pure LSM cathodes, and a slope of -0.29 and an activation energy of 1.49 eV for LSM-YSZ composite cathodes. Furthermore, they state that the high activation energy and weak p_{O_2} dependence can be attributed to dissociative oxygen adsorption rate limiting steps [33]. Ostergard and Mogensen [34] also report a slope of ~ -0.3 for their p_{O_2} studies of LSM and the value is attributed to dissociative adsorption of oxygen.

Figure 4.21: Relationship between the oxygen partial pressure and the polarization resistance of a Ag/ organic LSM/YSZ symmetrical cell. Polarization resistances recorded from 0.2 atm to 0.002 atm (down) and from 0.002 atm to 0.2 atm (up) at 750°C and 800°C are shown.

The impedance spectra evolved from a symmetrical arc at high p_{O_2} to a distinctly asymmetrical arc at low p_{O_2} . All impedance data were fitted using a 2RQ equivalent

circuit. The changes in the resistances for the two RQ elements with respect to $\log pO_2$ were not consistent. This result may have been caused by the difficulty in separating the two arcs consistently using the nonlinear regression fitting when they overlap extensively. Consequently, the two arcs cannot be assigned to two processes in each electrode or to different behavior of each of the two electrodes.

4.4 Deconvolution study of LSM infiltrated YSZ cathodes

The performance of LSM infiltrated YSZ cathodes (with LSM current collectors) are extensively discussed in Chapter 03 of this dissertation. In this section, the deconvolution analysis of impedance spectra for those cathodes (mentioned in Chapter 03) and the results obtained for LSM infiltrated “improved” YSZ cathodes will be studied in detail.

Kungas et al. [35] have stated that the structural modifications either in infiltrated nanoparticles or the scaffold can result in a better performing SOFC cathode. Since the essentially 2-D LSM solution based cathodes resulted in comparatively low polarization resistances, one approach was to use a conventional YSZ powder scaffold that is relatively thin. The other approach was to create a YSZ scaffold by Hydrofluoric acid etching (HF etching) [35] of the commercially bought YSZ electrolyte.

Experimental:

The two LSM infiltrated YSZ scaffolds were prepared as follows:

- (i) Sample 1: YSZ powder (YSZ8-TC, surface area: $144 \text{ m}^2/\text{g}$), ink vehicle (from Dr. Sabolsky's group) and graphite powder (~ 325 mesh, Alfa Aesar) were mixed together (3:4:1 by weight) and “ball-milled” in a WIG-LBUG. Then, this paste was used to paint very thin YSZ scaffolds ($\sim 10 \text{ }\mu\text{m}$ after sintering) on both sides of a YSZ electrolyte and sintered at 1550°C for 2 hours. Then, the scaffolds were infiltrated with organic LSM solution ($\sim 20 \text{ }\mu\text{L}$, 10 infiltration steps) (while firing at 450°C after each infiltration of $2 \text{ }\mu\text{L}$), followed by final sintering at 800°C for 1 hour. The cell was characterized using Ag wires and Ag current collectors.

- (ii) Sample 2: An area on the YSZ electrolyte (defined by varnish) was covered with concentrated HF acid and was etched at room temperature for ~3 hours. After washing, the HF etching was repeated on the other side. The surface was lightly brushed and sonicated in water to remove all the etched particles from the surface. The HF covered areas were visibly roughened and not shiny compared to the varnish covered area. Then, varnish was applied again on the YSZ electrolyte to define the HF etched area and organic LSM solution (~ 10 uL) was deposited on both sides and fired at 900 °C for 1 hour in order to prepare organic LSM/HF etched YSZ symmetrical cells. The cell was characterized using Ag wires and Ag current collectors.

Results and Discussion:

The initiative to optimize these cathodes by improving the YSZ scaffold structure is a result of the deconvolution studies of the impedance data collected for LSM infiltrated YSZ scaffolds (with LSM current collectors) discussed in Chapter 03 (Figure 4.22).

Figure 4.22: Deconvoluted and simulated data for LSM infiltrated YSZ nanofiber scaffold (a) and powder scaffold (b) with LSM current collectors at 400 °C

Based on the deconvolution spectra shown in Figure 4.22, we used a double fractal Gerischer element in order to fit these data (parameters shown in Table 4.11). In general, Gerischer type impedance shapes tend to be present in relatively thick composite electrode structures. The cause for the Gerischer shape is believed to be the electrolyte resistance in the composite electrode structure [36]. The composite structure is analogous to that of a

porous metal electrode in contact with a fluid electrolyte. The electrochemical reaction occurs along the walls of the pore. De Levie assumed that the pores were uniform cylinders and showed that the observed impedance was mathematically the same as a Gerischer impedance [37].

Table 4.11: Normalized fitting parameters for LSM infiltrated YSZ scaffolds with LSM current collectors at 800 °C.

Symmetrical Cells		LSM/LSM infiltrated YSZ nanofiber scaffold /YSZ	LSM/LSM infiltrated YSZ powder scaffold /YSZ	
Element	Parameter	Value	Value	Units
Series R	R ₁	1.10	0.95	Ohmcm ²
Inductance	L	4.20E-07	4.91E-07	Hcm ²
Ge	R	0.21	0.30	Ohmcm ²
Ge	f	113	51	Hz
Ge	T	1.54E-03	2.23E-03	Ohmcm ²
Ge	U	0.760	0.848	
Ge	P	0.384	0.584	
Total Polarization R	R _p	0.21	0.30	Ohmcm ²
Activation Energy for ORR	E _a	1.3 (+/- 0.0)	1.5 (+/- 0.1)	eV

However, there are reports[38], [39] in which the authors demonstrated the use of a simple LR(RQ) equivalent circuit to fit the impedance data collected for LSM infiltrated YSZ cathodes.

Figure 4.23: Deconvoluted and simulated data for LSM infiltrated improved YSZ scaffolds (types i and ii) with Ag current collectors at 800 °C.

The impedance data collected for both LSM infiltrated improved YSZ scaffolds (Figure 4.23 and Table 4.12) were fitted using a LR(RQ)2 equivalent circuit. As noted by Jensen et al. [36], thin composite electrodes do not exhibit marked Gerischer impedance. However, the thin YSZ scaffold yielded a slightly asymmetrical arc which could be fitted with a double fractal Gerischer impedance.

Table 4.12: Normalized fitting parameters for LSM infiltrated improved YSZ scaffolds with Ag current collectors at 800 °C.

Symmetrical Cells		Sample (i)	Sample (ii)	
Element	Parameter	Value	Value	Units
Series R	R1	0.57	1.05	Ohmcm ²
Inductance	L	2.73E-07	1.03E-06	Hcm ²
RQ1	R2	0.50	1.26	Ohmcm ²
RQ2	R3	1.93	0.12	Ohmcm ²
RQ1	n1	0.812	0.827	
RQ2	n2	0.702	0.910	
RQ1	f1	298	1158	Hz
RQ2	f2	945	5688	Hz
RQ1	Q1	4.38E-03	4.92E-04	
RQ2	Q2	4.64E-03	5.87E-04	
Total Polarization R	R _p	0.49	0.71	Ohmcm ²
Activation Energy for ORR	E _a	1.3 (+/- 0.3)	1.5 (+/- 0.1)	eV

The activation energy values for oxygen reduction reaction and the R_p values calculated for these cathodes are comparable to the values reported in Chapter 03 for the LSM infiltrated YSZ cathodes. However, the R_s value reported for sample (ii) is higher than the typical R_s value at 800 °C for YSZ (~0.7 Ohmcm²) which may be due to poor sintering of the Ag current collector on HF etched YSZ surface. This result is surprising since the HF etching should have removed impurities likely to inhibit sintering. This attempt to recreate the infiltration methods reported in the literature [31] did not produce

a cathode with markedly superior performance (smaller polarization resistance) than the 2-D cathodes formed from solution based LSM cathodes with silver current collector. Kungas et al. [35] have reported a R_p value $\sim 0.5 \text{ Ohm cm}^2$ at 700°C for their LSM infiltrated HF etched YSZ scaffolds. Our HF etched YSZ surfaces showed a roughness to the naked eye. However, we were not able to get high quality SEM images of the HF etched surface (as Kungas et al. [35] have reported) to assure that the HF etching produced a well porous cathode, due to instrument limitations.

4.5 Summary

Results for the sintering study of LSM paste cathodes showed 1200°C as the optimum sintering temperature. Deconvolution of impedance data collected for LSM paste cathodes needed several RQ elements to fit the data. The performances of the LSM paste cathodes were almost same with different current collectors.

Solution based LSM cathodes showed very different results compared to the LSM paste cathodes. They yielded very low R_p values, higher peak frequencies and deconvolution spectra that can be fitted using one or two RQ elements. However, the performance of these solution based cathodes varies with different current collectors, which suggests that the current collector participates in the electrochemical reaction of solution based LSM cathodes. Using the activation energy as an indicator for the dominant electrode material, some of the cells appeared to be controlled by the metal and some by the LSM. In the former case, the impedance behavior of the metal electrode is synergistically improved by the presence of the LSM particles, possibly through inhibition of agglomeration of the metal particles. The solution based LSM cathodes with Ag current collectors (especially the solution based cathode sintered at 1200°C) exhibit less aging than LSM powder based cathodes over a five day experiment.

LSM infiltrated improved YSZ scaffolds with Ag current collectors yielded deconvolution spectra that did not show the presence of marked Gerischer impedance. However, the performance of these cathodes was not substantially superior to the results reported in Chapter 03.

4.6 Conclusion

LSM cathodes are typically developed using pastes prepared from commercial LSM powders that have undergone high temperature sintering steps during the synthesis processes. However, there are no reported attempts to develop LSM cathodes by evaporating a LSM precursor solution on the electrolyte (YSZ) followed by firing at a much lower sintering temperature. In this study, we have prepared solution based LSM cathodes using two different LSM precursor solutions. However, the performance of the solution based LSM cathodes cannot be directly compared with the LSM paste cathodes since their performance is directly dependent on the current collector. At this stage, it is not possible to propose a mechanism for the oxygen reduction reaction on LSM solution based cathodes with Ag current collector since we cannot differentiate whether the LSM or Ag or both LSM and Ag perform as the cathode material. Nevertheless, it would be possible to further improve this Ag-LSM “composite” to be used as a cathode in intermediate temperature solid oxide fuel cells (IT-SOFCs) due to its low polarization and activation energy values, stability over time and the simple method of preparation. Most importantly, since the peak frequencies for impedance data of LSM solution based cathode and LSM paste cathode (with the Ag current collector) are around two orders of magnitude apart, this disparity in frequency provides an opportunity to study the behavior of each electrode separately, without overlapping impedance elements. However, if only the properties of solution based LSM cathodes are needed to be studied further, multiple deposition and sintering steps must be followed in order to develop a relatively thicker electrode which would eliminate the participation of the current collector in oxygen reduction reaction of the solution based LSM cathode.

For the first time, we have carried out deconvolution studies of the impedance data collected for LSM infiltrated YSZ nanofiber cathodes and have shown that in both LSM infiltrated YSZ scaffolds (nanofiber and powder) possibly the same oxygen reduction reaction mechanism takes place.

4.7 References

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Chapter 05

LSM/YSZ Hybrid Cells

5.1 Introduction

One of the major limitations in SOFC characterization studies using impedance spectroscopy is the difficulty to separate processes related to anode and cathode due to their overlapping peak frequencies [1]. As we have discussed in Chapter 04, impedance spectra for powder based LSM cathodes result in peak frequencies in the 1-10 Hz range while the impedance spectra for solution based LSM cathodes (sintered at 800⁰C or 900⁰C) with Ag current collectors result in peak frequencies about 2 to 3 orders of magnitudes higher. We took advantage of this property to prepare “LSM/YSZ hybrid cells” in order to isolate and study the powder based LSM cathode and the solution based LSM cathode separately with minimal effects from each other. Figure 5.1 shows an example of a Cole-Cole plot and a –Z'' (negative out of phase impedance) vs log frequency plot with equivalent circuit fitting (2 RQ elements) of impedance data collected for a LSM/YSZ hybrid cell at 800⁰C.

Figure 5.1: Cole-Cole plot (a) and Negative out of phase impedance vs log frequency plot with equivalent circuit fitting (b) for a LSM/YSZ hybrid cell with Ag current collectors at 800⁰C.

As discussed in detail in Chapter 04, it is known that the Ag current collector is involved in the oxygen reduction reaction of solution based LSM cathodes, which might result in a complex oxygen reduction reaction mechanism that cannot be explained at this stage. However, since the current collector did not show any effect on powder based LSM

cathodes, this study would be more beneficial in terms of investigating the oxygen reduction process on a single LSM powder based cathode.

The oxygen reduction reaction mechanism on LSM/YSZ systems has been extensively studied using model cathodes. Since LSM is primarily an electron conductor, one can expect the surface path to be predominant for the oxygen reduction reaction. However, previous work have suggested that both the surface and bulk path simultaneously reduce oxygen on LSM cathodes. Depending on the cathode microstructure (thickness, area, porosity, particle size) and conditions applied (pO_2 , temperature, polarization) either the surface path or the bulk path (Figure 5.2 [4]) would be predominant [2] - [5]. Since most of these studies have been carried out on dense LSM electrodes, the effects of gas diffusion on oxygen reduction mechanism of porous LSM cathodes are overlooked most of the time [4]. Most of the time, porous cathodes are not convenient for comparison studies due to the complexity of microstructure (variations in TPB length, pore size, particle size, surface area etc.) [6] which in turn might result in different rate determining steps. Nevertheless, previous work [6], [7] have reported that the porous LSM cathodes predominantly reduce oxygen via the surface path under cathodic polarization conditions. Siebert et al. [8] had shown that the surface oxygen reduction pathway is favored for LSM cathodes under low anodic or cathodic polarization conditions while Adler's review [3] mentions that the porous LSM cathodes reduce oxygen via the surface pathway near the open circuit voltage (OCV). Brichzin et al. [5] and Fleig et al.'s [9] studies on thin film dense LSM microelectrodes suggest that the bulk path is favored under cathodic polarization conditions while the surface path is favored under anodic polarization conditions for the oxygen reduction reaction due to the changes in oxide ion vacancies of LSM.

In the same way, various elementary steps have been proposed as the rate determining step(s) of the oxygen reduction reaction on LSM. Gas phase oxygen diffusion, surface diffusion of adsorbed oxygen and oxygen incorporation to YSZ at TPB are some of them [5] – [7], [9].

Figure 5.2: Surface and bulk paths for oxygen reduction reaction on a porous cathode [4].

5.2 Experimental

As mentioned in Section 4.2, a powder based LSM cathode was painted on one side of the YSZ electrolyte (tape was used to define the area and the thickness) and sintered at 1200 °C for 1 hour. On the other side of the electrolyte, a solution (organic) based LSM cathode was prepared (as mentioned in Section 4.3) and sintered at 900 °C for 1 hour to prepare the LSM/YSZ “hybrid” cell. Two different hybrid cells (cell A and cell B) were prepared using the same procedure. Then, these cells were electrochemically characterized using Ag current collectors and Ag wires. In order to increase the porosity of the Ag current collector, a very thin layer of the diluted commercial silver paste was used.

Both Cell A and Cell B were first characterized at 800 °C, 750 °C and 700 °C at the open circuit voltage (OCV) using impedance spectroscopy. Then, the cells were brought back to 800 °C and characterized at OCV. After that, Cell A was characterized under applied DC voltages and Cell B was characterized under applied DC currents. The LEVM/LEVW program was used to fit the collected impedance data to equivalent circuits.

5.2.1 Temperature Study

Experimental

As mentioned above, LSM/YSZ hybrid cells were prepared and both Cells A and B were electrochemically characterized at 800 °C, 750 °C and 700 °C at the OCV. For the

temperature study of both cells, impedance analysis was carried out by applying an AC voltage and recording the AC current. Then, the impedance data were fitted using a simple LR (RQ)(RQ) equivalent circuit.

Results and Discussion

As shown in Figure 5.1, the RQ1 equivalent circuit element is assigned to the powder based LSM cathode and the RQ2 element is assigned to the solution based LSM cathode. As shown in Table 5.1, R2, Q1 and n1 are the parameters associated with the powder based LSM cathode while R3, Q2 and n2 are the parameters associated with the solution based LSM cathode. R1 is the series resistance of the cell.

Table 5.1: Summary of results obtained for the temperature study of LSM/YSZ hybrid cells.

	Temperature (°C)	R1 (Ohmcm ²)	R2 (Ohmcm ²)	Q1	n1	R3 (Ohmcm ²)	Q2	n2
Cell A	800	0.73	5.95	3.38E-02	0.831	0.68	2.29E-03	0.726
	750	1.05	13.00	3.14E-02	0.823	1.45	1.43E-03	0.751
	700	1.62	26.96	2.91E-02	0.818	2.65	1.03E-03	0.762
	Activation Energy (eV)	0.7 (+/-0.0)	1.4 (+/-0.1)			1.2 (+/-0.1)		
Cell B	800	0.69	6.39	1.01E-02	0.727	0.98	5.94E-04	0.826
	750	0.91	15.90	1.01E-02	0.717	2.90	6.20E-04	0.792
	700	1.35	37.63	9.41E-03	0.716	6.68	5.77E-04	0.774
	Activation Energy (eV)	0.6 (+/-0.0)	1.6 (+/-0.1)			1.7 (+/-0.2)		

The activation energy values associated with R2 range from 1.4 (+/-0.1) to 1.6 (+/-0.1) for Cells A and B, which agree with the activation energy for the oxygen reduction reaction on a typical LSM cathode [1]. As shown in Table 4.3, the organic solution based LSM cathode sintered at 900 °C usually shows activation energy around 1.30 (+/-0.14) for the oxygen reduction reaction (Table 4.3), which agrees with Cell A's E_a calculated for R3. But, for Cell B this value is relatively high. “Q” is the constant phase element (CPE) and “n” is the

exponent associated with “Q”. Capacitance (C) can be calculated using equation 5.1 [10] and it provides information about the degree of involvement of a material’s surface, interfaces and bulk in the oxygen reduction reaction reaction [3]. According to the results shown in Table 5.1, both Q1 and n1 show a slight variation with the temperature.

$$C = (R^{1-n}Q)^{1/n} \quad (5.1)$$

5.2.2 LSM/YSZ Hybrid Cell Characterization under Polarization

Experimental

Following the temperature study (Section 5.2.1), one LSM/YSZ hybrid cell (Cell A) was characterized under applied DC voltages and the other LSM/YSZ hybrid cell (Cell B) was characterized under applied DC currents using the experimental protocol shown below in Table 5.2. Two impedance spectra were recorded one after the other at each condition to check the drifting of the data with time and for noise cancellation through data averaging. However, since noise did not significantly affect the collected data in this system, the second impedance spectrum collected at each condition was used for the analysis. The powder based LSM cathode was used as the working electrode. Collected data was fitted into a LR(RQ)2 equivalent circuit using LEVM/LEVMW software and the resistances associated with each LSM cathode was calculated at each condition.

Table 5.2: Experimental protocol used for impedance analysis of LSM/YSZ hybrid cells under applied DC voltages (Cell A) and DC currents (Cell B).

	Cell A	Cell B
1)	800 deg EIS OCV2	800 deg EIS OCV2
2)	Potentiostatic 20 min, 0.01 V	Galvanostatic 5s, 0.00 mA
3)	800 deg EIS 0.01 V	800 deg EIS 0.00 mA
4)	Potentiostatic 20 min, 0.02 V	Galvanostatic 15 min, 0.25 mA
5)	800 deg EIS 0.02 V	800 deg EIS 0.25 mA
6)	Potentiostatic 15 min, 0.03 V	Galvanostatic 15 min, 0.45 mA
7)	800 deg EIS 0.03 V	800 deg EIS 0.45 mA
8)	Potentiostatic 15 min, 0.04 V	Galvanostatic 15 min, 0.60 mA
9)	800 deg EIS 0.04 V	800 deg EIS 0.60 mA
10)	Potentiostatic 15 min, 0.05 V	Galvanostatic 15 min, 0.80 mA
11)	800 deg EIS 0.05 V	800 deg EIS 0.80 mA

12)	800 deg EIS OCV3	800 deg EIS OCV3
13)	Potentiostatic 15 min, 0.06 V	Galvanostatic 15 min, 1.0 mA
14)	800 deg EIS 0.06 V	800 deg EIS 1.0 mA
15)	Potentiostatic 15 min, 0.07 V	Galvanostatic 15 min, 1.2 mA
16)	800 deg EIS 0.07 V	800 deg EIS 1.2 mA
17)	800 deg EIS OCV4	Galvanostatic 15 min, 1.5 mA
18)	Potentiostatic 15 min, -0.01 V	800 deg EIS 1.5 mA
19)	800 deg EIS -0.01 V	Galvanostatic 15 min, 1.8 mA
20)	Potentiostatic 15 min, -0.02 V	800 deg EIS 1.8 mA
21)	800 deg EIS -0.02 V	Galvanostatic 15 min, 2.1 mA
22)	Potentiostatic 15 min, -0.03 V	800 deg EIS 2.1 mA
23)	800 deg EIS -0.03 V	Galvanostatic 15 min, 2.5 mA
24)	Potentiostatic 15 min, -0.04 V	800 deg EIS 2.5 mA
25)	800 deg EIS -0.04 V	800 deg EIS OCV4
26)	800 deg EIS OCV5	Galvanostatic 15 min, -0.25 mA
27)	Potentiostatic 15 min, -0.05 V	800 deg EIS -0.25 mA
28)	800 deg EIS -0.05 V	Galvanostatic 15 min, -0.5 mA
29)	Potentiostatic 15 min, -0.06 V	800 deg EIS -0.5 mA
30)	800 deg EIS -0.06 V	Galvanostatic 15 min, -0.75 mA
31)	Potentiostatic 15 min, -0.07 V	800 deg EIS -0.75 mA
32)	800 deg EIS -0.07 V	Galvanostatic 15 min, -1.0 mA
33)	Potentiostatic 15 min, -0.08 V	800 deg EIS -1.0 mA
34)	800 deg EIS -0.08 V	Galvanostatic 15 min, -1.3 mA
35)	Potentiostatic 15 min, -0.09 V	800 deg EIS -1.3 mA
36)	800 deg EIS -0.09 V	800 deg EIS OCV5
37)	800 deg EIS OCV6	Galvanostatic 15 min, -1.6 mA
38)		800 deg EIS -1.6 mA
39)		Galvanostatic 15 min, -2.0 mA
40)		800 deg EIS -2.0 mA
41)		Galvanostatic 15 min, -2.5 mA
42)		800 deg EIS -2.5 mA
43)		Galvanostatic 15 min, -3.0mA
44)		800 deg EIS -3.0 mA
45)		Galvanostatic 15 min, -3.6 mA
46)		800 deg EIS -3.6 mA
47)		800 deg EIS OCV6

Results and Discussion – Anodic Polarization

When a positive DC voltage/current is applied to the hybrid cell, the powder based LSM electrode which is used as the working electrode acts as the anode ($2\text{O}^{2-} \rightarrow \text{O}_{2(g)} + 4\text{e}^-$) while the solution based LSM electrode acts as the cathode ($\text{O}_{2(g)} + 4\text{e}^- \rightarrow 2\text{O}^{2-}$). When a negative DC voltage/current is applied to the hybrid cell, the reverse reactions take place

making the powder based LSM electrode the cathode ($\text{O}_{2(g)} + 4\text{e}^- \rightarrow 2\text{O}^{2-}$) and the solution based LSM electrode the anode ($2\text{O}^{2-} \rightarrow \text{O}_{2(g)} + 4\text{e}^-$).

The impedance data collected for the anodically polarized hybrid cells initially (at low positive voltages/currents) agreed with the LR(RQ)2 equivalent circuit. However, with increasing anodic polarization, there appeared to be another low frequency arc (for both Cells A and B) which was included in the equivalent circuit as a parallel RC element (Figure 5.3). The appearance of this low frequency arc limited the deconvolution of impedance data at higher anodic polarization conditions and also limited the ability to deduce an accurate total resistance (R_t) value which would be consistent with the R_t value calculated from the potentiostatic/galvanostatic experiment (Figure 5.5 (b) and (h)).

Figure 5.3: Cole-Cole plot (a) and Negative out of phase impedance vs log frequency plot with equivalent circuit fitting (b) for a LSM/YSZ hybrid cell under 70 mV applied current at 800 °C. The solid lines in (b) show the contributions of the three elements (RQ1, RQ2 & RC) in the equivalent circuit.

In order to investigate the origin of this low frequency arc, the polarization experiment was repeated with a powder based LSM/YSZ (prepared as mentioned in Section 4.2) and a solution based LSM/YSZ (prepared as mentioned in Section 4.3) symmetrical cells to obtain the results shown in Figure 5.4.

From the observations in Figure 5.4, it is evident that the low frequency arc appears only on the powder based LSM cathodes at anodic polarization conditions. Hence, we can confirm that the low frequency arc observed in LSM/YSZ hybrid cells is also associated with the powder based LSM cathode but not with the solution based LSM cathode.

Figure 5.4: Negative out of phase impedance vs log frequency plots for different applied positive voltages at 800 °C for (a) powder based LSM/YSZ symmetrical cell and (b) solution based LSM/YSZ symmetrical cell.

Figure 5.5: (a) Current vs. time plots for Cell A (potentiostatic experiment). (b) Potential vs. time plots for Cell B (galvanostatic experiment).

Figure 5.5 presents the results obtained for potentiostatic (Cell A) and galvanostatic (Cell B) experiments for anodic polarization. After 15 minutes the current/voltage becomes almost constant. Total resistance for Cell A = applied voltage/ final current and the total resistance for Cell B = final voltage/ applied current.

Figure 5.6: Fitting parameters of equivalent circuit elements used for impedance data collected for Cell A ((a)-(f)) and Cell B ((g)-(l)) under anodic polarization (LSM paste electrode anode, LSM solution electrode cathode) at 800 °C. Note the sign change on the voltage axes for R3 and Q2.

Nearly constant series resistance for Cells A and B (Figure 5.6 (a) and (g)) show that delamination of electrodes or current collectors did not occur with applied anodic voltages. The total resistance (R_t) of Cell A (Figure 5.6 (b)) initially stays almost constant but gradually decreases after ~ 40 mV while the total resistance of Cell B (Figure 5.6 (h)) initially increases slightly but rapidly decreases after ~ 40 mV. Under these conditions, the R_t calculated from the impedance spectroscopy (blue diamonds) is always lower than the R_t calculated from the potentiostatic/galvanostatic experiment (Figure 5.5) (red squares), presumably due to the appearance of the low frequency arc. The added RC element used for Cells A and B equivalent circuits does not account for the discrepancy between R_t values, suggesting that this arc is not well described by the RC equivalent circuit element. The polarization resistance associated with the powder based LSM cathode (R_2) of Cell A shows a gradual decrease followed by a rapid decrease (Figure 5.6 (c)) while the R_2 of Cell B shows a slight increase followed by a rapid decrease and then a gradual decrease. Variations of the area normalized constant phase element (Q1) value associated with Cells A and B (Figures 5.6 (d) and (j)) show that it is not independent of the polarization but that the changes with applied voltage are small. Similarly, the changes in the exponent (n) are small.

Mogensen and Ostergard [11] have reported 10^{-5} Fcm^{-2} ($n=0.9$) as the Q value for the LSM-YSZ interface and 10^{-3} Fcm^{-2} ($n=0.6$) as the Q value associated with the adsorptive dissociation of oxygen on LSM. They have also reported that both the capacitances and

exponent values are independent of the applied overpotential [11]. Fleig et al. [12] have measured 10^{-3} Fcm^{-2} as the capacitance value associated with the oxygen exchange at the LSM cathode surface and 10^{-5} Fcm^{-2} ($n=0.8$) as the Q value between the LSM-YSZ interface. Chen et al. [7] reports a Q value of $5 \times 10^{-3} \text{ Fcm}^{-2}$ for surface diffusion of adsorbed oxygen species on LSM while Van Herle et al. [13] have reported a capacitance value of $2 \times 10^{-3} \text{ Fcm}^{-2}$ associated with the adsorbed oxygen layer on LSM. Furthermore, Jiang et al. [14] have attributed their observed $0.018 - 0.032 \text{ Fcm}^{-2}$ capacitance values to surface adsorption and diffusion process of oxygen. Since the value of Q1 for both Cells A and B range from 0.01 to 0.04 Fcm^{-2} (C values calculated using the equation given above range from $\sim 7 \times 10^{-3} \text{ Fcm}^{-2}$ to $\sim 7 \times 10^{-4} \text{ Fcm}^{-2}$), we can suggest that Q1 is either associated with the capacitance at the gas phase-electrode interface or the process of surface adsorption and diffusion of oxygen. Also, any mechanism would have to account for the very weak dependence of the Q and n values with respect to the applied voltage.

The activation energy associated with R2 (at OCV) range from 1.4 (+/- 0.1) eV to 1.6 (+/- 0.1) eV which is comparable to previously reported E_a values associated with surface diffusion of adsorbed oxygen (1.3 eV- 1.6 eV) [6], [7] and oxygen adsorption and surface diffusion (1.49 eV – 2.0 eV) [9], [10] processes.

When the powder based LSM cathode is under anodic bias, oxygen gas is produced from the $2\text{O}^{2-} \rightarrow \text{O}_{2(g)} + 4\text{e}^-$ reaction. Since the arc only appears under anodic current flow through the LSM paste electrode, we speculate that there is a mass transfer limitation from the points where the oxygen molecule is generated to the outer surface of the electrode. There is no low frequency arc associated with the diffusion of oxygen molecules to the reaction sites under cathodic current flow.

Researchers have reported LSM cathode deactivation (increased R_p) with anodic polarization mainly due to surface deactivation resulting from cation segregation and reduced oxide ion vacancies [16] – [18]. However, several other studies [5], [9], [18], [19] have shown that the anodic polarization results in cathode activation (decreased R_p) due to internal cracking of the cathode which results in higher TPB length (and also increased surface area for oxygen adsorption). la'O et al. [19] have observed on thin dense LSM

films that the magnitude of cathode activation is very high in comparison to the amount of TPB length increased due to electrode cracking with anodic polarization. The cracking is caused by generation of gas bubbles at the LSM/YSZ interface with high gas pressure. From the Nernst equation, one can demonstrate that an overpotential of +60 mV (at 800 °C) can generate an O₂ gas pressure ~13 times higher than the atmospheric O₂ partial pressure (0.2 atm). Furthermore, the authors suggest that the rate limiting step of their oxygen reduction reaction does not occur at the TPB but rather on the surface of the LSM cathode, which means that the rate-limiting step is the oxygen adsorption and the surface diffusion on LSM [19]. Furthermore, la'O et al.'s [19] Auger Electron Spectroscopy (AES) studies on anodic polarized LSM cathode surfaces did not provide any evidence for cation migration. Brichzin et al. [5] have reported that the surface path for oxygen reduction reaction is more favored under anodic bias conditions on dense microdot LSM films. They also observed extrusions in the LSM cathodes after large anodic polarization and reported that high currents were correlated with these extrusions, during their I-V studies. Previous studies [5], [9], [18], [19] suggest that the stress related to high local pO₂ inside the cathode (due to oxygen generation under anodic bias) results in these extrusions or cracking inside the cathode. Based on these, we hypothesize that the same “cracking” phenomenon might have occurred in our porous LSM paste electrodes (under anodic polarization) which increased the surface area for “oxygen desorption and surface diffusion” reaction which in turn decreases the polarization and total resistance as observed. Such a physical effect would cause changes in the polarization resistance at zero current (open circuit) after sufficient exposure of the LSM electrode to anodic current. As noted above, the resistance variation we observed (Figure 5.7 (a) and (b) for Cell A and B respectively) for the low frequency (gas diffusion) arc (R4) appears to be associated with this phenomenon.

Figure 5.7: Variation of resistance (R_4) associated with low frequency (gas diffusion arc) with applied voltage for Cell A (a) and Cell B (b). The values are based on an assumed RC equivalent circuit for the gas diffusion process.

According to Figure 5.7, the resistance for the oxygen gas diffusion inside the cathode appears initially due to limited porosity but stays almost constant at high anodic voltages. Given the uncertainty in the R_4 values, interpretation of the trend is subject to considerable uncertainty. The plots suggest that with relatively low voltages, there is sufficient porosity inside the cathode for oxygen gas diffusion to yield a nearly constant diffusion resistance.

Summary for the LSM paste electrode:

- The E_a associated with R_2 (at OCV) suggests that the “surface diffusion of adsorbed oxygen” or “oxygen adsorption and surface diffusion” reaction are associated with the rate limiting step.
- Values of Q_1 compare reasonably well with the capacitance values for surface adsorption and diffusion for the gas-electrode interface
- The appearance of low frequency arc is assigned to the gas phase oxygen diffusion from the reaction sites to the bulk
- Decreasing resistances (R_2 and R_t) and variations of R_4 with increasing anodic polarization may occur due to increased surface area due to the internal cracking of LSM cathode during O_2 generation.

Results and Discussion – Cathodic Polarization

Figure 5.8: (a) Current vs. time plots for Cell A (potentiostatic experiment). (b) Potential vs. time plots for Cell B (galvanostatic experiment).

Figure 5.8 presents the results obtained for potentiostatic (Cell A) and galvanostatic (Cell B) experiments with cathodic polarization. After 15 minutes the current/voltage becomes almost constant. Total resistance for Cell A= applied voltage/ final current and the total resistance for Cell B = final voltage/ applied current.

LSM cathode activation (decreased polarization resistance) upon cathodic polarization is a well-known phenomenon [17], [18], [20]. Cation desegregation which removes surface passivating phases such as SrO or La_2O_3 , generation of oxygen vacancies due to partial reduction of manganese ions and microstructural evolution are some of the reported reasons for the activation process. Each of these possible mechanisms enhances the oxygen reduction reaction and decreases the polarization resistance under cathodic bias [17], [18], [20].

Figure 5.9: Fitting parameters of equivalent circuit elements used for impedance data collected for Cell A ((a)-(f)) and Cell B ((g)-(l)) under cathodic polarization at 800 °C. Note the positive voltages for R3 and Q2 plots.

Similar to the observations for the anodic polarization conditions, the series resistances stays almost constant while R_t and R_2 show a decreasing trend with the cathodic polarization for both Cells A and B (Figure 5.9). However, the total resistance values calculated using potentiostatic/galvanostatic experiments (Figure 5.8) (red squares) are lower than the resistances calculated using impedance data (blue diamonds). The reason for this discrepancy might be due to a low frequency inductive loop that can result in a lower X-axis intercept which would yield a lower R_t value. Figure 5.10 shows the appearance of low frequency inductance (red circle) in impedance data collected using negative current (LSM paste electrode as the cathode).

Figure 5.10: Cole-Cole plot (a) and Negative out of phase impedance vs log frequency plot (b) for a LSM/YSZ hybrid cell under -3.6 mA applied current at 800 °C.

Q_1 values which range from 0.008 to 0.03 Fcm^{-2} (C values calculated using the equation mentioned before range from $\sim 2 \times 10^{-3} \text{ Fcm}^{-2}$ to $\sim 2 \times 10^{-2} \text{ Fcm}^{-2}$) show a decreasing pattern with applied negative bias for both Cells A and B. The value of Q_1 is comparable with a capacitance for the gas phase - electrode interface or of the surface adsorption and diffusion process of oxygen. Also, as previously mentioned, the activation energy calculated for R_2 (at OCV) favors a surface oxygen adsorption and diffusion process.

The low frequency arc due to gas phase oxygen diffusion impedance is not observed under cathodic conditions. For both Cells A and B, cathodic polarization experiments were carried out after they were anodically polarized which means that they may have undergone microstructural changes (if internal cracks occurred) to increase the porosity. Therefore the gas phase oxygen diffusion from the bulk to the reaction sites occur without restraint, so that this process is not prominent in the impedance spectrum.

Furthermore, as mentioned in the experimental section, two impedance spectra were recorded (one after the other) at each condition. For most of the spectra, a slight drift in the impedance data was visible at low frequencies (Figure 5.11) suggesting that slow changes occur at the powder based LSM cathode.

Figure 5.11: Cole-Cole plot (a) and Bode plots (b) and (c) showing the slight drift in impedance spectra at low frequencies for Cell A at 0.01 V, 800 °C.

As mentioned before, no attempt was made to analyze the oxygen reduction reaction on solution based LSM cathode with Ag current collector due to the expected complexity of the mechanism owing to the evidence of Ag current collector's participation in the oxygen reduction reaction. However, the trends of the parameters associated with the solution based cathode are presented with respect to applied cell voltage.

Current – Over Voltage plots

Current density is the area normalized applied current. The calculated current densities were multiplied by the respective area normalized resistances to calculate the overvoltages (η). For cell A, the impedance spectra were recorded under applied potential conditions. Therefore, the currents were calculated by dividing the applied voltages by the total resistance values (calculated from impedance data).

Figure 5.12: Current-over voltage plots for series resistance (R1), resistance for powder based LSM cathode (R2) and resistance for solution based LSM cathode (R3) of Cell A ((a), (c), (e)) and Cell B ((b), (d), (f)), respectively.

According to the current-over voltage plots in Figure 5.12, the series resistance (R1) and the resistance for solution based LSM cathode (R3) show Ohmic behavior which means these resistances are independent of the applied voltage. However, R2 does not show Ohmic behavior. The current-overvoltage plots resemble Butler-Volmer behavior. Researchers commonly use the Butler-Volmer equation (equation 5.2) when proposing a mechanism for oxygen reduction reaction and for computer simulations. However in order

to describe a reaction using Butler-Volmer equation, only the current should change with the applied voltages and all the other parameters should remain constant.

Butler-Volmer equation:

$$i = i_0(\exp((\alpha_A)f\eta) - \exp(-\alpha_Cf\eta)) \quad (5.2)$$

i = current

i_0 = exchange current

η = over potential

α_A = anodic transfer coefficient

α_C = cathodic transfer coefficient

In other words, the resistances, Q and n values measured at OCV should be constant, irrespective of the history of the cathode. However, our results (Table 5.3) show that the cathode properties were changing with the applied voltages. Hence, we cannot further analyze our data using the Butler-Volmer equation and deduce useful information.

Table 5.3: Parameters recorded for Cell A and Cell B at open circuit voltage (800 °C).

	Experiment	R2	Q1	n1	R3	Q2	n2	f1	f2	History
Cell A	OCV1	5.95	0.0338	0.831	0.68	0.00229	0.726	1.10	1170	Initial measurement
	OCV2	6.65	0.0333	0.828	0.83	0.00190	0.735	0.98	1030	After temperature study
	OCV3	7.11	0.0326	0.827	0.83	0.00162	0.740	0.93	1210	After +40 mV
	OCV4	5.77	0.0320	0.830	0.84	0.00175	0.730	1.22	1220	After +70 mV
	OCV5	6.12	0.0314	0.829	0.89	0.00163	0.733	1.17	1170	After -40 mV
	OCV6	4.81	0.0307	0.833	1.09	0.00153	0.731	1.59	1000	After -90 mV
Cell B	OCV1	6.39	0.0102	0.727	0.98	0.00059	0.826	7.00	1304	Initial measurement
	OCV2	7.78	0.0105	0.719	1.33	0.00065	0.808	5.00	979.9	After T study
	OCV3	10.7	0.0111	0.709	1.62	0.00074	0.790	3.00	803.4	After +45 mV
	OCV4	6.98	0.0102	0.713	1.67	0.00067	0.797	6.00	800	After +100 mV
	OCV5	7.49	0.0101	0.712	1.72	0.00068	0.796	6.00	774.3	After -45mV
	OCV6	5.56	0.0094	0.717	1.80	0.00066	0.800	10.0	728.7	After -90 mV

Figure 5.13: Resistance of the powder based LSM cathode as a function of the applied voltage for Cell A (a) and Cell B (b) respectively. Resistance values at open circuit voltages OCV 1 (red), OCV 2 (orange), OCV 3 (purple), OCV 4 (black), OCV 5 (blue) and OCV 6 (green) are shown in different colors.

As shown in Figure 5.13; for Cell A, R2 (paste electrode) initially increases after positive voltages (+40 mV) and then decreases (+70 mV). Q1 and n1 are approximately constant. After negative voltages, R2 initially increases (-40 mV) and then sharply decreases (-90 mV). Q1 decreases somewhat while n1 remains constant. Similarly, for Cell B, R2 (paste electrode) initially increases with positive voltages (+45 mV) and then decreases (+100 mV). Q1 and n1 are approximately constant. After negative voltages, R2 initially increases (-45 mV) and then sharply decrease (-90 mV). Q1 shows a decreasing trend and n1 remains constant. Based on previous discussion and the literature, the changes can be assigned to microstructural evolution of the LSM, or slow movement of cations towards or away from the surface. What is unique to this study is that the slow changes in polarization resistance are occurring for overpotentials less than 100 mV and current densities less than 10 mA/cm^2 . Most previous work has reported changes after large voltages or large currents.

As noted above, the slow changes in LSM properties prevent the use of the Butler Volmer equation to analyze the current-overvoltage patterns in Fig. 5.9. This observation suggests that many mathematical simulations of LSM cathodes which incorporate Butler-Volmer kinetics must be viewed with caution.

5.3 Summary

LSM/YSZ hybrid cells were prepared using powder based and solution based LSM cathodes on each side of an YSZ electrolyte. Since the peak frequencies of processes for these two cathodes are several orders-of-magnitude apart, we are able to isolate and study the powder based LSM cathode independent of the other electrode. The solution based LSM cathode with Ag current collector was used merely as a counter electrode. However, observed parameters for both electrodes are presented for usefulness of further analysis.

A low frequency arc assigned to gas phase diffusion appeared with anodic polarization but not with the cathodic polarization. Comparison of the obtained parameters with the reported data in the literature supports the occurrence of the oxygen reduction reaction via surface path. However, further experiments are needed to support this hypothesis. Also, we are not able to analyze the data using Butler-Volmer equation since measurements at OCV show that the cathode is changing with applied voltages (in mV range).

5.4 Conclusion

LSM/YSZ hybrid cells provided a straightforward method to isolate and study only the powder based LSM cathode even under applied DC voltage/current. According to our knowledge, a direct method to study the behavior of a single electrode (with minimal effects from the other cell components) at applied DC voltages/currents had not been reported before.

Based on the parameters measured for the LSM cathode, hypotheses are presented for the oxygen reduction pathway. However, further experiments are needed for verification. Comparatively high peak frequencies associated with the solution based LSM cathodes (with Ag current collector) provides an opportunity to use them as counter electrodes when studying other different cathode materials with low peak frequency impedances.

Also, we have shown that the Butler-Volmer equation cannot be used to deduce mechanisms on cathodes that have changing properties with applied voltages. Furthermore, it would be worthwhile to investigate the changes associated with the powder based LSM

cathode. After anodic polarization, the microstructure of the cathode can be analyzed to observe whether any “cracks” have occurred. Also, the cell can be kept at OCV for a longer time (as opposed to 15 minutes) to see whether any of these changes are reversible. These hybrid cell experiments can be continued with higher applied DC voltages/currents and also the experiment order can be changed (ie. Cathodic polarization followed by anodic polarization).

5.5 References

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Appendix A

Figure 1: Polarization resistances recorded over time during the aging experiment for organic LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ at (a) 700 °C and (b) 800 °C.

Figure 2: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of organic LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ.

Figure 3: Polarization resistances recorded over time during the aging experiment for aqueous LSM solution cathode (with Ag current collector) sintered at 800 °C on YSZ at (a) 700 °C and (b) 800 °C.

Figure 4: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of aqueous LSM solution cathode (with Ag current collector) sintered at 800 °C on YSZ.

Figure 5: Polarization resistances recorded over time during the aging experiment for aqueous LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ at (a) 700 °C and (b) 800 °C.

Figure 6: Polarization resistances recorded at (a) 700 °C and (b) 800 °C for aging of aqueous LSM solution cathode (with Ag current collector) sintered at 900 °C on YSZ.

**PREPARATION OF SOLID OXIDE FUEL CELL CATHODES AND
ANALYSIS BY IMPEDANCE SPECTROSCOPY**

Juwana Hennadige Lalanthi Kaushalya de Silva

**Dissertation submitted to the Eberly College of Arts and Sciences
at West Virginia University in partial fulfillment of the requirements
for the degree of**

Doctor of Philosophy in Chemistry

C. Eugene Bennett Department of Chemistry

APPROVAL OF THE EXAMINING COMMITTEE

Harry Finklea, Ph.D., Chair

Fabien Goulay, Ph.D.

Justin Legleiter, Ph.D.

Alan Stolzenberg, Ph.D.

11/14/2014

Date

Nianqiang Wu, Ph.D.