Structural and Electrochemical Characterization of Two Proton Conducting Oxide Thin Films for a Microfabricated Solid Oxide Fuel Cell

by

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ABSTRACT

The use of proton conducting oxide materials as an electrolyte offers the potential to reduce the operating temperature of a solid oxide fuel cell (SOFC), leading to improved thermal management and material compatibility. However, many proton conducting materials have not yet been investigated for residual stress and electrochemical properties in thin film form. This research characterizes the thermomechanical and electrochemical properties of two promising materials: Yttria doped Barium Cerate (BaCe$_{0.9}$Y$_{0.1}$O) and Terbium doped Strontium Cerate (SrCe$_{0.95}$TbY$_{0.05}$O), for use in a microfabricated SOFC ($\mu$SOFC). Uniform, crack-free thin films of both compositions were produced by sputter deposition. Films with thickness ranging from 150 nm to 600 nm were deposited on a fused silica substrate. The desired composition was achieved for both films at a deposition temperature of 575°C, though minor secondary phases were also present. Residual stress for different film thicknesses was measured as a function of temperature using the wafer curvature technique. All films exhibited an initial compressive residual stress (from -200 to -600 MPa) and a significant tensile stress hysteresis upon thermal cycling, leaving a final residual stress at room temperature that ranged from -200 to +200 MPa. The average modulus-CTE product for films of each material was found to be $\sim$ -0.65 MPa/°C, which is 3-4 times smaller than that of the bulk materials. Electrochemical performance was assessed using impedance spectroscopy. Measurements were taken in three gas atmospheres (ambient air, dry air, and 5% H$_2$ + 95% Ar) from 200 to 500°C. Bulk conductivity in air was found to be 6.57x10$^{-4}$ S/cm at 473°C for BaCeYO and 2.64x10$^{-4}$ S/cm at 424°C for SrCeTbO. Though somewhat lower, these values compare well with the conductivity for bulk yttria stabilized zirconia (YSZ), the most common SOFC electrolyte: $\sim$ 1 x 10$^{-3}$ S/cm at 500°C. Prior research indicates that conductivity and activation energy are a strong function of the quantity of water vapor in the test atmosphere. The lack of water vapor in this work most likely explains the lower conductivity and higher activation energy. The activation energy in ambient air was 0.7 eV for BaCeYO and 1.0eV for SrCeTbO, suggesting that these materials should have comparable or better conductivity at lower temperatures than bulk YSZ which has a value of 0.8 eV. This research shows that these proton conducting oxides are viable and promising materials for lowering the temperature of a $\mu$SOFC. Future work on these films should include electrochemical tests in a controlled, humidified atmosphere and performance tests of these materials in a $\mu$SOFC.

Thesis Supervisor: Brian L. Wardle
Title: Boeing Assistant Professor of Aeronautics and Astronautics
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List of Nomenclature

\( A \) Cross-sectional area (electrolyte film thickness x length of the electrode)
\( d_s \) Thickness of the substrate
\( d_f \) Thickness of the film
\( E_A \) Activation energy
\( E_f \) Biaxial modulus of the film
\( E_s \) Young’s modulus of the substrate
\( \overline{E_s} \) Biaxial modulus of the substrate
\( k \) Boltzmann’s constant
\( L \) Distance between electrodes
\( R \) Radius of curvature
\( Rl \) Resistance of bulk material
\( Z \) Impedance
\( \alpha_f \) Coefficient of thermal expansion of the film
\( \alpha_s \) Coefficient of thermal expansion of the substrate
\( \kappa \) Curvature
\( \sigma_f \) Biaxial stress of film
\( \sigma_s \) Stress of substrate
\( \nu_s \) Poisson’s ratio of the substrate
\( \omega \) Radial frequency
1 Introduction

As the world’s need for alternative energy sources grows more acute, fuel cells are increasingly gaining attention as a clean and efficient source of electric power. Fuel cell technology has been developing steadily over the last several decades, but has faced significant commercial and technological hurdles. Fuels cells have typically required pure hydrogen gas as their fuel, expensive precious metals in their construction and/or high operating temperatures, all of which have prohibited their widespread adoption. Recent advances have increasingly addressed these limitations and fuel cell technology seems poised for early-stage commercialization. There is still much work to be done, however. The ultimate goal of the research presented in this thesis is to help develop a viable, portable fuel cell by reducing the operating temperature through the use of new materials. This thesis characterizes a relatively new type of material, known as a proton conducting oxide, for use in a small, microfabricated solid oxide fuel (μSOFC).

1.1 Motivation for Microfabricated Solid Oxide Fuel Cells

In its most basic form, a fuel cell is comprised of three layers of materials – a cathode, an electrolyte, and an anode – which combine hydrogen and oxygen to produce electricity and water. Fuel cells are a particularly attractive source of power because they are highly efficient (up to 60%), produce only water as a by-product, and have no moving parts (reducing complexity and increasing reliability). Fuels cells have potential applications ranging from power plants to automobiles to cellular phones. Fuel cells come in a variety of technologies, such as proton exchange membrane (PEM), direct methanol (DMFC) and solid oxide (SOFC), each with its own advantages and
disadvantages. All of the technologies operate on the same basic principle of combining hydrogen and oxygen and transporting ions across the electrolyte, but they do so using different materials and different mechanisms. This research is focused on solid oxide fuel cell technology.

Solid oxide fuel cells have several advantages over other fuel cell technologies: they are the most efficient at converting hydrogen (or hydrocarbon fuel) into electricity (up to 60%), have the highest power density (up to 1.8 W/cm²)\(^1\) [1], and have the greatest fuel flexibility. Unlike most fuel cells, which require the use of pure hydrogen, SOFCs are more tolerant of contaminants and are therefore able to use hydrogen derived from a variety of hydrocarbon fuels. This is a significant commercial advantage because it obviates the need for pure hydrogen, which is both difficult and dangerous to handle. SOFC’s, though, are not without their disadvantages. The primary disadvantage of SOFC technology is the relatively high operating temperature (600-1000°C), which poses a considerable technological challenge for materials development and thermal management. A second, related, disadvantage of the technology is the long startup required to reach the high operating temperature, making the SOFC impractical for quick-start applications.

As a result of the high operating temperatures, SOFCs have typically been applied to large, stationary applications. Now, however, by using microfabrication techniques and construction, SOFCs may be a promising portable technology. Microfabrication techniques are those typically employed by the semiconductor and MEMS industries, consisting of thin films, released membranes and micro- and nano-scale features. A microfabricated SOFC, in the context of this research, would take the form of multiple

\(^1\) Anode-supported planar cell stack at 800°C.
released membranes (on the order of 10 μm x 10 μm each) comprised of a tri-layer of thin films (the anode, cathode and electrolyte) and supported by a silicon substrate. The fuel cell would provide a power output of 0.1–1.0 W/cm² for use primarily in portable electronic devices.

In addition to its small size and portability, a microfabricated SOFC has a number of advantages over the macroscale version. First, the lower thermal mass dramatically reduces the time to reach the operating temperature, making the SOFC more practical for quick-start applications. Second, the thinner electrolyte has less ohmic resistance and hence fewer losses and higher net power output. Third, a thinner electrolyte (<1 μm) has been shown to have better ionic conductivity, thus offering improved electrochemical performance at a lower temperature (600°C vs. 800-1000°C) [42]. Finally, microfabrication may offer the opportunity to increase or tailor the triple-phase boundary, improving electrochemical performance. The triple phase boundary (TBP) is the region where the gas phase (the hydrogen or oxygen), the electrode, and the electrolyte are all in contact. The TPB drives the kinetics of the electrode reaction and so improving it will also improve the performance of the fuel cell.

1.2 Motivation for Proton Conducting Oxides

The motivation for studying proton conducting oxide materials is that they offer the potential to lower the operating temperature (<500°C) of a solid oxide fuel cell, addressing the primary disadvantage of SOFC technology. A proton conducting oxide would be used as the electrolyte in the SOFC in place of more conventional materials such as yttria stabilized zirconia (YSZ). The electrolyte is the material layer sandwiched between the anode and the cathode. With a conventional electrolyte, the SOFC produces
electricity by transporting oxygen ions from the cathode, through the electrolyte, to the anode. A proton conductor, however, transports protons (hydrogen ions) across the electrolyte instead of oxygen ions. Due to the nature of the reactions, proton conduction requires less energy than oxygen-ion conduction which results in a lower operating temperature.

Though there are many materials known to conduct protons, it is only relatively recently (early 1980’s) [41], that a class of proton conducting ceramics was discovered that meet the requirements for a SOFC application. Most importantly among the requirements are that the materials are chemically stable at temperatures above ~300 °C, exhibit high protonic conductivity but low electronic conductivity, and are impermeable to the hydrogen and oxygen gases. The original materials investigated of this class were barium cerate (BaCeO) and strontium cerate (SrCeO) [41]. It has since been discovered that doping these materials with rare earth elements, such as yttrium and terbium, greatly improves the protonic conduction. There has also recently been research into related materials and alternative doping elements. Nonetheless, barium cerate- and strontium cerate-based oxides remain among the best proton conducting materials and are therefore the materials of choice for this research. The specific materials characterized in this work are yttria-doped barium cerate (BaCeYO) and terbium-doped strontium cerate (SrCeTbO).

1.3 Objective and Scope of Thesis

The objective of this thesis is to investigate the use of proton conducting oxide materials in a microfabricated solid oxide fuel cell application. The scope of the research is three-fold: to demonstrate the feasibility of producing the materials of interest in thin
film form (<1 μm thick), to characterize the residual stress and thermal expansion properties of the resulting films, and to characterize the electrochemical performance of the materials. The approach taken is largely experimental, employing analytical techniques to assess the film’s structure (x-ray diffraction and atomic force microscopy), residual stress (wafer curvature), and electrochemical conductivity (impedance spectroscopy).

The two materials investigated in this research, yttria-doped barium cerate (BaCeYO) and terbium-doped strontium cerate (SrCeTbO), are relatively complex compounds and producing them as thin films can not be taken as a given. Indeed, producing uniform, crack-free films with the desired composition proved to be non-trivial, but was a necessary first step before they could be considered viable micro-SOFC materials.

The residual stress and thermal expansion characteristics of thin films are also critically important to understand before using them in a device. Nearly all thin films have an internal, or residual, stress, as a result of the deposition process used to create them. The state and magnitude of the stress is highly dependent on the material, processing conditions and thickness, among other factors. If the magnitude of the stress is large relative to other layers in the device or to the supporting structure, the film can crack, delaminate, or otherwise fail. Similarly, the thermal expansion characteristics must also be assessed in order to prevent failure through design. Devices such as SOFCs are subjected to thermal cycles during their operation. The different layers of materials must have compatible coefficients of thermal expansion (CTEs) or, again, the films may
fail. The materials presented here are characterized in terms of both residual stress and thermal expansion for several different thicknesses.

Evaluating the electrochemical performance of the materials is important in predicting how well they will perform in a fuel cell application. Electrochemical performance measures the ability of the material to conduct ions. In this research the electrochemical performance – conductivity and activation energy - is characterized for both materials over a range of operating temperatures in three different gas environments (air, dry air, and H₂ + Ar).
2 Background and Prior Work

The study of solid oxide fuel cells is inherently multi-disciplinary and this research draws on prior work and analytical techniques from a wide range of sources. The background and prior work presented here begins with a technical overview of the components and operation of a solid oxide fuel cell. This is followed by a discussion of proton conducting oxide materials in general and an introduction to two specific proton conducting materials: barium cerate and strontium cerate. Finally, the thin film deposition process, known as sputter deposition, is introduced, as well as the tools and analysis used to characterize the film's residual stress and electrochemical performance.

2.1 Background on Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) are highly efficient electrochemical devices for converting hydrocarbon fuels into electricity. A SOFC is a solid state device which combines hydrogen, oxygen and heat to produce electricity and water. In its most basic form a SOFC is comprised of a stack of three layers of materials: a cathode, an anode and an electrolyte. Oxygen, usually in the form of air, is supplied to the cathode where it is reduced into oxygen ions. The oxygen ions are then transported through the electrolyte to the anode. At the anode, the oxygen ions are combined with hydrogen to yield water and electrons. The electrons from the reaction are transported across an external load around the insulating electrolyte. Heat is added to the system to promote the chemical reactions. The operation of the fuel cell is illustrated in Figure 2.1.
Solid oxides are hard ceramic compounds of oxygen, which in the context of a fuel cell often refers to \( \text{ZrO}_2 \) (the compound of zirconium and oxygen), though other oxides can be used. In practice \( \text{ZrO}_2 \) is typically stabilized with yttrium to produce yttria stabilized zirconia (YSZ), a widely used electrolyte material. Such materials are required because they must meet several stringent criteria for success [1]:

- It must be dense and impermeable to the fuel and air gases
- It must have good ionic conductivity and low electronic conductivity at operating temperatures
- It must be stable in both oxidizing and reducing environments
- It must be thin to reduce the ionic resistance (losses)
- It should have a large surface area to maximize the current capacity
- It should have a compatible coefficient of thermal expansion (CTE) with respect to its supporting structure
- It must be economically viable
The remainder of this thesis investigates two alternative materials to YSZ for the SOFC electrolyte.

The other components of the SOFC are the electrodes (the anode and cathode) which can be made from a variety of different materials. The important criteria for these materials are that they are: porous (to allow the gas to contact the electrolyte), promote the desired chemical reaction, adhere to the electrolyte, and that they have a compatible CTE with the rest of the fuel cell. Noble metals such as platinum and palladium, though expensive, have been used successfully as electrodes, as have nickel and metal/YSZ blends (cermets). As with the electrolyte, there are numerous other possible material choices for the electrodes and research is on-going.

The discussion thus far has focused on the most common type of SOFC: one that conducts oxygen ions. It is, however, possible to create a fuel cell that conducts hydrogen protons instead. A proton-conducting SOFC operates on a similar principle as the fuel cell described above but uses a slightly different mechanism. Instead of transporting oxygen ions across the electrolyte, a proton-conducting SOFC transports hydrogen protons. In such a configuration, the anode now becomes the reducing catalyst to produce protons and electrons and the cathode becomes the oxidizing catalyst to combine electrons, oxygen and hydrogen protons to yield water. The difference between the two systems is illustrated in Figure 2.2.
Proton-conducting SOFCs hold the promise of lower operating temperatures with comparable or improved conductivity. However, developing such a fuel cell will require new materials for the electrolyte. These materials, known as proton conducting oxides, are the subject of this thesis.

2.2 Background on Proton Conducting Oxide Materials

Proton conducting oxides are materials that exhibit protonic conductivity in the presence of hydrogen. These materials differ from a typical oxide-ion conductor in that they conduct hydrogen protons rather than oxygen ions. There are a number of materials...
which conduct protons, but most either decompose at temperatures above 300°C or conduct only at temperatures over 1000°C [2]. There is however a class of perovskite-type oxide ceramics that are both stable and exhibit proton-conduction at moderately elevated temperatures (300°C - 1000°C). These materials have the general chemical composition AB$_{1-x}$M$_x$O$_3$, where A and B are the main constituents, M is a trivalent dopant, such as a rare earth element, and x is a dopant level less than 1. The two materials analyzed in this research are in this form: BaCe$_{0.9}$Y$_{0.1}$O$_3$ and SrCe$_{0.95}$Tb$_{0.05}$O$_3$ (yttria doped barium cerate and terbium doped strontium cerate, respectively).

The basic perovskite-type structure, without a dopant, has the general form ABO$_3$ (for example, BaCeO$_3$ or SrCeO$_3$) and an orthorhombic crystal structure. In this structure, component “A”, the large metal cation, occupies the center of the crystal, “B”, the small metal cation, occupies the corners, and oxygen, O, is in the center of the edges. This structure is illustrated in Figure 2.3.

Figure 2.3: Orthorhombic crystal structure of a perovskite-type oxide.
When this basic structure is doped with a rare earth element such as yttrium (Y) or terbium (Tb), the dopant displaces some of the small cations ("B"). This substitution causes the formation of oxygen ion vacancies in the structure. These vacancies, in turn, promote the formation of protons from hydrogen gas or water vapor. The proton then “hops” from one oxygen ion to the nearest neighboring one, producing proton conduction. The meaningful result of proton conduction is that it should have a lower activation energy than oxide ion conduction [11]. Thus, a proton conductor should have better conductivity at lower temperatures than an oxygen ion conductor.

2.3 Barium Cerate

Proton conduction in barium cerium oxide (BaCeO\textsubscript{3}) was first discovered in Japan circa 1980 by Hiroyasu Iwahara [3]. It was shown relatively soon after, however, that although BaCeO\textsubscript{3} exhibited proton-conduction, it was necessary to dope the compound with a rare earth element, such as yttrium\textsuperscript{2}, to produce sufficient conductivity. In this section, prior research into creating barium cerium yttrium oxide (BaCeYO) thin films is discussed as is research on BaCeYO conductivity.

2.3.1 Barium Cerium Yttrium Oxide Thin Films

Thin films of BaCeYO have a number of potential applications including solid oxide fuels cells, hydrogen separation membranes, hydrogen pumps, and hydrogen sensors [4]. Such high-current-drain applications, which use proton conductors as an electrolyte, require the use of thin films to minimize electrical losses in the electrolyte

\textsuperscript{2} There has been research on barium cerates doped with elements other than yttrium, such as neodymium (Nd), but these materials are not discussed here.
and reduce operating temperature [4]. Researchers have employed a variety of methods to create thin films of this material, including evaporation, electrostatic spray, sputtering, and spin coating. Many of these efforts are described here. In the body of prior work for BaCeYO, however, only material structure or conductivity (typically bulk) is investigated. An important, but yet unreported, property of the thin film is characterized in this thesis: residual stress. In addition, based on the literature review, it is possible that conductivity for very thin (200 – 600 nm) films of BaCeYO is also presented here for the first time.

Thin films of perovskite materials were first deposited by Muller et al. in 1963 using the grain-by-grain evaporation technique [5]. This technique, however, requires very high evaporation temperatures for BaCeO₃ (2130°C). Later, in 1994, a low temperature electrostatic spray pyrolysis (ESP) was used by Schooman et al [6]. This method produced barium cerate, but also produced secondary phases of Ce₂O₃ and Ba(OH)₂ [7].

In 1995, He et al. [7] deposited a 540 nm thick film of BaCe₀.₉Y₀.₁O₃ on single-crytalline MgO substrates using RF-magnetron sputtering techniques. The following sputtering conditions were used: 50 mm target-substrate distance, 100 W RF power, a gas atmosphere of 1:9 O₂-Ar mixture at a working pressure of 2x10⁻² mbar. These conditions produced deposition rates of approximately 600 nm/h. It was found that the phase purity of the films depended strongly on the substrate temperature. A relatively high temperature (750°C) produced a large amount of a secondary phase of Ce₂O₃ (or CeO₂). The optimal substrate temperature for obtaining the desired single phase of BaCeYO was found to be approximately 550°C.
Several researchers have also developed thin BaCeYO films using repeated spin-or dip-coating followed by sintering to achieve the desired film thickness and composition. Yamaguchi et al. [8] successfully used this technique in 2004 to create films 45 µm thick.

In 2004, Lee et al. [4] prepared a thin film of barium cerate using colloidal spray deposition method on porous NiO/BCY substrates. Dense, crack-free BaCeYO films with thickness of ~10 µm and a grain size of 2–7 µm were produced.

There has been little, if any, published work on the thermal/mechanical properties of BaCeYO thin films. However, in 2005, Yamanaka et al. [38] characterized the thermophysical properties of bulk BaCeO, calculating a linear coefficient of thermal expansion of 1.12x10^-5 (K^-1) between 300 and 1000°C.

### 2.3.2 Barium Cerate Conductivity and Fuel Cell Applications

A number of researchers have investigated the electrochemical performance of bulk BaCeYO and several have tested the material in fuel cell applications. For proper context, the results of these tests should be compared with the performance of a commonly used electrolyte such as yttria-stabilized zirconia (YSZ). Hibino et al. [11] found that the conductivity for bulk polycrystalline YSZ ranged from ~1 x 10^{-3} (S cm^{-1}) at 500°C to ~1 x 10^{-2} (S cm^{-1}) at 700°C in air. Hibino also reported an activation energy for YSZ of 0.84 eV.

In 1997 Guan [9] studied the conductivity of bulk 5% doped BaCeYO in the form of 2.2 cm diameter pellets. The group tested the material from 500°C to 800°C and in both oxygen/water vapor and hydrogen/water vapor atmospheres. They found that proton
Conduction is dominant at lower temperatures (500-600°C) and oxygen ion conductivity is dominant at higher temperatures. Protonic conductivity ranged from $1.9 \times 10^{-3}$ (S cm$^{-1}$) at 800°C in oxygen/water vapor atmosphere to $1.27 \times 10^{-2}$ (S cm$^{-1}$) at 800°C in a hydrogen/water atmosphere. Total conductivity in a hydrogen/water atmosphere ranged from $4.37 \times 10^{-3}$ (S cm$^{-1}$) at 600°C to $1.99 \times 10^{-2}$ (S cm$^{-1}$) at 800°C.

In 1998 Balachandran et al. [10] created disks of 5% doped BaCeYO measuring 22.5 mm in diameter and 2 mm thick. The group measured conductivity in a variety of atmospheres and found that total conductivity ranged from $5 \times 10^{-3}$ (S cm$^{-1}$) in argon to $2 \times 10^{-2}$ (S cm$^{-1}$) in oxygen at 600°C.

In 2002, Hibino [11] constructed a solid oxide fuel using BaCeY as the electrolyte and two sets of electrode materials. The group used pure platinum as reference electrodes and then tested Pd-loaded FeO as the anode and Ba$_{0.5}$Pr$_{0.5}$CoO$_3$ as the cathode. The electrolyte was a ground pellet of sintered BaCeY 1 mm thick. Using the Pt electrodes, conductivities for a 10% Y-doped BaCeY electrolyte ranged from $1.9 \times 10^{-3}$ (S cm$^{-1}$) at 400°C to $9 \times 10^{-3}$ at 600°C in a H$_2$ saturated with H$_2$O atmosphere. Hibino found that BaCeY conductivity was higher than for YSZ for temperatures below about 650°C, but that YSZ conductivity was higher than BaCeY for temperatures above 650°C. Activation energies were only reported for the 25% Y-doped composition, but these range from 0.41 eV (400-500°C) to 0.53 eV (550-800°C).

In 2005 Ito [12] fabricated a fuel cell test cell using a thin film electrolyte. Ito used pulse laser deposition to deposit a 0.7 μm thick BaCe$_{0.8}$Y$_{0.2}$O$_3$ film on a palladium film. The cathode was a perovskite paste that was screen printed on the electrolyte-palladium structure. The test cells were then operated from 400 - 600°C and measured a
power density of 0.9 – 1.4 W/cm². The conductivity of the film, measured using AC impedance, was about one order of magnitude lower than the bulk electrolyte. Measured conductivity ranged from \(-6 \times 10^{-4}\) S cm⁻¹ at 400°C to \(-9 \times 10^{-4}\) S cm⁻¹ at 600°C.

### 2.4 Strontium Cerate

Strontium cerium oxide (SrCeO₃) was the original proton-conducting oxide perovskite material discovered by Iwahara circa 1980 [41]. It was this discovery that led to the investigation of proton-conduction in other perovskite oxides, such as BaCeO₃. Strontium cerate tends to have slightly lower proton conductivity than barium cerate, but it also exhibits less oxygen-ion conductivity and is generally more stable [29]. In this section, prior research into creating strontium cerium terbium oxide (SrCeTbO) thin films is discussed as is research on SrCeTbO conductivity.

With BaCeO, the dopant element of choice has typically been yttrium, though other elements have been researched. There is not as clear a consensus with SrCeO, and dopants other than terbium (Tb) are often used, including thulium (Tm) [31], ytterbium (Yb) [35], and yttrium (Y) [29]. As a result there is much less data available for SrCeTbO. Because the dopant element can have a dramatic effect on the properties of the film, these other materials are not discussed in this section.

#### 2.4.1 Strontium Cerium Terbium Thin Films

Elbaccouch et al. [30] deposited thin film of SrCe₀.₉₅Tb₀.₀₅O using spin-coating in 2005. The group produced 200 nm thick films using one spin-coating cycle and
produced films up to 2 μm using multiple coating cycles. The films were homogeneous, continuous, crack-free and of the correct perovskite structure and composition. It was determined, however, that the surface morphology depended on the number of coating cycles. Thicker films exhibited a bi-layer structure with a highly porous top layer and a dense bottom layer.

There has been little, if any, published work on the thermal/mechanical properties of SrCeTbO thin films. However, in 2005, Yamanaka et al. [37] characterized the thermophysical properties of bulk un-doped SrCeO, calculating a linear coefficient of thermal expansion of $1.11 \times 10^{-5}$ (K$^{-1}$) between 300 and 1000°C.

As with BaCeYO, the body of prior work for SrCeTbO covers material structure or conductivity (typically bulk). An important, but yet unreported, property of SrCeTbO thin films is characterized in this thesis: residual stress. In addition, based on the literature review, it is possible that conductivity for very thin (200 - 600 nm) films of SrCeTbO is also presented here for the first time.

### 2.4.2 Strontium Cerate Conductivity and Fuel Cell Applications

In 1998, Dionysiou et al. [39] investigated the conductivity of bulk SrCeTbO. The group produced samples in bar form measuring 1.8 x 7.4 x 21 mm with electrodes in the form of silver paint. Conductivity was $5.6 \times 10^{-5}$ (S/cm) in 20% O$_2$ + 80% N$_2$ atmosphere and $7.51 \times 10^{-3}$ (S/cm) in a hydrogen containing atmosphere (5% H$_2$ + 95% He), both at 900 °C. This increase in conductivity in a hydrogen atmosphere was given as proof that the material is a good proton conductor.
In 1999, Qi et al. [40] also produced SrCeTbO samples in bar form measuring 1.8 x 7.4 x 21 mm with silver paint electrodes. The group reported a total conductivity of $5.6 \times 10^{-5}$ (S/cm) in air at 900 °C.

2.5 Sputter Deposition

The thin films analyzed in this research were created using sputter deposition. The properties of thin films are highly dependent on the method of deposition and the processing parameters. It is therefore necessary to understand the basic sputter deposition process and the variable parameters. In the following section the basic process is described, as are the process parameters and their effects on the film.

2.5.1 Background on the Sputtering Process

Sputter deposition is one of several methods available to create thin films. Sputter deposition is a physical vapor deposition (PVD) method by which atoms of the desired material are physically ejected from a source (known as the target) by energetic ions, and deposited on the desired substrate. Other deposition methods include thermal and electron-beam evaporation (also PVD processes), chemical vapor deposition (CVD), and wet-physical methods such as sol-gel. Sputter deposition has several advantages over other methods including low deposition temperature, lack of any chemical reactions (apart from desired oxidation) and relatively high deposition rates.
The classic configuration of a RF or DC sputter deposition system is shown in Figure 2.4. The basic system consists of a vacuum chamber, power supply, target and substrate.

As shown, the process takes place in a vacuum chamber with the target as the cathode and the substrate as the anode. The chamber is evacuated and then filled with an inert gas such as argon. A current is then passed between the anode and cathode in order to generate an electromagnetic field. In the presence of this magnetic field the argon is...
energized and develops into a plasma. A plasma is a weakly ionized gas comprised of electrons, ions, and neutral atomic and molecular species that exhibit a collective behavior. It is this plasma that produces the actual sputtering. The positive gas ions are accelerated toward the cathode (the target) where they bombard the surface and eject atoms of the source (target) material. These atoms are then accelerated toward the anode (the substrate) where they are deposited on the substrate and impinge on the growing film.

There are a number of variations available on the basic sputtering configuration. Differences include RF versus DC power, diode versus magnetron, and geometrical configurations. This research was conducted using a reactive (oxidizing) RF magnetron system. RF power was required because only electrically conductive target materials can be sputtered with a DC current. High resistivity (greater than $\sim 10^6$ ohm-cm at 100 volts) materials, such as the ceramics used in this research, cannot be DC sputtered. Instead, employing the fact that the impedance of dielectrics drops with increasing frequency, an RF power supply is used to pass current through the target. Magnetron sputtering has the advantage of higher deposition rates and reduced operating pressures. The specific geometry of the system is described in Section 3.2.

There are a number of parameters in the sputtering process which strongly affect the material properties of the film. These include the base pressure, working pressure, sputter gas composition and substrate temperature. The base pressure is the pressure in the chamber before the inert gas is injected, or in other words, it is the extent of the vacuum. The most important consequence of the base pressure is that it is related to the
number of impurities in the film. The lower the base pressure, the fewer foreign atoms exist that could enter the film causing impurities.

The working pressure, also known as the sputtering gas pressure, is the pressure of the gas(es) injected into the chamber. This parameter can have a number of different and complex effects, but the prominent effect is on the residual stress of the film. Low pressures tend to yield compressive residual stresses, while higher pressures tend to yield more tensile stress. At low pressure there are fewer atomic collisions so gas molecules can directly peen the surface of the film, compressing it ("atomic peening" is discussed further in section 2.6.2). At high pressure, however, there are more molecules and therefore more atomic collisions. These collisions slow down the gas molecules and reduce the amount of atomic peening, which leads to a more tensile stress state. In addition, higher pressures are conducive to the development of columnar grains with intergranular voids—a microstructure that exhibits tensile stress.

The composition of the sputter gas(es) has a number of effects on the film. First, the choice of the inert gas is important. Argon is a commonly choice for sputtering, but it is not the only one. Heavier gases can increase atomic collisions and slow down molecules, leading to a tensile stress as described above. Similarly, lighter gases can increase the effect of atomic peening and increase the compressive stress. In addition, some amount of the sputter gas gets trapped in the film and different gases can have different effects on the film's material properties. Second, an additional "reactive" gas can be introduced. The reactive gas is often oxygen, in a ratio of between 5% and 50% to the inert gas, and is used to create oxide thin films. For example, sputtering a pure
titanium (Ti) target in an atmosphere of argon and oxygen will lead to a film of titanium oxide (TiO₂).

The last parameter, substrate temperature, has a complex effect which is highly material dependent and is typically understood only empirically. Substrate temperature can have a significant impact on residual stress, film composition, microstructure, and film material properties.

2.6 Residual Stress

Residual stress is inherent in most thin films and is highly dependent on a variety of factors, including: material composition, substrate, film thickness, deposition conditions and operating environment. Residual stress can cause a number of failure modes in the film and therefore must be understood and well-characterized before designing the film into a system. Residual stress and its origins are introduced in this section, followed by a discussion of the characterization technique.

2.6.1 Background and Importance of Residual Stress

Nearly every thin film exhibits some amount of internal, or residual, stress even in the absence of external loads. This stress develops during the deposition process (growth stress) and then is often further influenced by the film’s physical environment after deposition (induced stress). The total residual stress is often times broken into intrinsic (growth stress) and extrinsic (stresses from loads and environmental changes) [26]. The stress can be either tensile or compressive and the magnitude can often be quite large
relative to the material’s failure stress. Residual stress has the effect that if the film were to be removed from the substrate its in-plane dimensions would change and may also deflect out-of-plane. As a result, residual stress can induce a number of serious problems including deformation, fracture, delamination and microstructural changes in the material. It is therefore critically important to understand and properly characterize a film’s residual stress before designing it into a system. Failure to do so can lead to a poorly performing system or one that fails completely.

2.6.2 Origins of Residual Stress

Residual stress develops during the film deposition process and is highly dependent on the materials involved and the process parameters. Though the exact mechanism by which the stress develops is not yet fully understood for all materials, there is a general consensus on how the stress varies as the film grows. At the early stages of the deposition process the film is slightly compressive. As the film grows the stress becomes tensile and then, as the film continues to grow, the stress becomes more compressive, ultimately reaching a steady-state value that is either compressive or tensile.

![Residual Stress vs. Film Thickness](image)

**Figure 2.5:** Residual stress vs. film thickness (illustrative), adapted from [26].
The different stages of film stress correlate with sequential stages of film growth. The initial stage of film growth is the “island nucleation” stage. During this early stage deposited atoms coalesce around a distribution of nucleation sites that have formed on the substrate. The source of the compressive stress that arises during this stage is normally attributed to surface or interface stress. The idea is that islands become firmly attached to the substrate early in their growth. As the islands continue to grow in volume, the radius of the attachment point cannot expand at the same rate, if at all, because it is “perfectly adhered” to the substrate. This causes a strain in the islands and to a compressive stress in the film.

The second stage of film growth is that of “island contiguity” or “island-to-island coalescence”. During this stage the islands of material grow to the point where they begin to merge together. It is during this phase that the stress becomes less compressive and ultimately tensile. The widely accepted model for the development of this tensile stress is the Hoffman-Nix mechanism. The work of Hoffman and Dolijack [27] and later by Nix [33], explain the change in stress in terms of closing the small gaps between the impinging islands to form grain boundaries. As the islands begin to make contact with one another, each island is still an independent entity with a relatively large surface area and thus a high surface energy. As they continue to merge, the interface becomes a grain boundary and the islands become a single contiguous film. This effect reduces the overall surface area of the film and thus lowers the systems net energy. The process causes the participating islands to be strained elastically leading to the tensile stress.

The final stage of film growth is simply “continued growth”. As the film continues to grow the stress becomes compressive once again, ultimately approaching a
steady-state value. The explanation for this compressive stress seems to be that it is due to an excess number of atoms in the film. The current thinking in the literature is that excess atoms do not have enough energy to be driven into interstitial sites in the crystal. Instead these atoms will migrate into the grain boundaries. The excess atoms in the grain boundaries lead to a compressive stress in the film [26].

The sputter deposition process, as opposed to other deposition processes, also adds its own stress generating mechanism. Sputtered atoms bombard the film with relatively high kinetic energies. This causes damage to the surface of the film in the form of excess interstitials and leads to a compressive stress. This mechanism is known as "atomic peening" and is analogous to the peening process in metals on the macro scale, which also leads to compressive stresses.

Figure 2.6: Illustration of atomic peening in a crystal lattice (from [32]).

Stresses in the film can also be induced after deposition by external influences. A wide variety of factors can cause induced stresses including temperature change with a
difference in coefficients of thermal expansion (CTEs) between bonded elements, piezoelectric response, inertial forces, chemical reactions, plastic or creep deformations, or applied loads. In this research, thermal cycles and differing CTEs are of significant concern and will be discussed in more detail.

2.6.3 Characterizing Residual Stress

Residual stress can not easily be measured directly. Instead, it is measured indirectly by exploiting the fact that the stress of the film tends to distort the shape of underlying substrate. A disk-shaped substrate, such a wafer, will tend to bow under the force created by the residual stress of the film. The stress will force the film-substrate structure into a convex shape if the film stress is compressive and a concave shape if the stress is tensile, as illustrated in Figure 2.7.

Figure 2.7: Film under residual tensile (left) and compressive stress (right) causes bending.
Converting this physical deformation into a value of residual stress requires measuring the shape change, typically taken as curvature change, of the substrate before and after film deposition. The curvature is typically measured using a laser scanning instrument (described in further detail in the Experimental Procedures chapter), which detects vertical displacement at points across the diameter of the wafer. This change in vertical displacement can be converted to a value for the average curvature of the substrate. This curvature can then be converted to residual stress by use of the Stoney formula. The Stoney formula was first given by Stoney in 1909 [46] and is extremely useful because it requires no knowledge of the film beyond its thickness. The formula is shown below:

\[
\sigma_f = \frac{E_s d_s^2}{6R(1-\nu_s)d_f} = \frac{\overline{E}_s d^2}{6R d_f}
\]  

(2.1)

where \( \sigma_f \) is the residual stress of the film, \( E_s \) is the Young’s modulus of the substrate, \( d_s \) is the thickness of the substrate, \( R \) is the radius of curvature measured for the film-substrate system (as shown in Figure 2.7), \( \nu_s \) is Poisson’s ratio of the substrate, \( d_f \) is the thickness of the film, and \( \overline{E}_s \) is the biaxial modulus of the substrate.

Through the use of curvature measurements, knowledge of the substrate material properties (typically well-characterized materials such as single crystal silicon) and the film thickness, a measure of the residual stress can be obtained.

**Coefficient of Thermal Expansion**

A critically important film property is the coefficient of thermal expansion (CTE). In a solid oxide fuel cell, as in other multilayer devices, the materials must have
compatible CTEs to avoid cracking, or otherwise failing, during thermal cycling.

Characterizing the residual stress of the film is one way to determine the CTE. Once the baseline value for residual stress at room temperature has been established, the film can then be subjected to a thermal cycle. The resulting residual stress versus temperature curve is related to the CTE by the following:

$$\frac{\partial \sigma}{\partial T} = \bar{E}_f (\alpha_s - \alpha_f)$$  \hspace{1cm} (2.2)

where \(\frac{\partial \sigma}{\partial T}\) is the slope of the residual stress-temperature plot, \(\bar{E}_f\) is the biaxial modulus of the film, and \(\alpha_s\) and \(\alpha_f\) are the CTE of the substrate and the film, respectively.

Measuring the (linear) slope of the stress-temperature plot gives the \(\bar{E}_f \Delta \alpha\) product, or “modulus-CTE” product, which is a function of the substrate CTE. Calculating the biaxial modulus and CTE of the film requires an additional analysis which is not conducted in this research.

2.7 Electrochemical Performance

The electrochemical performance of a material can be determined using a technique known as impedance spectroscopy. Impedance spectroscopy provides a measure of resistance of the material of interest which can then be converted into values for conductivity and activation energy. This technique is described in detail in the following section.
2.7.1 Impedance Spectroscopy - Background and Technique

The general approach to impedance spectroscopy is to apply an AC potential, over a range of frequencies, to an electrode-material system (an electrochemical cell) and measure the resulting current (amplitude and phase shift) through the cell. Measuring conductivity as a function of frequency has the advantage of allowing the film resistance to be separated from the electrode resistance, since each is 'active' at different frequency ranges.

In the following section, the mathematics of impedance spectroscopy is introduced, drawing heavily from the work of Barsoukov et al. [33] and from [13]. The method involves calculating impedance from excitation signal and the resulting current, plotting the impedance data on a Nyquist plot, fitting an equivalent circuit, understanding how different resistances are observed, and ultimately calculating a value for conductivity.

![Figure 2.8: Schematic of impedance measurement technique.](image)

Impedance spectroscopy begins with the application of an AC potential for the system shown in Figure 2.8. The excitation signal, as a function of time, is:

\[ E(t) = E_0 \cos(\omega t) \]  
(2.3)
where $E(t)$ is the potential at time $t$, $E_0$ is the amplitude, and $\omega$ is the radial frequency (the relationship between radial frequency $\omega$ (radians/second) and frequency $f$ (hertz) is:

$$\omega = 2\pi f$$

The resulting steady state current is:

$$I(t) = I_0 \cos(\omega t - \phi)$$

(2.4)

where $I$ is the current at time $t$, $I_0$ is the current amplitude and $\phi$ is the phase shift.

The impedance, $Z$, of the system can be calculated using an expression analogous to Ohm’s law:

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\alpha \xi)}{I_0 \cos(\alpha \xi - \phi)} = Z_0 \frac{\cos(\alpha \xi)}{\cos(\alpha \xi - \phi)}$$

(2.5)

The above expression can expressed as a complex function, using Euler’s relationship:

$$\exp(j \varphi) = \cos \varphi + j \sin \varphi,$$

the excitation voltage becomes:

$$E(t) = E_0 \exp(j \omega t)$$

(2.6)

and the current response becomes:

$$I(t) = I_0 \exp(j \omega t - j \phi)$$

(2.7)

which allows impedance to be written as a complex number:
\[ Z = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0 (\cos\phi + j\sin\phi) \quad (2.8) \]

The impedance, \( Z \), can then be plotted on a Nyquist plot, with the real component on the x-axis and the negative of the imaginary component on the y-axis, as shown in Figure 2.9. Each point on the curve is the measured impedance, \( |Z| \), at frequency, \( f \).

![Nyquist plot with impedance vector](adapted from [13]).

The semicircular shape, or arc, in Figure 2.9 is indicative of a single “time constant”. Electrochemical impedance plots often contain more than one time constant, with each time constant (semicircle on Nyquist plot) representing a different physical phenomenon in the system. Such phenomena include material resistance, electrode resistance, and resistance across the grain and grain boundary of the material, among many others. In general, electrode resistance is identified at the lowest frequencies on the Nyquist plot, followed by grain resistance and then material resistance as frequency increases, as shown in Figure 2.10.
The plot is analyzed by fitting the data to an equivalent circuit model. Equivalent circuit models are usually comprised of common electrical elements such as resistors, capacitors and inductors. A simple equivalent circuit with one time constant, to fit the data above, can be represented by a resistor and capacitor in parallel, as in Figure 2.11.

Analyzing impedance data with several arcs, and therefore multiple time constants, requires more complex circuits. Sample impedance data with two arcs and the related equivalent circuit is shown in Section 3.5.2.
Calculating Conductivity and Activation Energy

Once the appropriate equivalent circuit has been fit to the impedance data, the resistance due to the electrolyte, and any other resistances, can be determined as the R₁, R₂...Rₓ which solve the circuit. As illustrated in the example in Figure 2.10, this research takes R₁, R₂, and R₃ as the resistance of the bulk material, grain and electrodes, respectively. In this research, R₁ is used to calculate the conductivity of the material (electrolyte) which is common practice in electroceramics. The conductivity, σ, is calculated as follows:

$$\sigma = \frac{L}{AR} \quad (2.9)$$

where L is distance between electrodes, A is a cross-sectional area (which, in this research, is equal to electrolyte film thickness x length of the interdigitated electrode), and R is the resistance of the electrolyte.

The activation energy, $E_A$, of the material can also be calculated by:

$$E_A = -km \quad (2.10)$$

where $k$ is the Boltzmann constant [$k = 8.617 \times 10^{-5} \text{ eV K}^{-1}$] and $m$ is the slope of the line of the natural log of conductivity plotted against the inverse of temperature (in Kelvin).

Activation energy is the energy that must be overcome in order for a reaction to occur. In the context of this research, a material with lower activation energy will be conductive at a lower temperature, a highly desirable outcome for a SOFC application. The concept of activation energy is also useful in that it allows for electrochemical comparison across materials.
Electrode Materials

In order to test the conductivity of the sample, an electrode must be affixed to the electrolyte. The common choice for an electrode for BaCeYO and SrCeTb is platinum, as discussed below, and is the choice in this work.

In their work with BaCeYO, Lee et al. [4] used platinum for the anode and cathode material. Guan [9] also used a platinum mesh affixed with silver paste. Hibino [11] tested a 3 wt % Pd-loaded FeO anode and a Ba$_{0.5}$Pr$_{0.5}$CoO$_3$ cathode, but used pure platinum as a reference electrode. In a 2004 study of BaCeYO [14], Hibino again used platinum electrodes.

In their work with SrCeTbO, Matsumoto et al. [35] used porous platinum electrodes. Dionysiou et al. [39] and Qi [40] used silver paint. Iwahara [41] used both platinum and nickel for the anode and a perovskite-type oxide for the cathode in his early research on un-doped SrCeO.
3 Experimental Procedures

This chapter contains a description of the experimental work performed in this research. The chapter is broadly divided into two sections: depositing the thin films and analyzing the films. In the first section, the production of sputtering targets, the sputtering conditions and the choice of substrate material are all discussed. The second section contains a discussion of the resulting thin films and the tools and analyses used to determine film thickness and uniformity, residual stress, and electrochemical performance.

1.1 Target Preparation

The target is the source material for the sputter deposition process. Though many types of materials may be sputtered, this research utilizes ceramic materials, and thus requires a ceramic target. In general, producing a ceramic target consists of the following steps: determining the precursor materials and their quantity, mixing the precursors, calcining the mixture, re-mixing the calcined powders, forming the target, and sintering the target. During calcining the powders are heated in order to decompose the carbonates of the precursor materials and form the desired material compound. During sintering, the powders are again heated, to a higher temperature than during calcining, in order fuse the particles together and create a dense, ceramic target that can withstand repeated sputtering runs. The details of creating the particular targets for this research are described below.
3.1.1 Preparation of BaCeY and SrCeTb Targets

Several targets of both BaCeY and SrCeTb were prepared using the same method. These methods were based on several prior works [4,7,9,11,29,] and advice from experienced colleagues in the Department of Material Science and Engineering at MIT. To be compatible with the available sputtering system, targets were required to be in disk form approximately two inches in diameter and 1/8 inch thick.

Barium cerium yttrium targets were prepared from three precursor materials: barium carbonate (BaCO$_3$), cerium dioxide (CeO$_2$) and yttrium oxide (Y$_2$O$_3$). Strontium cerium terbium targets also used three precursors: strontium carbonate (SrCO$_3$), cerium dioxide (CeO$_2$) and terbium oxide (Tb$_4$O$_7$). The precursor materials were obtained in a powder form from Alfa Aesar Corp [47].

The amount of each precursor required was determined by calculating the desired stoichiometry of the final target material, which is also the desired composition of the film. As was discussed in Section 2.5, the sputtering process ejects atoms of the target material and deposits them onto the substrate, creating a film with a stoichiometry approximately equal to that of the target. The barium cerate target was to be 10% doped with yttrium. The strontium cerate target was 5% doped with terbium. These dopant levels were deemed an appropriate starting point based on prior research (discussed in Sections 2.3 and 2.4). The detailed stoichiometric calculations are shown in Figures 3.1 and 3.2 (note that oxygen is not explicitly part of the precursor calculation because the reactions utilize oxygen from the atmosphere during calcining).
Molar Calculation for BaCe₉Y₁O₃

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Weight</th>
<th>Desired Ratio</th>
<th>Weight Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>137.33</td>
<td>137.33</td>
<td>1 mol BaCe₉Y₁O₃ = 320.32 g</td>
</tr>
<tr>
<td>Ce</td>
<td>140.12</td>
<td>0.9</td>
<td>126.10</td>
</tr>
<tr>
<td>Y</td>
<td>88.91</td>
<td>0.1</td>
<td>8.89</td>
</tr>
<tr>
<td>O</td>
<td>16</td>
<td>3</td>
<td>48</td>
</tr>
</tbody>
</table>

C 12.01

Precursor Calculation

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Element</th>
<th>Molar Calculation</th>
<th>Grams req'd for 200g of BaCeYO</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCO₃</td>
<td>Ba</td>
<td>1 mol BaCO₃ = 197.34 g</td>
<td>123.21 g</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Ce</td>
<td>1 mol CeO₂ = 172.12 g</td>
<td>96.72 g</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>Y</td>
<td>1 mol Y = 112.91 g</td>
<td>7.05 g</td>
</tr>
</tbody>
</table>

Figure 3.1: Target composition calculations for BaCe₉Y₁O₃.

Molar Calculation for SrCe₀₉₅Tb₀₅O₃

<table>
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<tr>
<th>Element</th>
<th>Atomic Weight</th>
<th>Desired Ratio</th>
<th>Weight Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>87.62</td>
<td>87.62</td>
<td>1 mol SrCe₀₉₅Tb₀₅O₃ = 276.68 g</td>
</tr>
<tr>
<td>Ce</td>
<td>140.12</td>
<td>0.95</td>
<td>133.11</td>
</tr>
<tr>
<td>Tb</td>
<td>158.925</td>
<td>0.05</td>
<td>7.95</td>
</tr>
<tr>
<td>O</td>
<td>16</td>
<td>3</td>
<td>48</td>
</tr>
</tbody>
</table>

C 12.01

Precursor Calculation

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Element</th>
<th>Molar Calculation</th>
<th>Grams req'd for 200g of SrCeTbO</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCO₃</td>
<td>Sr</td>
<td>1 mol SrCO₃ = 147.63 g</td>
<td>106.72 g</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Ce</td>
<td>1 mol CeO₂ = 172.12 g</td>
<td>118.20 g</td>
</tr>
<tr>
<td>Tb₄O₇</td>
<td>Tb</td>
<td>1 mol Tb = 186.93 g</td>
<td>6.76 g</td>
</tr>
</tbody>
</table>

Figure 3.2: Target composition calculations for SrCe₀₉₅Tb₀₅O₃.
The desired amounts of each precursor were carefully weighed to ±5 mg on a powder scale and combined. The powder mixture was combined with YTZ (95% ZrO$_2$, 5% Y$_2$O$_3$) grinding media, obtained from Tosoh Corporation [48] and methanol in a 1:1:1 ratio. The mixture was then tumbled (in a custom tumbler) for at least 24 hours to ensure proper mixing. The mixture was removed from the tumbler and dried in a beaker on a heated mixing plate (set at 100°C and 250 rpm). The dried mixture was placed in an alumina combustion tray (obtained from Alfa Aesar) and calcined in a furnace at 1000°C for 12 hours (with a heating and cooling rate of 5°C/min).

The calcined powder was again mixed with grinding media and methanol in the same 1:1:1 ratio. A “binder” was then added to this mixture. The binder, Poly(methylmethacrylate) (PMMA) [47], was added in the quantity of 1% of the total weight of the original precursor powders. The binder helps the loose powder to hold its shape when pressed into the disk mold. The binder burns off in the sintering process and is not part of the final composition. This mixture, including the binder, was again tumbled for at least 24 hours and then dried on a hot plate under the same conditions as described above. The desired quantity of the dried mixture to make each target (~36g) was then ground with a mortar and pestle and placed into a stainless steel mold. The mold was pre-cleaned with isopropanol and then lubricated with stearic acid dissolved in acetone. The powder in the mold was pressed to 30,000 lbs using a uniaxial press.

The calcined powder was now in the desired form (2” dia x 1/8” thick disk). The disk was placed on an alumina combustion tray and sintered in the furnace at 1450°C for 12 hours (with a ramp rate of 3°C/min). The sintered target was removed from the furnace. Ceramic targets are inherently brittle, so to improve the structural integrity each
target was bonded to a solid copper disk (also of dimensions 2” dia x 1/8” thick) using silver paste. The completed target was now ready for use.

3.1.2 Target Composition

Target composition was assessed primarily using x-ray diffraction (XRD). The BaCeYO target was also assessed using wavelength dispersive spectrometry (WDS). The XRD scan settings were as follows: scan speed of 2.0°/min, sampling interval of 0.01° and angles measured from 10-90°.

Analysis of the XRD scans of the BaCeYO target shows that the desired phase was achieved. SrCeTbO is a much less common material and so there were no reference XRD data to compare against. However, the target does match the reference data for strontium cerate Sr(CeO)₃, which is a reasonable proxy for terbium-doped SrCeO₃³. The XRD scans are shown in Figures 3.3 and 3.4.

³ The author was not able to obtain an XRD scan of SrCeTbO from the literature search or from the analysis software, Jade. However, because the dopant level is small (5%), the likely effect on the XRD scan is a small shift of peaks to the left or right, with respect to the scan of SrCeO. The significant peaks should retain their shape and spacing.
Figure 3.3: XRD scan of BaCeYO sputtering target compared to the standard for BaCeYO.
The composition of the BaCeYO target was also assessed using wavelength dispersive spectrometry (WDS) using an electron probe (JEOL JXA-733 Superprobe) in Department of Earth, Atmospheric and Planetary Sciences at MIT. WDS analysis provides a measure of the quantity of each element in the material (in terms of an atomic percentage). Based on the chemical composition, BaCe$_{0.9}$Y$_{0.1}$O$_3$, the elements barium (Ba), Cerium (Ce) and Yttrium (Y) should appear in a ratio of approximately 10:9:1 (Ba:Ce:Y). The amount of oxygen (O$_3$) is not reliably measured using WDS [49]. As shown in Table 3.1 there appears to be a small excess of cerium and a small deficiency of...
yttrium. This may indicate the presence of unwanted cerium oxide as was discovered in the films of BaCeYO and discussed in Section 3.3.1. A WDS analysis for SrCeTbO was not performed.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Normalized to Ba</th>
<th>Expected (Stoichiometric)</th>
<th>Measurement Error%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>38.3</td>
<td>10</td>
<td>10</td>
<td>1.7%</td>
</tr>
<tr>
<td>Ce</td>
<td>47.4</td>
<td>12.4</td>
<td>9</td>
<td>0.7%</td>
</tr>
<tr>
<td>Y</td>
<td>1.8</td>
<td>0.5</td>
<td>1</td>
<td>9.4%</td>
</tr>
</tbody>
</table>

Table 3.1: WDS results for BaCeYO target composition.

Two tools, X-ray diffraction spectroscopy and wavelength dispersive spectrometry, were used to assess the composition of the sputtering targets prior to film deposition. XRD is the more commonly applied tool for assessing these types of compounds and analysis of the results shows that the targets do have the desired composition. WDS is less commonly applied and served here a secondary check. Analysis of the WDS results for BaCeYO indicates that the target may have a small excess cerium and a small deficiency of yttrium. Nonetheless the WDS results are reasonably close to the desired composition and thus the targets are considered approximately stoichiometric.

### 3.2 Sputter Deposition

The sputtering system used in this research was a Kurtis Lesker reactive RF magnetron system with a sputter gun configuration located in the Department of Material Science and Engineering at MIT. The system is illustrated in Figure 3.5. The system has three target locations (A, B, and C in Figure 3.5), consisting of a copper mounting plate
atop a magnet, which is water cooled from behind (this configuration is referred to as a “sputter gun”). The targets are inclined 30 degrees from vertical and have a working distance of approximately 9 cm. The substrate is suspended on a rotating stage above the targets in the center of the chamber. The substrate can be heated from behind with using halogen bulb. Vacuum in the chamber is achieved via two vacuum pumps – a mechanical pump to reach 0.8 Torr, followed by a cryo-pump to reach a vacuum up to 10^{-7} Torr. The remainder of this section discusses the sputtering parameters used in this research.
Figure 3.5: Schematic of the Kurtis Lesker sputtering system used in this research, top and side view [32].
3.2.1 Sputtering Parameters

Sputter deposition parameters can have a significant effect on the properties of the resulting film, as discussed in Section 2.5. The parameters of interest primarily include the working pressure of the sputtering gas, sputtering gas composition, power and substrate temperature. This research did not attempt to investigate how varying these parameters would affect the specific materials in question. Instead, baseline values were used for each parameter based on prior research on these materials, and on sputtered ceramic oxides in general. As necessary, these baseline values were adjusted to achieve the desired material composition and were henceforth held constant.

The only parameter that was varied significantly was the substrate temperature. The maximum temperature of the system was $575 \, ^\circ C$ and this produced the purest film composition. Temperatures slightly lower than $575 \, ^\circ C$ produced significant amounts of the secondary phases such cerium oxide. Temperatures much lower (several hundred degrees) than $575 \, ^\circ C$ did not produce the desired composition at all. This is consistent with the findings of He et al. [7] who found that the composition of BaCeY was highly temperature dependent.

The following sputtering parameters were used for the deposition of both materials after initial trial depositions:

<table>
<thead>
<tr>
<th>Sputtering Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working pressure</td>
<td>10 mtorr</td>
</tr>
<tr>
<td>Gas composition</td>
<td>9:1 argon:O2</td>
</tr>
<tr>
<td>RF power</td>
<td>70 watts</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>$575 , ^\circ C$</td>
</tr>
</tbody>
</table>

Table 3.2: Sputter deposition parameters used in this research.
The sputtering power was limited to 70 watts because it was found to be near the threshold power at which both ceramic targets would crack and become unusable. The result was that the deposition rate was a relatively low 130 nm per hour. It was also determined that a maximum ramp rate of approximately 30 watts per hour could be used without cracking the targets.

3.2.2 Achieving Uniform Film Thickness

In order to characterize residual stress using wafer curvature and the Stoney formula, the film must have a relatively uniform thickness across the substrate. Indeed, for the film to ultimately be used in a fuel cell device the film must be uniformly thick as well. This proved to be a significant challenge with the available sputtering system.

The thickness profile was found to follow the equation below [15].

\[
\frac{d}{d_0} = \left[1 + \left(\frac{S}{h}\right)^2\right]^{1/2} \frac{1 + \left(\frac{l}{h}\right)^2 + \left(\frac{S}{h}\right)^2}{\left[\left(\frac{l}{h}\right)^2 + \left(\frac{S}{h}\right)^2\right]^{1/2} + \left(\frac{l}{h}\right)^2} \quad \text{Eq. 3.1}
\]

Where \(S\) is the radius of the target, \(l\) is the distance from the center of the substrate and \(h\) is distance from the target to the substrate. The ratio \(d/d_0\) is the ratio of the film thickness at \(d\), the distance from the center of the substrate, and at the center of the substrate \(d_0\), as illustrated in Figure 3.6.
Figure 3.6: Position and dimensions of target and substrate (adapted from [15]).

This equation yields the general thickness profile shown in Figure 3.7. The shape of the profile is marked by a significant depression at the center of the film and increasing thickness moving away from the center, peaking at distance $l = S$.

Figure 3.7: General thickness profile for a sputtered thin film (from [15]).
This equation was applied to the sputtering system used in this research. All parameters of the system were fixed, with the possible exception of \( h \), the distance from the target to the substrate, which was previously fixed at \( h=3 \) inches. This distance was varied using equation 1.1 and plotted in Figure 3.8. The plot clearly shows that to achieve uniform thickness with the given configuration, it would be necessary to position the substrate at a distance of approximately 1.5 inches from the target.

![Thickness Uniformity vs. Substrate Distance from Target](image)

**Figure 3.8: Thickness profile as a function of target-substrate distance, \( h \) (\( h \) is in inches).**

A new substrate holder was fabricated to position the wafer at the appropriate distance from the target (\( h=1.5" \), \( S/h = 4/3 \)). An integrated heat shield was also added in order to keep the substrate at the desired temperature, now that the wafer was farther from the
heat source. This new position allowed for the deposition of nearly uniformly thick films. The thickness profile for a nominally 300nm thick film is shown in Figure 3.9. The thickness varies less than 15% over the middle 80% of the diameter of the wafer. The middle 80% is the relevant region used in the wafer curvature measurements and residual stress calculations (as discussed in Section 3.4). Thickness measurements for the films are discussed in Section 3.3.2.

Figure 3.9: Film thickness profile for a 300nm BaCeYO film.

3.2.3 Substrate

The substrate chosen for the film deposition was a fused silica wafer. Fused silica is a high-purity synthetic amorphous silicon dioxide. This material was chosen for several reasons. First, silica is amorphous and thus eliminates the potential for epitaxial crystal growth that could occur with a silicon substrate. Though the ultimate fuel cell
device would be constructed from a silicon wafer, the electrolyte would be deposited on a bilayer of silicon nitride and a cathode material, which would most likely be amorphous. Second, the fused silica is a good choice for impedance spectroscopy because it is electrically insulating and stable at high temperatures. Third, the amorphous nature allows for higher quality x-ray diffraction analysis of the sputtered thin films, because there is not a very large peak (as with a silicon substrate) dominating the plot and obscuring the smaller peaks of interest.

The fused silica wafers were obtained from Mark Optics, Inc [50]. The wafers were 100 mm (+/- 0.2 mm) in diameter, 500 um (+/- 25 um) thick, had one flat and were polished on one side. The fused silica used has the following mechanical properties [50]:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic (Young’s) Modulus</td>
<td>72.7 GPa</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>31.4 GPa</td>
</tr>
<tr>
<td>Modulus of Rupture</td>
<td>52.4 MPa</td>
</tr>
<tr>
<td>Bulk Modulus</td>
<td>35.4 GPa</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.16</td>
</tr>
<tr>
<td>Biaxial Modulus (calculated)</td>
<td>86.5 GPa</td>
</tr>
<tr>
<td>Density</td>
<td>2.201 g/cm³</td>
</tr>
</tbody>
</table>

**Table 3.3: Mechanical properties of fused silica from Mark Optics [50].**

Before deposition the wafer was cleaned with rinses of acetone, methanol and isopropynol, in that order. The wafer was then blown dry with compressed filtered air.
3.3 Film Composition and Thickness

Stoichiometry and thickness uniformity of both sputtered films are discussed here because both properties are important to the residual stress and electrochemical characterizations presented in Chapter 4.

3.3.1 Film Composition

As with the composition of the target material, the composition of the films were determined using x-ray diffraction (XRD) and wavelength dispersive spectrometry (WDS). The XRD scan settings were as follows: scan speed of 2.0 °/min, sampling interval of 0.01° and angles measured from 10-90°.

Analysis of the XRD scan of the BaCeYO film shows that the desired phase was achieved, but that there is also a secondary phase of cerium oxide, possibly associated the excess cerium identified in the WDS analysis of the target. As mentioned above, there were no reference data for SrCeTbO, so the sample was again compared to strontium cerate Sr(CeO)₃, which is a reasonable proxy for terbium-doped SrCeO₃. While the sample does appear to contain strontium cerate, it also appears to contain several other phases: Ce₁₁O₂₀ (cerium oxide), SrO₁.₉₇₈ (strontium oxide), and SrTbO₃ (strontium terbium oxide). Due to the complicated XRD pattern and the signal noise, it is not possible to conclusively identify the phases, however it is believed that the sample does contain at least some SrCeTbO. The scans for BaCeYO and SrCeTbO are shown in Figures 3.10 and 3.11, respectively.
Figure 3.10: XRD scan of BaCeYO film compared to the standard for BaCeYO.
As with the WDS analysis for the BaCeYO target, the expected ratio of Ba:Ce:Y in the film is approximately 10:9:1. As shown in Table 3.4, there appears to be an excess of both Ce and Y. This is consistent with both the target WDS analysis (see Table 3.1) and the analysis of the film XRD scan, which shows there is a secondary phase of cerium oxide. The elements for SrCe$_{0.95}$Tb$_{0.05}$ are expected to be in the ratio 10:9.5:0.5 for Sr:Ce:Tb. As shown in Tables 3.5 there appears to be a deficiency of Ce. This could also be consistent with the other phases shown in the XRD analysis of SrCeTbO film in Figure 3.11.
### Table 3.4: WDS results for BaCeYO film.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Normalized to Ba</th>
<th>Expected (Stoichiometric)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>10.5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Ce</td>
<td>21.5</td>
<td>20.5</td>
<td>9</td>
</tr>
<tr>
<td>Y</td>
<td>2.5</td>
<td>2.4</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 3.5: WDS results for SrCeTbO film.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Normalized to Sr</th>
<th>Expected (Stoichiometric)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>8.3</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Ce</td>
<td>4</td>
<td>4.8</td>
<td>9.5</td>
</tr>
<tr>
<td>Tb</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The films, although not stoichiometric, did contain the desired phases of BaCeYO and SrCeTbO.

#### 3.3.2 Film Thickness

Thickness was measured using a Tencor P-10 Surface Profilometer, which operates by moving a stylus across a step change in height/thickness. In order to create the necessary step change between the substrate and the film, each wafer was masked in eight locations across the diameter using a small amount of White-Out® office correction fluid. The White-Out® was applied before deposition and was then easily removed after deposition with a razor blade and acetone. The masking pattern begins 0.25 inches from the left edge of the wafer (with the flat at the top) and locations were then spaced 0.75 inches thereafter, as shown in Figure 3.12 below.
The results of the film thickness analysis are shown in Figure 3.13 for BaCeYO. The thickness varies less than ± 10% over the middle 80% of the diameter. The film is thicker at the edges of the wafer, but this was expected. It is common for film thickness to increase at edges of the wafer, especially if the target has a smaller diameter than the wafer (in this case a 2” target was used for a 4” wafer) [17]. The SrCeTbO film had a similar thickness profile with the same ± 10% over the middle 80% of the diameter. The relevant area of the film for curvature measurement is the middle 80%, as discussed in Chapter 2. Greater uniformity could certainly be achieved with a dedicated or optimized sputtering system.
Figure 3.13: Film thickness profiles for 200, 300, and 500 nm thick BaCeYO films.

3.4 Film Analysis – Residual Stress

Residual stress is calculated using the Stoney formula based on wafer curvature. This calculation is described in detail in the Prior Work chapter. The curvature of the wafer was measured using a Tencor FLX-2320 Thin Film Stress Measurement System.

The basic theory of operation of the Tencor is that curvature is measured using a laser which is scanned across the surface of the substrate. The laser beam is passed through a lens to ensure that it impinges perpendicular to the surface. A photodetector records the angle of the reflected beam. A perfectly flat substrate will have zero angle of deflection. Each angle of deflection can be translated into a vertical displacement and
then collectively into a radius of curvature for the wafer. A schematic of this system is shown in Figure 3.13.

![Schematic of laser scanning instrument](image)

**Figure 3.14: Schematic of a laser scanning instrument used for measuring substrate curvature (adapted from [32]).**

Curvature is approximately related to displacement by the relation:

$$\kappa = \frac{\partial^2 w}{\partial x^2}$$  \hspace{1cm} \text{Eq. 3.2}

where $\kappa$ is the curvature, $w$ is the out-of-plane displacement, and $x$ is the distance from some reference point. Quinn [32] found that the uncertainty in the curvature measurements on the same Tencor 2320 to less than +/- 1%. Quinn determined this by examining the variation of 30 measurements taken along the same line the wafer. To convert the displacement data into a radius of curvature, a quadratic equation was fit to the displacement versus position data. The coefficient of the quadratic term was then taken as one-half the radius of curvature.

A base curvature measurement was taken on each bare wafer at room temperature prior to film deposition. Vertical displacement data consisted of 50 data points evenly
spaced across the inner 80% of the diameter of the wafer. The measurement was then repeated after film deposition. The change in curvature between the wafer with and without the film was used to calculate the residual stress of the film. Each wafer, with film, was then subjected to two identical thermal cycles. The wafer was heated to 500°C at a rate of 2.0°C per minute, held at 500°C for one to three hours and then cooled to room temperature at 2.0°C per minute. The cycle was then repeated. The thermal cycles were used to simulate the operating environment the film would experience in a fuel cell device and therefore explore hysteresis in the intrinsic components of residual stress.

Curvature data was analyzed to determine if there was an annealing effect in the film, what consequence it held for residual stress and whether any changes were permanent or continued to vary with temperature.

3.5 Film Analysis – Conductivity

Electrochemical performance of the film was analyzed using impedance spectroscopy. The theory of this technique is described in Section 2.7. In practice, this technique had two experimental components, fabricating electrodes and measuring impedance, which are described below.

3.5.1 Electrode Fabrication

Thin, closely spaced (metal) electrodes were required to conduct the AC signal through the thin film. For this research, platinum electrodes were chosen and were applied to the film using photolithography and sputtering. Platinum is known to be a
catalyst for BaCeYO and SrCeTbO as discussed in Section 2.7. The procedure is described below.

The fused silica wafer with film was cleaned with an acetone and isopropanol rinse and spun dry at 3000 rpm for 40 sec and further dried on a hot plate at 150°C for 2 minutes. The wafer was then spin-coated with a negative photoresist, NR7, at 700 rpm for 10 seconds and 3000 rpm for 30 sec. The coated wafer was pre-baked at 150°C for 1.5 minutes on a hot plate. The electrode pattern mask was placed on the wafer and the photoresist was exposed to UV light for 40 seconds. The exposed wafer was then post-baked at 150°C for 1.5 minutes on a hot plate. The cured photoresist was developed in Futurexx RD6 developing solution for 30 sec and rinsed in deionized water and dried.

Next, a 150 nm thick film of platinum was sputtered onto the wafer. The sputtering conditions were: room temperature, 5 mtorr working pressure, 100 % argon atmosphere, and DC magnetron sputtering at 50 watts. The wafer was then soaked in acetone to lift-off the photoresist layer. This resulted in three patterns of interdigitated platinum electrodes, referred to as Pattern 14, 15 and 16. A die-saw in the Experimental Materials Laboratory at MIT was used to dice the wafer into 11 mm x 11 mm squares (just beyond the perimeter of each electrode pattern), so that each pattern could be tested individually.

The first pattern, pattern 16, has “fingers” measuring 100µm in width and spaced 100µm apart. Pattern 15, has similar geometry as pattern 16 but the fingers are 50µm wide and 50µm apart. Pattern 14 also has the same geometry, but the fingers are 25µm wide and 25µm apart. The different electrode width and spacing of each of the patterns changes the distance of the conduction path through the film as well as the length of the
triple phase boundary (TPB). As a result, different electrochemical properties of the film may be highlighted with each pattern. This is discussed further in Section 4.2. Sample interdigitated electrodes are shown in Figure 3.14. The outer dimensions of the electrode are 10mm x 10mm.

Figure 3.15: Electrode schematic (Pattern 15), left, and electrodes patterned on fused silica, right [17].

3.5.2 Impedance Measurement

Impedance spectroscopy measurements were taken using a custom microprobe station in the Department of Material Science at MIT. The film sample, now patterned with electrodes, was diced into 11 mm x 11 mm dies and placed on a heated sample holder, consisting of a small metal disk measuring 1.5 inches in diameter and electrically heated from bottom. The sample temperature was measured by a thermocouple positioned on the top side of the sample. The electrodes were electrically connected via
platinum wire leads to a Solartron 1260 Impedance/Gain Phase Analyzer. Sample temperature was controlled using LabView data acquisition software and impedance was recorded with ZPlot software [53]. Measurements were either taken in ambient air, or in a sealed, gas-tight chamber containing either dry air (purchased) or a hydrogen mix (5% H₂ + 95% Ar).

The sample was heated from room temperature to ~ 500 °C at a rate of 5°C/minute and then cooled at the same rate. The sample was held at each temperature for 15 minutes to ensure it had reached steady state. Beginning at 200°C, impedance was measured every 50°C during heating and cooling. At each temperature interval, impedance was measured over a range of frequencies, from 10 MHz to 10 mHz.

The following is an example of deriving a measurement of conductivity from the impedance data. The raw impedance data is first plotted on a Nyquist plot, as described in Section 2.7 and shown in Figure 3.16. The Nyquist plot, in this case, clearly shows the expected arc shape, but the arc appears to be “squashed”. This appearance is indicative of two arcs, or two “time constants”, rather than just one.
Figure 3.16: Sample impedance data plotted on a Nyquist plot with time constants superimposed. Data is from a 500 nm thick BaCeYO film at 473°C.

The above impedance data can be fit with the equivalent circuit shown in Figure 3.17, using ZView software [53]. The circuit contains an inductor, L1, and two resistor-capacitor (RC) elements, one for each time constant. R1 and R2 are the resistors. A CPE is a “constant phase element” and acts somewhat like a capacitor⁴. The R1-CPE1 and R2-CPE elements represent the larger left arc and the smaller right arc in Figure. 3.16, respectively).

---

⁴ A constant phase element is a non-intuitive circuit element that was “invented” while looking at response of real-world systems. This element accounts for the fact that the center of the arc sometimes does fall on the x-axis as an ideal capacitor would but, instead, the center is some distance below the axis. The depressed center is generally interpreted to mean that some property of the system is not homogenous or that there is some distribution of the value of some physical property of the system. The important point is that it provides a useful modeling element for analyzing the system even if the cause is not determined [51].
Figure 3.17: Equivalent circuit used to curve fit the impedance data in Figure 3.15.

Solving for the elements of the equivalent circuit yields the following values for the R1, C1, R2, C2, and L, shown in Table 3.6.

<table>
<thead>
<tr>
<th>Element</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>3023</td>
<td>ohms</td>
</tr>
<tr>
<td>C1</td>
<td>1.07E-10</td>
<td>farads</td>
</tr>
<tr>
<td>R2</td>
<td>1802</td>
<td>ohms</td>
</tr>
<tr>
<td>C2</td>
<td>5.94E-08</td>
<td>farads</td>
</tr>
<tr>
<td>L1</td>
<td>8.10E-06</td>
<td>henries</td>
</tr>
</tbody>
</table>

Table 3.6: Solved values for equivalent circuit elements (example).

As described in Section 2.7, conductivity, $\sigma$, is then be calculated using Equation 2.9:

$$\sigma = \frac{L}{AR}$$

where L is distance between electrodes, A is a cross-sectional area (which is equal to electrolyte film thickness x length of electrode), and R is the resistance of the electrolyte. In this case there are two time constants and thus two values of resistance and conductivity. R1, in this case, represents the resistance of the film and R2 most likely represents the resistance of the grain boundaries within the film. The inductor, L, represents the inductance of the coaxial cable used to connect the Solartron to the electrodes. This inductance had been previously characterized by a colleague [17]. The
capacitors, C1 and C2 represent the capacitance of the film and the grain boundaries, respectively.

This calculation is repeated for each temperature, electrode pattern, film thickness and film material. The results are presented and discussed in Section 4.2.
4 Results and Discussion

The research presented in this thesis has three objectives: to demonstrate the feasibility of producing BaCeYO and SrCeTbO in thin film form (<1 μm thick), to characterize the residual stress and thermomechanical properties of the resulting films, and to characterize the electrochemical performance of the materials. In Section 3.2.2, it was shown that is possible to produce uniform thickness, crack-free films with the desired composition using sputter deposition. The results of characterizing residual stress, modulus-CTE product, and electrochemical performance are presented below. At the end of the chapter, a brief discussion of the microstructure of the films is also presented.

4.1 Residual Stress and Thermomechanical Properties

The results from the residual stress and thermal cycling tests are presented in this section. Each film was subjected to between one and four thermal cycles, as described in Section 3.4, and residual stress was derived as a function of temperature using wafer curvature measurements. Three different film thicknesses were analyzed (200, 400, and 600 nm) for each material. This thickness range was chosen because it represents likely values to be used in a μSOFC device (though the maximum thickness is also limited in practice by the slow deposition rate).
4.1.1 Residual Stress - BaCeYO

The residual stress versus temperature results for the three BaCeYO films are shown in Figures 4.1 - 4.3. The three films show the same general trend: an as-deposited initial compressive stress followed by a net tensile stress hysteresis which results in a small tensile or slightly compressive final stress state.

![Residual Stress vs T (3 Cycles) BaCeY 200nm](image)

**Figure 4.1:** Residual stress vs. temperature for a 200nm thick BaCeYO film.
Figure 4.2: Residual stress vs. temperature for a 400nm thick BaCeYO film.

Figure 4.3: Residual stress vs. temperature for a 600nm thick BaCeYO film.
The magnitude of the initial residual stress is relatively small, ranging from -261 to -482 MPa, for the 200 and 600 nm thick films, respectively. The final stress state and hysteresis are also relatively small (compared to similarly deposited YSZ films [32]). The maximum values are for the thickest (600 nm) film: 156 MPa and 638 MPa for final stress and hysteresis, respectively. These results are summarized later in Table 4.1. The 600 nm sample, however, was not annealed for as long an interval as the others, so the final stress magnitudes are likely to be somewhat higher than reported. Nonetheless, the stress magnitudes are relatively small compared to other materials considered for use in a μSOFC. Quinn [32] measured initial stresses up to -1.4 GPa for sputtered thin films of YSZ.

The observed hysteresis has also been witnessed in other works on sputtered thin films [32] and is believed to be an annealing effect which relieves the compressive stress caused by impurities or atomic peening (as discussed in Section 2.6.2). In each of the figures, it can be seen that the hysteresis is successively less with multiple or longer thermal cycles. It is reasonable to expect that with the appropriate thermal cycle the hysteresis would disappear completely. There are some differences among Figures 4.1-4.3, due to slight variations in the thermal cycles, which should be noted. The three thermal cycles performed on the 200 nm film in Figure 4.1 were completed in one continuous, automated run. This plot, therefore, is the best example of the decreasing hysteresis. In Figures 4.2 and 4.3 there was a delay between thermal cycles. In Figure 4.2 the delay was between the end of cycle 2 (after the “Cooling 2” stage completed) and the beginning of cycle three (before “Heat 3”) began. In Figure 4.3 the delay was between the end of cycle 1 and the beginning of cycle 2. In both cases, the film was
exposed to room atmosphere and temperature for several days between the cycles. The
effect of this delay is evident in that the stresses before and after the delay are not the
same, as they are in Figure 4.1, even though the films experienced no other processing.
In both cases, the stress state is more compressive at the start of the new cycle than it was
at the end of the previous cycle ( \( \sigma = -213.9 \) MPa and \( \sigma = -215.3 \) MPa for the 400 and
600 nm films, respectively). Regardless, the films eventually resume a similar
temperature-stress profile during the new thermal cycle. A similar phenomenon has been
observed in thin-film sputtered YSZ \cite{32}. The reason for this difference in stress is
unclear. It could be that the films absorbed some gas molecules from the atmosphere,
causing a compressive stress (swelling), that were then expelled upon being heated. This
is just speculation, however, and more work would be required to determine the
mechanism. It is not believed that this phenomenon affects the final stress, the hysteresis,
or the profile of the stress-temperature curve.

4.1.2 Residual Stress - SrCeTbO

The results of the residual stress experiments on SrCeTbO films are very similar
to those of the BaCeYO analysis. Again, the films show consistent behavior, as seen in
Figures 4.4 to 4.6: a relatively small initial compressive stress followed by a tensile
hysteresis that decreases with annealing, resulting in a small compressive or slightly
tensile final stress state. The magnitude of the initial residual stress ranges from -344 to -
570 MPa, in the 600 and 200nm thick films, respectively. Maximum observed hysteresis
was \( \sim +400 \) MPa, in both the 400 and 600nm thick films. Final stress magnitudes were
small: -232 MPa for the 200nm film, and 56 and 28 MPa for the other two thicknesses. These results are summarized later in Table 4.1.

Again, as in the BaCeYO analysis, the plots all exhibit a small disconnect between the end of the first thermal cycle and the beginning of the second cycle (\( \sigma = -50.1 \) MPa, \( \sigma = -31.9 \) MPa, \( \sigma = -29.4 \) MPa for the 200, 400 and 600 nm films, respectively). The reason for this is the same delay between thermal cycles as described in Section 4.1.1. The disconnect is smaller in magnitude than in the BaCeYO cycles because the length of the delay was smaller (<12 hours). The reason is again unclear but is not believed to materially affect the results.

Figure 4.4: Residual stress vs. temperature for a 200nm thick SrCeTbO film.
Figure 4.5: Residual stress vs. temperature for a 400nm thick SrCeTbO film.

Figure 4.6: Residual stress vs. temperature for a 600nm thick SrCeTbO film.
<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>σ deposited (MPa)</th>
<th>σ final (MPa)</th>
<th>hysteresis (MPa)</th>
<th>σ deposited (MPa)</th>
<th>σ final (MPa)</th>
<th>hysteresis (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>-261</td>
<td>-112</td>
<td>149</td>
<td>-570</td>
<td>-232</td>
<td>338</td>
</tr>
<tr>
<td>400</td>
<td>-231</td>
<td>120</td>
<td>352</td>
<td>-344</td>
<td>56</td>
<td>399</td>
</tr>
<tr>
<td>600</td>
<td>-482</td>
<td>156</td>
<td>638</td>
<td>-357</td>
<td>28</td>
<td>385</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of results of the residual stress analysis.

Several trends are observed in the residual stress results, with regards to material and film thickness. First, the thinnest 200nm films of both materials showed the least hysteresis and their stress remained compressive throughout the thermal cycling. Second, the hysteresis of the BaCeYO films appears to vary directly with thickness, while the SrCeTbO films show more consistency in their hysteresis. Third, a trend not seen is that of the as-deposited stress becoming more compressive with thickness, as a result of atomic peening. This could be because the stress has already reached a plateau (as shown in Figure 2.5) at some thickness less than 200 nm, as was observed by Quinn [32] in sputtered YSZ films. While these trends are interesting, it should be noted that only one sample per material and thickness was tested. Therefore, drawing any firm conclusions would require more testing. The above results have an approximate certainty of ±20 MPa, which was calculated by Quinn, using similar equipment and processes.

4.1.3 Thermomechanical Properties

As discussed in Section 2.6.3, the residual stress data from the thermal cycle can be used to deduce mechanical properties of the film. Specifically in this case, it is
possible to determine the modulus-CTE product, which is taken as the slope of the residual stress-temperature curve. The slope was determined using linear-least squares for the final cooling cycle of each sample. The final cooling cycle was used because it exhibited the least amount hysteresis and is therefore likely to be most representative of the film’s annealed value for the modulus-CTE product. The modulus-CTE product for each film is shown in Table 4.1. The R-squared value for the linear curve fit was at least 0.98 for all slope calculations.

| Film Thickness (nm) | Modulus-CTE product (MPa/°C) | | | | |
|---------------------|-----------------------------|-----------------------------| | | |
|                     | BaCeYO | SrCeTbO | Undoped BaCeO (Bulk) | Undoped SrCeO (Bulk) | |
| 200                 | 0.65   | 0.48    | -2.4                | -1.5                | |
| 400                 | 0.75   | 0.62    |                     |                     | |
| 600                 | 0.74   | 0.74    |                     |                     | |

Table 4.2: Modulus-CTE product for three film thickness of BaCeYO and SrCeTbO. (Material properties for bulk BaCeO and SrCeO from [38], material properties for the silica substrate are from [50]).

The modulus-CTE product was fairly close in value across the thicknesses tested and even between films. The possible exception is the SrCeTb 200 nm film which showed a slightly lower value (-0.48 MPa/°C). Because there was only one sample for each thickness, it is not possible to say whether the lower value is due to scatter or if it has a physical significance. The modulus-CTE product for the films of both materials is significantly lower (by a factor of ~3 - 4) than that of the bulk material. The large difference between the bulk and thin film results also serves as evidence of the need to continue to characterize the material properties of thin films if they are to be reliably designed into microfabricated devices.
4.2 Electrochemical Performance

The electrochemical performance of the materials is presented in this section. The section begins with the conductivity results and activation energy calculations for tests conducted in ambient air. This is followed by the electrochemical performance results for samples tested in two controlled atmospheres: dry air, and 5% H$_2$ + 95% Ar. Finally, the section concludes with a discussion of the information that is provided by using different electrode patterns (the electrode patterns are described in Section 3.5.1).

In the ambient air electrochemical tests, seven BaCeYO samples were tested: four thicknesses (200, 400, 500 and 600 nm) each with one to three electrode patterns (patterns 14, 15, 16) as described in Section 3.5.1. Two samples were tested for SrCeTbO: one thickness (600 nm) with two electrode patterns (patterns 14, 15). Conductivity results for both materials, tested in ambient air as a function of temperature, are presented in Figure 4.7. For clarity, results from other researchers are shown in Figure 4.8, along with a subset of the data presented in Figure 4.7.

As can be seen, in Figure 4.7 the data are roughly divided into two groups. The group to the left contains the 200, 400, and 600 nm thick BaCeYO films for two electrode patterns – pattern 15 and pattern 16. This group experienced nearly identical processing conditions and all show very similar results. There appears to be no significant differences among, or correlation to, film thickness. That the two different electrode patterns show similar results is not surprising because the conductivity is normalized by the electrode geometry (see eq. 2.9). That they are so similar is, in fact, confirmation that
the impedance tests and analyses are working as expected, measuring the conductivity of the film.

Figure 4.7: Conductivity, \( \sigma \), versus temperature for BaCeYO (three thickness and two electrode patterns) and SrCeTb (one sample), tested in ambient air. Note: "p16" and "p15" in the legend refer to electrode pattern 16 and pattern 15, respectively.
Figure 4.8: Conductivity vs. temperature for BaCeYO and SrCeTbO shown with results from prior work [9,11,12]. Prior work is for BaCeYO unless otherwise noted.

The group to the right is interesting in that the results indicate better conductivity at all temperatures than the group to the left. This group contains the thickest SrCeTbO sample (600 nm) and one BaCeYO sample, “BaCeY 500nm”, for two electrode patterns (15 and 16). The BaCeYO sample is unique in that it had been deposited under slightly different conditions than the other films and tested several months earlier. The sample was tested using the same equipment and under the same conditions. The reason for the improved conductivity is unclear. The slight variation in processing conditions were as follows: sputtered at 60 watts instead of 70 watts, sputtered from a different target (though both targets were made at the same time from the same materials), and this film was annealed during the process of the conductivity tests, which reached the same
maximum temperature (500°C) as the other films, but the sample did not experience a separate thermal cycle prior to measurement. In addition to different processing conditions, other possible explanations for the difference are: the presence of impurities in either set of films or a higher relative humidity on the day of testing. The presence of water vapor in the testing atmosphere is known to improve protonic conductivity [18] (relative humidity was not recorded during testing). None of these reasons can be confirmed without additional investigation. The reason for the higher conductivity in the SrCeTbO sample is also unclear. It is possible that the SrCeTbO is a better proton conductor, but more samples will have to be tested in a controlled humidified atmosphere to confirm this.

As shown in Figure 4.8, the conductivity for the BaCeYO films is slightly lower than reported values. This is not surprising because there are several differences between this research and prior work. First, all of the reported conductivities were for tests conducted in humidified hydrogen, which, as has already been discussed, is known to significantly improve proton conduction. Second, this research tested samples at lower temperatures (from 200-500°C in this work compared to 400-800°C in prior work). As has been shown, conductivity improves at higher temperatures. Lastly, Guan [9] and Hibino [11] report values for bulk BaCeYO. Only Ito [12] tests a thin film (700 nm thick) of the material and those conductivity results are on the same order of magnitude as the results of this research (though Ito’s results show a lower activation energy than this research). The conductivity reported by Ito is about an order of magnitude lower than that of bulk BaCeYO as reported by Iwahara [12]. Ito suggests that the lower conductivity of the film compared to bulk may be a result of an interface resistance.
between the electrodes and the film in their setup. Also shown in this figure is the conductivity for bulk YSZ as reported by Hibino. While the bulk YSZ was also only tested at higher temperatures, the activation energy, given by the slope of the conductivity line, is similar to that of the materials tested in this research. This indicates that the proton conducting oxides should have conductivities comparable to or better than YSZ at lower temperatures.

The activation energy, $E_A$, for each sample was calculated by plotting the natural logarithm of the conductivity versus the inverse of the temperature (in Kelvin) and taking the slope of the resulting line. The results are presented in Table 4.3. Also presented in the table is the value for conductivity for each sample measured at the maximum experimental temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Film Thickness (nm)</th>
<th>Activation Energy (eV)</th>
<th>Conductivity (S/cm) [at max temp]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCeYO</td>
<td>200</td>
<td>1.1</td>
<td>4.86E-04 [522°C]</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.2</td>
<td>3.42E-04 [504°C]</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.7</td>
<td>6.57E-04 [473°C]</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>1.3</td>
<td>3.27E-04 [532°C]</td>
</tr>
<tr>
<td>SrCeTbO</td>
<td>600</td>
<td>1.0</td>
<td>2.64E-04 [424°C]</td>
</tr>
</tbody>
</table>

Table 4.3: Activation energy and conductivity (at the maximum experimental temperature) for BaCeYO and SrCeTbO, measured in ambient air.

Activation energies for BaCeYO are not specifically reported in earlier works, but by observing the slope of the temperature-conductivity curve, it can be inferred that they have a lower activation energy than was observed in this research. Activation energy for proton conduction in perovskite oxides in general has been reported to be ~0.6 to 0.7 eV
This value compares favorably with the 500nm BaCeYO sample, which showed a higher conductivity than the other samples and had an activation energy of 0.7 eV.

Activation energies for SrCeTbO are not reported. However, for a rough comparison, activation energies for bulk SrCeTmO are reported as 0.85 and 0.67 eV, in dry air and wet air respectively, and 0.69 and 0.48 eV, in dry and wet 10%H₂ + 90%He, respectively [31]. The activation energy for the SrCeTbO sample in this research was somewhat higher at 1.0 eV. Based on this prior work, it seems that activation energy is a strong function of humidity for these materials.

One sample of each material was evaluated for electrochemical performance in a controlled atmosphere. The results of the analysis are shown in Table 4.4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atmosphere</th>
<th>Temp (°C)</th>
<th>Conductivity (S/cm)</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCeYO 600nm</td>
<td>Dry Air</td>
<td>500</td>
<td>1.3E-05</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>5% H₂ + 95% Ar</td>
<td>298</td>
<td>1.8E-05</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>401</td>
<td>3.3E-04</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>502</td>
<td>2.0E-03</td>
<td></td>
</tr>
<tr>
<td>SrCeTbO 600nm</td>
<td>Dry Air</td>
<td>401</td>
<td>4.8E-06</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>502</td>
<td>6.7E-05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5% H₂ + 95% Ar</td>
<td>400</td>
<td>6.9E-06</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>502</td>
<td>1.6E-03</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.4: Activation Energy and Conductivity (at the maximum experimental temperature) for BaCeYO and SrCeTbO measured in dry air and a hydrogen mix (5% H₂ + 95% Ar).

The tests were conducted in dry air and a hydrogen gas mix (5% H₂ + 95% Ar). As can be seen, both materials showed an order of magnitude decrease in conductivity in dry air at 500°C versus ambient air. This is not surprising since the atmosphere contained no
water vapor to promote the proton conduction. Both materials also showed an order of magnitude increase in conductivity in the 5% H₂ + 95% Ar atmosphere at 500°C versus ambient air. This is also not surprising given the abundance of hydrogen. But there is still no water vapor in the H₂/Ar atmosphere, so there is a question as to what conductivity is actually being measured, protonic or electronic. To help answer the question, the activation energy was calculated. The BaCeYO sample exhibited an activation energy of 0.9 eV. This is comparable to the E_A observed in the ambient air tests, as well as to the expected E_A of protonic conduction (~0.6 to 0.7 eV). Therefore, it is likely that BaCeYO exhibits protonic conductivity. The SrCeTbO sample, however, yields an E_A of 2.3 eV, which is much higher than the E_A of protonic conduction and indicative of electronic conduction due to the reduction of hydrogen [45]. Therefore it is likely that the SrCeTb test did not measure protonic conductivity, most likely due to the lack of water vapor in the test atmosphere.

The results of the equivalent circuit modeling that yield the conductivity values are given in Figure A.2 in the Appendix. It was possible to determine the contribution to conductivity (resistance) by looking at the relative values of CPE1 and CPE2, and R1 and R2. In this type of modeling, the capacitance of the bulk material is typically on the order of picofarads and capacitance of the grain/grain boundary is on the order of nanofarads [45]. Also, the resistance of the bulk should be much greater than that of the grain/grain boundary. These trends can be seen in the data and, so, CPE1 and R1 are taken as the capacitance and resistance of the bulk material and are the values used to calculate the conductivity reported here.
4.3 Microstructure

The microstructure of the films was examined using an atomic force microscope (AFM). The goal of the analysis was to investigate the grain size of the materials. The samples used were the 600 nm thick BaCeYO and SrCeTbO films after annealing. The film samples analyzed had not undergone electrochemical testing. The AFM images for both materials, at 500nm and 1µm scales, are given in Figures 4.9 – 4.12. The images appear to show grain clustering, which has also been observed in sputtered YSZ films [32] and is indicative of columnar grain growth. Grain size for both materials appears to be on the order of 10-50 nm based on Figures 4.9 – 4.12.

The AFM scans are also useful in reporting surface roughness. The 600 nm thick BaCeYO had a root mean square (RMS) roughness of 12.2 nm. The 600 nm thick SrCeTbO had a RMS roughness of 22.9 nm. This compares to the roughness of a YSZ thin film deposited in the same system of 8.9, 24, and 11 nm deposited on SiO₂ at 25, 300, and 600°C, respectively [44].
Figure 4.9: AFM scan of 600nm thick BaCeYO (500nm scale). Left and right images are of the same measurement. The left image displays brightness which is used to calculate depth, and therefore roughness, and the right image shows texture.

Figure 4.10: AFM scan of 600nm thick BaCeYO (1µm scale).
Figure 4.11: AFM scan of 600nm thick SrCeTbO (500nm scale).

Figure 4.12: AFM scan of 600nm thick SrCeTbO (1μm scale).
5 Conclusion and Recommendations

The conclusions which can be drawn from the thin film deposition and the residual stress, thermomechanical and electrochemical analyses are presented in this section. Following this are recommendations for continued research on the materials and their properties investigated in this work.

5.1 Summary of Contributions

The research presented in this thesis has shown that is possible to create very thin films with uniform thickness of perovskite-type proton conducting oxides using sputter deposition, and has provided an initial characterization of the residual stress, thermomechanical and electrochemical properties of the materials. It was shown that the sputtered films are uniform, crack-free, and continuous and have the desired chemical composition. Though most parameters of the deposition process were not varied, the composition of the films did show a high dependence on the temperature of the substrate. The “best” composition (one that had only a minor second phase) was deposited with a substrate temperature of ~575°C for both materials considered (BaCe₀.₉Y₀.₁O and SrCe₀.₉₅TbY₀.₀₅O).

The results of the residual stress and thermomechanical characterization also showed promising results. The sputtered films exhibited a relatively small magnitude of as-deposited residual stress. The films did exhibit some stress hysteresis upon thermal cycling, but this disappeared with repeated cycles. Also, the films remained intact (i.e., uncracked) throughout the thermal cycles. These results indicate that the films could be designed into a μSOFC device without failing due to stress. Finally, the modulus-CTE
was determined and found to be 3-4 times lower than bulk values for both materials. The thermomechanical properties will aid in designing devices using these materials.

Electrochemically, impedance spectroscopy results and analyses indicate proton conduction in both films. The conductivity of the films was on the same order of magnitude as the only reported value of BaCeYO in thin film form, though the values were lower than for the bulk material. The difference in conductivities is most likely a result of the difference in atmospheres because all other reported values were measured in atmospheres with high levels of water vapor. As has been discussed, water vapor is known to significantly improve protonic conductivity and lower the activation energy. Nonetheless, the measured conductivities in this work are high enough at low temperature ($6.57 \times 10^{-4}$ (S/cm) at 473°C for BaCeYO and $2.64 \times 10^{-4}$ (S/cm) at 424°C for SrCeTbO, in ambient air) to warrant further investigation.

5.2 Recommendations Future Work

There is an abundance of future work based on the results from this thesis. Proton conducting materials and microfabricated solid oxide fuel cells are both exciting topics in terms of research potential and potential impact on the world. Future work stemming directly from this research can be best organized by the three goals of the thesis.

The first goal was to demonstrate the ability to produce a viable thin film of the desired material. Though this goal was achieved, there was no attempt to optimize the process or investigate the effect of varying the sputter deposition parameters. It is likely that by changing the process parameters, a single phase film (without a second cerium oxide phase) and/or a film with better electrochemical performance could be created for
either the BaCeYO or SrCeTbO material. Detailed microstructural characterization, along with identification of mechanisms affecting microstructure, needs to be determined to fully understand the results and trends identified in this work (e.g., the low modulus-CTE product for both films versus bulk and the change in stress during the delays in measurements). This work should be done as a function of processing (sputtering) and post-processing parameters.

The second goal was to characterize the residual stress and thermomechanical characteristics of the films. The research presented here provides a great foundation and starting point for a more rigorous investigation of the thermal and mechanical properties of the materials. Specific work could include sampling many more films to determine the repeatability of the deposition process and to gain a reliable average for the modulus-CTE product. It would also be useful to measure the biaxial modulus of the film (e.g. through bulge testing or buckled membrane height measurements as in [52]) and thereby calculate the CTE. Lastly, it would be useful to determine the appropriate thermal cycle required to eliminate the stress hysteresis, so that the film could be reliably designed into a device.

The third goal was to characterize the electrochemical performance. This work has really only just begun and there are many issues left to investigate. The most important contribution in this area would be to test a much larger sample size under a controlled environment of hydrogen gas and water vapor. Comparing conductivity and activation energy in a dry atmosphere versus a humidified atmosphere would conclusively show proton conduction. Additionally, it would be interesting to investigate the effect of variations in the deposition process on electrochemical performance. Lastly, this
research was confined to one doping level for each material. However, it has been shown that the doping level has a large effect on the electrochemical performance. In particular, for bulk BaCeYO, a 25% Y-doping level shows the best electrochemical performance [11] as compared to the 10% doping used in this research. Investigations into other doping levels are therefore warranted.

Given the protonic conductivity observed in this work, the best and most exciting future work would be to insert these materials into a microfabricated solid oxide fuel cell and measure their performance at relatively low operating temperatures.
Appendix A

The information provided in this appendix includes: the equivalent circuit used in the impedance modeling, the results of the impedance modeling, raw data from the controlled atmosphere tests, and representative Nyquist plots of the impedance data.

![Equivalent circuit used to model impedance.](image)

**Figure A.1: Equivalent circuit used to model impedance.**

The model (as described in Section 3.5.2) returns values for each element along with values for the phase angle of the constant phase elements, CPE1 and CPE2. A perfect capacitor would have a phase angle of 90°, which is equivalent to a CPE P value of 1.

The model elements are described in Table A.1 and the results of the model are shown in Table A.2. Note that the results for 600 nm thick BaCeYO film with pattern 16 were best fit with an equivalent circuit model containing one inductor and only one RC circuit, and therefore there are no results for R2 and CPE2 for this sample.

<table>
<thead>
<tr>
<th>Element</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>Inductance of connector cables</td>
<td>Henries</td>
</tr>
<tr>
<td>R1</td>
<td>Resistance (bulk material)</td>
<td>Ohms</td>
</tr>
<tr>
<td>CPE-1 T</td>
<td>Capacitance Magnitude (bulk)</td>
<td>Farads</td>
</tr>
<tr>
<td>CPE-1 P</td>
<td>Capacitance Phase Angle (bulk)</td>
<td>(angle)*</td>
</tr>
<tr>
<td>R2</td>
<td>Resistance (grain )</td>
<td>Ohms</td>
</tr>
<tr>
<td>CPE-2 T</td>
<td>Capacitance Magnitude (grain)</td>
<td>Farads</td>
</tr>
<tr>
<td>CPE-2 P</td>
<td>Capacitance Phase Angle (grain)</td>
<td>(angle)*</td>
</tr>
</tbody>
</table>

*The angle of CPE P is measured as: 1 = 90°, 0.5 = 45°.

**Table A.1: Description of values returned by equivalent circuit model in Fig. A.1.**
Table A.2: Equivalent circuit elements values from impedance modeling. Samples tested in ambient air.

The following three figures (Figures A.2 – A.4) are representative Nyquist plots for the impedance data. The sample in all of the plots is the 400 nm thick BaCeYO film at 500°C. The difference among the three plots is the electrode pattern (pattern 14, 15, and
16). Figure A.2 is a plot from pattern 16, the coarsest pattern. Figure A.4 is the plot of the data from pattern 14, the finest pattern. The different patterns make it possible to analyze different aspects of the system (as described in Section 3.5.1). As can be seen in Figure A.4 the second arc (to the right) becomes more prominent. This resistance is likely the due either to the electrodes or the grain and grain boundary, and is easier to analyze in this plot.

![Graph](image)

**Figure A.2**: BaCeYO 400nm, pattern 16, 504°C (ambient atmosphere).
Table A.3 and Figures A.5 - A.11, contain raw data and representative Nyquist plots for the electrochemical tests conducted in a controlled atmosphere. As can be seen in Figures A.5 - A.11, the arcs formed in the Nyquist plots are not as smooth as those formed in the ambient air tests. The reason for this is that different test equipment was
used (though the same Solartron Impedance analyzer was used). The different setup used a binary temperature controller rather than a proportional controller. This resulted in large temperature swings during measurements. As a result, it was not possible to properly fit the data with an equivalent circuit. On the advice of Hertz [17] an approximate arc was fitted by hand and the resistance was taken as the diameter of the arc. As a result, only resistances are reported in Table A.3, rather than values for each equivalent circuit element.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atmosphere</th>
<th>Temp (°C)</th>
<th>Resistance (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCeYO 600nm</td>
<td>Dry Air</td>
<td>500</td>
<td>557,580</td>
</tr>
<tr>
<td></td>
<td>5% H₂ + 95% Ar</td>
<td>298</td>
<td>381,250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>401</td>
<td>21,469</td>
</tr>
<tr>
<td></td>
<td></td>
<td>502</td>
<td>3,560</td>
</tr>
<tr>
<td>SrCeTbO 600nm</td>
<td>Dry Air</td>
<td>401</td>
<td>342,130</td>
</tr>
<tr>
<td></td>
<td></td>
<td>502</td>
<td>24,819</td>
</tr>
<tr>
<td></td>
<td>5% H₂ + 95% Ar</td>
<td>400</td>
<td>238,400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>502</td>
<td>1,045</td>
</tr>
</tbody>
</table>

Table A.3: Equivalent circuit elements values from impedance modeling. Samples tested in a controlled atmosphere of dry air or 5% H₂ + 95% Ar.
Figure A.5: BaCeYO 600nm, pattern 16, 500°C (dry air).

Figure A.6: BaCeYO 600nm, pattern 16, 502°C (5% H2 + 95% Ar).
Figure A.7: BaCeYO 600nm, pattern 16, 401°C (5% H2 + 95% Ar).

Figure A.8: BaCeYO 600nm, pattern 16, 298°C (5% H2 + 95% Ar).
Figure A.9: SrCeTbO 600nm, pattern 15, 502°C (Dry Air)

Figure A.10: SrCeTbO 600nm, pattern 15, 401°C (Dry Air).
Figure A.11: SrCeTbO 600nm, pattern 15, 502°C (5% H2 + 95% Ar).

Figure A.6: SrCeTbO 600nm, pattern 15, 400°C (5% H2 + 95% Ar).
References


[17] Joshua Hertz, Department of Material Science and Engineering, MIT.


[43] I. Kosacki, H.L. Tuller, “Mixed conductivity in SrCe_{0.95}Yb_{0.05}O_3 protonic conductors”, *Solid State Ionics*, vol. 80, pp. 223-229, 1995.


[45] H. Tuller, Department of Material Science and Engineering, MIT, personal communication.


WF3937X02032190.

[51] [www.consultrsr.com/resources/eis/cpe1.htm](http://www.consultrsr.com/resources/eis/cpe1.htm)


[53] ZView and ZPlot software by Scribner Associates Inc. ([//scribner.com](http://scribner.com)).