

ABSTRACT

Title of Dissertation: THE ROLES OF MATERIAL, SURFACE, & MICROSTRUCTURAL EFFECTS IN DEVELOPING CERAMICS FOR ENERGY APPLICATIONS

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Ceramics have a wide variety of applications for energy conversion and other industries because of their unique properties. Conduction of multiple charged species simultaneously enables their use as membranes, electrodes, and more. Perovskites especially, have highly tunable features, and can be modified through doping, surface coating, and microstructure. In this work, each of those approaches was used to improve and/or characterize ceramic components for either proton conducting membranes or solid oxide fuel cells (SOFCs). In the case of membranes, perovskites have limited electronic conductivity, which reduces their ability to permeate hydrogen. Through changing the dopants used in existing perovskite compositions, the electronic conductivity was improved dramatically allowing its use as an n-type conductor. This was achieved by using Pr as a dopant, which introduces electronic

conductivity due its multivalent nature. It also has a favorable ionic radius for proton conduction, which is required for hydrogen permeation. In the case of fuel cells, both performance and stability need to be improved for their widespread adoption. The surface chemistry and physical properties of two major cathode materials were evaluated, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC). Both are susceptible to the formation of unwanted secondary phases during operation as SOFC cathodes. By studying the surface chemistry of LSCF it was possible to better understand the mechanism of cathode degradation. In the case of LSCF, it was found that electrostatic forces that result from a chemical potential difference between the bulk and surface, promote the segregation of Sr cations from the bulk which is responsible for the degradation. However, the behavior of SSC was more difficult to determine. In SSC, cation segregation was far more dependent on the grain orientation than LSCF and therefore was more difficult to quantify, and the techniques used for improving stability in LSCF were unsuccessful when applied to SSC. Additionally thin films deposited through atomic layer deposition (ALD) were tested as a means of enhancing the performance of LSCF. Due to the challenges of using ALD on porous substrates, the role of variables in the deposition process that can be widely implemented were studied, with a focus on oxygen vacancies. It was found that the choice of oxidizer and the addition of an annealing step can dramatically improve the effectiveness of thin film electrode coatings. Although ALD may not be practical for modifying SOFC electrodes, these are process steps that can be easily implemented by other researchers to improve their existing approaches. Finally, the role of microstructure was addressed as well. Tuning the

porosity of SOFC anodes is essential for large scale fabrication of fuel cells and improving their performance and reliability. A microstructure featuring a hierarchal porosity was able to improve the performance of SOFC anodes, especially at lower temperatures and fuel ratios. Improvements in microstructure will allow the fabrication of larger scale SOFCs that are more reliable and mechanically stronger, with minimized performance losses associated with using a thicker anode. The primary scientific merit of this research is demonstrated in the work on cathode degradation and coatings. There the focus was on using a methodology based on a fundamental material property, oxygen vacancies, which are essential to many applications of metal oxides. With this type of approach, it is possible to apply similar techniques to other areas of research involving metal oxides or thin films. The main engineering merit of this research is evaluating the relationship between microstructure, SOFC performance, and large SOFC production. Commercialization of SOFCs requires that they are as effective as possible outside of ideal conditions (pure fuel, high temperatures). Hierarchal porosity has been shown to improve performance under both conditions and can also be applied to cathodes.

THE ROLES OF MATERIAL, SURFACE, & MICROSTRUCTURAL EFFECTS
IN DEVELOPING CERAMICS FOR ENERGY APPLICATIONS

by

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Dedication

This is dedicated to my friends and family.
They have always loved and believed in me,
especially when I am doubting myself.
This would not have been possible without them.

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Table of Contents

Dedication	ii
Acknowledgements	iii
Table of Contents	v
List of Tables	vii
List of Figures	viii
List of Abbreviations	xii
Chapter 1: Introduction	1
1.1 Non-Stoichiometry & Doping.....	1
1.2 Conductivity in Ceramics	2
1.3 Proton Conducting Membranes	3
1.4 Solid Oxide Fuel Cells	5
1.4.1 Operation of Solid Oxide Fuel Cells.....	5
1.4.2 Introduction to Electrolytes.....	6
1.4.3 Introduction to Cathodes.....	8
1.4.4 Introduction to Anodes	10
1.5 Quantifying Electrochemical Kinetics	11
1.5.1 Electrochemical Impedance Spectroscopy	11
1.5.2 Distribution of Relaxation Times.....	13
Chapter 2: Proton Conducting Membranes.....	14
2.1 Mixed Conductors as Membranes	14
2.2 Experimental Methods: Proton Conducting Membranes.....	15
2.2.1 Materials Synthesis	15
2.2.2 Characterization of Materials.....	16
2.2.3 Conductivity Measurements	16
2.3 Results & Discussion: Proton Conducting Membranes.....	16
2.3.1 Crystal Structure and Stability	16
2.3.3 Conductivity in Oxidizing Atmospheres	24
2.4 Conclusion: Proton Conducting Membranes	26
Chapter 3: Degradation in SOFC Cathodes	27
3.1 Introduction to Cathode Degradation.....	27
3.2 Experimental Methods: Cathode Degradation.....	29
3.2.1 Sample Preparation	29
3.2.2 Characterization Methods	30
3.3 Results & Discussion: Cathode Degradation.....	32
3.3.1 Effect of Temperature	32
3.3.2 Effect of Time	34
3.3.3 Effect of pO_2	36
3.3.4 Effect of pCO_2	41
3.3.6 Mechanisms of Cathode Degradation.....	43
3.3.7 Mitigation of Cathode Degradation	46
3.4 Degradation in Next Generation Cathodes	47
3.5 Modifying Next Generation Cathodes	51
3.6 Conclusion: Cathode Degradation	54

Chapter 4: Cathode Surface Modification	56
4.1 Overview of Atomic Layer Deposition.....	56
4.2 Sample Preparation: Cathode Surface Modification.....	59
4.2.1 Symmetric Cell Fabrication	59
4.2.2 Atomic Layer Deposition.....	60
4.2.3 Characterization Methods	60
4.3 Results & Discussion: Cathode Surface Modification.....	61
4.3.1 Effect of Different Film Compositions	61
4.3.2 Effect of Film Oxidizer.....	62
4.3.3 Effect of Film Annealing	64
4.3.4 DRT Analysis of Cathodes	66
4.3.5 Surface Chemistry of ALD coatings on dense LSCF	68
4.3.6 ALD of Full Cells	70
4.4 Conclusion: Cathode Surface Modification.....	71
Chapter 5: Anode Microstructure	72
5.1 Anode Porosity: Scale Up and Performance.....	72
5.2 Experimental Methods: Anode Microstructure	74
5.2.1 Tape Casting	74
5.2.2 Lamination & Sintering	74
5.2.3 Characterization of 25cm ² Fuel Cells	75
5.2.4 Characterization of Button Cells.....	75
5.3 Results & Discussion: Anode Microstructure.....	76
5.3.1 Anode Microstructure & Porosity.....	76
5.3.2 Scale Up of Half Cells	79
5.3.3 Performance of Button Cells.....	83
5.4 Conclusion: Anode Microstructure	88
Chapter 6: Conclusion.....	89
6.1 Summary of Results: Proton Conducting Membranes	89
6.2 Summary of Results: Cathode Degradation.....	89
6.3 Summary of Results: Cathode Surface Modification	91
6.4 Summary of Results: Anode Microstructure	91
Chapter 7: Future Work	92
7.1 Future Work: Proton Conducting Membranes.....	92
7.2 Future Work: Cathode Degradation.....	93
7.3 Future Work: Cathode Surface Modification	93
7.4 Future Work: Anode Microstructure	94
Bibliography	95

List of Tables

TABLE I. Comparison of lattice parameters before and after reduction.	18
Table II. Activation energies at varying dopant concentrations from conductivity measurements in 5% H₂ in N₂ with added moisture.....	21
Table III: List of compositions used in tape casting.....	74

List of Figures

Figure 1.1: Crystal structure of perovskite lattice. A and B denote the two cation sites, X represents the anion.....	3
Figure 1.2: Examples of applications for proton conducting membranes. (a) Proton conducting membrane for steam reforming and water gas shift reactions. (b) Membrane and catalyst system for hydrocarbon valorization.	4
Figure 1.3: Diagram of overpotential losses associated with SOFC operation.....	8
Figure 1.4: Diagram showing ORR active sites for a) Exclusively electronic conductor on GDC (basic TPB) b) MIEC and GDC interface (triple-phase and dual-phase boundary) c) Increased reaction sites with additional ionic conducting phase on MIEC.	10
Figure 1.5: Diagram showing the layers in anode-supported and electrolyte-supported SOFCs..	11
Figure 2.1: Phase and structure of Pr-doped SrCeO₃. (a) XRD spectra of each dopant level (b) The lattice parameters a, b, c, and unit cell volume V.....	17
Figure 2.2: Redox stability of Pr doped SrCeO₃. (a) XRD spectra of SrCe_{0.9}Pr_{0.1}O_{3-δ} before and after reduction in H₂ for 18 h; with insert focusing on primary peaks (b) SEM image of SrCe_{0.9}Pr_{0.1}O_{3-δ} pellet as sintered (c) SEM image of SrCe_{0.9}Pr_{0.1}O_{3-δ} pellet after testing in reducing atmosphere.....	19
Figure 2.3: Conductivity of Pr doped SrCeO₃. (a) Arrhenius plot of SrCe_{1-x}Pr_xO_{3-δ}, x = 0, 0.1, and 0.2, exposed to 5% H₂ in N₂ with 3% moisture. 5% Eu doped SrCeO₃ is shown for comparison.(b) Conductivity as a function of dopant concentration in 5% H₂ and 95% N₂ with 3% moisture at 600 °C and 800 °C as a function of dopant level.....	20
Figure 2.4: pO₂ dependence of conductivity of SrCe_{0.9}Pr_{0.1}O_{3-δ} in reducing atmospheres; a mixture of H₂ and N₂. (a) Effect of pO₂ on conductivity at different temperatures. (b) Arrhenius plot of SrCe_{0.9}Pr_{0.1}O_{3-δ} in a 10% H₂ atmosphere with and without water....	22
Figure 2.5: pO₂ dependence of SrCe_{0.9}Pr_{0.1}O_{3-δ}. In (a) High pO₂ atmosphere with moisture, and (b) High pO₂ atmosphere without moisture.	24
Figure 3.1: Overview of procedure for using Trainable WEKA segmentation in ImageJ to determine particle size distribution (a) original image (b) surface particles identified by Trainable WEKA highlighted in original image.	30
Figure 3.2: EDS of particles found to grow on LSCF after aging for 25 hours at 850°C in synthetic air.	31
Figure 3.3: Temperature effect on LSCF cation segregation. LSCF dense samples were aged for 25 hours in synthetic air at (A) 500°C, (B) 600°C, (C) 700°C, (D) 800°C, and (E) 900°C. (F) Sintered surface microstructure (G) average particle size and surface coverage as a function of temperature (H) particle size distribution at each temperature.	33
Figure 3.4: Aging time effect on LSCF cation segregation at 700°C. Dense LSCF samples were aged at 700°C for (A) 25, (B) 50, (C) 75, and (D) 100 hours in synthetic air. (E) Unaged polished sample (F) average particle size and surface coverage of SrO as a function of aging time. (G) Particle size distribution as a function of time.	35

Figure 3.5: pO ₂ effect on LSCF cation segregation. LSCF dense samples were aged at 700°C for 25 hours in (A) 1% O ₂ (B) 21% O ₂ (C) 50% O ₂ (D) 100% O ₂ (E) 100% N ₂ . (F) SrO particle size distribution with different pO ₂ 's. (G) Particle size and surface coverage of SrO as a function of log pO ₂ ..	37
Figure 3.6: XRD of polished unaged LSCF surface and aged for 25 hours in CO ₂ gas environment at 700°C.	39
Figure 3.7: Raman spectroscopy of pristine LSCF surface and aged for 25 hours at 700°C in each gas environment (a) without CO ₂ (b) with CO ₂ .	40
Figure 3.8: Environment effects on surface chemistry of LSCF. XPS of Sr 3d spectra in (A) different O ₂ environments and (B) pristine LSCF. LSCF lattice Sr peaks are shown in green and surface segregated Sr peaks are shown in blue. (C) The ratio of surface segregated Sr and Sr in LSCF lattice as a function of O ₂ . LSCF samples were aged at 700°C for 25 hours in the listed environment.	40
Figure 3.9: pCO ₂ effect on LSCF cation segregation. LSCF dense samples were aged at 700°C for 25 hours in (A) ambient air, (B) 1% CO ₂ /20% O ₂ , (C) 10% CO ₂ /20% O ₂ (D), 50% CO ₂ /20% O ₂ , (E) 80% CO ₂ /20% O ₂ and (F) 80% CO ₂ /20% N ₂ . (G) Particle size (nm) and particle quantity (#) as a function of log pCO ₂ . (H) SrO particle size distribution as different pCO ₂ 's.	42
Figure 3.10: Effects of CO ₂ on surface chemistry of LSCF. XPS of Sr 3d spectra in (A) different O ₂ environments and (B) pristine LSCF. LSCF lattice Sr peaks are shown in green and surface segregated Sr peaks are shown in blue. (C) The ratio of surface segregated Sr and Sr in LSCF lattice as a function of pCO ₂ . LSCF samples were aged at 700°C for 25 hours in the listed environment.	43
Figure 3.11: Possible driving forces and cation segregation mechanism. (A) Lattice constant and surface coverage as a function of pO ₂ . The red square shows the lattice constant of LSCF. The purple circle symbols represent SrO surface coverage of LSCF aged at 700°C in different pO ₂ 's for 25 hours. (B) Non-stoichiometry as a function of pO ₂ . The color bands represent different oxygen stoichiometry zone of LSCF at different temperatures. The region highlighted in purple is the oxygen stoichiometry of interest ($\delta = 0.03\text{--}0.06$), which are achieved at 800°C in synthetic air or at 700°C between pO ₂ = 10 ⁻¹ to 10 ⁻⁴ atm. (C) O ₂ and CO ₂ effect on nucleation. Sr diffusion is mitigated once no oxygen-containing gaseous species are present. SrO nucleation occurs once O ₂ is present, promoting the diffusion, nucleation, and eventually agglomeration. (D) O ₂ and CO ₂ effect on growth. Carbonates are formed with the presence of CO ₂ , which limit the surface migration.	45
Figure 3.12: A-site stoichiometry effect on LSCF cation segregation. A site deficient (La _{0.6} Sr _{0.4}) _{0.95} Co _{0.2} Fe _{0.8} O ₃ (LSCF095) dense samples were aged at 700°C for 25 hours in (A) 1% O ₂ , (B) 50% O ₂ , (C) 50% CO ₂ (balanced with 20% O ₂ , 30% N ₂) with (D) a higher magnification.	47
Figure 3.13: Aging time effect on SSC cation segregation at 700°C. Dense SSC samples were aged at 700°C for (A) Select SSC grain after 12 hours, (B) Select SSC grain after 25 hours, (C) SSC surface after 25, (D) 50, (E) 75 and (F) 100 hours in synthetic air....	48
Figure 3.14: pO ₂ effect on SSC cation segregation. LSCF dense samples were aged at 700°C for 25 hours in (A) 100% N ₂ (B) 1% O ₂ (C) 21% O ₂ (D) Ambient air (E) 50% O ₂ (F) 100% O ₂	49

Figure 3.15: EDS study of SSC aged in 1% O ₂ for 25 hours at 700°C (a) SEM image (b) EDS mapping (c) Elemental mapping & EDS study of SSC aged in synthetic air for 100 hours at 700°C (d) SEM image (e) EDS mapping (f) Elemental mapping.	50
Figure 3.16: Electron Backscatter Diffraction mapping of dense SSC aged for 100 hours in ambient air at 700°C.	51
Figure 3.17: XRD spectra of commercial SSC in comparison with sol-gel synthesized A-site deficient SSC. (A) Full XRD spectra (B) Magnified image of primary peak.	52
Figure 3.18: (A) EIS spectra of SSC-GDC cathodes on GDC symmetric cells at different temperatures. (B) Electrode impedance derived from EIS measurements as a function of time at 625°C for the symmetric cells in ambient air.	52
Figure 3.19: Different SSC compositions aged at 600°C in 100% N ₂ for 25 hours, seen at two magnifications. (A) SSC (B) Sm _{0.475} Sr _{0.475} CoO ₃ (C) Sm _{0.475} Sr _{0.5} CoO ₃	54
Figure 3.20: Different SSC compositions aged at 600°C in 100% O ₂ for 25 hours, seen at two magnifications. (A) SSC (B) Sm _{0.475} Sr _{0.475} CoO ₃ (C) Sm _{0.475} Sr _{0.5} CoO ₃	54
Figure 4.1: Diagram showing the 4 steps of the Atomic Layer Deposition Cycle	57
Figure 4.2: Diagram of parameters during each step of the ALD process and their impact on the properties of the deposited film.	59
Figure 4.3: Diagram showing placement of symmetric cell and full cell within the ALD chamber..	60
Figure 4.4: EIS spectra of symmetric cells with LSCF-GDC cathodes with and without ALD coatings. 25 layers of TiO ₂ was deposited at 150°C using water as oxidizer and TDMAT as precursor. 25 layers of ZnO was deposited at 150°C using water as oxidizer and DEZ as precursor. 25 layers of V ₂ O ₅ was deposited a 175°C using ozone as oxidizer and VTOP precursor.	62
Figure 4.5: EIS spectra of symmetric cells with 25 layers of TiO ₂ deposited at 150°C. One with water and one with ozone.	63
Figure 4.6: EIS spectra of symmetric cells with 16 layers of ZnO deposited at 150°C. One with water and one with ozone.	64
Figure 4.7: Symmetric cells coated with TiO ₂ with each oxidizer that have also been annealed in 100% N ₂ at 400°C for 1 hour prior to EIS measurements. (A) EIS spectra at different temperatures showing the effect of annealing. (B) ASR of each symmetric cell as a function of temperature.....	65
Figure 4.8: Symmetric cells coated with ZnO with each oxidizer that have also been annealed in 100% N ₂ at 400°C for 1 hour prior to EIS measurements. (A) EIS spectra at different temperatures showing the effect of annealing. (B) ASR of each symmetric cell as a function of temperature.....	66
Figure 4.9: DRT spectra of LSCF-GDC cathode with each TiO ₂ film at various temperatures.....	67
Figure 4.10: DRT spectra of LSCF-GDC cathode with each ZnO film at various temperatures.....	68
Figure 4.11: XPS spectra for Oxygen 1s peak of TiO ₂ coated samples of dense, polished LSCF after TiO ₂ deposition, with and without annealing.	69

Figure 4.12: XPS spectra for Oxygen 1s peak of ZnO coated samples of dense, polished LSCF after ZnO deposition, with and without annealing.	70
Figure 4.13: IV curves and EIS spectra comparison of LSCF-GDC full cells with and without 16 layers of ZnO deposited on the cathode side.	71
Figure 5.1: Photos of button cells, large scale cell, and diagram of button cell reactor.	76
Figure 5.2: (A) Low magnification images of anode microstructure with different amounts of pore former. (B) Higher magnification images of anode microstructure taken using backscatter mode.	77
Figure 5.3: Porosity of anodes with different amounts of pore former. Porosity was quantified through trainable WEKA segmentation from SEM images.	79
Figure 5.4: Sintering and curvature of large scale cells. (A) Diagram showing the placement and orientation of large-scale cells in the furnace. (B) Displacement measurements of large-scale cells in both directions. Open symbols ($\square$) denote uniform porosity anodes, triangles ($\blacktriangledown$) denote graded anodes, and diamonds ($\blacklozenge$) denote 4 layer anodes. (C) Diagram showing how displacement is defined.	82
Figure 5.5: Electrochemical measurements including IV curves and EIS spectra for full cells with identical SSC-GDC cathodes and 3 layers of ASL consisting of uniform porosity.	83
Figure 5.6: Comparison of performance between uniform and graded porosity anodes including IV curves and EIS spectra.	85
Figure 5.7: Electrode ASR as a function of porosity varied with temperature and fuel ratio. H ₂ balanced with N ₂ at (A) 600°C (B) 625°C (C) 650°C. Constant fuel ratio with varying temperature. (D) 50% H ₂ & 50% N ₂ (E) 75% H ₂ & 25% N ₂ (F) 100% H ₂	86
Figure 5.8: Electrochemical measurements including IV curves and EIS spectra for full cells with uniform porosity and varying sizes of pore former	87
Figure 5.9: IV curves of 4 layer ASL full cells. Two uniform cells of 6g and 9g standard 10 μ m pore former are shown, as well as 3/6/9/12g anode with 10 μ m, and 6/6/9/12 anode with 3 μ m PMMA in the layer closest to the electrolyte and 10 μ m for remaining layers.	88

List of Abbreviations

ALD	Atomic layer deposition
atm	atmospheres
ASR	Area-specific resistance
BBP	Benzyl butyl phthalate
BSE	Back scattered electron
BCZYYb	Barium cerium zirconium yttrium ytterbium oxide
CTE	Coefficient of thermal expansion
D95	$\text{Sm}_{0.475}\text{Sr}_{0.475}\text{CoO}_3$
DEZ	Diethyl zinc
D_M	Dopant of metal “M”
DRT	Distribution of Relaxation Times
DSm	$\text{Sm}_{0.475}\text{Sr}_{0.5}\text{CoO}_3$
DSr	$\text{Sm}_{0.5}\text{Sr}_{0.475}\text{CoO}_3$
EBS	Electron Backscatter Diffraction
EDS	Energy Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
GDC	Gadolinium doped ceria
HOR	Hydrogen oxidation reaction
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
IV	Current voltage characteristic curve
<i>J</i>	permeation
LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$
LSCF095	$(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$
LSM	Lanthanum strontium manganate
MIEC	Mixed ionic electronic conductor
MIPEC	Mixed ionic electronic protonic conductor
η	overpotential
OCV	Open circuit voltage
ORR	Oxygen Reduction Reaction
PCEC	Proton conducting electrolysis cell
PCFC	Proton conducting fuel cell
$p\text{CO}_2$	Partial pressure of CO_2
PMMA	Polymethyl methacrylate
$p\text{O}_2$	Partial pressure of O_2
ppm	Parts per million
PVB	Polyvinyl butyral
sccm	Standard cubic centimeter per minute
SEM	Scanning Electron Microscope
SOEC	Solid oxide electrolysis cell
SOFC	Solid oxide fuel cell
SSC	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$
TDMAT	Tetrakis(dimethylamido)titanium
TEM	Transmission electron microscope
TPB	Triple phase boundary
$\text{V}_\text{o}^{\bullet\bullet}$	Oxygen vacancy
VTOP	vanadium tri-isopropoxide
WEKA	Waikato Environment for Knowledge Analysis
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
YSZ	Ytria stabilized zirconia

Chapter 1: Introduction

1.1 Non-Stoichiometry & Doping

Ceramics are used in a wide variety of renewable energy and sensor applications including catalysis, energy production, chemical conversion, gas sensors, and coatings.¹⁻⁷ This is made possible by their ability to participate in surface reactions, respond to their surroundings (temperature and gas environment), and conduct charge carriers. All these abilities are the result of non-stoichiometry, meaning that many ceramics have chemical formulas that cannot be represented as a ratio of whole numbers. The ceramics discussed in this work are metal oxides and often exhibit a deficiency in oxygen when exposed to a high temperature or an oxygen deficient gas environment. These are referred to as point defects. The predominant forms of point defects are vacancies and interstitials which can be represented in Kröger-Vink notation. The materials in this work overwhelmingly feature oxygen vacancies which are denoted as $V_O^{\bullet\bullet}$. V signifies that the defect is a vacancy, O represents oxygen, and $\bullet\bullet$ represents the 2 positive charges of the defect.

There are also the charged species which are electrons (n) and holes (p). Since the material as whole must retain a neutral charge, this is balanced by the generation of charged species within the bulk of the material. This response to gas environment is the working principle behind gas sensors. Many properties of ceramics can be fine-tuned through doping which is the intentional introduction of defects. Here, one or more of the elementals are replaced with another that has a different oxidation state.

This creates a stable population of charged defects in the material and causes an insulating material to become a semi-conductor.

1.2 Conductivity in Ceramics

Ceramics are known to conduct a wide variety of charged species including electrons/holes, ions, and protons.^{8–10} The exact mechanism for each species varies but it is always related to the population of charged defects and the crystal structure of the material. In the case of electronic conductivity, compositions with multivalent dopants tend to exhibit a greater degree of electronic conductivity.^{11,12} This is attributed to the formation of polarons which enable to transport of electrons and holes between the atoms in the crystal lattice. Ions, in this case oxygen, is conducted as oxygen ions swap places with vacancies. Finally, proton migration in ceramics occurs through the Grotthus mechanism.¹⁰ Here a proton attached to an oxygen atom as a hydroxyl group is oriented and swapped between adjacent oxygen atoms in the lattice. All these mechanisms are dependent on the composition and structure of the material, which influences the mobility of the charged species.

One class of materials capable of conducting all of these species is the perovskite. The perovskite crystal structure is well studied and nearly ubiquitous in renewable energy and the semiconductor industry. Perovskites consist of 2 cations and 1 anion in a ABX_3 ratio, as seen in **Figure 1.1**.

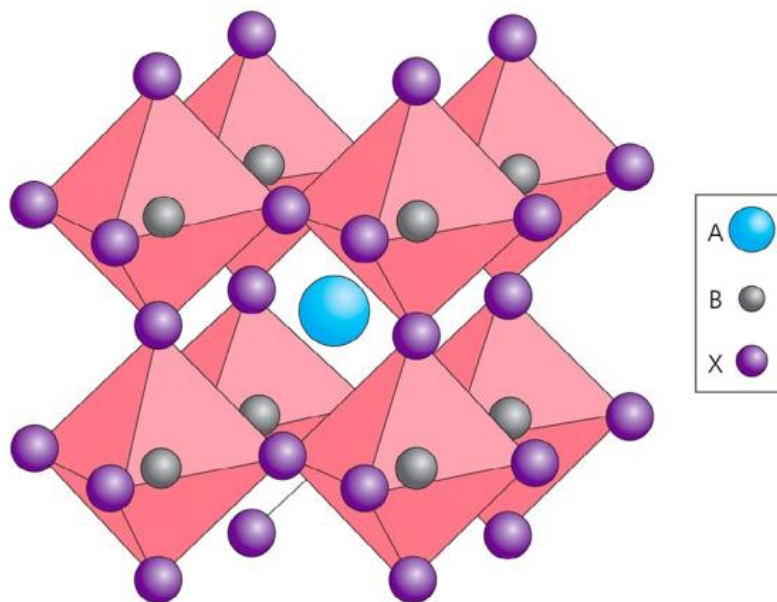


Figure 1.1: Crystal structure of perovskite lattice. A and B denote the two cation sites, X represents the anion.¹³

The reason that perovskites are so widely used is that there are so many elements that can be combined to form perovskites. This is further enhanced by the possibility of doping the either the A-site, the B-site, or both. In addition to tuning the concentration of charged species, the dopants are also able to affect the lattice parameters and therefore the mobility.

1.3 Proton Conducting Membranes

The ability of perovskites to conduct multiple charge species enables their use as hydrogen membranes. When both electrons and protons are transferred simultaneously, it is possible to permeate hydrogen, which has important applications for energy conversion. This is described in the equation below.

$$J_{H_2} = A e^{\frac{-E_a}{RT}} \quad (1.1)$$

Here J refers to the permeation flux of a species, A is the pre-exponential factor, E_a is the activation energy for conduction, R is the universal gas constant, and T is the temperature. The high thermal stability and H_2 permeation of mixed ionic electronic conducting (MIEC) perovskite oxides make them ideal for water-gas shift (1.2), steam methane reformation (1.3), and more.^{3,14,15}



Because membranes can drive a reaction by removing a product, in this case hydrogen, this lowers the temperature of existing industrial processes and promote their efficiency. This is known as Le Chatelier's principle. In combination with a catalyst, this process can also be used to convert methane to longer chained hydrocarbons, which is a very energy intensive process. Examples of membranes and their applications are shown in **Figure 1.2**.

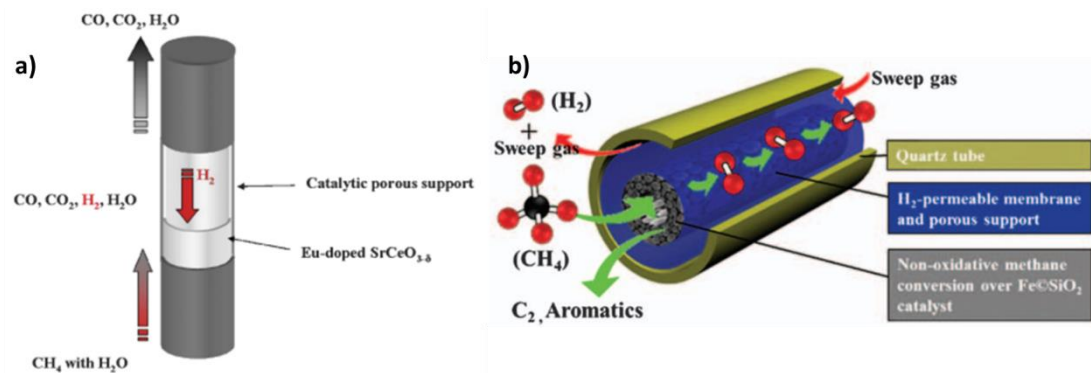


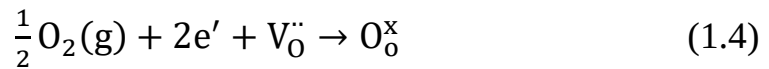
Figure 1.2: Examples of applications for proton conducting membranes. (a) Proton conducting membrane for steam reforming and water gas shift reactions.¹⁴ (b) Membrane and catalyst system for hydrocarbon valorization.¹⁶

Iwahara et al was the first reported study of a perovskite for membrane applications and used doped SrCeO₃, which is still used to this day.^{17,18} Ongoing research focuses primarily on new dopants and improving fabrication. The main challenge of proton conducting membranes is electronic conductivity, which is often the limiting factor for hydrogen permeation.^{8,14}

1.4 Solid Oxide Fuel Cells

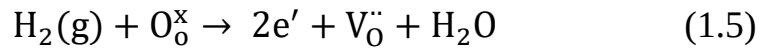
1.4.1 Operation of Solid Oxide Fuel Cells

Solid Oxide Fuel Cells (SOFCs) can provide an effective means of clean energy production that takes advantage of existing fossil fuel infrastructure but produces less pollution and greenhouse gas emissions. SOFCs consist of a cathode, electrolyte, and anode that conduct ions from the air side (cathode) to the fuel side (anode). At the cathode O₂ is adsorbed onto the surface and reduced, becoming lattice oxygen. The oxygen reduction reaction (ORR) at the cathode is shown in equation 1.4



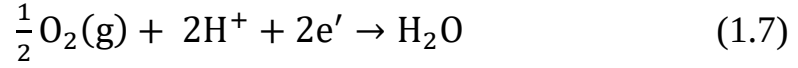
Next the ions diffuse through the electrolyte, driven by the difference in chemical potential. At the anode, the oxygen reacts with hydrogen or a hydrocarbon fuel.

Equation 1.5 shows the reaction for hydrogen in the anode.



As seen in equation 1.5 The hydrogen oxidation reaction (HOR) takes place at the anode. Here the electrons that are produced are the current that the cell creates. The water that is produced diffuses out of the anode with the remaining fuel. In addition to SOFCs, there are also Proton Conducting Fuel Cells (PCFCs). These function in a

very similar manner but instead have the following reactions take place at the anode and cathode respectively.



1.4.2 Introduction to Electrolytes

Unlike the mixed conductivity perovskites used for membranes, the materials for SOFC electrolytes must have minimal electronic conductivity. Otherwise, this creates a leakage current. The two most common electrolyte materials are yttria stabilized zirconia (YSZ) and gadolinium doped ceria (GDC). YSZ has lower conductivity overall but has negligible electronic conductivity.¹⁹ This results in a higher cell voltage but also less power density due to the increased resistance. YSZ requires high operating temperatures to overcome the low conductivity, this manifests as activation polarization at low current densities. High temperatures increase the cost of making and operating SOFCs, lower their long term stability, and hinder the use of SOFCs in real-life applications. In comparison to YSZ, GDC has higher conductivity, but ceria undergoes reduction from a Ce^{4+} to Ce^{3+} , which increases the number of electrons, therefore lowering the cell voltage. The Nernst equation (1.8) describes the relationship between temperature, gas environment and the open circuit voltage (OCV).

$$OCV = \frac{RT}{4F} \ln\left(\frac{p\text{O}_2^{cathode}}{p\text{O}_2^{anode}}\right) \quad (1.8)$$

R is the universal gas constant, T is temperature, F is the faraday constant, $pO_2^{cathode}$ and pO_2^{anode} are the partial pressures of oxygen at the cathode and anode respectively.

In this work, GDC was chosen since the reduced voltage is mitigated by operating at a lower temperature and the higher conductivity of GDC makes it a better choice for operating SOFCs at lower temperatures. GDC has an additional benefit over YSZ, which is that it is more chemically compatible with cathodes. Regardless of the electrolyte composition, it must be as thin as possible without any leaks, because all materials will contribute ohmic resistance to the SOFC. An example of this is shown in **Figure 1.3**. The first drop in OCV, from 1.2 to 1.0 is due to leakage current through the electrolyte. Ohmic losses are due to the electrical contacts and resistance of the bulk of the electrolyte. Activation loss occurs when the current density is too low for an electrochemical process to occur. Finally, mass transfer or polarization overpotential occurs when there are not enough reactants for a process to achieve high current densities.

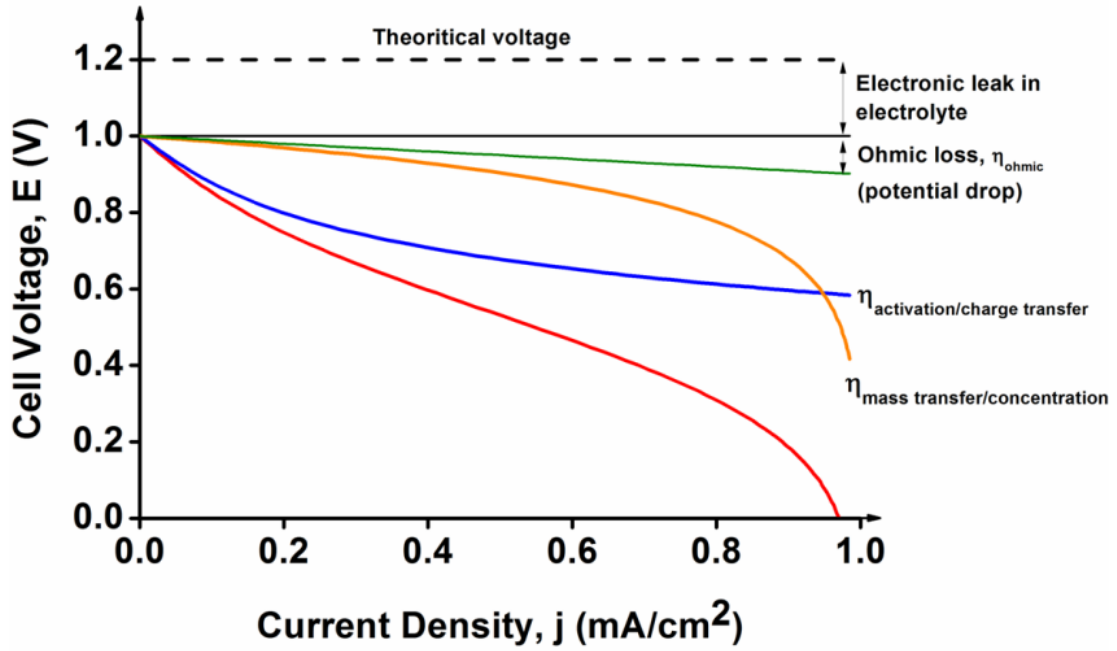


Figure 1.3: Diagram of overpotential losses associated with SOFC operation.²⁰

These performance losses are described by equation 1.9 below

$$\eta_{Total} = \eta_{activation} + \eta_{ohmic} + \eta_{polarization} \quad (1.9)$$

Where η represents each overpotential, which can be thought of as a loss in chemical potential energy needed to complete an electrochemical process.

1.4.3 Introduction to Cathodes

A major bottleneck for adopting SOFC technology, however, is the cathode. At typical SOFC operating temperatures, the cathode is subject to degradation by means of cation segregation.^{21–23} High temperatures cause unwanted reactions and coarsening that degrade performance over time.^{23–25} Unfortunately, temperature is also the driving force for the ORR in addition to cathode degradation. Therefore, if the kinetics of the cathode could be improved, it would address the issues of cathode degradation, as well as the other challenges mentioned previously.

The ORR activity of the cathode is also driven by the cathode's composition, lattice, structure, and surface chemistry.^{1,26,27} Many well-studied cathode compositions, such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) are perovskites. As seen in Equation (1.4) SOFC cathodes need both ionic and electronic conductivity. Here the A-site is known to influence the oxygen conductivity by adding $\text{V}_\text{O}^{\bullet\bullet}$. Meanwhile the B-site promotes electronic conductivity which is why it typically consists of multivalent transition metals.^{26,28,29} While the principles are like those of membranes, in the case of SOFC cathodes, oxygen conductivity is required instead of protonic. Also, unlike membranes which must be dense, cathodes require a large surface area to facilitate more sites for ORR. The reaction occurs at the Triple Phase Boundary (TPB) of the cathode, which is where all the components (oxygen, electrons, and $\text{V}_\text{O}^{\bullet\bullet}$) are present. Typical cathodes will consist of both cathode and electrolyte materials. **FIGURE 1.4** shows the effect that different types of conductors have on the TPB. The presence of mixed conductors allows additional interface between the cathode and electrolyte materials.

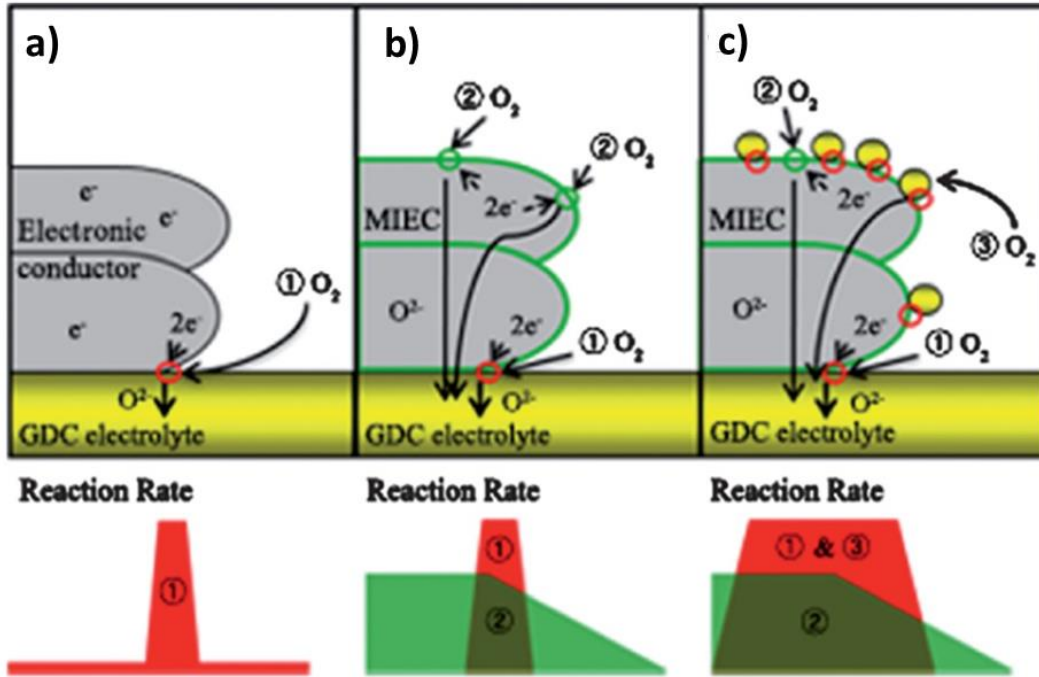


Figure 1.4: Diagram showing ORR active sites for a) Exclusively electronic conductor on GDC (basic TPB) b) MIEC and GDC interface (triple-phase and dual-phase boundary) c) Increased reaction sites with additional ionic conducting phase on MIEC.³⁰

1.4.4 Introduction to Anodes

Like cathodes, SOFC anodes are also composites that consist of two phases to increase the overall performance. Most cathodes consist of either Ni-YSZ or Ni-GDC. NiO is used with electrolyte materials because once it reduces to metallic Ni, it leaves behind open pores that enable gas diffusion, while also being catalytically active and conducting electrons. **Figure 1.5** shows the two most common types of SOFC configurations.

High performance SOFCs are almost always anode supported cells (ASCs). In this configuration, the anode is produced first and forms the bulk of the SOFC. Next the electrolyte is attached either before sintering or deposited as a coating. Finally, the cathode is deposited. As seen in **Figure 1.5**, the electrolyte dominates the structure of

the electrolyte supported cell. This adds significant ohmic resistance but is much easier to produce in large quantities before adding virtually any type of cathode or anode. The major challenge with ASC anodes is that they typically form the backbone of the SOFC so mechanical and thermal properties must be considered as well as performance. But this configuration has much lower ohmic resistance, which is mainly derived from the electrolyte. Ongoing research into anodes focuses primarily on scaling up or performance. There is also a myriad of additional problems such as redox stability, coking tolerances, and sulfur tolerance.^{31–33}

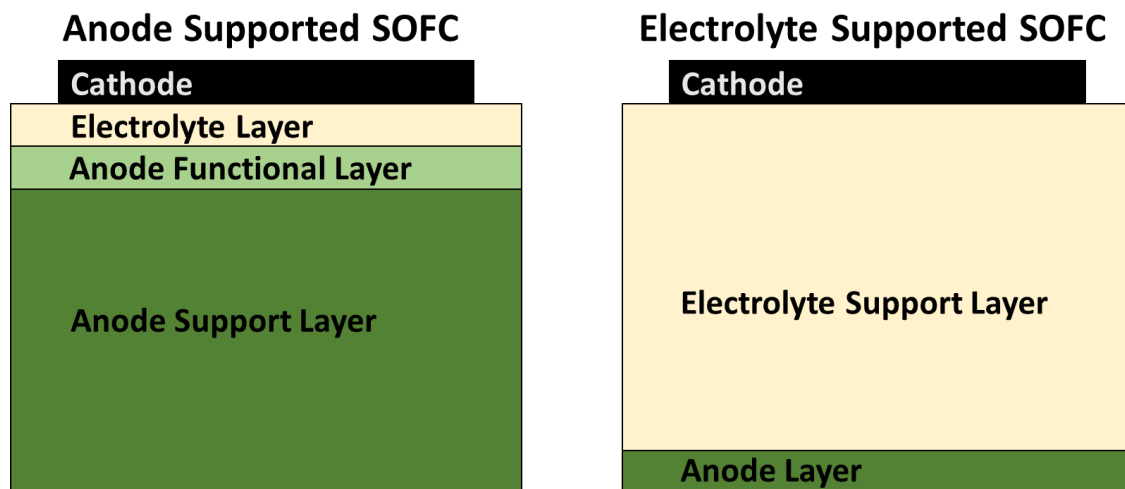


Figure 1.5: Diagram showing the layers in anode-supported and electrolyte-supported SOFCs

1.5 Quantifying Electrochemical Kinetics

1.5.1 Electrochemical Impedance Spectroscopy

Qualifying the performance of membranes and SOFCs was done with electrochemical testing. One of the most common measurements is that of Electrochemical Impedance Spectroscopy (EIS). Here an AC voltage is applied while

the impedance is measured in a frequency sweep. When this is applied to a pure resistor this is expressed with the following equation:

$$V(t) = V_o \sin(\omega t + \phi) = I_o \sin(\omega t)R \quad (1.20)$$

However, electrochemical processes have characteristic frequencies/time constants, so they do not act purely as resistors. Instead, impedance is used to account for the frequency dependence of the system.

$$Z(\omega) = Z'(\omega) + iZ''(\omega) \quad (1.21)$$

Here Z is the total resistance, Z' is the real component, and Z'' is the imaginary component of impedance. When these are plotted together, the result is a Nyquist plot. In a Nyquist plot, the x intercept represents the total ohmic impedance. The arc that follows is often a superposition of overlapping arcs, each representing a different electrochemical process. In the case of membranes, the most important value is the bulk conductivity, which is represented by the first arc. A second arc corresponds to other material properties such as grain boundary conductivity. In SOFCs, the electrolyte material and thickness determine the ohmic impedance. The arcs are a combination of each process occurring in the electrodes including, gas diffusion, ORR, and HOR. By fitting the impedance into an equivalent circuit, it is possible for each electrochemical process occurring in a membrane or SOFC to be represented by a circuit element. The circuit element most commonly used is called a Voigt element, which is a resistor in parallel with a capacitor, that together are in series with a second resistor.

1.5.2 Distribution of Relaxation Times

EIS curves can be further analyzed by mapping them on a frequency or time domain. As mentioned previously, EIS is done with a frequency sweep and each arc corresponds to some process with a unique reaction rate or time constant. Rather than plotting the real versus imaginary components of impedance, the distribution of relaxation times (DRT) method uses a frequency or time domain. By plotting in terms of time or frequency, it is possible to see each process separately. There are several ways to do this, all of which start with the following equation:

$$Z(\omega) = R_{\infty} + R_p \int_{-\infty}^{\infty} \frac{G(\tau)}{1+i\omega\tau} d\ln\tau \quad (1.22)$$

Here $Z(\omega_i)$ is the impedance, R_{∞} is the ohmic resistance, R_p is the polarization resistance, and $G(\tau)$ is a normalized function that equals 1 upon integration, and τ is the time constant. Since there are multiple possible solutions that can equal 1, there are several methods that go on to calculate the actual solution such as Fourier Transforms, Maximum Entropy, and Tikhonov Regularization.^{34–37} In this work, the DRT tools package for Matlab was used which uses Tikhonov Regularization and requires a regularization parameter (λ) to define the solution. For this the value of $\lambda=10^{-4}$ was used. DRT plots plot γ as a function of time constant or frequency. γ is defined in the equation below.

$$\gamma(\ln\tau) = \sum_{m=1}^M x_m \varphi_{\mu}(\ln\tau - \ln\tau_m) \quad (1.23)$$

Here, x_m is a parameter for approximating the system as a Voigt element, φ is a radial basis function, and μ is a shape function for the width and height of the peaks.

Chapter 2: Proton Conducting Membranes

2.1 Mixed Conductors as Membranes

High-temperature solid-state ion conductors have numerous applications ranging from SOFCs/SOECs to gas separation membranes and sensors.³⁸ Specifically, proton conducting membranes can be used for the separation of H₂ gas from various feedstocks. Perovskites have been widely studied for use as high-temperature proton conductors due to their tunable properties.^{17,39,40} However, the fixed oxidation state of strontium limits the electronic conductivity of SrCeO₃. The majority charge carriers within SrCeO₃ are protons, and have limited hydrogen permeation due to the relatively lower electronic conductivity.¹⁴ Improving the conductivities of these materials will also enhance the performance of PCFC's and PCEC's. Electrodes based on mixed conductors can achieve a higher triple phase boundary (TPB) compared to composites of single-species conductors. This is demonstrated by the high performance of triple-conducting oxides as electrodes.⁴¹

Different dopants are known to change the chemical, structural, and electrical properties of perovskite oxides. The effectiveness of SrCeO₃ with different dopants (D= Eu, Sm, Y, Yb, Tm, Tb) on Ce sites for use in hydrogen permeation membranes has been studied.^{11,42-44} These dopants will introduce oxygen vacancies with their +2 and +3 oxidation states forming D''_{Ce} or D'_{Ce} respectively. D_{Ce} represents a dopant in a cerium site, and ' denotes the charge number. These oxygen vacancies play an important role in controlling the functionality of materials, such as oxygen ion diffusivity, catalytic sites for the dissociation of H₂O into OH⁻, and the generation of electrons and holes.

Computational work by Bai et al. demonstrated that polarons formed by certain dopants have minimal charge trapping effects and beneficially distort the lattice.¹² Univalent dopants of +3 would form oxygen vacancies but not polarons. This is supported by literature comparing the effects of different dopant types. Past experimental and theoretical work has found improved conductivity in multivalent compared to univalent dopants, suggesting that polarons do contribute to electronic conductivity through a charge hopping mechanism.^{11,12,45} Pr specifically was chosen as a dopant because of its lower ionization energy compared to similar lanthanides, meaning that Pr may be reduced at a higher pO_2 compared to other dopants.¹² Additionally, the ionic radii of Pr and Ce are similar to each other, which is important because smaller B-site atoms may hinder the ability of Pr to change oxidation state and promote secondary phase growth.⁴⁶ At the time this research was performed, Eu was also significantly more expensive than Pr. Although the difference in cost has decreased, Eu is currently 3-5 times more expensive than Pr at major suppliers such as Alfa Aesar and Sigma Aldrich.

2.2 Experimental Methods: Proton Conducting Membranes

2.2.1 Materials Synthesis

$SrCe_{1-x}Pr_xO_{3-\delta}$ ($x=0, 0.05, 0.10, 0.20$) were prepared through solid-state synthesis. Precursors of stoichiometric $SrCO_3$ (Sigma Aldrich, $\geq 99.9\%$ trace metals basis), CeO_2 (Alfa Aesar, 99.9% REO), and Pr_6O_{11} (Alfa Aesar, 99.5% REO) were weighed and then ball-milled in ethanol for 24 hours. The solvent was evaporated, and the solute was ground before calcination at $1300^\circ C$ for 6 hours.

2.2.2 Characterization of Materials

X-ray Diffraction (XRD) was conducted using a Bruker D8 Advance with Cu-K α radiation, and the identification of secondary phases was done using Bruker Diffrac.Eva software. Determination of lattice parameters was done through Le Bail fitting performed with Topaz. Microstructure characterization and EDS were performed with a Hitachi Su70 SEM.

2.2.3 Conductivity Measurements

Conductivity measurements were conducted on dense pellets. SrCe_{1-x}Pr_xO_{3- δ} powders were pressed in a 10 mm die with a hydraulic press. The pressed pellets were then sintered at 1450 °C for 4 hours. The pellet was placed between gold mesh layers that were held between ceramic plates within a custom-built alumina reactor for conductivity measurements in controlled gas environments. The pO_2 was adjusted by varying N₂, H₂, and O₂ flow rates. The flow of gases was controlled using a mass flow controller. The pO_2 was measured downstream with a Zirox SGM5 oxygen sensor. Moisture was added by flowing the gas into a bubbler held at ambient temperature. The conductivity of the pellet was measured by electrochemical impedance spectroscopy (EIS) using a 1470E Cell Test System (Solartron) with a 1455A Frequency Response Analyzer (Solartron). Measurements were performed with a 50mV AC signal across the frequency range of 1 MHz to 1 Hz.

2.3 Results & Discussion: Proton Conducting Membranes

2.3.1 Crystal Structure and Stability

The stability and conductivity of doped SrCeO₃ is highly dependent on its structural

properties. **Figure 2.1 (A)** shows X-ray diffraction (XRD) of $\text{SrCe}_{1-x}\text{Pr}_x\text{O}_{3-\delta}$ with $0 < x < 0.2$. There are no visible peaks other than that of the orthorhombic SrCeO_3 perovskite phase up to 10% dopant concentration, suggesting 10% would likely be the maximum doping level to form solid solution of $\text{SrCe}_{1-x}\text{Pr}_x\text{O}_{3-\delta}$. Above 10% dopant concentration some secondary phases can be seen, specifically Sr_2CeO_4 , Sr_2PrO_4 and Pr_2O_3 . The lattice parameters of Pr doped SrCeO_3 were evaluated based on the peak positions of XRD measurements, and the corresponding lattice parameters are summarized in **Figure 2.1 (B)**. All lattice parameters (a , b , c) and the cell volume (V) decrease as Pr doping concentration increases because of the decrease in B site average ion radii (0.85 Å and 0.87 Å for Pr^{4+} and Ce^{4+} respectively in six-fold coordination). Additionally, the increased dopant amount also increases the oxygen vacancy concentration, since Pr^{4+} is more likely to be reduced than Ce^{4+} .¹²

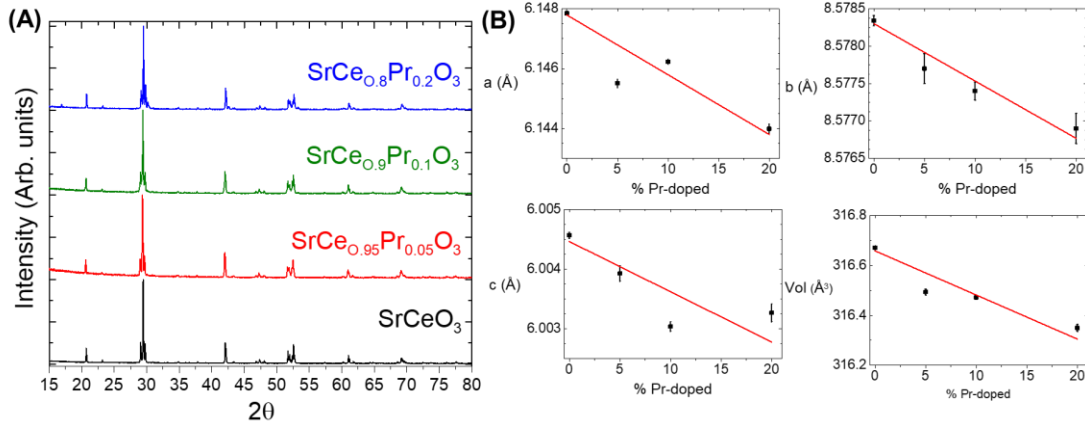


Figure 2.1: Phase and structure of Pr-doped SrCeO_3 . (a) XRD spectra of each dopant level (b) The lattice parameters a , b , c , and unit cell volume V .⁴⁷

Stability in reducing conditions is crucial for hydrogen permeation membrane and SOFC/SOEC anode applications. As multivalent Pr is introduced to SrCeO_3 , the changes in Pr oxidation states during reduction and oxidation may induce lattice

expansion/shrinkage, leading to the formation of secondary phases or material failure. Secondary phases would inhibit permeation and impact electrode polarization even if total conductivity were to increase.⁴⁸ Therefore, XRD and SEM were used to study the gas environment effects on crystal structure and microstructure, respectively.

As shown in **Figure 2.2 (A)**, XRD of $\text{SrCe}_{0.9}\text{Pr}_{0.1}\text{O}_{3-\delta}$ has a perovskite structure with no formation of secondary phases after reduction in 5% H_2 in N_2 with 3% humidity at 900°C . In addition, the characteristic peaks of $\text{SrCe}_{0.9}\text{Pr}_{0.1}\text{O}_{3-\delta}$ shift to a lower angle, indicating that the lattice parameters increase after reduction, as listed in **Table 1**. This is likely due to the reduced oxidation state of Pr and its greater ionic radius. Similar studies on $\text{BaZr}_{1-x}\text{Pr}_x\text{O}_3$ have also observed a similar effect upon reduction.⁴⁶ **Figure 2.2 (B) and (C)** shows the microstructure of the dense $\text{SrCe}_{0.9}\text{Pr}_{0.1}\text{O}_{3-\delta}$ surface before and after reduction. Both fresh and unreduced samples show a dense microstructure without any cracks and do not show signs of new phase having nucleated on or in between the grains, indicating that the $\text{SrCe}_{0.9}\text{Pr}_{0.1}\text{O}_{3-\delta}$ is stable in both oxidizing and reducing conditions.

TABLE I. Comparison of lattice parameters before and after reduction.

Composition	a (Å)	b (Å)	c (Å)	Volume (Å ³)
$\text{SrCe}_{0.9}\text{Pr}_{0.1}\text{O}_{3-\delta}$ - initial	6.1477	8.5784	6.0027	316.5670
$\text{SrCe}_{0.9}\text{Pr}_{0.1}\text{O}_{3-\delta}$ - reduced	6.1521	8.5862	6.0121	317.5781

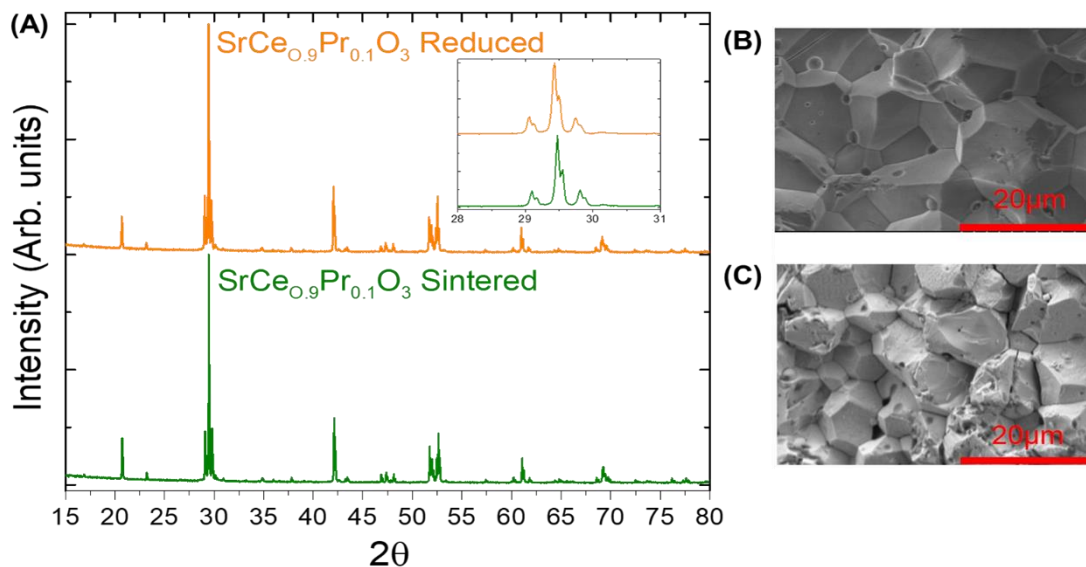


Figure 2.2: Redox stability of Pr doped SrCeO₃. (a) XRD spectra of SrCe_{0.9}Pr_{0.1}O_{3- δ} before and after reduction in H₂ for 18 h; with insert focusing on primary peaks (b) SEM image of SrCe_{0.9}Pr_{0.1}O_{3- δ} pellet as sintered (c) SEM image of SrCe_{0.9}Pr_{0.1}O_{3- δ} pellet after testing in reducing atmosphere.⁴⁷

2.3.2 Conductivity in Reducing Atmospheres

Conductivity of Pr-doped SrCeO₃ was evaluated as a function of dopant concentration by measuring the temperature dependence of conductivity in an atmosphere of 5% H₂, 95% N₂ with 3% moisture. **Figure 2.3 (A)** shows Arrhenius plot of total conductivity of SrCeO₃ with different Pr doping levels and 5% Eu for comparison.⁴⁹ Pr showed higher conductivity at all dopant levels and temperatures. The activation energies for conductivity were calculated from the slope of log of conductivity multiplied by temperature from **Figure 2.3 (A)**, and the resulting values are shown in **Table II**.

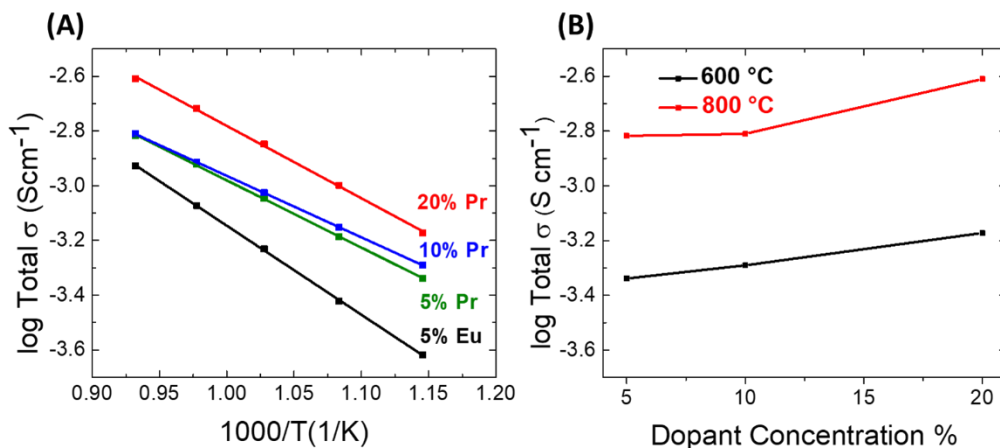


Figure 2.3: Conductivity of Pr doped SrCeO_3 . (a) Arrhenius plot of $\text{SrCe}_{1-x}\text{Pr}_x\text{O}_{3-\delta}$, $x = 0, 0.1$, and 0.2 , exposed to 5% H_2 in N_2 with 3% moisture. 5% Eu doped SrCeO_3 is shown for comparison.⁴⁹ (b) Conductivity as a function of dopant concentration in 5% H_2 and 95% N_2 with 3% moisture at 600 °C and 800 °C as a function of dopant level.⁴⁷

The Eu doped SrCeO_3 had activation energy higher than all the Pr-doped samples. Among the Pr-doped compositions, the 20%-doped sample had the highest activation energy despite having the highest conductivity. The 10%-doped sample had the lowest activation energy but had about the same conductivity as the 5%-doped sample. This suggests that there may be multiple conductivity mechanisms resulting from the presence of secondary phases and that the dominant charge species changes with temperature. Past studies on the similar composition $\text{SrCe}_{0.9}\text{Eu}_{0.1}\text{O}_{3-\delta}$ found CeO_2 formation after H_2 exposure, which increased conductivity due to the n -type nature of CeO_2 .⁵⁰ Therefore, the increase in conductivity of the 20% Pr sample may be due to the contribution from secondary phases, as suggested by the XRD results.

Table II. Activation energies at varying dopant concentrations from conductivity measurements in 5% H₂ in N₂ with added moisture.

Composition	E _a (eV)
SrCe _{0.95} Pr _{0.05} O _{3-δ}	0.57
SrCe _{0.90} Pr _{0.10} O _{3-δ}	0.53
SrCe _{0.80} Pr _{0.20} O _{3-δ}	0.61
SrCe _{0.95} Eu _{0.05} O _{3-δ}	0.72

Figure 2.3 (B) shows the conductivity of Pr doped SrCeO₃ in moist 5% H₂ and 95% N₂ with varying dopant concentrations at 600°C and 800 °C. The total conductivity increases with the dopant concentration over a wide range of temperatures. Despite the higher conductivity, the secondary phases formed by 20% doping could be problematic for long-term stability and may hinder hydrogen permeation if used as a membrane.⁵⁰ Computational work by Bai et al. reported that in the case of Pr-doped SrCeO₃, it is not energetically favorable for Pr to reach a Pr⁺² oxidation state.¹² Instead, an additional electron will localize on a Ce⁺⁴ site, reducing it to Ce⁺³. If we consider the reduced forms of each B-site atom; Ce⁺³, Pr⁺³, and Eu⁺²; their ionic radii are 1.01 Å, 0.99 Å, and 1.17 Å respectively. Computational work by Mather and Islam discusses the effect of ionic radius on proton conductivity and defect association.¹⁰ Their work suggests that the ionic radius of the dopant directly affects the binding energy of the $M'_{Ce}OH_O^\bullet$ defect cluster (where M denotes the B-site element), and the optimal dopant ionic radius for proton conduction in SrCeO₃ is about 0.89 Å. The ionic radius of Pr⁺³ is closer to this than the larger ionic radius of Eu⁺², which is reflected in the difference in activation energies that we observe.

In addition to temperature dependence, oxygen partial pressure (pO_2) dependence on conductivity of Pr-doped $SrCeO_3$ was conducted to determine the dominant charge species for transport over a wide range of pO_2 's. Since an increase in Pr dopant concentration increases conductivity and the 10% sample was the highest dopant level to retain pure phase, 10% Pr-doped $SrCeO_3$ was selected as the composition of interest. **Figure 2.4 (A)** shows the pO_2 dependence of conductivity for $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$ between 800°C and 900°C. The pO_2 was measured with an oxygen sensor and adjusted by tuning the flow rates of H_2 and N_2 .

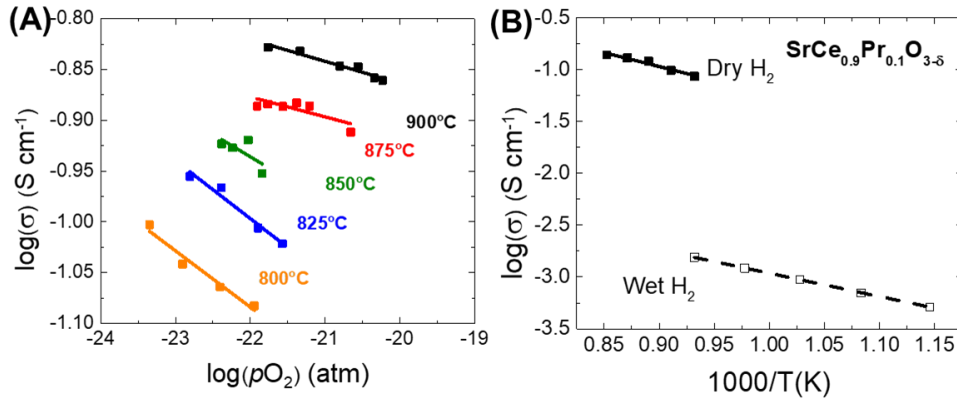


Figure 2.4: pO_2 dependence of conductivity of $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$ in reducing atmospheres; a mixture of H_2 and N_2 . (a) Effect of pO_2 on conductivity at different temperatures. (b) Arrhenius plot of $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$ in a 10% H_2 atmosphere with and without water.⁴⁷

In reducing conditions (dry H_2), the conductivity of $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$ increases with pH_2 , demonstrating that $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$ exhibits *n*-type electronic behavior. In our prior work on acceptor doped $SrCeO_3$, *n*-type behavior was also observed in reducing conditions and has already been discussed in detail.^{11,48,49} In summary, we can expect the behavior in reducing conditions to be governed by the following equations, which are expressed in Kröger-Vink notation.

$$O_O^x \leftrightarrow V_O^{\bullet\bullet} + 2e' + 1/2 O_{2(g)}; K_O = \frac{[V_O^{\bullet\bullet}]n^2 P_{O_2}^{1/2}}{[O_O^x]} \quad (2.1)$$

$$H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^x \leftrightarrow 2OH_O^\bullet; K_{H_2O} = \frac{[OH_O^\bullet]^2}{[V_O^{\bullet\bullet}][O_O^x]P_{H_2O}} \quad (2.2)$$

$$H_{2(g)} + 2O_O^x \leftrightarrow 2OH_O^\bullet + 2e'; K_H = \frac{[OH_O^\bullet]^2 n^2}{[O_O^x]^2 P_{H_2}} \quad (2.3)$$

$$2Pr_{Ce}^X + O_O^x \leftrightarrow 2Pr_{Ce}' + V_O^{\bullet\bullet} + 1/2 O_{2(g)}; K_R = \frac{[Pr_{Ce}']^2 [V_O^{\bullet\bullet}] P_{O_2}^{1/2}}{[Pr_{Ce}^X]^2 [O_O^x]} \quad (2.4)$$

$$Pr_{Ce}^X + e' \leftrightarrow Pr_{Ce}'; K_{Pr} = \frac{[Pr_{Ce}']}{[Pr_{Ce}^X]n} \quad (2.5)$$

Here, $V_O^{\bullet\bullet}$ denotes oxygen vacancies of net charge +2, $OH_O^\bullet$ denotes a hydroxyl group occupying an oxygen site (net charge +1), and n represents the concentration of electrons. The subscripts denote the lattice site that is being occupied and the superscript represents the charge of the species. For instance, O_O^x , Pr_{Ce}^X , and Pr_{Ce}' refer to a neutral charged oxygen in an oxygen site and a neutral and negatively charged Pr atom in a ceria site respectively. Vacancies and electrons are generated as the material is reduced and oxygen is lost from the lattice, expressed in Equation (2.1). In Pr-doped case, the reduction of Pr^{+4} to Pr^{+3} leads to further oxygen loss and electron charge carrier gain, hence the n-type behavior shown in Equations (2.2)-(2.5). This behavior was also observed in our prior work on Eu-doped $SrCeO_3$, which also exhibited n-type conductivity and behaved as a mixed conductor.^{11,49}

Figure 2.4 (B) is an Arrhenius plot showing the differences in conductivity between Pr-doped $SrCeO_3$ in 10% H_2 atmosphere with and without 3% humidity. The activation energies were calculated to be 0.63 eV and 0.53 eV respectively. The activation energy for proton conduction is less than that of oxygen ions, but greater than for electrons.^{51,52} We expect a greater concentration of electrons than protons in dry conditions as the introduction of moisture would raise the effective pO_2 . Thus, this is in agreement with our observed activation energies and previously reported n-

type conductivity.⁵³ Compared to Eu-doped SrCeO₃, Pr doping led to significantly higher conductivity in reducing atmospheres both with and without moisture.^{48,49} In the case of Eu doping, Eu⁺² and Eu⁺³ both act as acceptors within the B-site of SrCeO₃. This can be represented by the defect relation below.

$$Eu'_{Ce} + e' \leftrightarrow Eu''_{Ce}; K_{Eu} = \frac{[Eu''_{Ce}]}{[Eu'_{Ce}]n} \quad (2.6)$$

Both Eu and Pr are known to have a +2 oxidation state. However, as mentioned previously, in the case of Pr, Ce⁺⁴ is more likely to reduce to Ce⁺³ rather than Pr⁺³ to become Pr⁺². We attribute the increased conductivity of SrCe_{0.9}Pr_{0.1}O_{3-δ} relative to SrCe_{0.9}Eu_{0.1}O_{3-δ} to reduced defect association and the polaron hopping model described by Bai et al.¹²

2.3.3 Conductivity in Oxidizing Atmospheres

The results for pO_2 dependance in the high pO_2 regime are shown in Figure 2.5. In oxidizing conditions (O₂/N₂ mixture with moisture), as pO_2 increases, the conductivity decreases until pO_2 reaches $\sim 10^{-2}$ - 10^{-3} atm.

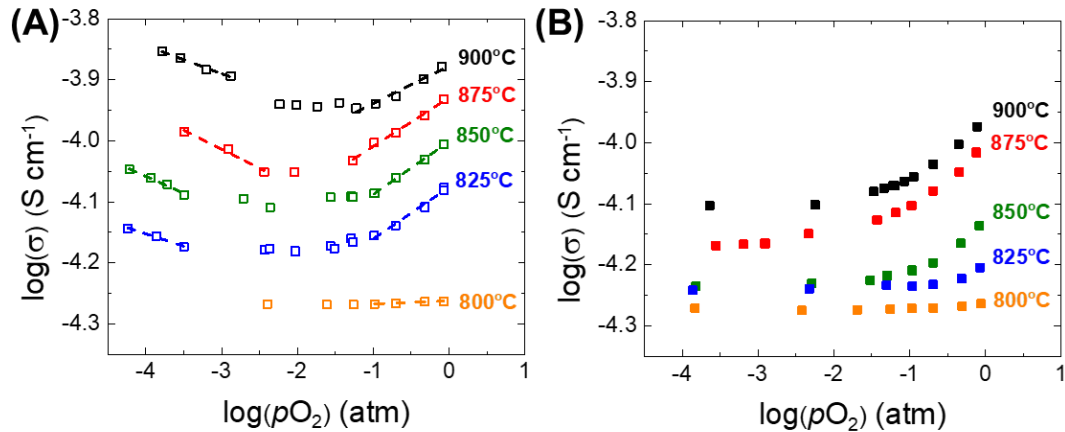


Figure 2.5: pO_2 dependence of SrCe_{0.9}Pr_{0.1}O_{3-δ}. In (a) High pO_2 atmosphere with moisture, and (b) High pO_2 atmosphere without moisture.⁴⁷

Once pO_2 is higher than $\sim 10^{-2}$ - 10^{-3} atm, the conductivity shows a p-type dependence as pO_2 increases, as is common in acceptor-doped perovskites.^{11,54-56} Prior work by Song et al. has observed p-type behavior in Eu-doped $SrCeO_3$ in oxidizing conditions and defect relations have been established for acceptor doped $SrCeO_3$.⁵⁶ Eu-doped $SrCeO_3$, exhibits higher conductivity in oxidizing atmosphere than $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$.

Unlike Pr, Eu remains an acceptor dopant at high pO_2 and the conductivity observed in Pr-doped $SrCeO_3$ in dry air is similar to that of undoped $SrCeO_3$.³⁹ Comparing the results in wet and dry conditions in **Figure 2.5 (A)** and **Figure 2.5 (B)**, the conductivity of $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$ is significantly higher in wet conditions than in dry conditions. This suggests that the protonic conductivity of $SrCe_{0.9}Pr_{0.1}O_{3-\delta}$ is relatively higher than its oxygen ion conductivity. Equation 2.2 describes how moisture is incorporated into the lattice resulting in protonic conductivity. The resulting hydroxyl groups result in protonic conduction through the Grotthus mechanism.⁵⁷ High protonic conductivity has been reported in doped strontium cerates and similar perovskites and is known to depend greatly on the dopant.^{10,54,55,58} Regarding protonic conduction in Eu-doped $SrCeO_3$, Song et al. reported reduced conductivity upon the addition of moisture in oxidizing conditions.⁵⁶ This fits our expectation that the ionic radius of Pr is more favorable for protonic conduction than Eu based on previously reported computational work.¹²

Note that the total conductivity is several orders of magnitude higher in reducing conditions than in oxidizing conditions, as shown in the difference in Y-axis values between Figure 2.4 and Figure 2.5. Such an increase has also been reported in

Pr-doped BaCeO₃.⁵⁹ The high electron and hole conductivity achieved by these multivalent dopants is essential for use in hydrogen permeation membranes and SOFC/SOEC electrodes. Our results demonstrate that SrCe_{0.9}Pr_{0.1}O_{3-δ} is an MIEC under both reducing and oxidizing conditions, albeit with greater conductivity in reducing environments due to the reduction of multivalent Pr dopant.

2.4 Conclusion: Proton Conducting Membranes

In this work, we synthesized Pr doped SrCeO₃ and determined the conductivity as a function of temperature and pO_2 . Pr doped SrCeO₃ demonstrated much higher conductivity under low pO_2 conditions than in high pO_2 conditions, mainly due to the increase in n -type conductivity as a result of the reduction of Pr. The increase in Pr dopant level increases the total conductivity. However, the formation of secondary phases is observed for compositions above 10% doping level, which can be detrimental to electrochemical performance despite the increased total conductivity. Therefore, 10% Pr doping appears to be the optimized level for forming solid solution. In addition, the structure and stability of SrCe_{0.9}Pr_{0.1}O_{3-δ} was evaluated, showing no secondary phase formation after redox cycles. This indicates that it has a great potential as an MIEC for gas separation membranes and SOFC/SOEC anodes operating in reducing conditions. As a new dopant for SrCeO₃, Pr shows greater conductivity compared to our previous Eu-based compositions under reducing conditions.^{11,50}

Chapter 3: Degradation in SOFC Cathodes

3.1 Introduction to Cathode Degradation

Perovskites are widely used for high temperature electrochemical conversion applications such as solid oxide fuel cells (SOFCs) and oxygen permeation membranes, because of their high oxygen activity, conductivity, and tunable nature.^{2,19,60} Generally, multiple dopants are used in both A and B sites of ABO_3 perovskites to achieve desired properties. However, their high oxygen activity toward gas-solid reactions simultaneously causes stability issues after long-term operation at high temperature, mainly cation segregation. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), one of the most commonly used SOFC cathodes and the most representative case for this degradation mechanism, along with similar Sr-doped perovskite cathodes,^{61–63} are susceptible to Sr ion diffusion to the cathode surface as a primary source of degradation. Once the insulating SrO phase is formed on the surface, it blocks active sites and impedes electron conduction.^{64–67} This atomic migration occurs during SOFC operation and degrades the performance.⁶⁸ Cation segregation has been shown to be a significantly greater problem than other degradation mechanisms such as microstructural changes.^{69–75} A gas impurity in air, namely CO_2 , is also shown to cause degradation issues for perovskite materials.^{76–78} Understanding the surface cation segregation mechanism is critical to mitigating the degradation process.

Intensive research has been conducted regarding strontium segregation on LSCF. Studies on the driving force for Sr-segregation suggest that lattice strain between cations (elastic energy) and surface charge (electrostatic energy) are responsible, but the exact mechanisms are difficult to ascertain.^{79–83} The composition of the A and B-

sites of perovskites, as well as oxygen non-stoichiometry, is found to affect Sr-segregation.⁸¹ Previous work showed the effects of oxygen partial pressure (pO_2), moisture, and mechanical strain on cation segregation process.^{64,82,84,85} However, the temperature and pO_2 range in previous studies were performed only in a small window. Thus, proposed mechanisms based on limited testing conditions might not fully represent the full situation. At high-temperature, the gas-solid interactions between gaseous molecules and the solid surface are expected to strongly influence surface chemistry of these perovskites, but the driving force for segregation and the influence of gas environment is rarely discussed. How pO_2 and carbon dioxide partial pressure (pCO_2) mutually affect the surface cation segregation process is still unclear. Moreover, since the gas environment and the strain are considered as the major causes of cation segregation, testing conditions (ambient, vacuum) and samples preparation (especially in the case of thin film studies) would likely affect the results.^{24,25,66,86}

Here the surface cation segregation of LSCF is systematically studied over a wide range of conditions that resemble SOFC operation to elucidate the fundamental surface segregation mechanism and the dominant governing factors for these segregation processes. Instead of using thin films, we decide to monitor the segregation process on bulk LSCF so that our observation might not be affected by the substrate lattice strain. Dense, polished LSCF samples were aged in a controlled environment to carefully explore the roles of temperature, time, gas compositions on surface segregation. Our results show that there is a specific window of temperature and pO_2 that facilitates SrO segregation. Also, we demonstrate how the gas environment, such

as CO₂ concentration, directly impacts the segregation process and cross-reference our findings with the proposed driving forces in the literature.

3.2 Experimental Methods: Cathode Degradation

3.2.1 Sample Preparation

Dense samples were made by pressing commercially available La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF), (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O₃ (LSCF095), and Sm_{0.5}Sr_{0.5}CoO₃ (SSC) powder (Praxair) with a hydraulic press. The resulting discs were sintered in air at 1400°C for 4 hours for LSCF. Once sintered, the discs were polished with SiC sandpaper down to 8μ and then polished with diamond polishing particles to 0.25μ. This enables observation of grain boundaries with SEM. The polished samples were aged in environmentally controlled reactors. Gas flow rates were controlled with mass flow controllers and the gas environment was verified with a Zirox SGM5EL *p*O₂ sensor. The gases O₂, N₂, CO₂, and H₂ (Airgas, ultra-high purity) were used to create each testing environment.

Samples of A-site deficient SSC; Sm_{0.475}Sr_{0.475}CoO₃ (D95), Sm_{0.475}Sr_{0.5}CoO₃ (DSm), and Sm_{0.5}Sr_{0.475}CoO₃ (DSr) were synthesized with the sol-gel method. Metal nitrates of Sr(NO₃)₂, Sm(NO₃)₃ · 6H₂O, Co(NO₃)₂ · H₂O were added to water heated to 120°C. Citric acid and ethylenediaminetetraacetic acid (EDTA) were added as chelating agents. The pH was adjusted to 7 before drying the water. The precipitate was heated to 400°C for combustion and then fired at 900°C. The powder was ground and pressed similarly to the LSCF.

3.2.2 Characterization Methods

The surface morphology is monitored using scanning electron microscopy (SEM), and the precipitated particle size and distribution are further quantified through image analysis. After aging conditions were met, the surface of each sample was studied using a Hitachi Su70 SEM. The subsequent images were then analyzed using ImageJ. The Trainable WEKA Segmentation plugin for ImageJ was used to distinguish between the background and particles. The resulting image could then be quantified to determine the particle frequency and size distribution. An analysis of the surface particles was then carried out using ImageJ software and the Trainable WEKA Segmentation plugin (WEKA).⁸⁷ An example of this process is shown in **Figure 3.1**. Particle phase and surface phases were studied with a Bruker D8 powder X-ray diffractometer (XRD) with Cu K α radiation. Raman spectroscopy was performed using an Yvon Jobin LabRam ARAMIS confocal Raman microscope.

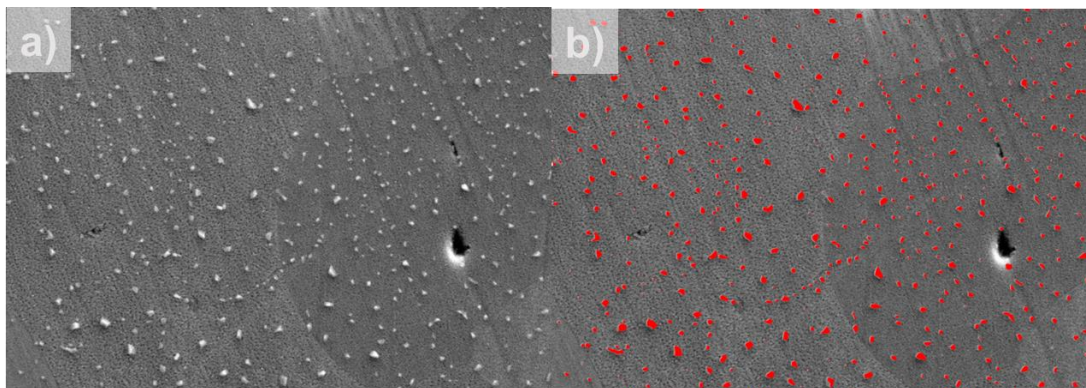


Figure 3.1: Overview of procedure for using Trainable WEKA segmentation in ImageJ to determine particle size distribution (a) original image (b) surface particles identified by Trainable WEKA highlighted in original image.²¹

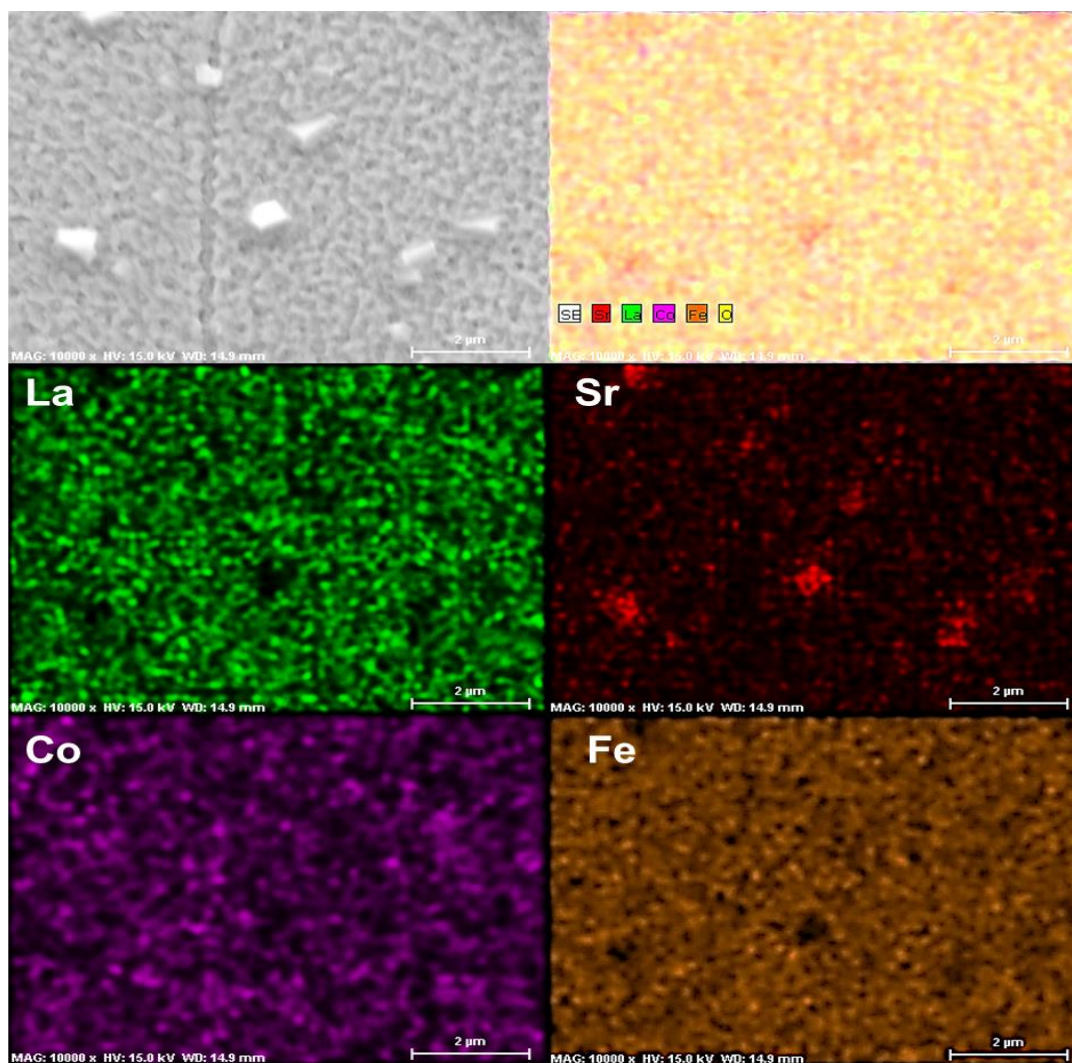


Figure 3.2: EDS of particles found to grow on LSCF after aging for 25 hours at 850°C in synthetic air.²¹

EDS measurements confirmed that the particles on the surface were Sr-rich phases. **Figure 3.2** shows an EDS scan of an aged LSCF sample and the resulting particles. The resolution of the EDS was too low to resolve the smaller particles that grew under certain conditions, but is sufficient to confirm that the particles contain Sr and O.

3.3 Results & Discussion: Cathode Degradation

3.3.1 Effect of Temperature

Operating temperature is a primary contributor to the thermodynamic stability of the LSCF surface and can be used to understand the growth conditions for Sr-based secondary phases in addition to its cause. **Figure 3.3** shows the SrO segregation on the LSCF surface as a function of temperature after aging in synthetic air for 25 hours. The Sr-rich nature of the particles was verified through EDS measurements (**Figure 3.2**). No SrO is detected for the sample aged at 500°C (**Figure 3.3 (A)**), and above 600°C, SrO particles start to form, indicating that thermal energy is one of the key factors that determines segregation kinetics. These particles tend to agglomerate at higher temperatures. Above 800°C (**Figure 3.3 (E)**), some grains exhibited pores that grow with increasing temperature, and the degree of porosity is dependent on crystalline grain orientation. Similar increases in surface roughness and pores have been observed elsewhere but are not discussed in detail.^{79,88–90} These pores were likely formed by Sr diffusing out of the lattice in large quantities and leaving behind pores. It appears that the grain orientation determines the roughness of these grains, suggesting that grains terminated with a Sr plane may allow more Sr to diffuse out of these grains.

The surface morphology of an as sintered LSCF sample (1400°C) is shown in **Figure 3.3 (F)**. Note that there are neither particles nor defects despite the high temperature. The grain boundaries are clearly observed, and the “verticality” shows the growth of each grain. This demonstrates the stability of LSCF stable at high

temperature, and that the SrO segregation can only occur in a specific temperature range.

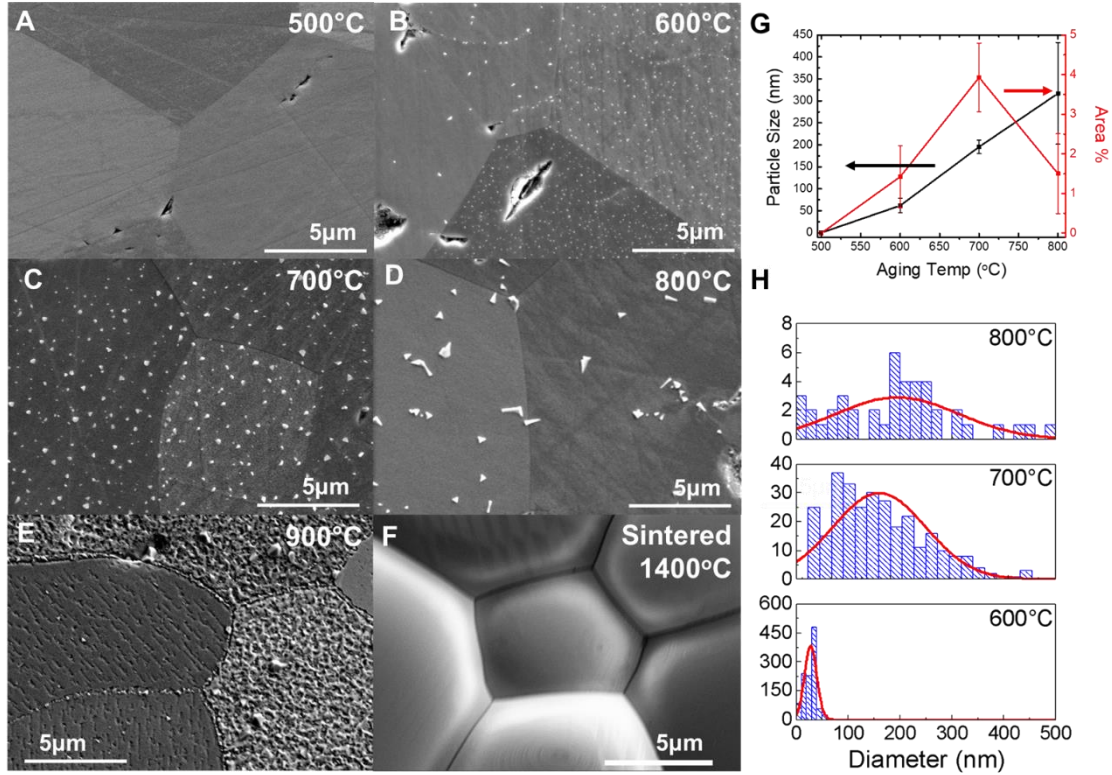


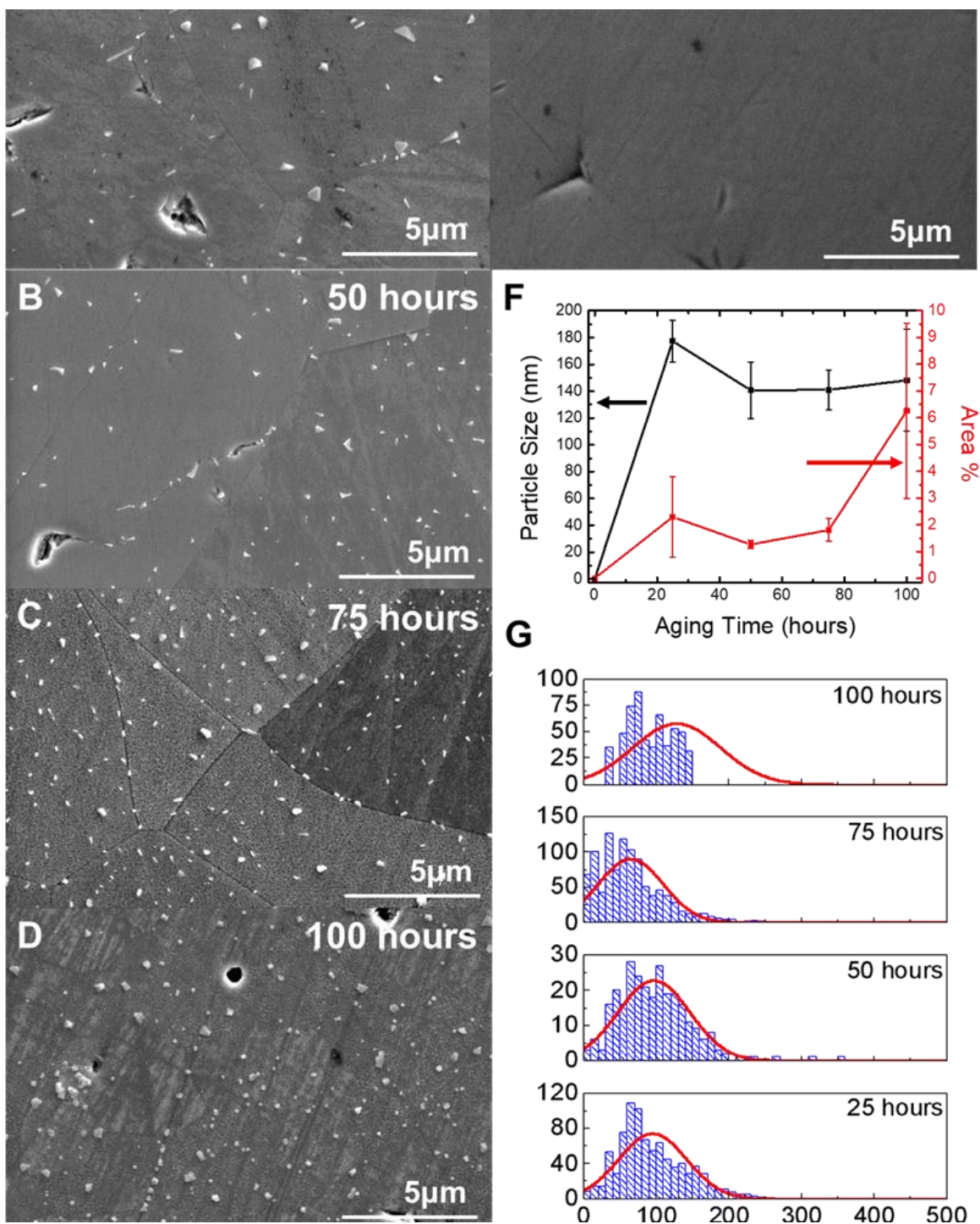
Figure 3.3: Temperature effect on LSCF cation segregation. LSCF dense samples were aged for 25 hours in synthetic air at (A) 500°C, (B) 600°C, (C) 700°C, (D) 800°C, and (E) 900°C. (F) Sintered surface microstructure (G) average particle size and surface coverage as a function of temperature (H) particle size distribution at each temperature.²¹

The particle size and surface Sr coverage as a function of temperature is summarized in **Figure 3.3 (G)**. The precipitated particle distribution at different temperatures is determined using image analysis, as shown in **Figure 3.3 (H)**. Temperature significantly affects the precipitated SrO particle size and quantity. When aged at 600°C, the average particle size is about 60 nm in diameter. The increase in temperature thermally activates surface Sr diffusion and promotes the agglomeration of segregated particles. However, the surface Sr coverage decreases at

800°C, compared to the one at 700°C, as a result of the vertical growth of SrO particle to lower the surface energy. The trend of increasing particle size but not surface coverage with temperature, as seen in **Figure 3.3 (G)**, suggests Ostwald ripening above 700°C. As a result of these pores and the high level of surface coverage, particle size distribution was not done above 800°C.

3.3.2 Effect of Time

Dense LSCF samples were aged at 700°C for different amounts of time to determine the cation segregation kinetics, **Figure 3.4 (A-D)** shows the LSCF surface after each aging time. The amount of surface covered by particles appears to increase significantly in the first 25 hours and subsequently plateau with further aging. As expected, no secondary phase in the unaged sample can be seen on the pristine surface, **Figure 3.4 (E)**. Aging time also appears to increase the maximum particle size and the quantity of particles as shown in the particle size and surface Sr coverage plot in **Figure 3.4 (F-G)**. A similar trend in aging time in air was reported by Niania *et al.*,⁸² in which there was a local minimum in surface area coverage, albeit under different temperatures and pressures. The local minimum at 50 hours may be attributed to Ostwald ripening, which also occurs with increasing temperature, leading to vertical growth of the larger particles and thus less surface coverage.



In addition, grain boundaries became easier to distinguish after aging even when no SrO segregation was observed, which may be the result of thermal etching caused by Sr diffusion through the grain boundaries. Finally, it can also be seen that some grains stand out relative to their neighbors, exhibiting either more numerous smaller particles or fewer larger particles. This is especially clear at 75 hours, **Figure 3.4 (C)**. The effect of grain orientation on secondary phase formation has been observed in other works and is attributed to different defect formation energies for each grain orientation.⁸⁰

3.3.3 Effect of pO_2

To observe effects of gas composition on the surface cation segregation of LSCF, 700°C was chosen as the temperature of interest because temperature effects dominate the surface precipitation above 800°C and the kinetics are too slow below 600°C. The pO_2 effects on the LSCF surface are shown in **Figure 3.5**. The increase in pO_2 , **Figure 3.5 (A-D)**, shows that the amount of SrO particles reaches a maximum at $pO_2=0.21$ atm, (**Figure 3.5 (B)**). In 100 % N_2 , there were no observable SrO particles on the LSCF surface (**Figure 3.5 (E)**). Thus, the lack of available oxygen molecules prevents the nucleation of surface particles. This suggests that without oxygen molecules, Sr nucleation and agglomeration into particles is severely hindered. On the other hand, higher pO_2 (0.5 and 1 atm) did not necessarily create more secondary phase as seen in **Figure 3.5 (F-G)**.

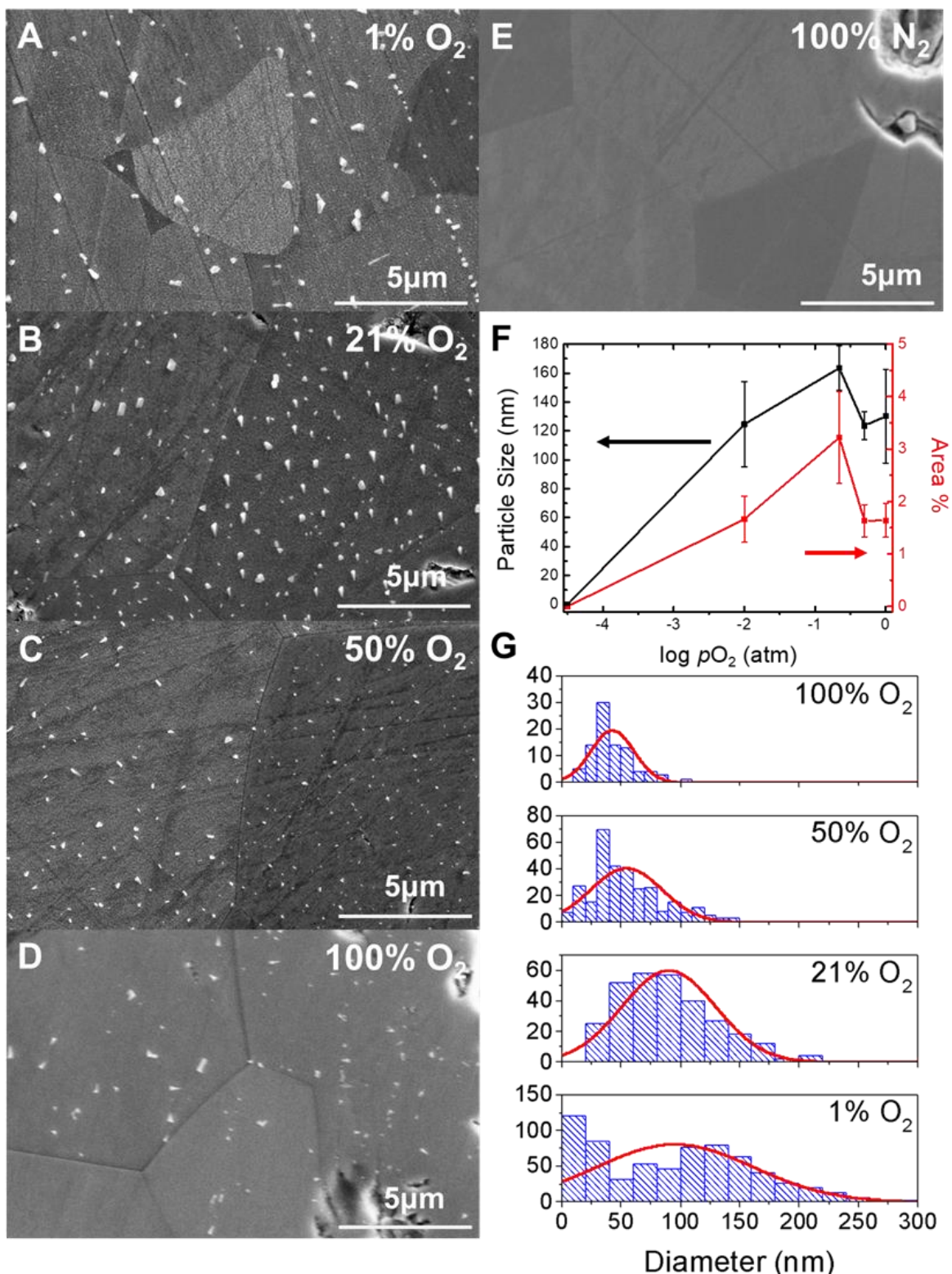


Figure 3.5: pO_2 effect on LSCF cation segregation. LSCF dense samples were aged at 700°C for 25 hours in (A) 1% O_2 (B) 21% O_2 (C) 50% O_2 (D) 100% O_2 (E) 100% N_2 . (F) SrO particle size distribution with different pO_2 's. (G) Particle size and surface coverage of SrO as a function of $\log pO_2$.²¹

The particle size distribution in different pO_2 's is shown in **Figure 3.5 (G)**. The change in pO_2 level directly impacts the size and quantity of SrO segregation. Both the particle size and the Sr surface coverage first increase and then decrease with the increase in pO_2 , as shown in **Figure 3.5 (F)**. Niania et al.⁸² also observed that SrO segregation on LSCF is more pronounced in air than pure O_2 , and they conclude that either H_2O or CO_2 in air is likely the main cause. However, their observations were done in a low-pressure environment possibly influencing the degree of contribution from gas-phase impurities. On the other hand, our results are based on a controlled gas environment where the impurity level of H_2O and CO_2 were clearly accounted for, indicating that pO_2 is the main cause. This pO_2 dependence has a peak around $pO_2=0.21$ atm. This suggests that pO_2 modulates cation segregation and SrO nucleation through multiple mechanisms, which could be the combination of the surface nucleation mechanism or the electrostatic potential that are generated between surface and bulk.^{91,92}

The surface composition after aging LSCF in different gas environments was evaluated using XRD, (**Figure 3.6**) and Raman Spectroscopy (**Figure 3.7**) but did not show significant changes in nearly all aging environments. The XPS Sr 3d spectra of aged LSCF and fresh LSCF were shown in **Figure 3.8 (A)**. Peaks of Sr within the bulk of LSCF lattice along with surface segregated Sr are shown in green and blue, respectively. The peak intensities of these two species have a strong dependence on gas environment. The high intensities of surface segregated Sr peaks indicate that the surface segregation is more severe at that testing condition. We used the ratio of those characteristic peaks to quantify the degrees of surface segregation as a function of

pO_2 , as shown in **Figure 3.8 (C)**, respectively. The black line in the plot represents the ratio for the baseline sample (fresh, unaged LSCF). Samples aged in 1% and 20% O_2 show the highest degree of SrO segregation, which is consistent with the observation from SEM morphologies.

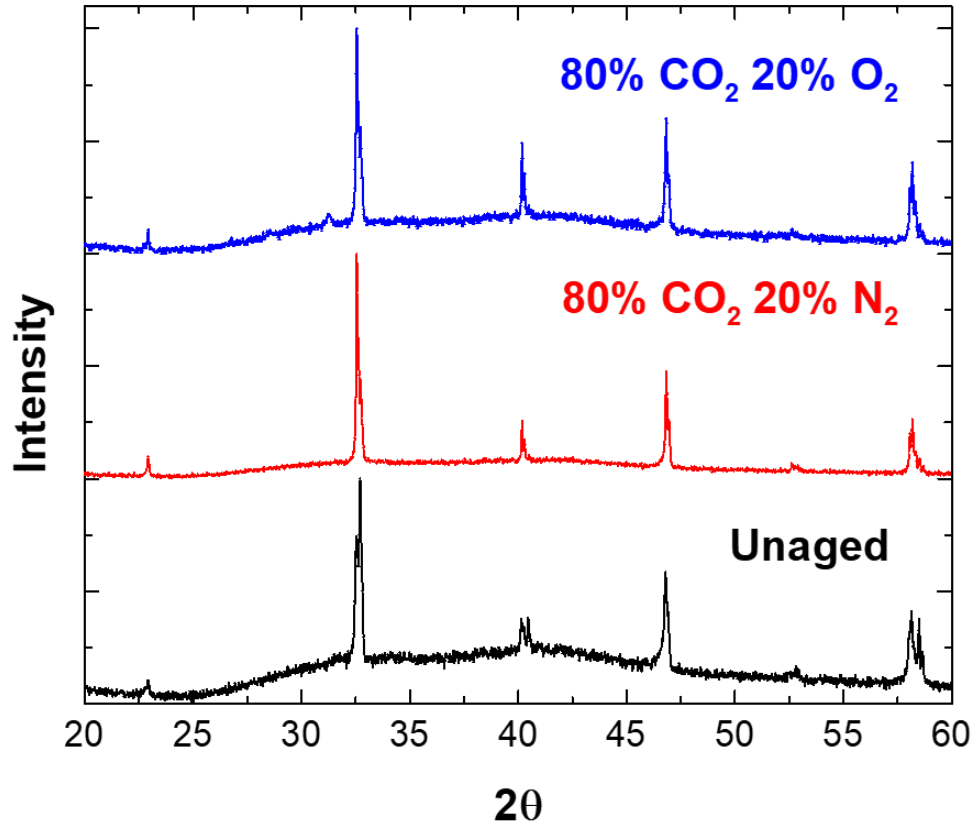


Figure 3.6: XRD of polished unaged LSCF surface and aged for 25 hours in CO_2 gas environment at $700^\circ C$.²¹

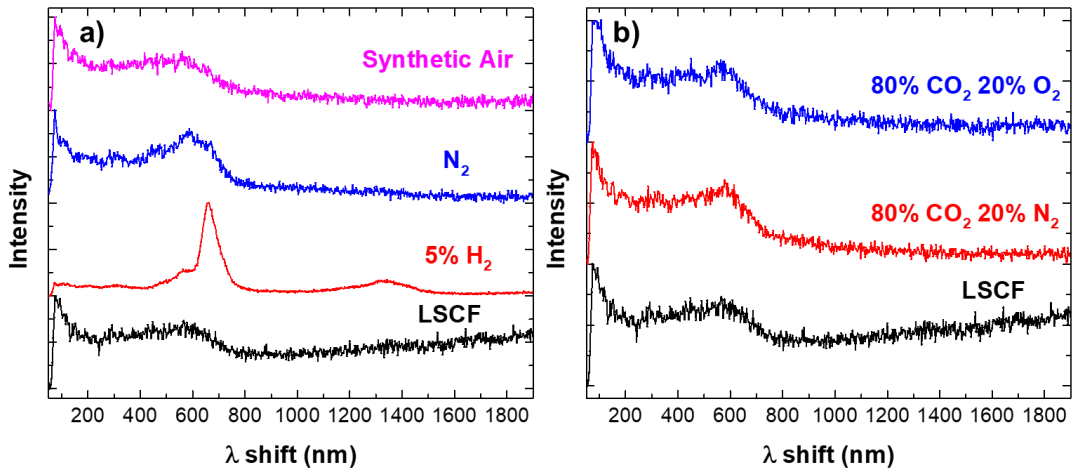


Figure 3.7: Raman spectroscopy of pristine LSCF surface and aged for 25 hours at 700°C in each gas environment (a) without CO₂ (b) with CO₂.²¹

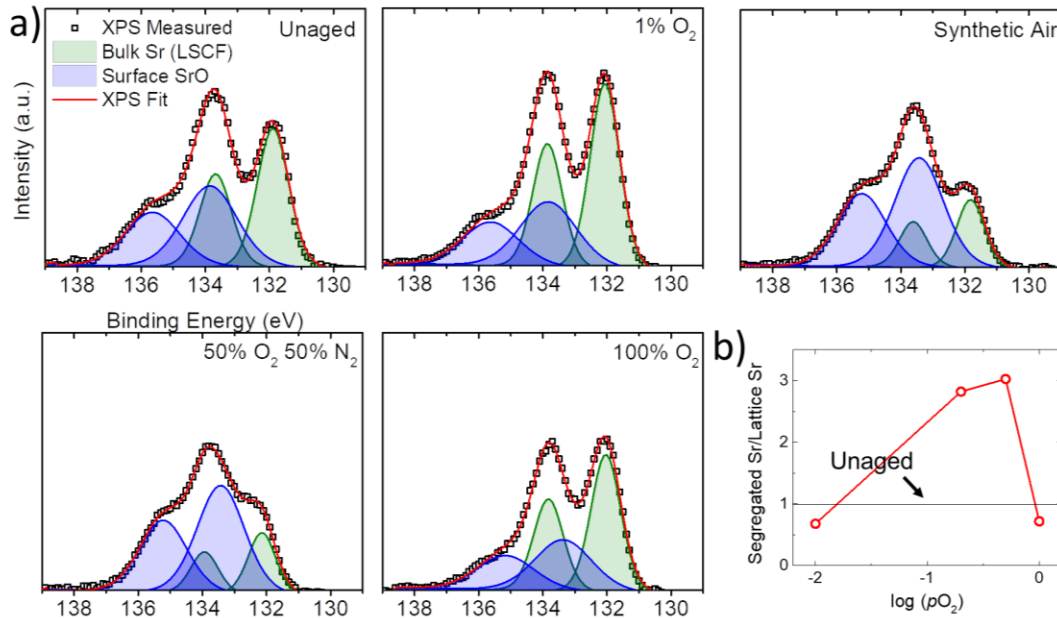


Figure 3.8: Environment effects on surface chemistry of LSCF. XPS of Sr 3d spectra in (A) different O₂ environments and (B) pristine LSCF. LSCF lattice Sr peaks are shown in green and surface segregated Sr peaks are shown in blue. (C) The ratio of surface segregated Sr and Sr in LSCF lattice as a function of O₂. LSCF samples were aged at 700°C for 25 hours in the listed environment.²¹

3.3.4 Effect of $p\text{CO}_2$

Figure 3.9 shows the LSCF surface evolution with varying $p\text{CO}_2$ and corresponding particle size analysis and distribution curves. As the $p\text{CO}_2$ increases from its ambient air value (200-400ppm) to 80% CO_2 (**Figure 3.9 (A)-(F)**), the particle size decreases, except in an O_2 free environment (**Figure 3.9 (F)**). Note that the formation of SrO particles aligns at scratches created during sample polishing, confirming that the defects on the surface are active nucleation sites for Sr segregation, which is consistent with results observed by Niania et al.⁸² The particle size as a function of $p\text{CO}_2$ is shown in **Figure 3.9 (G)**, where an inverse relationship is observed between $p\text{CO}_2$ concentration and the particle size.

This suggests that CO_2 not only promotes the nucleation of SrO but also limits the surface diffusion, or agglomeration, of SrO. The open symbol denotes CO_2 aged samples in 80% CO_2 /20% N_2 (without O_2). In this case, the particles are considerably larger (**Figure 3.9 (F)**). This implies that even when O_2 molecules are absent in the system, the presence of oxygen-containing CO_2 promotes the growth of surface strontium carbonates. Theoretical calculation results also suggest high stability of SrCO_3 in low $p\text{O}_2$ environments.^{93,94} One study on aging LSCF in the presence of CO_2 showed that the LSCF surface Sr segregation became self-limiting in the presence of CO_2 , reaching a steady state only when CO_2 was present.⁹⁵ Thus it is hypothesized that a carbonate layer is formed on the nucleating SrO particles once CO_2 is present, and as the SrO surface is passivated by CO_2 , the agglomeration process is subsequently limited.

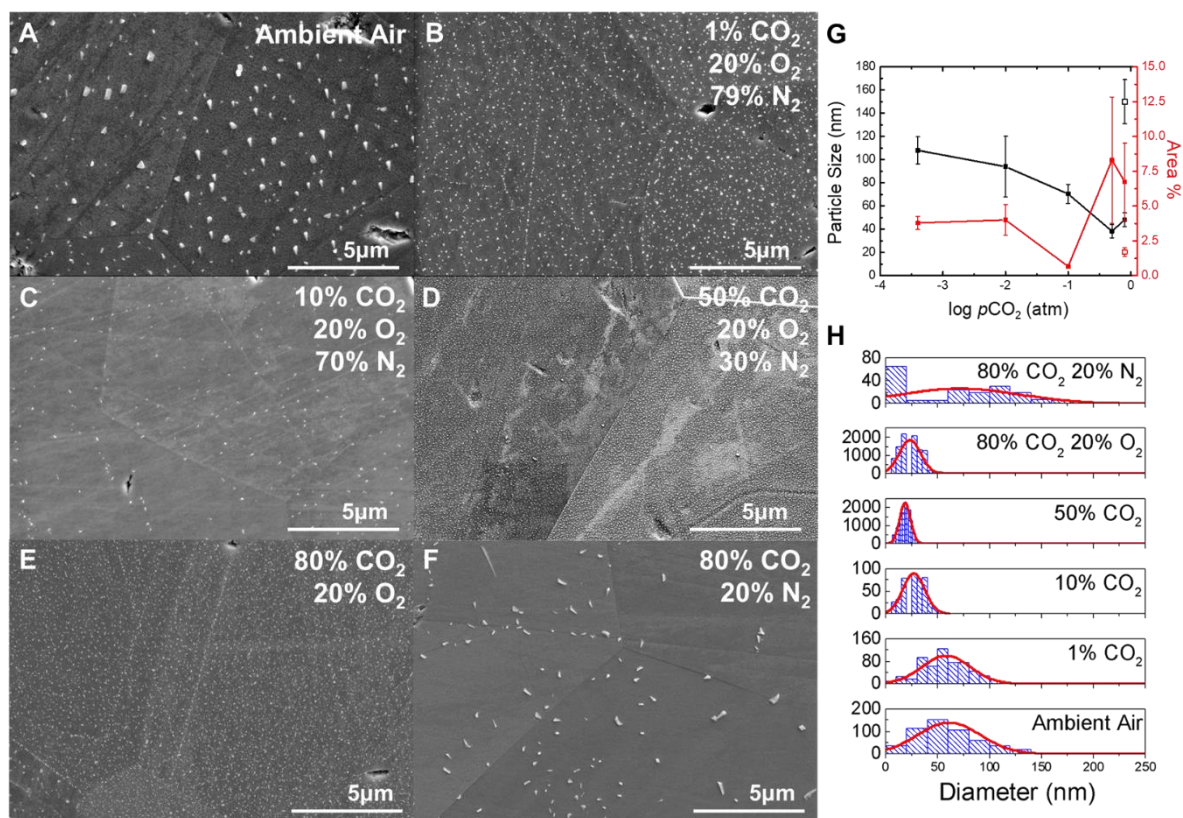


Figure 3.9: pCO₂ effect on LSCF cation segregation. LSCF dense samples were aged at 700°C for 25 hours in (A) ambient air, (B) 1% CO₂/20% O₂, (C) 10% CO₂/20% O₂ (D), 50% CO₂/20% O₂, (E) 80% CO₂/20% O₂ and (F) 80% CO₂/20% N₂. (G) Particle size (nm) and particle quantity (#) as a function of log pCO₂. (H) SrO particle size distribution as different pCO₂'s.²¹

However, CO₂ generally increases the number of particles, suggesting that CO₂ only interacts with segregated Sr rather than the whole surface, blocking agglomeration but not nucleation. The area coverage relationship is less straightforward compared to the one between area coverage and pO₂ but suggests that despite the massive increase in the quantity of particles, their smaller size does not lead to total surface coverage. This is seen in **Figure 3.9 (G)**; the drop in area coverage from 50% CO₂ to 80% CO₂ may be due to particles too small to be quantified. The SrO particle size distribution as a function of CO₂ concentration is summarized in **Figure 3.9 (H)**, and the presence of CO₂ decreases the particle size from over 200 nm to 50 nm, and the quantity of particles

increases from tens to thousands. XPS studies of LSCF aged in CO₂, **Figure 3.10**, show that SrO signals are higher than baseline (**Figure 3.8 B**), suggesting that the presence of gaseous CO₂ molecules actively interact with the surface Sr of LSCF. It is also worth mentioning that despite the much larger particle size observed in the 80% CO₂ with N₂ sample, the 80% CO₂ with O₂ shows a higher degree of Sr segregation according to XPS. The larger particle size may be attributed to the increased stability of SrCO₃ in low pO_2 environments.^{93,94}

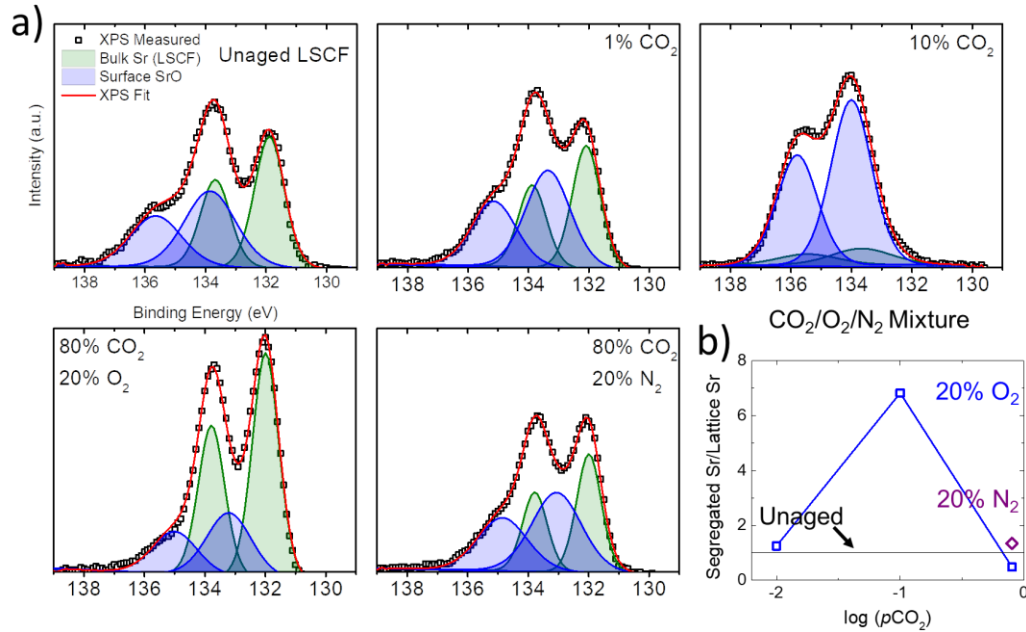


Figure 3.10: Effects of CO₂ on surface chemistry of LSCF. XPS of Sr 3d spectra in (A) different O₂ environments and (B) pristine LSCF. LSCF lattice Sr peaks are shown in green and surface segregated Sr peaks are shown in blue. (C) The ratio of surface segregated Sr and Sr in LSCF lattice as a function of pCO_2 . LSCF samples were aged at 700°C for 25 hours in the listed environment.

3.3.6 Mechanisms of Cathode Degradation

Figure 3.11 (A-B) shows the lattice constant and oxygen non-stoichiometry (δ) as a function of pO_2 respectively. This data is derived from the experimental results that were reported by Fukuda et al.⁹⁶, Kuhn et al.⁹⁷, and Stevenson et al.⁹⁸. The ranges

of δ values at 600°C, 700°C, and 800°C are highlighted in black, red, and blue color bands. The non-stoichiometry of LSCF also affects space charge (electrostatic energy), this can be compared to samples tested at different conditions but with similar δ to examine whether electrostatic energy is the main driving force. This figure indicates that the sample aged at 800°C in synthetic air has a similar δ as the one aged at 700°C between $pO_2=10^{-2}$ and 10^{-4} atm. However, these samples yield different degrees of segregation, suggesting that the difference in δ might also not be directly related to the main driving force. This indicates that gaseous oxygen-containing molecules, solid-state defect chemistry of oxides, and the surface free energy are the three main factors controlling the segregation level. **Figure 3.11(C)** shows the proposed mechanism behind Sr surface segregation. The intensive variables, temperature and pO_2 , control the thermodynamic status of segregation. At low temperature (<500°C), there is insufficient thermal energy for significant amounts of segregation. While, at high temperatures (1400°C), no cation segregation takes place because the free energy of La-Sr-Co-Fe-O in its perovskite phase is lower.⁹⁹

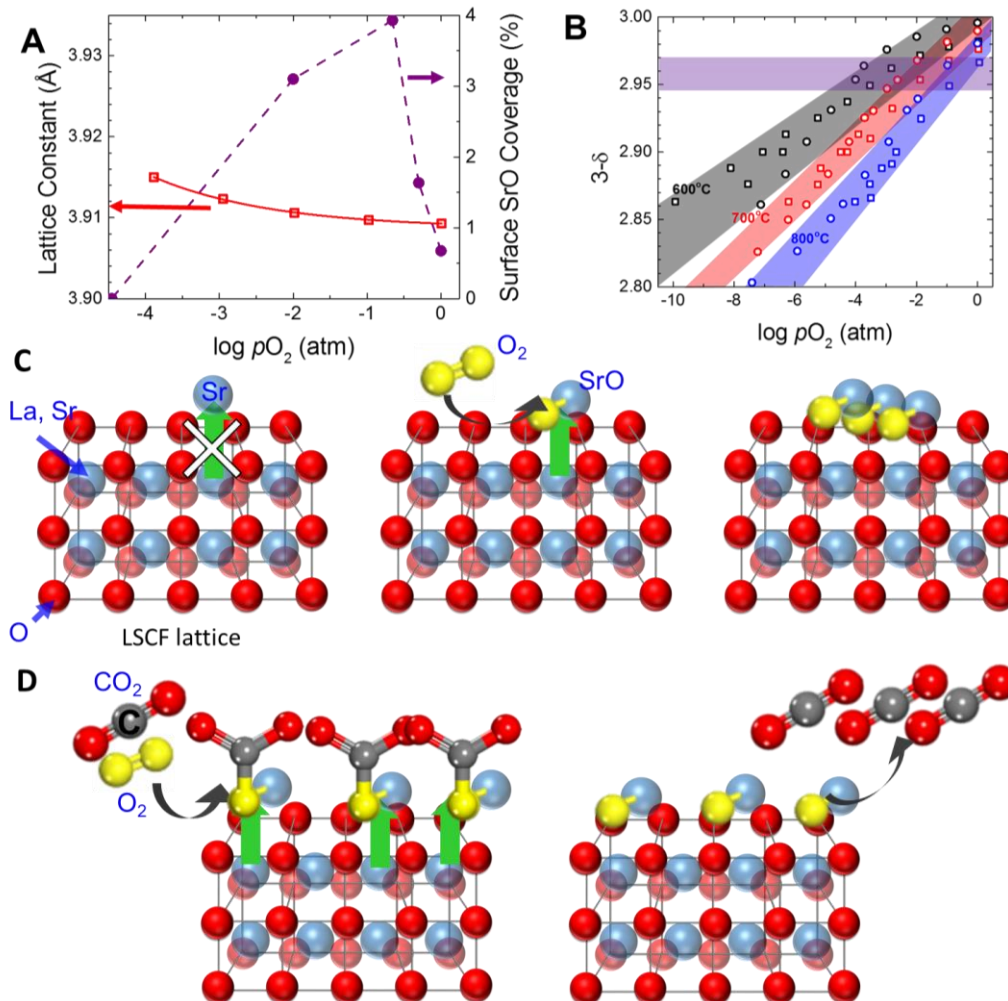


Figure 3.11: Possible driving forces and cation segregation mechanism. (A) Lattice constant and surface coverage as a function of pO_2 . The red square shows the lattice constant of LSCF.⁹⁷ The purple circle symbols represent SrO surface coverage of LSCF aged at 700°C in different pO_2 's for 25 hours. **(B)** Non-stoichiometry as a function of pO_2 . The color bands represent different oxygen stoichiometry zone of LSCF at different temperatures. The region highlighted in purple is the oxygen stoichiometry of interest ($\delta = 0.03-0.06$), which are achieved at 800°C in synthetic air or at 700°C between $pO_2 = 10^{-1}$ to 10^{-4} atm. **(C)** O_2 and CO_2 effect on nucleation. Sr diffusion is mitigated once no oxygen-containing gaseous species are present. SrO nucleation occurs once O_2 is present, promoting the diffusion, nucleation, and eventually agglomeration. **(D)** O_2 and CO_2 effect on growth. Carbonates are formed with the presence of CO_2 , which limit the surface migration.²¹

Significant presence of oxygen-containing molecules in the environment creates an oxygen chemical potential between the bulk and surface causing a driving force for ion diffusion. These surface molecules also react with diffused Sr cations and

nucleate into particles at the surface. At high pO_2 case, it is hypothesized that the presence of oxygen reduces surface particle growth because of the defect chemistry. Here, the lower δ value, and higher concentration of lattice oxygen stabilizes lattice Sr through coulombic interactions. This stabilizing effect, was reported by Ding et al.⁸¹ and Oh *et al.*,⁶⁴ should explain the reduced particle formation. After Sr segregation, SrO moves freely on the surface and tend to agglomeration into larger particles.

Once CO₂ is present, the particle size of segregated SrO decreased dramatically. Experiments on LSF and LSCF suggest that CO₂ passivates their surface and block reactions. In this scenario it is likely that SrCO₃ forms as transient intermediate SrCO₃ as in **Figure 3.11 (D)**.^{94,95} Since CO₂ preferably adsorbs onto the Sr sites, it creates the oxygen chemical potential at the surface and promotes the nucleation process through the formation of carbonates. These intermediate carbonates tend to limit the surface migration of Sr-containing species, causing the isolated particles. In this way, the presence of CO₂ was used to track the development of segregated particles.

3.3.7 Mitigation of Cathode Degradation

To understand the A-site stoichiometry effect on cation segregation, A-site deficient (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O₃ (LSCF095) was also aged in the same conditions as the stoichiometric LSCF. The surface morphologies of aged LSCF095 in different pO_2 and pCO_2 environments is shown in **Figure 3.12**. The deficiency in A-site stoichiometry of LSCF successfully suppresses SrO segregation in different pO_2 's, as shown in **Figure 3.12 (A-B)**, compared to stoichiometric LSCF in **Figure 3.5 A & C**. This suggests that the presence of O₂ and available Sr cations on the surface are needed to initiate SrO nucleation. However, A-site deficiency shows no effect on CO₂ induced

cation segregation compared to A-site stoichiometric LSCF, as shown in **Figure 3.12** (C). This evidence shows that gaseous CO₂ molecules actively promote SrO nucleation.

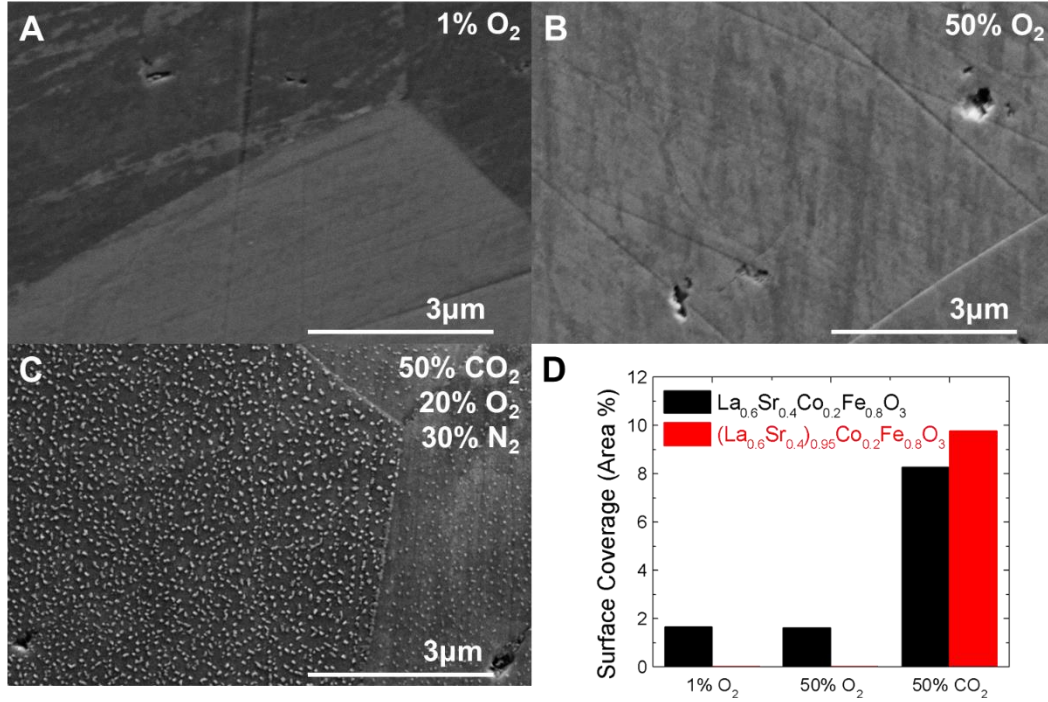


Figure 3.12: A-site stoichiometry effect on LSCF cation segregation. A site deficient (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O₃ (LSCF095) dense samples were aged at 700°C for 25 hours in (A) 1% O₂, (B) 50% O₂, (C) 50% CO₂ (balanced with 20% O₂, 30% N₂) with (D) a higher magnification.²¹

3.4 Degradation in Next Generation Cathodes

In addition to studying LSCF, this experimental approach was extended to Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC), which is a more recently developed cathode material compared to LSCF. **Figure 3.13** shows the microstructure of SSC aged at 700°C in synthetic air as a function of time. Although both LSCF and SSC are perovskites, they clearly have different degradation mechanisms. Rather than particles nucleating on the entire surface, there are distinct grains in which the majority of cation segregation takes place. **Figure 3.13 (A-B)** show two such grains at 12 and 25 hours respectively. Some particles are visible elsewhere, but the majority are nucleating

inside these grains. Over time they become more defined and eventually particles coat the entire surface as seen in **Figure 3.13 F**. Although LSCF also showed that particle growth was dependent on grain orientation, it was not nearly to this extent. It is also clear that the presence of grains that drive cation segregation complicates the quantification of particle growth and surface coverage on the SSC surface.

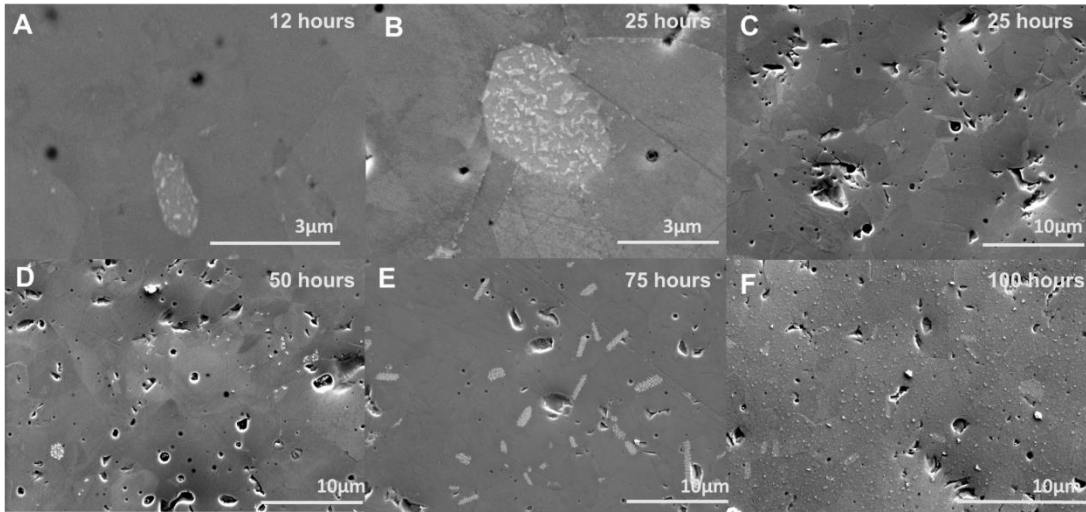


Figure 3.13: Aging time effect on SSC cation segregation at 700°C. Dense SSC samples were aged at 700°C for (A) Select SSC grain after 12 hours, (B) Select SSC grain after 25 hours, (C) SSC surface after 25, (D) 50, (E) 75 and (F) 100 hours in synthetic air.

To determine the mechanism of cation segregation in SSC, the relationship between pO_2 and microstructure was studied as well. **Figure 3.14** shows the effect of pO_2 on the SSC surface aged at 700°C in synthetic air for 25 hours. Again, there are some major differences compared to LSCF. In the case of SSC, the lack of oxygen did not inhibit the growth of surface particles, as seen in **Figure 3.14 (A)**. Although particles as well as grains are observed at all pO_2 values, it is shown that increasing pO_2 will reduce particle growth. There were also no significant differences between ambient and synthetic air. Since the growth of particles is not dependent on the presence of oxygen, then the mechanism for particle growth in SSC must also be

different than in LSCF. A review of the literature on SSC degradation showed that this degradation mechanism has not been reported in prior work.

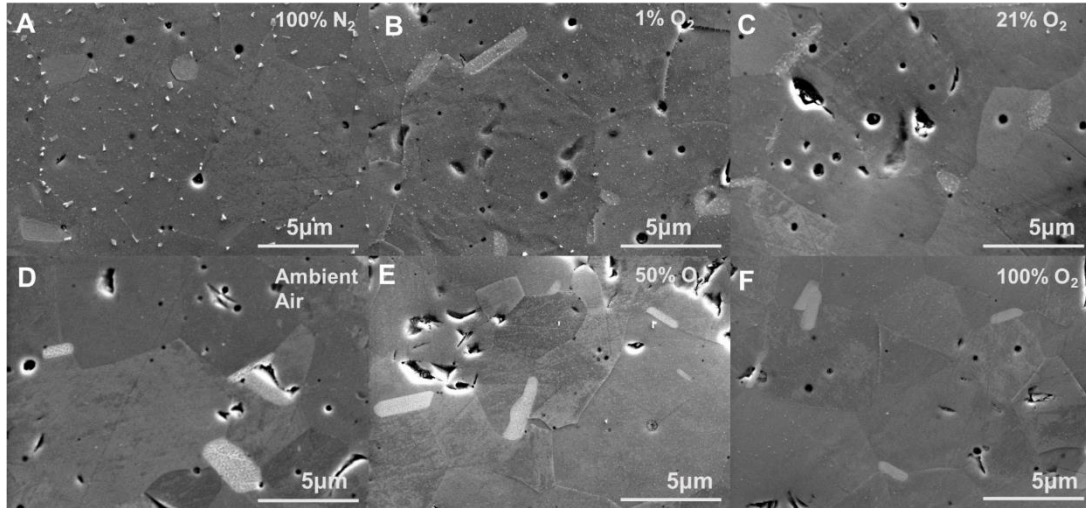


Figure 3.14: pO₂ effect on SSC cation segregation. LSCF dense samples were aged at 700°C for 25 hours in (A) 100% N₂ (B) 1% O₂ (C) 21% O₂ (D) Ambient air (E) 50% O₂ (F) 100% O₂

Analysis of the surface chemistry of aged SSC was performed with EDS.

Figure 3.15 shows EDS mapping of two aged SSC samples, one with small surface particles and one with large ones. In both scans, the grains that drive cation segregation are visible and were shown to be rich in Sm instead of Sr, which was entirely unexpected. Unfortunately, the EDS did not have enough resolution to determine the composition of the particles. The rest of the SSC surface seemed to contain an even distribution of all the elements. This suggests that the particles are a Sr-rich secondary phase, formed by the diffusion of Sr out of the grains and onto the surface. As a result, the Sm stayed in the grains which explains why they have a greater concentration of Sm. Since cation segregation in SSC seems to be more restricted to specific grains, that could be why SSC is regarded as a more stable cathode than LSCF.⁹⁹

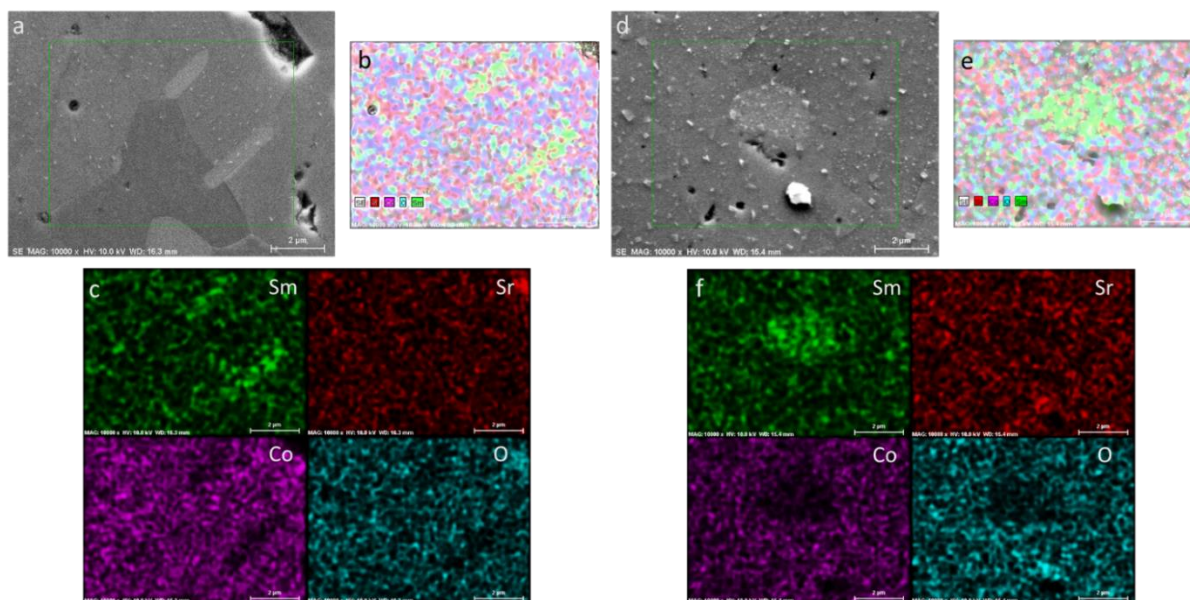


Figure 3.15: EDS study of SSC aged in 1% O₂ for 25 hours at 700°C (a) SEM image (b) EDS mapping (c) Elemental mapping & EDS study of SSC aged in synthetic air for 100 hours at 700°C (d) SEM image (e) EDS mapping (f) Elemental mapping

To determine the effect of grain orientation on cation segregation, EBSD was performed on aged SSC to determine the orientation of select grains. **Figure 3.16** shows the electron backscatter diffraction (EBSD) mapping of SSC aged for 100 hours at 700°C. Unfortunately, the mapping of grain orientation did not clearly determine the orientation of the grains that promoted cation segregation. This was attributed to insufficient polishing and sample drift. Since the composition of the particles was also undetermined, an in-depth study on the mechanism of cation segregation in SSC would require more advanced characterization techniques such as TEM. And it would have to be done on cathodes aged in many different conditions and quantifying particles on each grain may be required.

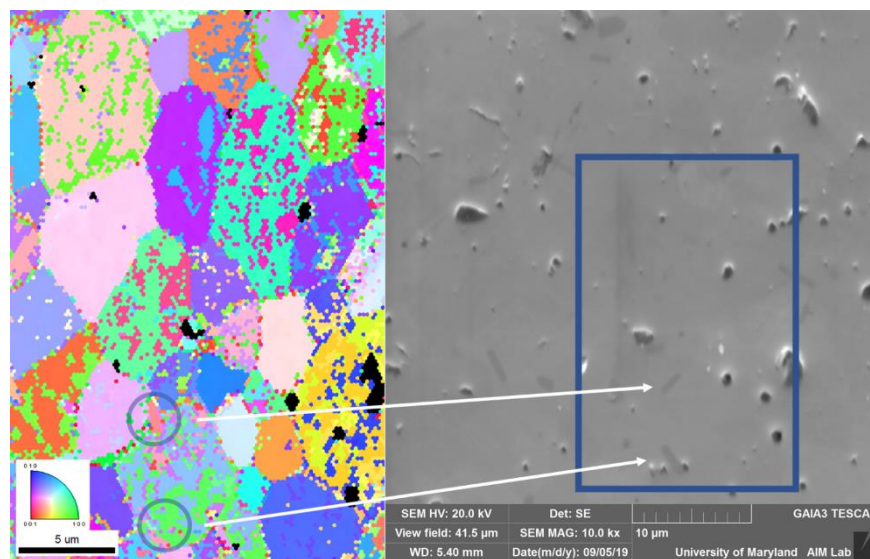


Figure 3.16: Electron Backscatter Diffraction mapping of dense SSC aged for 100 hours in ambient air at 700°C.

3.5 Modifying Next Generation Cathodes

The focus shifted to determining ways to mitigate the cation segregation in SSC rather than determination of the mechanism. While there exists a good deal of literature on LSCF with A-site deficient compositions, this has not been extended to SSC, despite it being a well-studied material. SSC-GDC composite cathodes were evaluated using symmetric cells. The compositions tested reflect those used for A-site deficient LSCF, which typically have 5% less La and Sr than the original LSCF.

First, these new compositions were synthesized with the sol-gel method.

Figure 3.17 shows the XRD spectra of synthesized A-site deficient SSC compositions. Each of them was successfully synthesized without any additional phases and have the same perovskite crystal structure. The insert, **Figure 3.17 (B)**, shows a magnified image of the primary peak. A small degree of peak shift is visible but there are no major differences between the compositions.

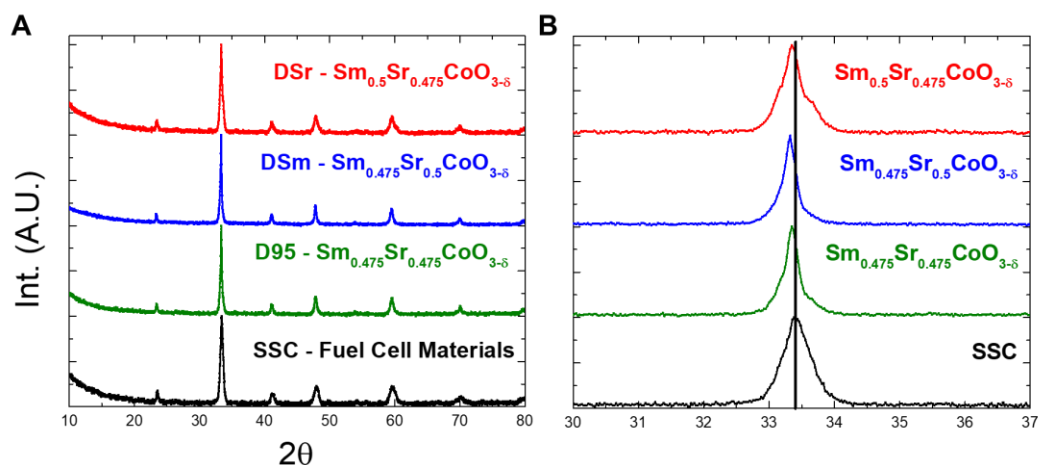


Figure 3.17: XRD spectra of commercial SSC in comparison with sol-gel synthesized A-site deficient SSC. (A) Full XRD spectra (B) Magnified image of primary peak.

The synthesized powders were used alongside commercial GDC powder to make composite cathodes and coated onto GDC symmetric cells. **Figure 3.18** shows the EIS spectra and long term stability of SSC-GDC symmetric cells with standard and A-site deficient SSC. The EIS spectra in **Figure 3.18 (A)** shows that there is no significant difference between the standard and A-site deficient SSC. While there was

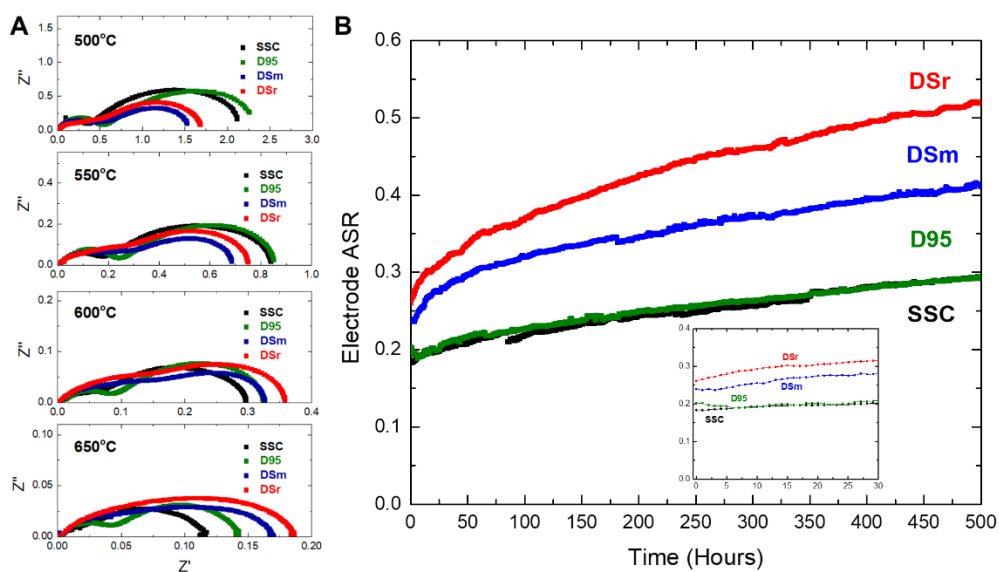


Figure 3.18: (A) EIS spectra of SSC-GDC cathodes on GDC symmetric cells at different temperatures. (B) Electrode impedance derived from EIS measurements as a function of time at 625°C for the symmetric cells in ambient air.

modest reduction in impedance at lower temperatures, this improvement was gone at 600°C and above. **Figure 3.18 (B)** shows the long term stability of each symmetric cell aged at 625°C in ambient air. The SSC deficient in both A-site elements was more stable than the other 2 compositions. However, it did not show better stability compared to base SSC. Though this approach was unsuccessful in improving the stability of SSC, the D95 composition had the same degradation rate demonstrating that SSC has a fundamentally different mechanism driving cation segregation.

Preliminary studies were done on the A-site deficient compositions to determine if the change in composition would affect the surface microstructure. **Figure 3.19** and **Figure 3.20** show the microstructure of SSC, D95, and DSm aged at 600°C in pure nitrogen and pure oxygen respectively. Pure nitrogen did not prevent particle growth and all compositions showed heavy amounts of particle nucleation. Grains with heavy cation segregation are seen in **Figure 3.19 (A)**, **Figure 3.20**, and **Figure 3.20 (B)**. All images show similar particle size distributions regardless of composition and gas environment. Thus A-site deficiency was not an effective way to mitigate cation segregation if applied to SSC.

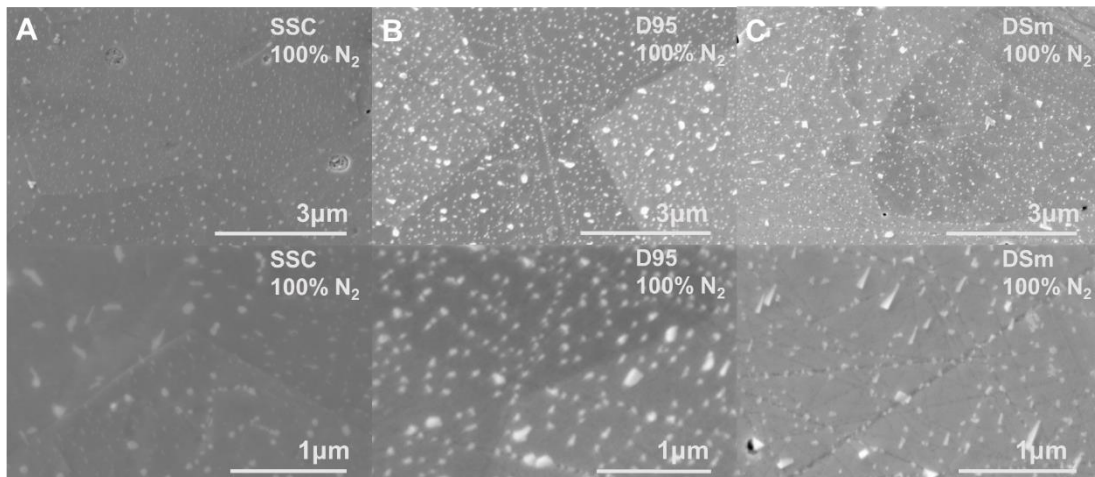


Figure 3.19: Different SSC compositions aged at 600°C in 100% N₂ for 25 hours, seen at two magnifications. (A) SSC (B) Sm_{0.475}Sr_{0.475}CoO₃ (C) Sm_{0.475}Sr_{0.5}CoO₃

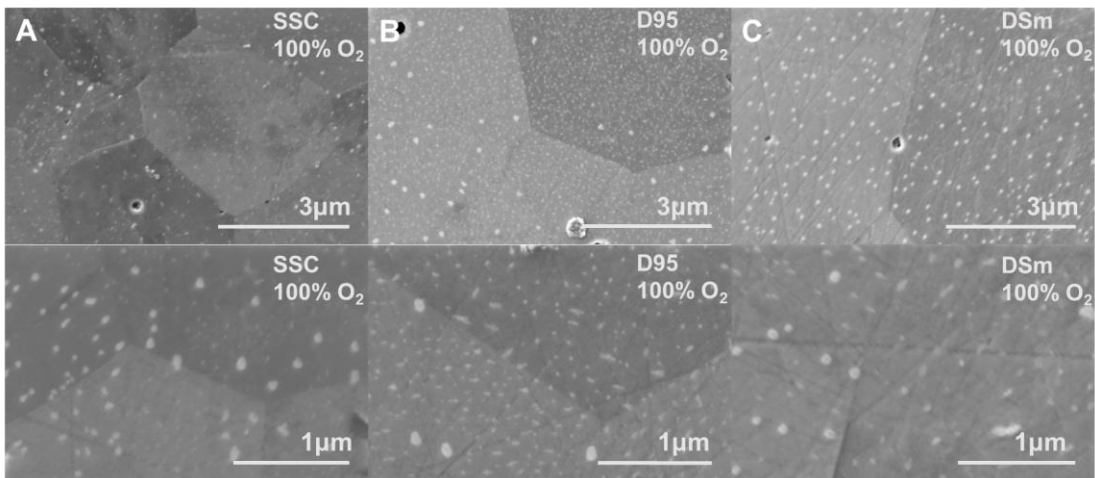


Figure 3.20: Different SSC compositions aged at 600°C in 100% O₂ for 25 hours, seen at two magnifications. (A) SSC (B) Sm_{0.475}Sr_{0.475}CoO₃ (C) Sm_{0.475}Sr_{0.5}CoO₃

3.6 Conclusion: Cathode Degradation

The LSCF surface microstructure after aging was found to vary greatly based on aging conditions of temperature, aging time, pO_2 , and pCO_2 . As expected, increased temperature and aging time drive surface SrO segregation, with the overall trends suggesting Ostwald ripening. The grain orientation is seen to impact the degree of

segregation. Sufficiently high temperatures also coarsen of the SrO particles and form pores on the surface because of significant amounts of Sr diffusing out of the lattice. A volcano-like trend in SrO segregation as a function of pO_2 is observed on LSCF, which is shown to be more stable in a pure O_2 or inert environment, such as N_2 . Lack of O_2 reactants at low pO_2 and the low oxygen vacancy concentration at high pO_2 are likely the causes of the decrease in SrO segregation level. Unfortunately, maximum SrO segregation occurs at around the pO_2 of air.

Gas phase impurities also affect SrO particle nucleation. The size of segregated particles is strongly influenced by pCO_2 , as the formation of carbonate intermediate species on the surface limit the mobility. Increasing pCO_2 seems to affect the mechanism of SrO aggregation while promoting SrO precipitation. The presence of CO_2 in the environment may cause preferential formation of $SrCO_3$ rather than SrO, and this $SrCO_3$, if formed, does not agglomerate to the same extent as SrO. A-site deficiency can limit SrO segregation, but once CO_2 is present, A-site deficiency has little to no effect on preventing cation segregation.

Extending this approach to other cathode materials showed that different compositions are subject to different mechanisms of degradation. In the case of SSC, it was far more dependent on grain orientation than LSCF, making the mechanism for cation segregation in SSC more difficult to determine. Unfortunately, applying the same methods used to improve the stability of LSCF was unsuccessful when used for SSC.

Chapter 4: Cathode Surface Modification

4.1 Overview of Atomic Layer Deposition

Surface modification of SOFC cathodes is a common way to improve their performance. One such method, atomic layer deposition (ALD) has been used to coat/deposit SOFC cathodes to enhance their performance through very thin films with the goal of blocking cation segregation and/or improve activity.^{100,101} The primary advantages of ALD for coating electrodes are its conformal nature and high control over coating thickness.¹⁰² ALD is widely used in the semiconductor industry for producing substrates, sensors, and microelectronics.

ALD is able to deposit a single self-limiting layer of a given material per cycle. This means that coating thickness can be precisely controlled. **Figure 4.1** shows a diagram of the 4 steps that make up a single ALD cycle. During ALD, first, the metallic precursor is exposed to the substrate allowing it to react with the surface but not adsorbed molecules. This precursor is a highly reactive metal-organic compound that will react with almost anything, but not with itself. Next, the excess precursor is purged with an inert gas. Then, the oxidizer is pulsed, allowing it to react with the adsorbed precursor, converting the exposed surface from a metal precursor into a metal oxide. Finally, the oxidizer is purged before the cycle repeats.

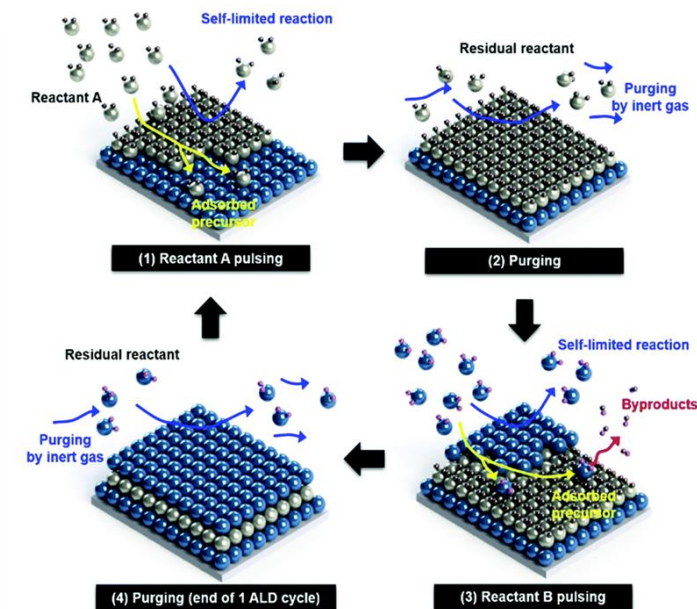


Figure 4.1: Diagram showing the 4 steps of the Atomic Layer Deposition Cycle.¹⁰³

Through a conformal coating, the impact on the cathode surface and thus the TPB is maximized. Discrete particles, such as those formed by solution infiltration, do not benefit the entire surface and may be subject to coarsening and morphology changes at high temperatures.¹⁰⁴ Unlike other conformal deposition processes, the chemistry behind ALD is self-limiting and as a result provides a fine degree of control over the coating thickness. This avoids depositing films that totally block gas diffusion with the cathode surface. Also, controlling the film thickness allows deposition of a film with ideal chemical and physical properties for a given application.^{105–107}

While ALD has been demonstrated to successfully enhance the performance of cathodes, this is not always the case. Recent studies show varying effects on electrode performance despite coatings of the same composition. Deposition of ZrO_2 was observed to enhance cathode performance in some works, but not others.^{101,108} The same discrepancy was observed with CoO_x deposition.^{100,109} These discrepancies are

due to the large number of variables in the deposition process. Differences in reactor type, ALD precursors, deposition conditions, as well as the cathode's microstructure and composition, can all contribute to the effect of the ALD coating on cathode performance. While a full study of each parameter is beyond the scope of this work, the review paper by Onn et al. provides an overview of the challenges in adapting ALD to porous substrates.¹¹⁰ This is further complicated by additional processes which may occur at testing temperatures such as cation segregation, phase changes of the films and microstructural evolution.^{111,112}

Here, the focus was on determining the effects of specific deposition parameters on cathode performance. Oxygen vacancies are also known to contribute to the ORR activity of cathode materials.^{113,114} The effect of oxygen vacancies on thin film properties has already been studied for other applications such as sensors and photoelectrodes.^{4,115,116} The use of a stronger oxidizer such as ozone instead of water results in more crystalline films with fewer oxygen vacancies and other defects. Annealing films without oxygen has also been used to tune the properties of thin films.^{117–119}

There are many variables within the ALD process, which complicates its application for modifying fuel cell electrodes. **Figure 4.2** shows a summary of the variables during the ALD process and the film properties that they influence. Intrinsic variables can be adjusted but are primarily optimized around the reactants, substrates, and ALD system. These may differ widely between different groups. On the other hand, post deposition annealing, and choice of oxidizer are independent of the equipment differences between labs. Thus, testing whether these could tune the performance of

ALD coated cathodes would be more valuable than simply reporting high performance cathodes.

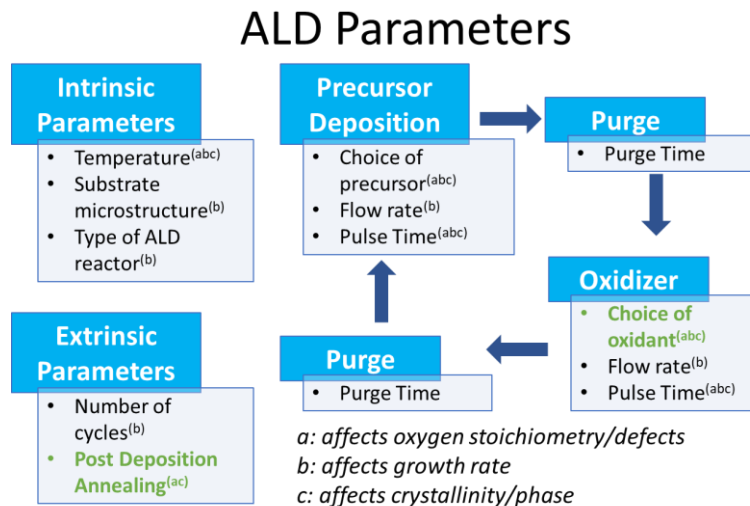


Figure 4.2: Diagram of parameters during each step of the ALD process and their impact on the properties of the deposited film.

4.2 Sample Preparation: Cathode Surface Modification

4.2.1 Symmetric Cell Fabrication

To fabricate the symmetric cells, pellets of GDC (Fuel Cell Materials) were made by pressing the GDC powder in a die and sintering at 1350°C. The pellets were briefly polished to remove any contamination and were then blade coated on both sides with an LSCF-GDC ink. This ink consisted of LSCF6428 powder (Praxair) in a 1:1 surface area ratio with GDC powder that was ball-milled together. ESL 441 (Ferro Scientific) was added to the mixture which was then dried in a Thinky centrifugal mixer. Finally, the cathode layers were then fired at 1080°C for 4 hours. The procedure for fabricating and testing full cells is discussed in detail in **Section 5.2**

4.2.2 Atomic Layer Deposition

The ALD was performed in a Beneq 500 ALD system, which is a flow based reactor using N_2 . Depositions of TiO_2 and ZnO were both performed at $150^\circ C$ for 16 cycles each, while V_2O_5 was deposited at $175^\circ C$. The steps of the cycle were a 1 second pulse time of precursor, a 10 second purge, 1 second pulse of oxidizer, followed by another 10 second purge. The precursors tetrakis(titanium) (TDMAT), diethylzinc (DEZ), and vanadium oxytriisopropoxide (VTOP) were used for TiO_2 , ZnO , and V_2O_5 respectively, while water and ozone were the oxidizer gases. Since ALD is a conformal process both sides of the symmetric cells had to be coated at once, while the cathode for full cells had to be coated while the anode was covered. This was achieved by using Kapton tape to cover openings. **Figure 4.3** shows the arrangement of both sample types inside the ALD chamber.

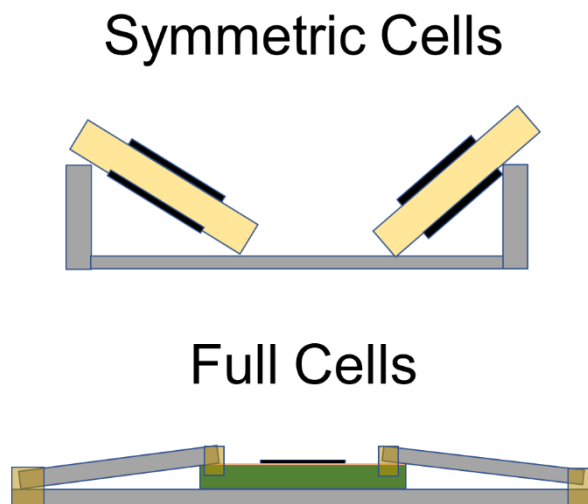


Figure 4.3: Diagram showing placement of symmetric cell and full cell within the ALD chamber.

4.2.3 Characterization Methods

Cells undergoing testing were coated with gold paste (Heraeus) on the electrodes and placed between gold mesh layers held by adjustable ceramic plates.

These plates were situated in a closed environment reactor. The conductivity of the pellet was measured by electrochemical impedance spectroscopy (EIS) using a 1470E Cell Test System (Solartron) with a 1455A Frequency Response Analyzer (Solartron). DRT measurements were performed on the EIS data using the DRT Tools software package with a λ (regularization parameter) value of 10^{-4} .³⁶

4.3 Results & Discussion: Cathode Surface Modification

4.4.1 Effect of Different Film Compositions

The metal oxides tested at the FabLab were TiO_2 , ZnO , and V_2O_5 . **Figure 4.4** shows the effect of 25 cycles of ALD for each metal oxide. Vanadium oxide was expected to enhance ORR activity due to its multivalent nature. TiO_2 is known to have oxygen vacancies and was expected to form SrTiO_3 in the presence of segregated Sr cations, which would be less insulating than SrO on the cathode. ZnO has been shown to improve the performance of LSCF through doping and can exhibit ORR activity when doped with Co or Fe.^{120,121} Ideally, it could achieve a similar affect through film-substrate interaction or interlayer diffusion with LSCF. Vanadium exhibited significantly worse performance, which is attributed to oxygen bonding to the film instead of reducing and being incorporated into the cathode. The other two materials showed better or comparable performance to the LSCF baseline, so they warranted further testing.

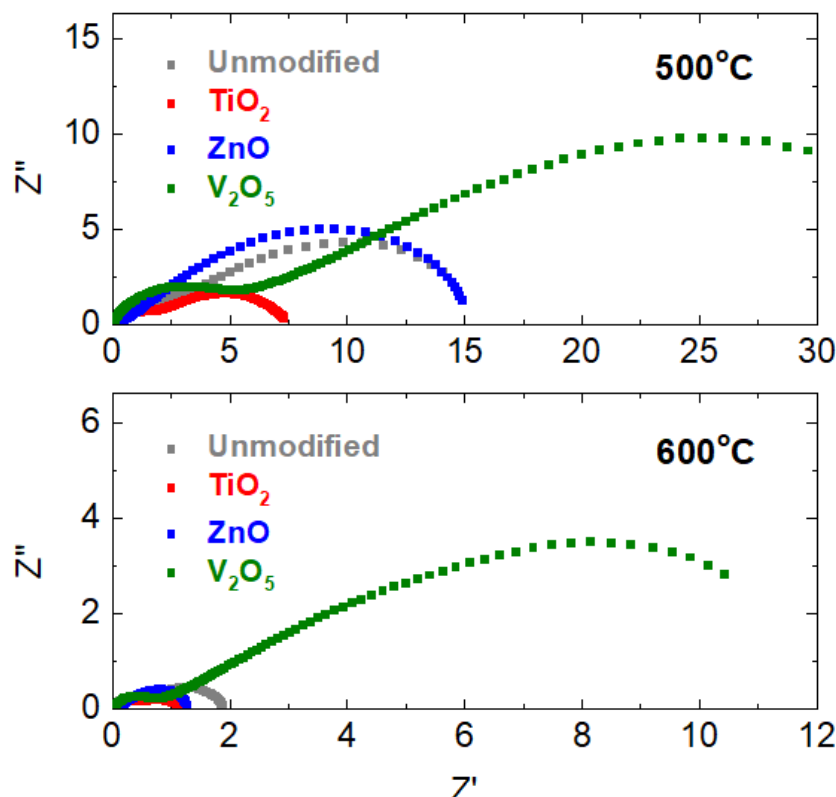


Figure 4.4: EIS spectra of symmetric cells with LSCF-GDC cathodes with and without ALD coatings. 25 layers of TiO_2 was deposited at 150°C using water as oxidizer and TDMAT as precursor. 25 layers of ZnO was deposited at 150°C using water as oxidizer and DEZ as precursor. 25 layers of V_2O_5 was deposited a 175°C using ozone as oxidizer and VTOP as precursor.

4.3.2 Effect of Film Oxidizer

Figure 4.5 shows the effect of on switching the oxidizer when depositing TiO_2 films. Ozone results in a coating with a lower concentration of $\text{V}_\text{O}^{\bullet\bullet}$ which is expected to reduce the ORR kinetics of the cathode. At low temperatures this difference between the two films is clearer, suggesting that the TiO_2 films crystallize at higher temperatures. This does correspond to the reported temperature of anatase formation in thin films.^{111,122,123} At higher temperatures, there was no significant difference between the two films, demonstrating that high temperatures undo any differences in defects once the films change phase.

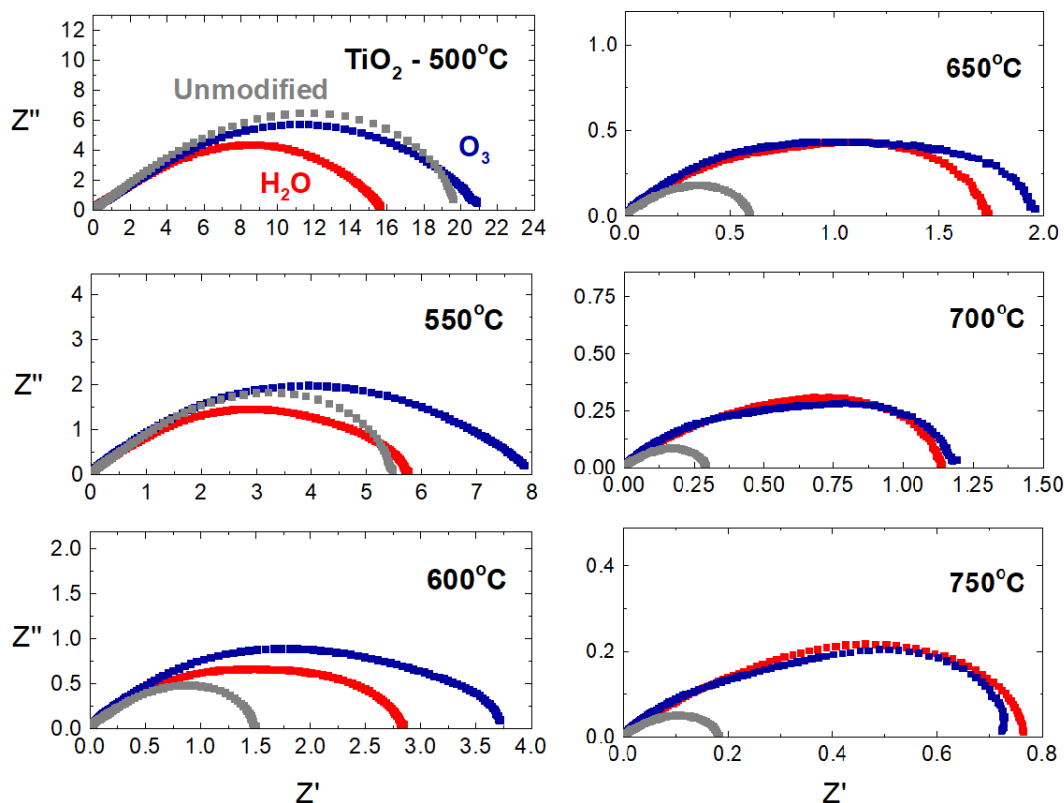


Figure 4.5: EIS spectra of symmetric cells with 25 layers of TiO_2 deposited at 150°C . One with water and one with ozone.

Figure 4.6 shows the differences in oxidizer for ZnO films. In the case of ZnO, both films were able to improve the performance of LSCF, and ozone oxidized film consistently showed higher impedance than the water oxidized one. The reduction in impedance compared to the uncoated LSCF was greater at lower temperatures but this effect did not go away at high temperatures. ZnO is known to crystallize below 600°C , yet there was still a difference in performance between the two films.¹²⁴ Since, both impedance curves had the same shape with only a difference

in size, the difference in performance is attributed to differences in film thickness caused by the oxidizer.

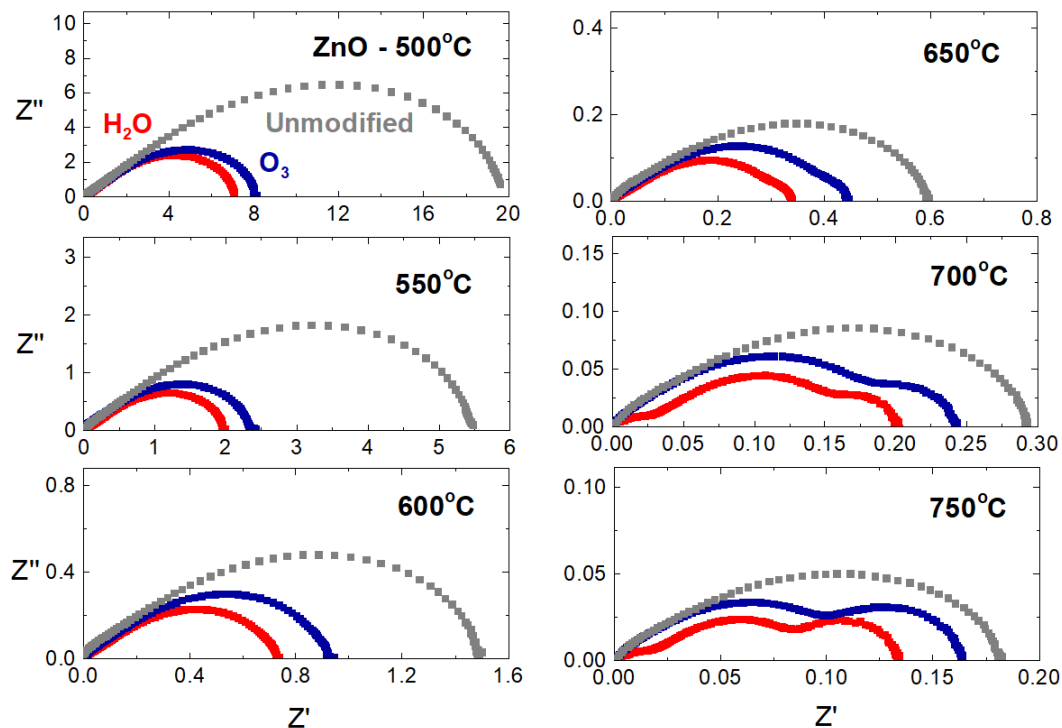


Figure 4.6: EIS spectra of symmetric cells with 16 layers of ZnO deposited at 150°C. One with water and one with ozone.

4.3.3 Effect of Film Annealing

Coated films were heated in pure N₂ up to 400°C and held for 1 hour prior to testing. The effect of annealing in nitrogen was tested on both compositions with both oxidizers. **Figure 4.7** shows the comparison between TiO₂ coated cathodes with and without annealing. In all cases, the additional annealing step reduced the impedance of the cathode. Both the water oxidized, and ozone oxidized films benefited from annealing. This effect was more pronounced at lower temperatures. At

higher temperatures there was still a difference between the annealed films. This would suggest that some defects formed during annealing are retained.

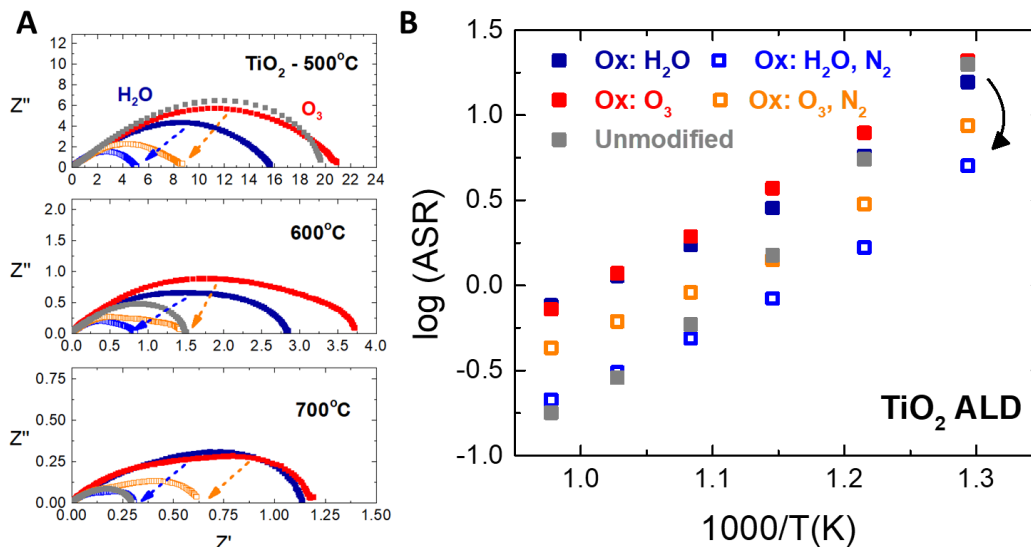


Figure 4.7: Symmetric cells coated with TiO₂ with each oxidizer that have also been annealed in 100% N₂ at 400°C for 1 hour prior to EIS measurements. (A) EIS spectra at different temperatures showing the effect of annealing. (B) ASR of each symmetric cell as a function of temperature.

The effect of annealing was less dramatic on ZnO films. **Figure 4.8** shows the effect of annealing on ZnO coated LSCF. The impedance slightly decreased for ozone, while increasing for water. The overall effect was also smaller compared to the TiO₂ films and wasn't strongly affected by temperature. Since the zinc films were modestly affected, it is possible that annealing is not enough to introduce significant amounts of $V_{\text{O}}^{\bullet\bullet}$ to the ZnO film. Although ZnO can form oxygen vacancies, it is still predominantly affected by Frenkel disorder.^{125,126}

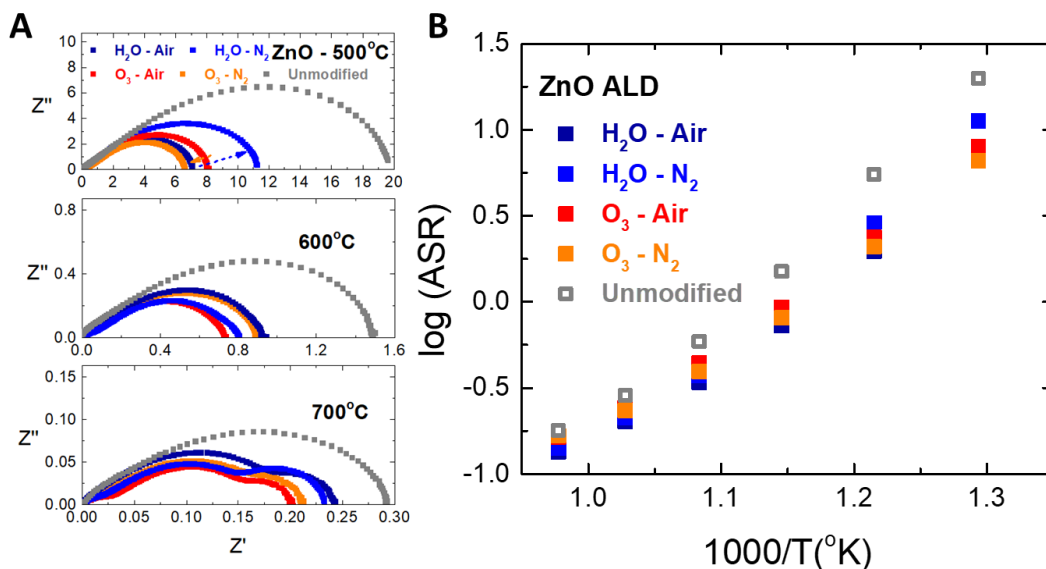


Figure 4.8: Symmetric cells coated with ZnO with each oxidizer that have also been annealed in 100% N₂ at 400°C for 1 hour prior to EIS measurements. (A) EIS spectra at different temperatures showing the effect of annealing. (B) ASR of each symmetric cell as a function of temperature.

4.3.4 DRT Analysis of Cathodes

Further analysis of the EIS spectra was performed using DRT in order to distinguish between different electrochemical processes occurring at the cathode/film surface. The DRT spectra for TiO₂ films are shown in **Figure 4.9**. All the spectra for TiO₂ coated cathodes exhibit spectra with the same relative shape albeit with different heights/areas. In order of decreasing area under the curve, and therefore faster electrode kinetics, the TiO₂ film oxidized with O₃ > H₂O oxidized > O₃ oxidized + N₂ annealing > H₂O oxidized + N₂ annealing, which could also match the order of decreasing oxygen content. This would suggest that reducing the oxygen content of the film enhances electrode kinetics. The annealed samples mainly reduced the resistances of the processes typically attributed to ORR and surface exchange.^{127,128} At 600°C and above, the films without annealing significantly increase the impedance

of all electrochemical processes. Also, as temperature increased, the gas diffusion process was hindered, this is attributed to the crystallization of TiO_2 that is less active for ORR than LSCF-GDC.

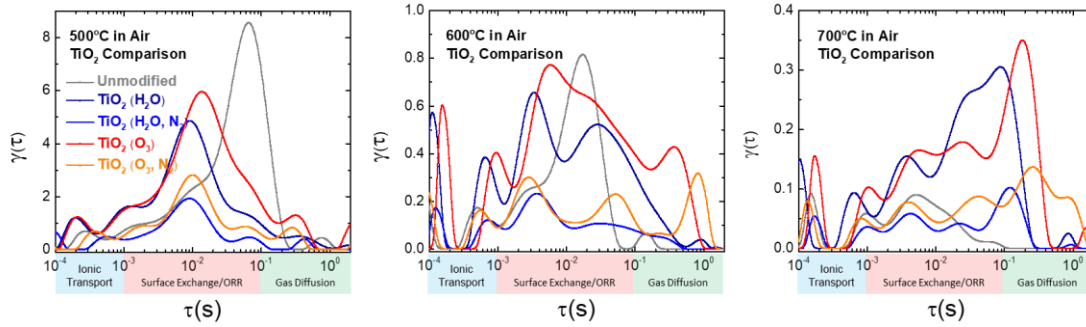


Figure 4.9: DRT curves of symmetric cells with each TiO_2 coating.

Figure 4.10 shows the DRT for ZnO films. The DRT curves for the ZnO coated cathodes were considerably smaller than that of the uncoated cathode. They also retained a similar shape suggesting that the films had similar properties despite the different conditions. At 700°C the ZnO films started to hinder electrochemical kinetics. All the films now showed a large peak in the gas diffusion region, suggesting that the films are now blocking active sites. This change appears to have happened more suddenly, unlike with TiO_2 films, which gradually blocked diffusion with temperature. Thus, this blocking may be attributed either to changes in the film morphology, crystal structure, or formation of a secondary phase.

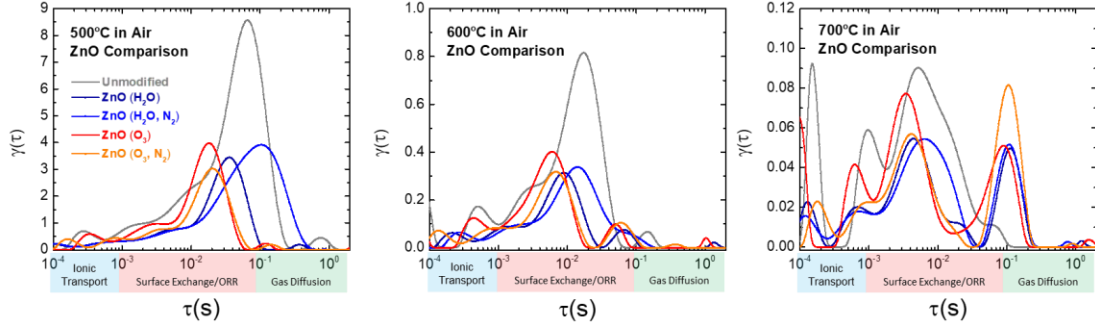


Figure 4.10: DRT curves of symmetric cells with each ZnO coating.

4.3.5 Surface Chemistry of ALD coatings on dense LSCF

Dense and polished samples of LSCF which were produced in the same way described in Section 3.2 were coated with ALD. **Figure 4.11** shows the XPS spectra for the Oxygen 1s peak for dense LSCF coated with 25 layers of TiO₂. Surprisingly, the ratio of oxygen vacancies to lattice oxygen was greater for the film deposited with ozone. There was also no clear effect on the oxygen peaks from the annealing process. This might suggest that the effect that TiO₂ has on cathode performance is not caused by vacancy concentration, but instead due to an interaction between the coating and the cathode at their interface. It may also be caused by to an interaction between the TiO₂ and the electrolyte.

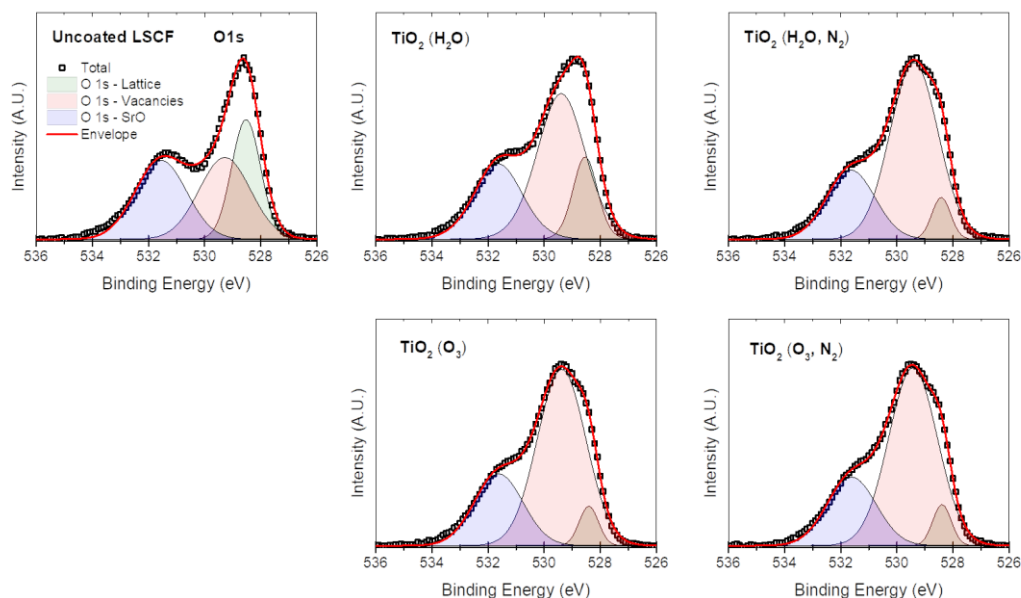


Figure 4.11: XPS spectra for Oxygen 1s peak of TiO_2 coated samples of dense, polished LSCF after TiO_2 deposition, with and without annealing.

XPS was also performed on ZnO coated films as shown in **Figure 4.12**. In the case of ZnO, the ratio between vacancy and surface oxygen was greater for the water oxidized film than the ozone oxidized one. The effect of annealing was only noticeable on the ozone oxidized film which showed signs of greater oxygen vacancies. This reflects the data seen in symmetric cells, which showed a modest effect from annealing.

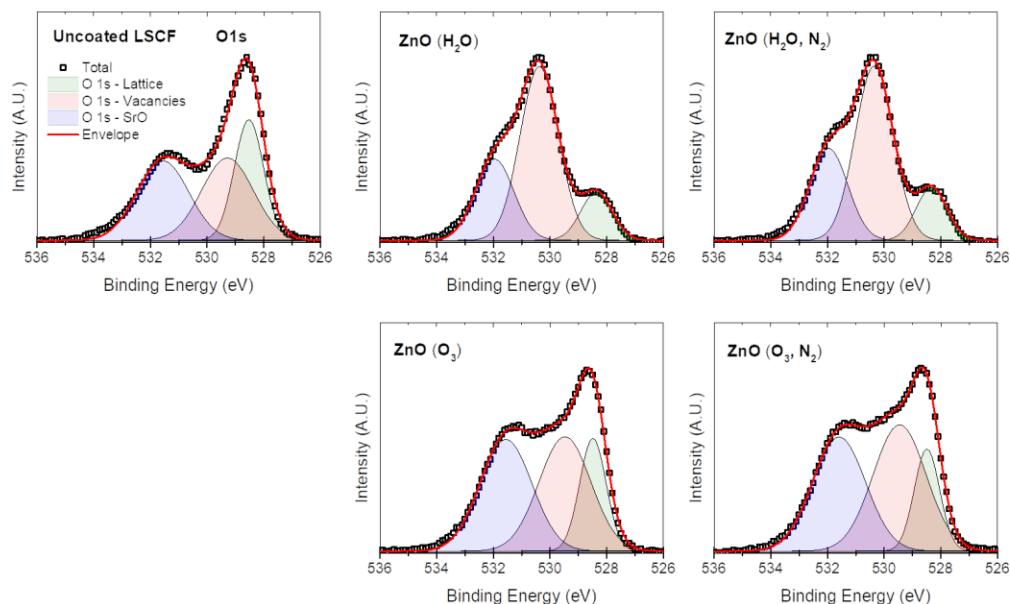


Figure 4.12: XPS spectra for Oxygen 1s peak of ZnO coated samples of dense, polished LSCF after ZnO deposition, with and without annealing.

4.3.6 ALD of Full Cells

Button cells with the same cathode were also used to evaluate the effects of ALD. **Figure 4.11** shows the effect of ZnO deposition on a LSCF-GDC cathode when used on a full cell. Both cells were heated up to 650C with the cathode side in ambient air, while the anode was in pure hydrogen. Unfortunately, the performance of the coated cell was significantly worse than the baseline. The open circuit voltage was lower in the coated which could indicate an interaction between the ZnO film and the electrolyte resulting in leakage current through electronic conductivity. The electrode impedance increased as well, which was unexpected. This was attempted several more times with different batches of cells. Even with lowering the reduction temperature of the full cells, there was a drop in performance for the coated cells. It is unclear why ALD hindered the performance of full cells but not symmetric cells. Due

to the porous structure of the cathodes, and the small thickness of the films, it would be difficult to determine the exact effects that the films have on cathode properties.

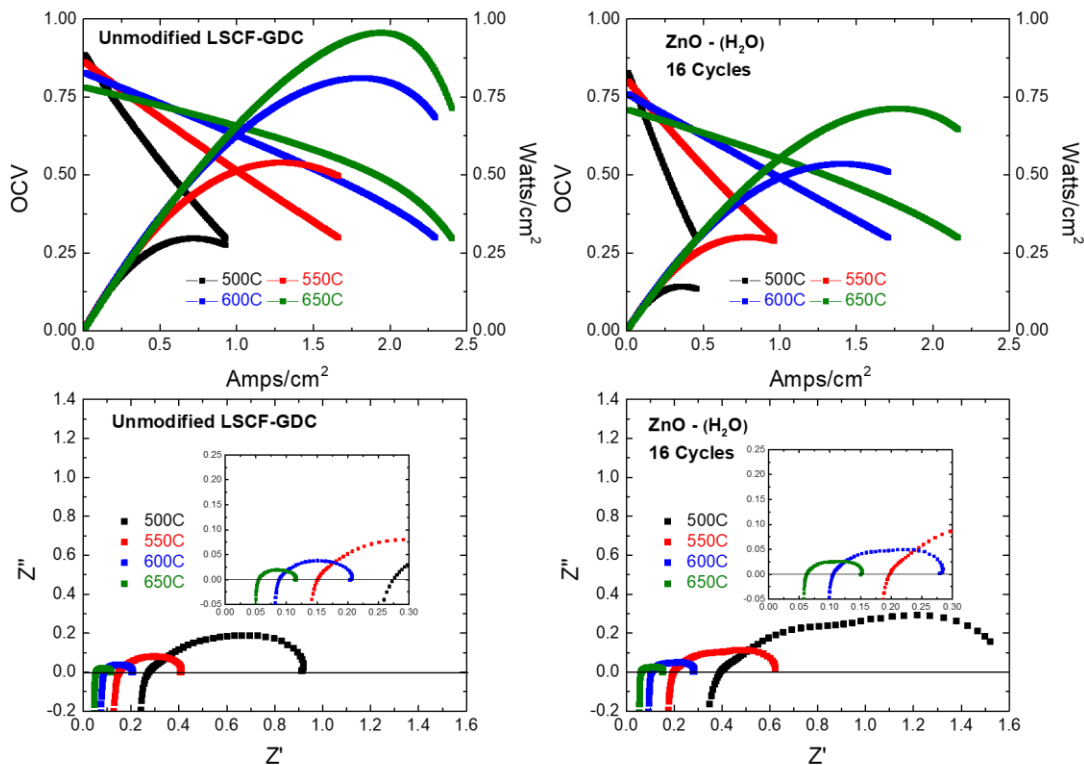


Figure 4.13: IV curves and EIS spectra comparison of LSCF-GDC full cells with and without 16 layers of ZnO deposited on the cathode side.

4.4 Conclusion: Cathode Surface Modification

Here, the electrochemical effects of two metal oxide coatings, namely TiO_2 and ZnO , were observed on LSCF-GDC composite symmetric cells. Both coatings improved performance, but the effect was heavily dependent on testing temperature. It was found that the choice of oxidizer used during the ALD process changed the effects of the ALD coatings. Post deposition annealing was also found to enhance the electrochemical performance for cells coated with TiO_2 but not ZnO . Our results show

that by annealing in a pure N₂ environment, there was further reduction in the ASR of the cells.

Unfortunately, while ALD allows conformal coating of electrode structures, it is a very complex process that requires significant optimization and proper equipment. The ability to adjust the defect concentrations in thin films would improve processing that already requires ALD. However, it may not be suitable or scalable to SOFCs. Other methods of cathode surface modification, specifically solution infiltration are much easier to perform and are still capable of providing significant improvements in performance.^{129,130} While developing more standardized approaches towards tuning thin film properties is important, there are additional variables that must be addressed before ALD can be widely used for SOFCs.

Chapter 5: Anode Microstructure

5.1 Anode Porosity: Scale Up and Performance

Advances in materials have allowed higher and more stable performance of SOFCs at lower temperatures.^{41,131} Yet ongoing challenges remain for large-scale adoption of SOFC technology. The tradeoff between performance, stability, and scalability cannot be ignored. Anode-supported SOFCs provide significantly higher performance because they can be produced with a very thin electrolyte. But anode-supported cells have proven challenging to fabricate in larger sizes. First, they are prone to warping during the sintering process, which results in poor sealing and places additional mechanical stress on the cell during operation.¹³² The degree of warping is known to increase with larger fuel cells.^{133,134} Both size and cell flatness

are crucial to SOFC stack design, which are mandatory for commercial power applications.^{135,136} The degree of porosity within the anode would also affect the warping of the cell during the sintering process because the voids would affect sintering and densification rates.¹³⁷ Sufficiently high discrepancies in shrinkage rates may also lead to significant mechanical stresses and delamination of the layers.^{132,138,139} Increasing the anode thickness would also improve the mechanical strength and flatness but by increasing the distance that fuel needs to diffuse, the performance of the cell would likewise be reduced.^{134,140} Together this presents a complex dynamic between performance and scaling up the size of SOFCs.

In this work, we used combinations of anode layers with varying microstructure, with an emphasis on porosity. By organizing the anode such that it was more porous towards the fuel and less porous towards the electrolyte, it was possible to improve the performance of thinner SOFC anodes but exhibited a modest effect on flatness. The effect of adjusting particle size was significantly less effective. This highlights the importance of using an anode functional layer (AFL) and the importance of increasing the triple phase boundary (TPB) near the electrolyte. suggests that an intermediate layer between the anode functional layer and the anode support can improve electrode performance. When considering the improved strength and flatness of a thicker anode, this approach results in high performance and scalable SOFCs without the added complexity of methods such as freeze casting. Graded anodes have the added benefit of exhibiting better performance at lower fuel ratios, which further increases their merit.

5.2 Experimental Methods: Anode Microstructure

5.2.1 Tape Casting

Each layer of the SOFCs, except for the cathode, was prepared through tape casting and subsequent lamination. For the anode support layer (ASL) coarse NiO (Alfa Aesar) and GDC (Nexceris) were ball-milled in ethanol and toluene with fish oil as a dispersant for 24 hours. 17g of polyvinyl butyral (Tape Casting Warehouse) and 12g benzyl butyl phthalate (Tape Casting Warehouse) were added as binder and plasticizer respectively before an additional 24 hours of ball milling. 2 hours prior to tape casting, a specified amount of polymethyl methacrylate (PMMA-Soken) was added to the slurry as the pore former. The late addition of pore former avoids dissolution of the PMMA by the toluene. The slurry was then mixed and subject to moderate vacuum prior to tape casting. The anode functional layer (AFL) was prepared in the same manner but using fine NiO (JT Baker) and without any pore former. Finally, the electrolyte was also prepared in the same manner using only GDC. The thickness of both the AFL and electrolyte are 15 μm . **Table III** shows the recipes for the tapes used in this study.

Table III: List of compositions used in tape casting

SOFC Layer	Solids	Dispersant	Solvent A	Solvent B	Binder	Plasticizer	Pore Former
Electrolyte	GDC - 60g	Fish Oil - 0.3g	Ethanol - 16g	Toluene - 16g	PVB - 5.6g	BBP - 3.6g	N/A
AFL	GDC - 26g; fine NiO - 24g	Fish Oil - 0.3g	Ethanol - 19g	Toluene - 19g	PVB - 5.5g	BBP - 3.2g	N/A
ASL	GDC - 80g; coarse NiO - 120g	Fish Oil - 1.5g	Ethanol - 37g	Toluene - 37g	PVB - 17g	BBP - 12g	PMMA 10um 0, 1.5, 3, 6, 9, 12g

5.2.2 Lamination & Sintering

The dried tapes were laminated using a roll laminator (PL-1200hp - Professional Laminating Systems). All 3 layers of ASL were laminated first. Then the

AFL and electrolyte were added one at a time. The layers were always stacked alternating between mylar-side and “air” side. The required shapes were then cut from the laminates with a laser cutter (Muse). The same laminates were used for the button cells (1.61 cm²), large scale cells (25cm²). The cut shapes were sintered between a pair of alumina plates (Nexceris) at 1450°C for 4 hours. A very slow ramp rate of 1°C /minute was used with holding temperatures of 225°C and 350°C.

5.2.3 Characterization of 25cm² Fuel Cells

The microstructure was observed with a Hitachi SU-70 SEM. To generate quantifiable images, button cells that were tested, and therefore fully reduced, were encased in epoxy and polished with gradually increasing grit. Final polishing was done using 0.25 micron diamond suspension (Leco) to create a totally smooth surface. Epoxy and backscatter mode allows one to distinguish between surface features and pores. The exact amount of porosity was quantified through FIJI using Trainable WEKA segmentation. The exact procedure is detailed elsewhere (WEKA/LSCF) but in short it uses machine learning to quantify details in an image. The flatness of the large scale cells was measured using a Keyence laser microscope taking height profile measurements through the center.

5.2.4 Characterization of Button Cells

For the button cells, cathode ink was prepared by ball milling SSC cathode powder (Praxair) with GDC for 24 hours. The suspension was stirred in a Thinky centrifugal mixer while ESL 441 (Ferro Scientific) was gradually added as a dispersant. The final product was then screen printed onto the button cells and fired at

950°C for 2 hours. Silver ink and mesh was used to form a current collector. The button cells were mounted on home-made reactors and sealed with ceramabond (Aremco). The performance of the cells is based on measurements taken after they had fully reduced as determined by steady state performance. Testing was done in a mix of N₂ and H₂ flowing through a water bubbler at ambient temperature. A total of 100 sccm of fuel was flowing to the anode side, while the cathode was in ambient air. **Figure 5.1** shows the appearance of button cells, large-scale cells, and a diagram of the home-made testing reactors.

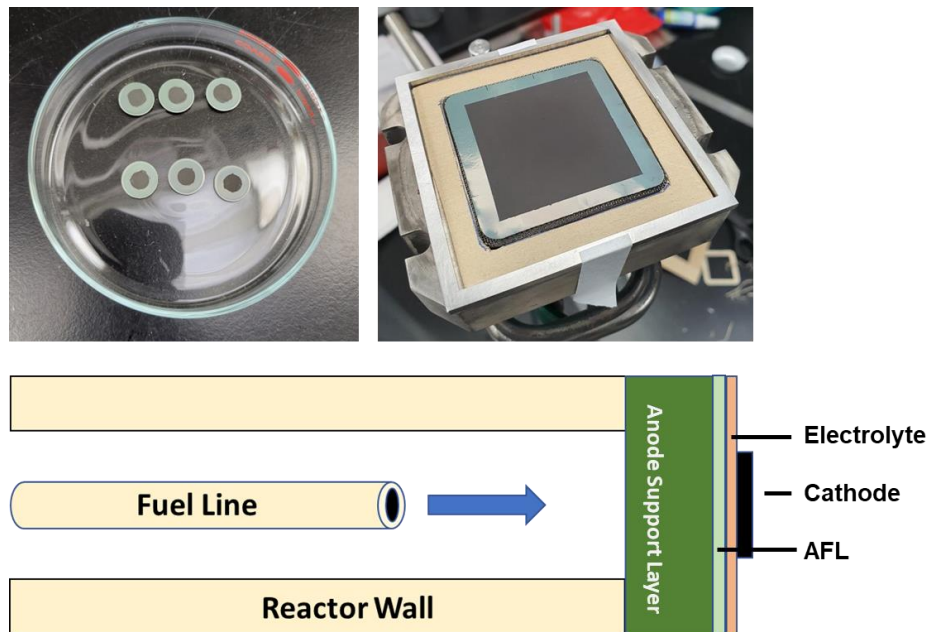


Figure 5.1: Photos of button cells, large scale cell, and diagram of button cell reactor.

5.3 Results & Discussion: Anode Microstructure

5.3.1 Anode Microstructure & Porosity

Porosity is fundamental to the performance of SOFCs. The anode must enable sufficient fuel flow to the electrolyte, have sufficient triple phase boundary (TPB) for

electrochemical activity, and enable sufficient diffusion of water vapor back out of the anode. Porosity in Ni-GDC and Ni-YSZ anodes is typically achieved through the reduction of the NiO to metallic Ni, leaving behind empty volume. **Figure 5.2** shows the microstructure of reduced anodes with different amounts of PMMA.

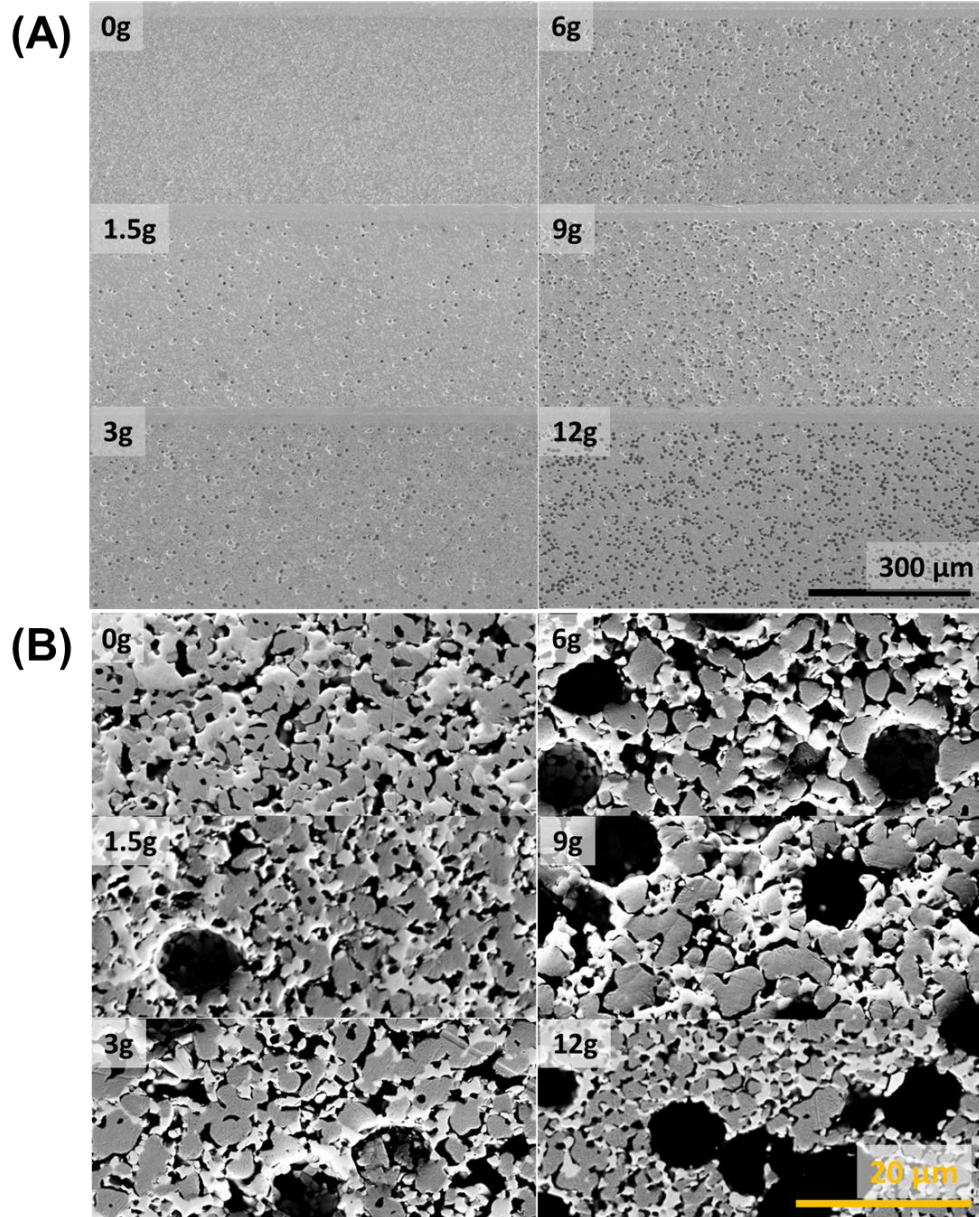


Figure 5.2: (A) Low magnification images of anode microstructure with different amounts of pore former. (B) Higher magnification images of anode microstructure taken using backscatter mode.

The addition of pore former creates larger regions that can promote gas diffusion closer to the electrolyte as they are significantly larger than the channels produced by Ni reduction. The pore diameter is close to 10 μm , which corresponds to the diameter of the pore former used. This means that sintering does not significantly reduce the pore size. Backscatter also confirms that the Ni and GDC are well distributed and therefore the anode has good connectivity. The thickness of the anode makes it challenging to determine parameters such as tortuosity through methods such as FIB-SEM, but the pore former is shown to be well distributed across the anode. The amount of porosity was quantified through WEKA Trainable Segmentation.⁸⁷ This is a machine learning plugin for FIJI, an enhanced version of the well-known ImageJ software. Multiple images at various magnification levels were processed. **Figure 5.3** shows the volume percentage of porosity in the anode as a function of added pore former weight. The porosity without any additional pore former is 17% and as expected gradually increases to 36.5%. PMMA was chosen for this study as its homogenous size results in a consistent microstructure and the pore size is known to affect performance.¹⁴¹ Finally, the size of the PMMA particles is an order of magnitude greater than the size of the channels produced by the reduction of NiO. This creates “macrochannels” that can promote a greater volume of gas diffusion.^{142,143} As long as the pores do not close during sintering, the size of the pore former is not expected to significantly impact the total porosity, but the NiO and GDC particle size will.^{138,144}

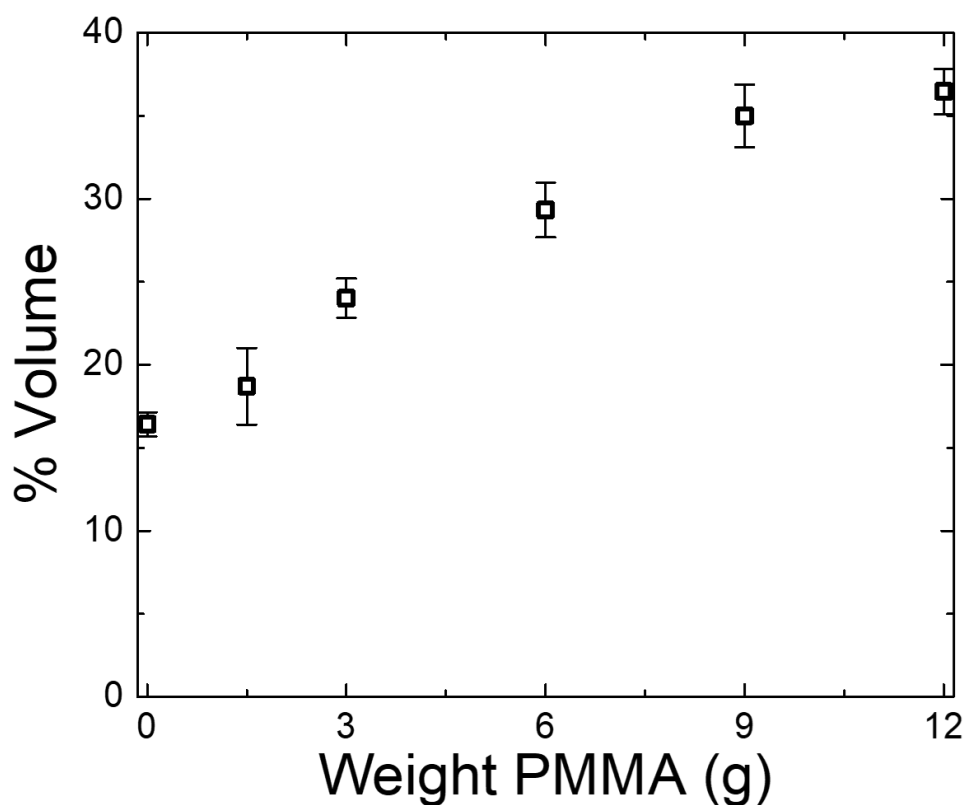


Figure 5.3: Porosity of anodes with different amounts of pore former. Porosity was quantified through trainable WEKA segmentation from SEM images.

5.3.2 Scale Up of Half Cells

For SOFCs produced through tape casting, the organics in the green tape significantly impact the production of cells. The combustion of dispersant, binder, plasticizer, and pore former which occurs during sintering can cause various defects, and even destruction of the entire cell. During heating, differences in thermal expansion and shrinkage rates between the layers cause tension and compression within the half cell. These differences are the result of different particle sizes, porosity, and composition between each layer of the SOFC. This results in warping of the cell before it reaches its final shape.^{132,145} Large scale fuel cells are significantly

more susceptible to this type of defect. Since the forces of tension and compression are applied across the entire cell, the total magnitude of force scales with size.¹³⁴ This is further complicated by non-uniformity in the hot zone of the furnace during sintering. The larger the cell, the greater the variation in temperature as it is heating. This presents a challenge for large scale adoption of fuel cells as high curvature can lead to poor sealing in stacks.^{135,146}

Although curvature is often attributed to the differences between layers, it is also influenced by the distribution of solids and organics.^{137,147} A thorough review and explanation of organic burnout is presented in Lewis, 1997.¹³⁷ As the laminates are heated, the organics initially form a liquid phase between the solid particles, which softens the cell. The removal of organics from laminated half-cells occurs as the organics combust into volatile gas which diffuses through the laminate to the surface through existing pore channels. As organics are removed, more porosity is available for additional diffusion. Defects occur in localized regions of limited mass transfer and can be mitigated by a low heating rate. Low heating rates reduce the differences in shrinkage rate between adjacent layers and promote flatness. Otherwise, delamination and fractures are possible.^{148,149} Hence the low ramp rate used in this study.

In this initial heating stage, the dense layers (the electrolyte and AFL) are densifying at a faster rate than the ASL. This is due to their reduced particle size and lower porosity. At low temperatures the half cells bend to be concave up despite the weight of the sintering plates. Currently, the dense layers are under tension and the ASL is under compression. At higher temperatures, the half cells warp in the other

direction. The dense layers would complete their sintering first so now there is a reversal of the curvature direction as the ASL densifies more than the dense layers.

Thus it was hypothesized that flatter cells could be achieved in two ways. The first was reducing the shrinkage of the ASL by adding pore former. Malzbender et al proposed adding a thin highly porous layer on the outside of ASL to match the shrinkage rate of the AFL and electrolyte. Unfortunately, this layer induced mechanical stress on the cell making it susceptible to damage during sealing or operation.¹³⁴ The second was to increase the compatibility between adjacent layers by giving them more similar properties, to hinder the mechanisms responsible for curvature. This was achieved by laminating ASL with different amounts of pore former such that the layers with the least amount of pore former were towards the electrolyte. Graded porosity anodes have been reported elsewhere but no studies have been made on the relationship between graded porosity and sintering properties.

To develop flatter 25cm² cells, the impact of pore former loading on the shape had to be quantified. **Figure 5.4 (B)** shows the effect of PMMA loading on the curvature of sintered large scale cells. Once sintered the half cells become concave down. This demonstrates that the shrinkage of the electrolyte and AFL at the top is less than the shrinkage of the ASL. This is reasonable given the smaller particle size of the solids in the thin layers and the lack of pore former. The differences between the layers result in the electrolyte and AFL being under compression, while the ASL is under tension, ultimately causing the curvature.^{134,150} The degree of curvature was strongly related to the amount of pore former in the anode. Higher amounts of organic content led to increased curvature due to the impact of organics on the pre-sintered

half-cell. However, further increasing porosity eventually resulted in flatter cells. This improvement in flatness is attributed to the reduced shrinkage in the ASL that more closely matches the shrinkage rates of the electrolyte and AFL. Several 4 layer anodes were tested as well, and as expected, they were significantly flatter. They were also less susceptible to variations in the furnace hot zone and appear less impacted by varying porosity.

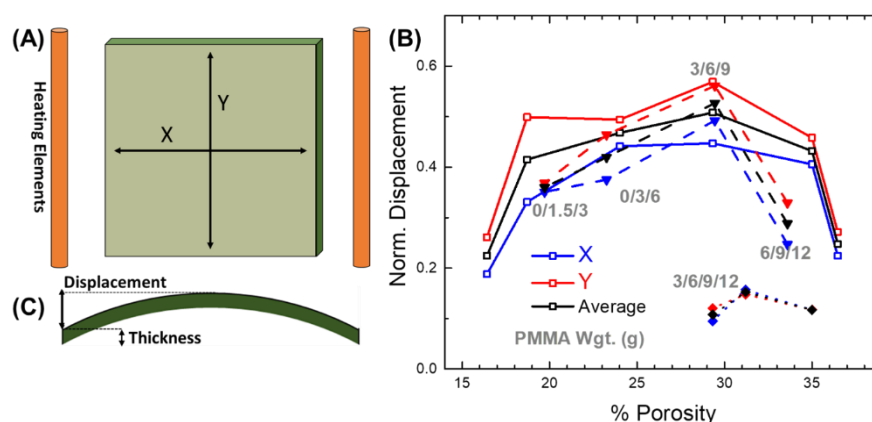


Figure 5.4: Sintering and curvature of large scale cells. (A) Diagram showing the placement and orientation of large-scale cells in the furnace. (B) Displacement measurements of large-scale normalized to cell thickness. Open symbols ($\square$) denote uniform porosity anodes, triangles ($\blacktriangledown$) denote graded anodes, and diamonds ($\diamond$) denote 4 layer anodes. (C) Diagram showing how displacement is defined.

At low porosity graded anodes had a modest effect on the flatness, but significant improvements in flatness were achieved at higher concentrations of pore former (6,9,12g, versus 9g). This strengthens the claim that increased porosity can improve the sintering of large scale cells. As long as the heating profile is slow enough to gradually combust all of the organics, this approach can be used to increase the flatness of large scale cells. Low amounts of pore former also resulted in flatter cells. It is hypothesized that the reduction of organic content in the ASL mitigates the

warping at low temperatures by making the ASL denser. 4 layer anodes did not seem to benefit from this, possibly because the porosity was too low in much of the anode.

5.3.3 Performance of Button Cells

Full cells with each amount of pore former were tested to determine the relationship between porosity and performance. **Figure 5.5** shows the IV curves and EIS spectra are shown for button cells with each loading of pore former. As porosity increased, the ohmic impedance decreased. At 12g the OCV decreased as well. This is the result of ceria in the electrolyte and AFL undergoing reduction to its +3 oxidation state resulting in greater electronic conductivity. This demonstrates that sufficiently high or low amounts of porosity can influence the cell beyond simply the anode performance. This effect would not occur in YSZ based SOFCs.

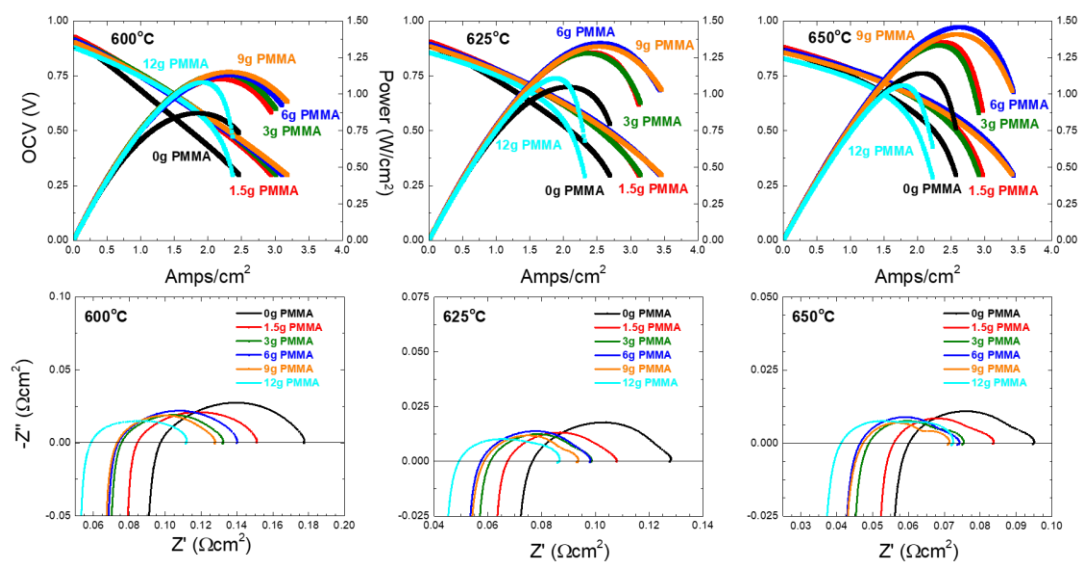


Figure 5.5: Electrochemical measurements including IV curves and EIS spectra for full cells with identical SSC-GDC cathodes and 3 layers of ASL consisting of uniform porosity.

The importance of porosity is shown to be heavily dependent on the temperature. At 600°C all the IV curves demonstrate similar performance except for the 0g and 12g anodes. Meanwhile, the anodes with intermediate porosity displayed similar performance to one another. The anode without pore former consistently had the highest electrode impedance which is attributed to insufficient porosity for gas diffusion. Despite the significantly higher impedance, the 0g anode performed better at 625°C and 650°C for higher current densities than the 12g anode. This is attributed to greater connectivity of the Ni and GDC. At higher temperatures, increased conductivity and reaction kinetics permit more of the anode to participate in the hydrogen oxidation reaction. The 12g anode had the lowest impedance at OCV but the IV shows a sharp drop at higher current densities. Since the size of the pore former is significantly larger than the gas diffusion channels formed by NiO reduction, it is expected that there is too much empty space in the anode, especially near the electrolyte. This would hinder the fuel cell reaction by limiting the triple phase boundary.

The effect of grading porosity with less porosity towards the electrolyte is shown in **Figure 5.6**. Here the anode with graded microstructure had lower electrode impedance and better peak power density at lower temperatures. However, at 650°C, the 3/6/9 anode showed a drop in performance at high current density suggesting concentration polarization. This may be due to having too much empty volume in its 9g layer.¹⁵¹ The 6/9/12 anode did not achieve as high power density but still performed reasonably well at 600°C. Since higher temperature drives reactions, and higher porosity anodes have fewer active sites, this drop in performance makes sense.

This is also reflected in the EIS curves. The 3/6/9 anode had the lowest impedance at OCV, likely because the layer with the least porosity helped increase the TPB near the electrolyte, which is from where the oxygen arrives for HOR.

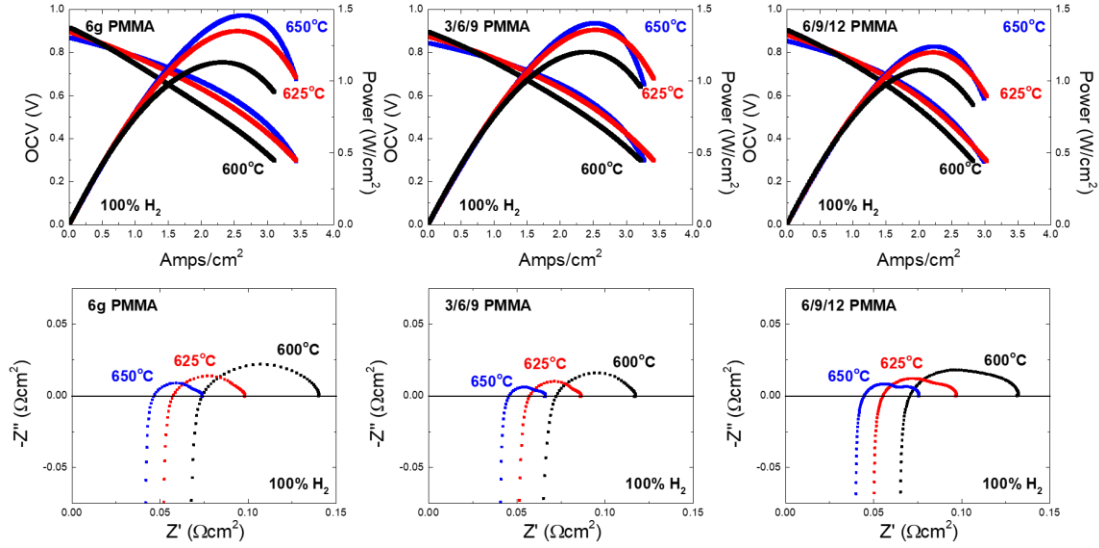


Figure 5.6: Comparison of performance between uniform and graded porosity anodes including IV curves and EIS spectra.

The effect of grading porosity and total porosity was evaluated over varying temperatures and fuel ratios. **Figure 5.7** shows electrode ASR as a function of porosity for homogenous and graded anodes. The 3/6/9 anode is as good or better than the standard 6g anode, which has approximately the same amount of porosity. The improvement occurs at lower temperatures and fuel ratios. The 6/9/12 anode was worse than its corresponding 9g anode. The improvement due to the graded porosity is attributed to the more efficient microstructure. The TPB close to the electrolyte is increased but the fuel is still able to reach further into the anode. Computational and experimental studies on graded anodes have suggested that reducing porosity in the

direction of the fuel flow increases the relative velocity of the fuel, thus improving the chemical kinetics.^{141,152}

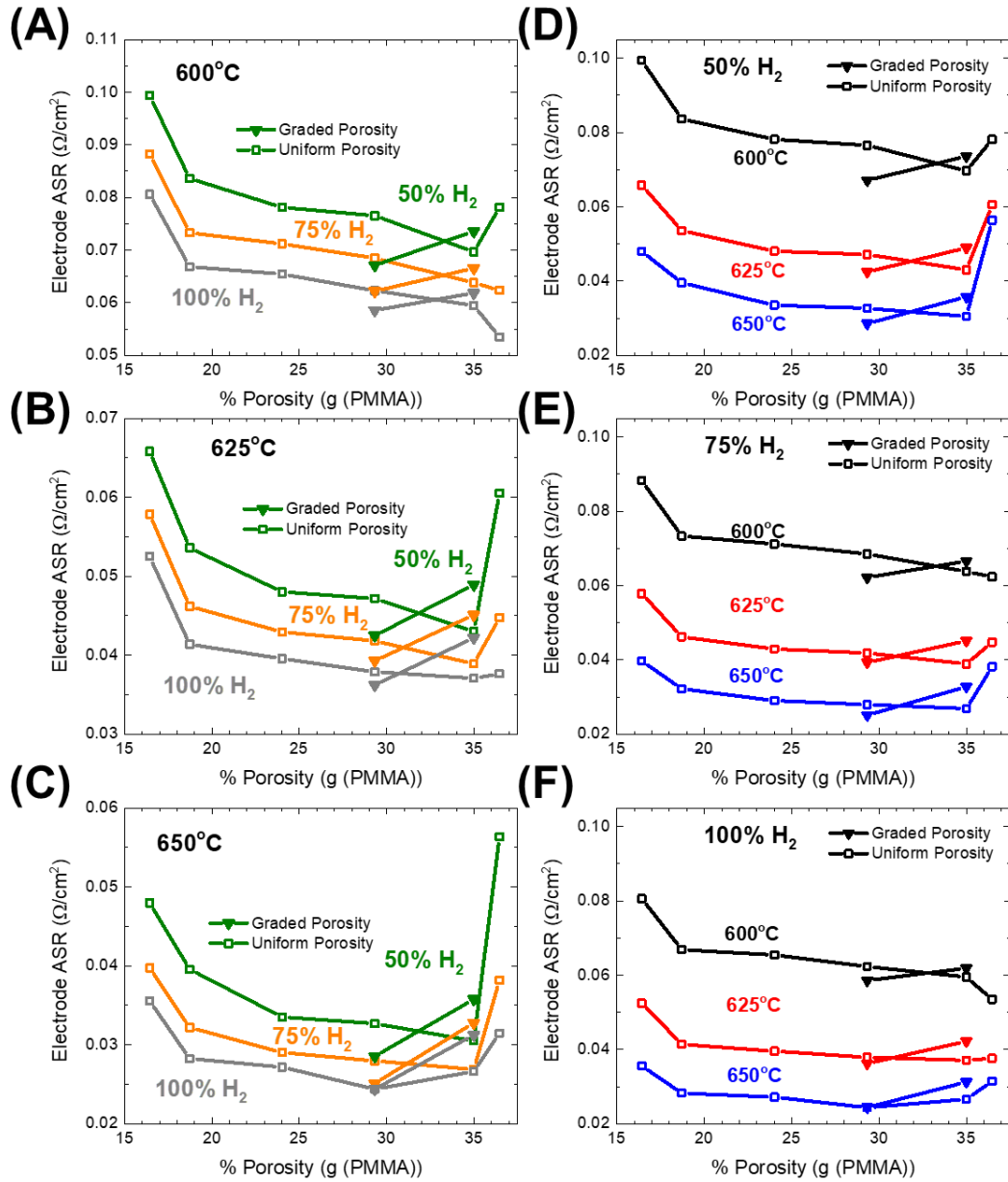


Figure 5.7: Electrode ASR as a function of porosity varied with temperature and fuel ratio. H_2 balanced with N_2 at (A) 600°C (B) 625°C (C) 650°C. Constant fuel ratio with varying temperature. (D) 50% H_2 & 50% N_2 (E) 75% H_2 & 25% N_2 (F) 100% H_2

To address the issue of concentration polarization in the cells, several pore former sizes were evaluated in addition to the standard 10 μm size pores. **Figure 5.8** shows the IV curves and EIS spectra for homogenous ASLs made with 6g of 1.5 μm , 3 μm , and 10 μm PMMA. The 3 μm PMMA showed the best performance at lower temperatures but was outperformed at higher current densities by the 10 μm PMMA cell. The 1.5 μm cell had the worst performance. Worth mentioning is that the EIS curves show similar performance for the two smaller pore sizes, which was better than the 10 μm pore anode. However, these measurements were only taken at OCV and do not reflect the reaction kinetics at high current density. This demonstrates that an optimal anode design will need to take both pore size and total porosity into account. This is further complicated for graded anodes, as this introduces many possible combinations of anode layers.

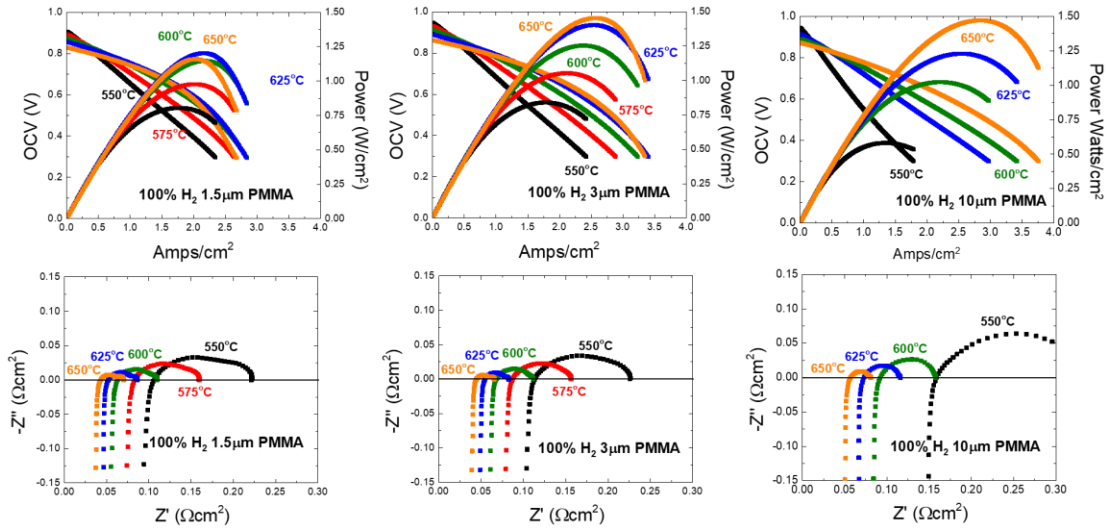


Figure 5.8: Electrochemical measurements including IV curves and EIS spectra for full cells with uniform porosity and varying sizes of pore former.

The ideal anode would have a 4th layer and be able to achieve similar performance to a thinner anode. **Figure 5.9** shows the IV curves for several 4 layer anodes. The best performing cell was the standard 6g ASL with 10 μ m pores. There was a significant drop in performance with the higher porosity 9g ASL. An anode with gradual reduction in porosity, the 3/6/9/12, did not perform as well as expected. The worst performing anode used one layer with 3 μ m pores towards the electrolyte in an unsuccessful attempt to boost the TPB, despite the high performance that was achieved using an anode with only 3 μ m pores. Further analysis is needed and testing is planned for 5 μ m PMMA.

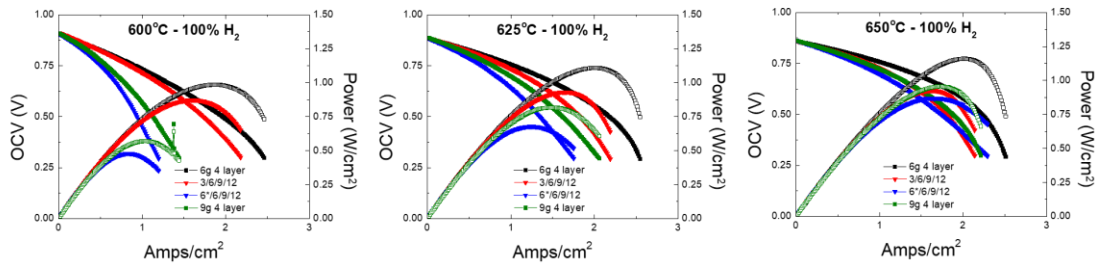


Figure 5.9: IV curves of 4 layer ASL full cells. Two uniform cells of 6g and 9g standard 10 μ m pore former are shown, as well as 3/6/9/12g anode with 10 μ m, and 6/6/9/12 anode with 3 μ m PMMA in the layer closest to the electrolyte and 10 μ m for remaining layers.

5.4 Conclusion: Anode Microstructure

Here we demonstrated the relationship between anode porosity, cell flatness, and performance. Improvements in performance were achieved through graded porosity enabling a more efficient microstructure with a high TPB near the electrolyte, and sufficient porosity for fuel flow and water exhaust. This also improved performance at lower fuel ratios, which is useful for commercialization.

Although graded microstructures did not been able to significantly improve flatness,

it is expected to improve the performance of 4 layer cells once pore size is considered. Thicker anodes are significantly flatter and would be mechanically stronger. Simultaneously improving performance and reliability would significantly promote adoption of SOFCs. This approach could be further extended to similar technologies such as electrolysis cells.

Chapter 6: Conclusion

6.1 Summary of Results: Proton Conducting Membranes

Pr was tested as a new dopant for SrCeO_3 and studied over a wide range of oxygen partial pressures ($p\text{O}_2$'s) and temperatures to determine its material and defect properties by measuring conductivity. In hydrogen Pr-doped SrCeO_3 was found to be chemically and structurally stable, up to a doping level of 10%. This composition exhibited greater conductivity than the previously reported Eu-doped SrCeO_3 . Under low $p\text{O}_2$ conditions Pr-doped SrCeO_3 exhibited n-type behavior with conductivity increasing with decreasing $p\text{O}_2$, demonstrating the electronic conductivity of SrCeO_3 is significantly enhanced by Pr doping. At high $p\text{O}_2$ conditions, Pr-doped SrCeO_3 exhibited p-type conductivity significantly lower than in reducing atmospheres. This is attributed to the +4 oxidation state of Pr. Much higher conductivity was observed in the presence of water affirming its protonic conductivity. This work demonstrates the effectiveness of Pr as a means of enhancing electronic conductivity in proton conducting perovskites.

6.2 Summary of Results: Cathode Degradation

Surface cation segregation on perovskite-type electrodes is a major issue that limits the durability of high-temperature solid-oxide fuel and electrolysis cells. This process is strongly dependent on composition, temperature, the external gas-environment, and gas-phase impurities, such as CO₂. To determine the mechanism behind cation segregation, LSCF is systematically evaluated under specific conditions to determine the origin of surface segregation and surface particle growth. Temperature is well understood to be the initial main driving force for cation segregation as it provides energy for cation diffusion. However, SrO particles appear under specific conditions which are dependent on the gas environment. The actual nucleation of harmful surface particles requires the presence of oxygen or gas-phase oxygen-containing molecules to form and grow SrO. It was found that oxygen also influences the defect chemistry of LSCF, that depending on the circumstances it can promote or suppress surface segregation through surface interactions between the bulk and the surface. Meanwhile, CO₂ was found to both promote the nucleation process and suppress surface migration of the nucleated particles. This dramatically altered the surface morphology compared to impurity-free oxygen.

We briefly evaluated A-site deficiency, a known method to improve the stability of LSCF. It was found that it can limit the SrO segregation in certain conditions but not in the presence of CO₂. This study demonstrates how gas-solid interactions can influence surface chemistry and phase separation. Though when applied to other materials, this approach was insufficient. In the case of SSC, the cation segregation was more heavily dependent on the crystal structure than gas environment. Different characterization methods would have been required for thorough understanding of its

degradation mechanisms. A-site deficiency was tested as a novel method of studying cation segregation and improving stability of SSC. Unfortunately, there was no clear effect from changing the composition either on symmetric cell performance or microstructure.

6.3 Summary of Results: Cathode Surface Modification

ALD was evaluated as a means of improving the performance of SOFC cathodes. Due to the many variables involved in the ALD process, which is further complicated by deposition on porous substrates, the effect of specific variables on cathode performance was studied. By changing the oxidizer used in ALD and annealing in nitrogen, it was possible to change the nature of the deposited films and observe an effect on cathode performance. TiO_2 and ZnO were affected differently by changes in oxidizer and the additional of an annealing step. The performance generally improved with less crystalline films, suggesting that defects play a role in promoting ORR. However, the exact mechanism is difficult to determine when applied to a porous substrate. Additionally, ALD was not able to improve the performance of full cells. It is unclear exactly why this occurred. The use of select variables can be used to improve consistency between different groups reporting ALD on SOFC electrodes and provide improved performance of proven procedures.

6.4 Summary of Results: Anode Microstructure

By tuning the porosity of SOFC anodes the relationships between cell flatness, electrochemical performance, and porosity were determined. Both high and low amounts of porosity improve flatness due to the different stages of the sintering

process but are not optimal for cell performance. Grading the porosity from minimal porosity near the electrolyte to higher porosity at the fuel side improves performance and can somewhat mitigate the performance losses if flatter cells are needed. This is more complicated in thicker anodes, where fuel flow appears to be more of a priority than increasing the triple phase boundary. Ongoing work suggests that thicker cells benefit more from a thicker porous region than a continually graded porosity anode. The size of the pores is also significant and several combinations of grading both total porosity and pore size may be necessary for optimal performance. This would allow the production of thicker cells that are flatter and stronger, without the corresponding performance losses.

Chapter 7: Future Work

7.1 Future Work: Proton Conducting Membranes

It was found that Pr is an effective dopant for SrCeO_3 . Its multivalent nature and favorable ionic radius promote conductivity for multiple charged species. More recently, membranes with multiple dopants have been demonstrated, with the most commonly used composition being BaCeZrYYbO_3 (BCZYYb).^{153,154} Few studies have used Pr either individually or as a second dopant. The disadvantage of Pr is its +4 oxidation state in oxidizing conditions, which could be mitigated by a second dopant.

7.2 Future Work: Cathode Degradation

Although it was possible to identify the degradation mechanism in LSCF, this was more difficult for SSC which demonstrated a different degradation mechanism seemingly based on grain orientation. Sophisticated characterization methods such as TEM cross sections may be able to examine the structure and composition of the particles in sufficient detail. In terms of cathodes, a novel characterization method has been reported for quantifying cation segregation in porous samples. Wang et al studied the change in composition of LSCF electrodes. First sample cells were placed in water to dissolve water-soluble phases on the surface. Next, they dissolved the entire cell in HCl. Both solutions were adjusted to the same molar ratio of HCl and the compositions were studied using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The difference in composition was used to measure the segregation of secondary phases. This approach would be able to quantify differences in surface chemistry in porous materials.

7.3 Future Work: Cathode Surface Modification

The challenge of ALD on SOFC electrodes is primarily due to the complex nature of ALD on porous substrates. Instead, ALD could be used to mitigate other issues with SOFC commercialization. The manifolds and interconnects that secure the cells and allow conduction of electricity while being subject to harsh conditions. Certain alloys, such as those containing chrome cause degradation of fuel cells.¹⁵⁵ Since these are dense materials that require stable surface chemistry, they are a much better candidate for ALD. If electrode surface modification is needed, solution

infiltration is a far simpler and more scalable process, with which we have been successful.

7.4 Future Work: Anode Microstructure

In addition to modifying the total porosity, we are still evaluating the effect of modifying the size of pore former, including grading of size. Furthermore, we plan to do dilatometry once our optical dilatometer becomes available to use. This will allow detailed study of the densification and curvature for our many laminates of varying porosity and thickness that have already been completed. This work will be valuable in scaling up SOFCs to even larger sizes and enabling wide-spread adoption.

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