Temperature Induced Deflection of Yttria Stabilized Zirconia Membranes

THESIS

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By

Andrew Scott Davis, B.S.
Graduate Program in Mechanical Engineering

The Ohio State University
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Thesis Committee:
Dr. Mark E. Walter, Advisor
Dr. Brian D. Harper
Solid oxide fuel cells (SOFCs) are electrochemical energy conversion devices capable of producing electrical power with high efficiency and low emissions. SOFCs are characterized by ceramic electrolyte membranes which transport oxide ions in the range of temperatures between 600°C and 1000°C. In order to facilitate efficient, low-range temperature operation the electrolyte is typically made very thin, on the order of 40 µm. SOFCs also employ porous electrodes on either side of the electrolyte which are then placed in contact with current collectors and seals. In the fuel cell environment, with high temperatures, substantial thermal gradients, mechanical loading between layers, as well as the desire to be able to thermally cycle the cell, one of the layers or components must provide mechanical support. It is typical for either the anode or electrolyte to provide the necessary mechanical support.

This thesis focuses on an electrolyte that is used for electrolyte-supported SOFC configuration. To address the need for mechanically robust electrolytes, NexTech Materials has developed the FlexCell™ electrolyte. This electrolyte design incorporates 40 µm thick conducting regions in a honeycomb pattern, and surrounding 200 µm thick stability regions. Various experiments on and determinations about this material and design must be made to ensure sufficient mechanical stability during fuel cell operation.
Thermal stresses from high temperatures, temporal and spatial temperature gradients, and differential thermal expansion of contacting materials, are critical issues within SOFCs. The critical property related to these issues, coefficient of thermal expansion (CTE), was measured in this work. An apparatus to measure the CTE of the FlexCell™ electrolyte material was designed and implemented. The average CTE of 3 mol% Y₂O₃-ZrO₂ (yttria stabilized zirconia or 3YSZ) was found to increase from 9 µm·m⁻¹·°C⁻¹ between room temperature (RT) and 180°C to nearly 11.5 µm·m⁻¹·°C⁻¹ from RT to about 650°C.

A torch heating experiment was performed to study thermal gradients. For 200 µm thick YSZ electrolyte samples it was found that heating experiment induced a directional dependence into unexpectedly large out-of-plane deflections. Digital image processing was used to capture deflection magnitudes which were compared against two finite element models. The two finite element models differed in how the through-thickness CTE variation was implemented. The first model contained a pseudo-continuous CTE gradient, whereas the second model contained an abrupt surface layer change in CTE. Both models were able to replicate the experimental results, thus pointing to CTE variation as the driving mechanism causing unexpected deflections in the experiments. Literature review and results from X-ray diffraction led to the conclusion that the tetragonal to monoclinic phase change in YSZ is the most likely reason for CTE change. It is proposed that the combination of heating and the initial tensile strain field are the root cause of this transformation.
This thesis is dedicated to the Lord, to my family, and to Laura.
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Vita

September 1, 1988 .........................................Born – Columbus, Ohio

June 2006 ..........................................................Worthington Kilbourne High School

December 2010 ...............................................B.S. Mechanical Engineering, The Ohio State University

2011 ...............................................................Graduate Teaching Associate, Department of Mechanical and Aerospace Engineering, The Ohio State University

2011 to 2012 .................................................Graduate Research Associate, Department of Mechanical and Aerospace Engineering, The Ohio State University

Fields of Study

Major Field: Mechanical Engineering
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Chapter 1: Introduction

1.1. Fuel Cells

Fuel cells are energy conversion devices which electrochemically combine a fuel and oxidant to produce electricity [1]. Fuel cells were first invented in the 1830’s by Sir William Grove; their operating principle, however, was discovered a few years earlier by Christian Friedrich Schönbein [2]. At their most basic level, fuel cells consist of two electrodes, the cathode and anode, which are separated by an electrolyte and connected via an external circuit. A set of reduction-oxidation (redox) reactions occur within the cell through the consumption of electrons (reduction) at the cathode and through the release of electrons (oxidation) at the anode. The electrons which are used up in the reduction reaction are supplied through the external circuit from the oxidation reaction. This general concept allows for a wide variety of specific implementations of fuel cells.

Fuel cells with vastly different electrodes, electrolytes, fuels, and oxidants have been invented and developed in the centuries since the concept was first discovered. In the modern age, they are grouped most generally as either low-temperature or high-temperature. Low-temperature cells operate at less than about 200°C while those cells that are considered high-temperature operate in the range of about 600° - 1000°C [2].
The groupings within low-temperature fuel cells include Alkaline (AFC), Polymer Electrolyte Membrane (PEMFC), and Phosphoric Acid fuel cells (PAFC). The two high-temperature types of fuel cells are Molten Carbonate (MCFC) and Solid Oxide fuel cells (SOFC). By combining information from [2,3], Table 1 provides an overview of these types of fuel cells, including applications and power capabilities as well as common materials used in each.

Table 1: Fuel Cell Overview [2,3]

<table>
<thead>
<tr>
<th></th>
<th>AFC</th>
<th>PEMFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temp. (°C)</td>
<td>&lt;100</td>
<td>60 – 120</td>
<td>150 – 220</td>
<td>600 – 800</td>
<td>600 – 1000</td>
</tr>
<tr>
<td>Anode reaction</td>
<td>H₂ + 2OH⁻ → 2H₂O + 2e⁻</td>
<td>H₂ → 2H⁺ + 2e⁻</td>
<td>H₂ → 2H⁺ + 2e⁻</td>
<td>H₂ + CO₃²⁻ → H₂O + CO₂ + 2e⁻</td>
<td>H₂ + O²⁻ → H₂O + 2e⁻</td>
</tr>
<tr>
<td>Cathode reaction</td>
<td>½ O₂ + H₂O + 2e⁻ → 2OH⁻</td>
<td>½ O₂ + 2H⁺ + 2e⁻ → H₂O</td>
<td>½ O₂ + 2H⁺ + 2e⁻ → H₂O</td>
<td>½ O₂ + CO₃⁺ → CO₂ + 2e⁻</td>
<td>½ O₂ + 2e⁻ → O²⁻</td>
</tr>
<tr>
<td>Applications</td>
<td>Transportation, space, military, and energy storage systems</td>
<td>Combined heat and power</td>
<td>Combined heat and power. Combined cycle adaptability and auxiliary power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Realized Power</td>
<td>Small plants 5-150 kW</td>
<td>Small plants 5-250 kW</td>
<td>Small-medium sized plants 50 kW-11 MW</td>
<td>Small plants 100 kW-3 MW</td>
<td>Small plants 1 kW-2 MW</td>
</tr>
<tr>
<td>Charge Carrier in Electrolyte</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>H⁺</td>
<td>CO₂²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>Common Electrolyte</td>
<td>KOH</td>
<td>Nafion ® (PTFE)</td>
<td>H₃PO₄ stabilized in a SiC based matrix</td>
<td>Li/K or Li/Na carbonate melt stabilized in an Al₂O₃ based matrix</td>
<td>Yttria stabilized zirconia (YSZ)</td>
</tr>
<tr>
<td>Anode</td>
<td>Pt/C</td>
<td>Pt</td>
<td>Pt/C</td>
<td>Ni-Al or Ni-Cr</td>
<td>NiO</td>
</tr>
<tr>
<td>Cathode</td>
<td>Pt/C</td>
<td>Pt</td>
<td>Pt/C</td>
<td>NiO</td>
<td>LaSrMnO₃ (LSM)</td>
</tr>
</tbody>
</table>

Among these varieties of fuel cells, PEMFCs have generated significant interest because of their low-temperature operation. On the other hand, there are significant
advantages to SOFCs, including higher efficiency (especially in combined heat and power applications), greater fuel flexibility, and less expensive raw materials. Countless research and developments efforts are currently being undertaken to explore promising SOFC concepts. Where there is a lack in adaptability and reliability, one will find numerous research opportunities. One such opportunity is in analyzing and mitigating stresses and failure caused by the high temperature operation of fuel cells [4 – 16]. These concerns limit SOFCs in how quickly they can be brought up to operating temperature, in how much they can be thermally cycled, and by how much materials within the cell can differ in terms of coefficient of thermal expansion (CTE). The remainder of this work will focus on SOFCs and more specifically on thermal expansion characteristics that are among the most crucial design challenges for SOFCs.

1.2. Solid Oxide Fuel Cells

Although the advent of fuel cells first began in the early to mid-19th century, the earliest traces of SOFC principles surfaced at the very end of the 19th century. Walther Nernst’s discovery of the electrolytic conduction of solid bodies at high temperatures in 1899 laid the foundation for the work of Baur and Preis in 1937, who operated the first ceramic fuel cell (SOFC) [1].

1.2.1. SOFC Operation
SOFCs, which operate at high temperatures (600° - 1000°C), are characterized by the solid, oxide-ceramic, oxygen ion conducting membrane which serves as the electrolyte for the cell. At the most basic level, and regardless of SOFC configuration, two electrodes are connected on either side to this electrolyte. These are the anode and cathode. Oxidation and reduction reactions occur on the anode and cathode sides of the cell, respectively. Representations of the various flows within the cell and these reactions are shown in Figure 1. The fuel in Figure 1 contains carbon monoxide (CO) and hydrogen (H₂) and flows over and thru the anode where it is oxidized. The oxidant, air or oxygen (O₂), flows over and thru the cathode where it is reduced.

Figure 1: Schematic of flows and reactions, after [1]
The electrons, which are given off in oxidation on the anode side and taken up in reduction on the cathode side, do not pass through the electrically insulating electrolyte; rather they travel across an external circuit from anode to cathode. The balance of electrical charge is maintained by the transport of oxide ions (O^{2-}) through the electrolyte membrane. These ions traverse the electrolyte by passing through oxygen vacancies in the electrolyte material, which is commonly Y_{2}O_{3} – ZrO_{2} (yttria stabilized zirconia or YSZ).

The electricity that is produced by a single cell is not enough to power anything meaningful, and as a result, cells are combined in series or in parallel to increase their electrical output. In order to combine the cells, an electrically conducting interconnect material is placed between consecutive cells. These connected cells are then referred to as a stack, with sizes ranging from two cells up to hundreds of cells in a single stack. A stack base unit schematic including electrolyte, electrodes, and interconnect is shown in Figure 2.

Figure 2: SOFC stack base unit
One can visualize the base unit shown in the schematic in Figure 2 stacked along with many other such units. These stacks are capable of producing electrical power in the kW to MW range. This power can be generated at electrical efficiencies as high as 50% [4]. The high SOFC efficiency is also combined with the advantage of high power density. Higher power density allows for compact cell and stack designs, reducing material costs and space requirements [17]. Another characteristic of such fuel cells is that they offer pollution free, or low-emission energy. In a cell operating with pure H\textsubscript{2} as fuel and pure O\textsubscript{2} as oxidant, the only reaction byproduct is H\textsubscript{2}O. Even in SOFCs operating with other fuel and oxidant mixtures, NO\textsubscript{x} and SO\textsubscript{x} emissions are very low [18]. These advantages and the wide range of electrical power capability allows for a similarly wide range of applications for SOFCs.

1.2.2. Applications

Along with the advancements in SOFC performance, new application possibilities arise. The most commonly discussed application for SOFCs and other high-temperature fuel cells, is stationary power generation. Most current SOFC systems operate in the low kW range; this makes their stationary power offering more viable for residential energy supply or small to medium sized combined heat and power applications [17]. Start-up times on the order of hours can be a disadvantage for SOFC stacks, as they need to be slowly brought up to operating temperature in order to mitigate effects of thermal
stresses. Even so, once they reach operating temperatures, their operation can be maintained and has been demonstrated for longer than 20,000 hours [17]. The heat produced during steady-state operation of a SOFC can be captured and utilized in one of two ways. Firstly, the heat can be used for heating in industrial or residential situations, that is, combined heat and power. Secondly, the heat can be used as part of a combined cycle with steam or gas turbine power generation cycles. Such combined cycle applications have been predicted to operate at efficiencies greater than 70% [18].

Non-stationary SOFC applications have been considered and developed as well. Due to the slow start-up and low cycle capabilities of SOFCs, they are not used as the main source of energy in mobile applications. However, SOFCs can be used as auxiliary power units (APU) for military, space, or transportation applications. Delphi Automotive Systems, for example, has been developing SOFCs as APUs for long-haul vehicles [2]. APUs would provide electrical power for HVAC, lights, navigation, entertainment, etc., thus eliminating the need for belt-driven alternators and making engines much more efficient.

1.2.3. Configurations

The size and shape of a SOFC stack is determined by the cell configuration that is utilized for a given application. There are a variety of cell configurations that are under consideration today. The most general descriptions of SOFC configurations are tubular and planar. Among tubular cells are the traditional -tubular and the segmented-cell-in-
series types. Planar cell designs consist of the traditional-planar and monolithic types. The traditional-tubular and segmented-cell-in-series varieties are cylindrical whereas the traditional-planar and monolithic ones are flat and sandwich-like. Each of the cell designs differ in the amount of dissipative losses they incur, the way in which fuel and oxidant are sealed from one another, and how cell-to-cell electrical connections are made [1].

1.2.3.1. Tubular

The traditional-tubular cell shown in Figure 3 is most commonly and importantly characterized by the fact that a seal is not needed. A critical design criterion for SOFCs is the separation of fuel and oxidant. In planar cells, this separation requires a designated seal. In tubular cells however, the tubular shape and thus dense, tubular electrolyte inherently separates the air, which commonly flows inside the tube, and fuel, which commonly flows outside.

The schematic cell representation in Figure 3 contains the critical layered structure of cathode-electrolyte-anode or as it is also named, the Positive electrode-Electrolyte-Negative electrode (PEN). The PEN structure in a tubular cell is distributed radially, which is the major distinction between cylindrical-type cells and flat, sandwich-like cells. The innermost layer of the PEN, usually the cathode, is the thickest of the layers so that it provides mechanical support for the cell. This thickness can limit the efficiency and fuel utilization of the tubular cell as a result of long electron paths and air paths to reach the
boundary between electrode and electrolyte. In some tubular cells, an additional support layer is located inside the PEN layers, on which the PEN is then deposited, in order to provide extra mechanical robustness [1]. This layer can further limit the cell’s performance.

![Image](image-url)

Figure 3: A traditional-tubular SOFC [18]

Fabrication techniques for tubular SOFCs offer challenges, however various deposition techniques are employed depending on the cell materials used. More detailed descriptions of the tubular cell fabrication processes are available [1,19]. In stacks comprised of tubular cells the interconnect is deposited as a narrow strip along the length of the tube. The interconnect of one cell is then placed in contact with another cell via nickel felt, as is shown in Figure 4. Stacks of tubular cells, also known as bundles, can be comprised of hundreds of tubes on the order of a meter in length. Of all the cell configurations, these tubular cells and stacks are the most developed and proven in research, however, they are limited by their relatively high dissipative losses. These
losses are attributed to the relatively long current path and thus high internal cell resistance.

The major design advantage which was mentioned previously is that the tubular designs do not require the difficult high temperature sealing that planar designs do. Tubular cells inherently accomplish sealing between the air and fuel since the dense electrolyte is a continuous cylinder, rather than a flat sheet with edges as an electrolyte is in a planar cell. Advances in tubular design concepts give them more long-term stability and they have been demonstrated more in actual plant applications [4]. However, tubular designs are higher in cost due to the relative difficulty of fabrication and they are less capable of high power densities than planar designs [20].

In between the traditional tubular cell and the planar cell designs, in terms of efficiency, is the segmented-cell-in-series (SCIS) configuration. There are various
geometric realizations of this type of cell, one from [19] is shown in Figure 5, but they each share the same common operating principle. Due to their configuration, cells are connected in series, both electrically and in terms of gas flow. Rather than one tube comprising one cell, as is the case for the traditional-tubular, each tube of a SCIS designed SOFC is comprised of several cells. As can be seen in the figure, from one cell to the next, fuel and oxidant travel inside and outside the tube, respectively. Similarly, series electrical current flows from the anode of one cell to the cathode of the next. Since it is able to reduce resistive losses, this configuration generates electrical power at slightly higher efficiencies than a similarly sized traditional tubular cell. Also advantageous to the SCIS-type cell is the fact that sealing is inherently included in its design without the designation of a specific seal material. The interconnect and electrolyte serve this purpose in conjunction. Although the SCIS can improve upon the efficiencies of the traditional-tubular cell, it is at least as difficult or more difficult to fabricate SCIS SOFCs. Both types of tubular cells also take up a lot of space for the power provided; that is, they lack power density.
1.2.3.2. Planar

Given the challenges with fabrication and the low power densities for tubular SOFCs, recent emphasis has been placed on developing planar concepts which excel in manufacturability and power density [17]. Planar SOFCs, as their name describes are flat cells whose operating layers are thin, flat plates that lie in a plane. Planar cells come in two main varieties: traditional-planar and monolithic cells. What planar designs overcome in manufacturability and power density, they lack in long-term stability and sealing.
An example of a traditional-planar cell configuration can be seen in Figure 6, with simple representations of each layer in the PEN structure. Also shown in the figure is the crossflow configuration, that is, perpendicular fuel and oxidant channels. Varying thicknesses within the PEN structure will be discussed further in this section. Additional flow configurations include coflow, parallel fuel and oxidant channels which flow in the same direction, and counterflow, parallel fuel and oxidant channels which flow in opposite directions. The main differences between each flow configuration are temperature and current density profiles, due to variations in heat transfer, mass transfer, and chemical reactions which take place [21]. Each flow configuration carries with it advantages and disadvantages such as, temperature profile, stress profile, and ease of manifolding. Generalizations as to the relative ranking of each of these advantages and disadvantages across the different flow configurations are not easily made, and so they must be considered on a case by case basis.

Figure 6: A traditional-planar cell [1]
Figure 7 shows a more complete representation of a planar SOFC stack with the essential sealing materials and manifolding shown. The interconnect is described as the separator, and Figure 7a shows an exploded view of a counterflow stack. The sealing material which goes around the edge of the entire cell as well as around each manifold port is of great importance. Without proper separation of fuel and oxidant, the traditional planar cell will not operate. Figure 7b gives a more detailed cross-sectional view of the seal and manifold ports.
In planar cells, stability and mechanical strength are derived from the support layer. The support layer can be the cathode, electrolyte, anode or a designated, inert support material. The layer that is selected to provide support is made considerably thicker than the other layers. Besides directly fixing the level of mechanical robustness, the choice of
which layer will carry mechanical loads also tends to dictate the thermal expansion of the PEN. Figure 8 shows the two most common planar configurations, electrolyte-supported and anode-supported. Electrode supported cells are advantageous because they allow for a thinner electrolyte which reduces the cell’s area specific resistance, which allows the cell to operate at lower temperatures. For the following reasons, the anode is generally selected over the cathode as a support material in electrode supported cells: (a) the anode material composition is stronger, providing more strength per unit thickness and (b) the anode is a better electrical conductor, allowing greater thicknesses without large rises in cell resistance.

Electrolyte supported cells demand less material than anode supported cells because the dense electrolyte is stronger than the porous anode. As can be seen in Figure 8 the support layer in an electrolyte supported cell can be as thin as 150 µm while the support layer in an anode supported cell is often as thick as 500 – 1500 µm. Anode supported cells allow for thinner (~10s µm), more electrochemically efficient electrolyte layers. A
current trend is to create electrolyte supported cells and combine their inherent advantage of using less material, while adding the electrochemical efficiency provided by thin electrolyte regions [22,23,24]. Electrolytes which combine these two advantages have thick support regions and thin active regions.

An example of an electrolyte supported cell whose electrolyte has both thick support regions and thin active regions is the NexTech Materials FlexCell™ [22], which is shown in Figure 9. As can be seen, there are thin (30 – 40 µm), hexagonal active regions which make up a majority of the cell area. These translucent regions are surrounded by a thick (~200 µm), opaque support structure which provides mechanical robustness for the cell. The FlexCell, with its thin active regions, produces electrical energy with great power density and efficiency while operating in the desired temperature range of 750° - 800°C [22]. The focus of the remainder of this thesis will be on the electrolyte material of the type used in the FlexCell.
Before moving on, a discussion of the monolithic SOFC design must be made. The monolithic cell, a schematic of which is shown in Figure 10, was proposed by Argonne National Laboratory in 1984 and offers the potential for high power density due to its large active area [19]. This large active area is provided by the corrugated PEN structure which can be seen in Figure 10. The corrugated structure creates gas channels and eliminates the need for structural elements that serve no electrochemical purpose. This elimination is done by manipulating the electrochemically active layers to embody structural characteristics. Manipulation of the PEN into a desired corrugated shape provides a high level of complication for materials selection and fabrication. Discussion of these challenges and the implications that flow configurations such as co- and cross-
flow, which are shown in Figure 10, have on these challenges is left to sources such as [1].

![Figure 10: Monolithic cell schematics [1]](image)

1.3. Problem Statement and Thesis Organization

As has been discussed, SOFCs are a promising technology that will play a role in future energy production. SOFCs offer clean electrical power at high electrical efficiency and power density. SOFCs are adaptable to a wide range of fuels without strict limitations on compositions or impurities. Their modular nature and scalability allow for a large range of distributed power production (W – MW) and a myriad of application possibilities from residential combined heat and power to military auxiliary power.

Working in opposition to these promising aspects, yet at the same time in intriguing cooperation with them in terms of providing motivation for research, are the challenges
presented of designing and manufacturing commercially viable SOFCs. As has been
alluded to above, SOFC technologies cultivate materials and design challenges. These
are brought about by their high temperatures (600° - 1000°C), thin ceramic layers (30 –
40 µm), and substantial thermal gradients that are inherent to their operation.

Among these challenges, the first two, high temperatures and thin ceramics provide
the framework for the motivation behind Chapter 2 of this thesis. Chapter 2 will focus on
the bulk thermal expansion of yttria stabilized zirconia electrolyte material. The
measurement apparatus, measurements taken, and method of calculation are discussed
along with the importance of knowing the CTE of all SOFC materials.

Chapter 3 derives its motivation from the SOFC-inspired challenge of using thin
ceramics which are heated to high temperatures. The influence of temperature gradients
and phase transformation on the deformation of YSZ electrolyte specimens is
experimentally demonstrated and theoretically analyzed with the finite element method.
Unexpectedly large and directionally-dependent thermal deflections are observed
experimentally. The reasons for such large deflections are proposed and discussed.
Chapter 3 is written in the form of a stand-alone journal article, as it is the desire of the
author to publish it. As such, some repetition of the basic introductory information is to
be expected.

The final chapter, Chapter 4, summarizes the experimental results and theoretical
analyses and provides concluding remarks. Chapter 4 also provides a brief description of
recommendations for future work.
Chapter 2: Thermal Expansion

2.1. Introduction to Coefficient of Thermal Expansion

As has been discussed, solid oxide fuel cells are designed to operate, and in fact are only able to operate at temperatures well above room temperature (RT). The generally accepted range of operation for SOFCs is 600° - 1000°C. This high temperature operation presents a design challenge for SOFC engineers. For SOFCs, since the temperature change from RT to operating temperature is large, the expansion that each component experiences will be proportionally large. Similarly, the change in temperature from the sintering state of the layered Positive electrode-Electrolyte-Negative electrode to RT is large (~1400°C), proportionally large contractions also occur. Equation 1 describes the coefficient of thermal expansion, $\alpha$, for a material at temperature $T$,

$$\alpha = \frac{\left(\frac{dL}{dT}\right)_T}{L_0}, \quad (1)$$

where $L_0$ is the length at room temperature and $\left(\frac{dL}{dT}\right)$ is the change in length over change in temperature. For most materials, $\alpha$ is a positive coefficient, which means that the quantity $\left(\frac{dL}{dT}\right)$ must be positive. This implies that for an increase in temperature by $dT$, 

\[\text{...}\]
there is an increase in length by \( dL \). Similarly, for a decrease in temperature by \( dT \), there is a decrease in length by \( dL \). Equation 1 can be rearranged and written to describe the stress free thermal strain (\( \varepsilon_t \)) that a given material experiences at a temperature \( T \) relative to a reference temperature \( T_0 \), which is shown in Equation 2.

\[
\varepsilon_t = \alpha(T - T_0)
\]  

(2)

SOFC operation at a temperature well above \( T_0 \) must then be accompanied by a proportionally large (\( \varepsilon_t \)). In order to know and design for these large strains, researchers and engineers must carefully characterize the CTE for all SOFC materials and compositions. If thermal expansions are not properly accounted for, there can be catastrophic complications which arise.

There are two ways in which large thermal strains can negatively affect and possibly cause SOFC stack failure. The first occurs by differential thermal expansion at uniform temperature and the second poses a problem due to temperature gradients. As has been presented, SOFCs are made up of at least 4 or 5 components. In general, each of these components has a different material composition. These component compositions vary widely, in fact Tietz [25] compiled CTE values for dozens of commonly used electrolytes, cathodes, interconnects, seals and anodes both experimentally and from literature. Based on his work, it has been shown that even within a given class of ceramic or metal, there can be variations in CTE. Once the CTE of each stack component has been determined, careful design and analysis can be performed. It should be noted that it
is common for there to be both ceramics and metals present in a SOFC stack, and that in general ceramics and metals have large differences in CTE value.

A key location where differential thermal expansion at uniform temperature comes into play is within the PEN structure. The anode, electrolyte, and cathode will each have a different ceramic composition, with anode layers commonly having metal particles dispersed throughout as well. With each material composition comes a different CTE, meaning that for a given temperature change each material will expand (or contract) by a different amount. For example, the cathode material analyzed by Tietz, La$_{0.65}$Sr$_{0.3}$MnO$_3$ (LSM), had a CTE of $\alpha = 12.0 \, \mu m \cdot m^{-1} \cdot °C^{-1}$ whereas the reported CTE of common electrolyte material, 8 mol% Y$_2$O$_3$ stabilized ZrO$_2$ (8YSZ), was $\alpha = 10.5 \, \mu m \cdot m^{-1} \cdot °C^{-1}$ [25]. This difference can result in issues within the SOFC stack. Differential thermal expansion causes stresses to be developed in a layered structure [10,15,26], and thus, PEN failure can occur.
Figure 11 demonstrates the way in which differential thermal contraction occurs. Under a given $\Delta T$, that is a change in temperature from the temperature at which the original length, $L_0$, was measured (commonly referred to as $T_0$), each individual layer, $i$, would expand or contract by an amount given in Equation 3, where $\alpha_i$ is the CTE of the $i^{\text{th}}$ layer.

$$\Delta L_i = \alpha_i(\Delta T)(L_0) \quad (3)$$

In the bilayer example shown in Figure 11, Layer 1 has a CTE that is greater than that of Layer 2. As such, and as is demonstrated by the size of the arrows in Figure 11, Layer 1 would contract more than Layer 2 for a negative $\Delta T$, as would be the case in cooling the
PEN structure from sintering temperature to room temperature. The layers are connected though, meaning that they are not able to contract as they would by themselves, and thus stresses develop. In the case of an electrolyte supported cell, the thick and considerably stiffer electrolyte dictates thermal expansion within the PEN. Stresses in the electrodes as a result of differential expansion from a change in temperature from \( T_0 \) to \( T \) develop according to Equation 4,

\[
\sigma_i = \frac{E_i}{1-\nu_i} (\alpha_E - \alpha_i)(T - T_0),
\]

(4)

where \( \sigma_i \) is the stress in each electrode, \( E_i \) the elastic modulus in each electrode, \( \nu_i \) the Poisson’s ratio in each electrode, \( \alpha_E \) the CTE of the electrolyte layer, \( \alpha_i \) the CTE of each electrode [10].

In the case shown in Figure 11 then, Layer 1 will experience tensile stress and Layer 2 will experience compressive stress. In a SOFC PEN structure, the layers are ceramic and thus with one or more layers experiencing tensile stress, the possibility for failure is greatly increased. Differential thermal expansion is not only an issue in the layered PEN, but it also occurs between the PEN structure and seal around its edge as well as between these seals and the interconnect. Insofar as there might be other components present, such as metal shims sandwiching the seals for spacing, or current collecting foams in between the PEN and interconnect, more differential thermal expansions do arise.

The second way that thermal deformation causes failure in SOFC stacks is via curvature and out-of-plane deflection. Temperature gradients are inherent to steady-state
SOFC operation [5,12,16]. As a result of heat transfer within the stack, fuel utilization, and current density variation, steady-state temperature gradients are established both in the plane of flat SOFC components as well as through the thickness of the PEN structure. An electrochemical-thermal model used by Selimovic et al. [12] demonstrates in-plane thermal gradients; an example output of their model is shown in Figure 12. They predict in-plane thermal gradients as high as almost 60 °C·mm⁻¹.

![Figure 12: An example thermal gradient (°C·mm⁻¹) distribution as determined by an electrochemical-thermal model [12].](image)

Depending on the flow configuration of a given stack, there will also be differences in temperature between the anode and cathode flow fields. As such, a temperature gradient through the thickness of the PEN structure is established which can cause slight out-of-plane deflection, which may be enhanced or reduced by the differences in CTE between PEN layers. Commonly, the ΔT between anode and cathode is not nearly as large as the ΔT between either RT and operating temperature or sintering temperature and operating...
temperature. As a result, through the thickness temperature gradient effects are not considered to be detrimental to a stack.

With the understanding that SOFC components and stacks must be designed to withstand CTE mismatch effects, the CTE value for all SOFC materials must be accurately known. As this work was centered on the SOFC designed by NexTech Materials, which is an electrolyte supported cell, it is imperative that the CTE of their electrolyte material be accurately characterized. The electrolyte material used in NexTech SOFC stacks is Y₂O₃ – ZrO₂ (yttria stabilized zirconia or YSZ). Literature values for yttria contents ranging between 3 and 10 mol% and temperatures between 100° and 1000°C vary from 8.5 to 11 µm·m⁻¹·°C⁻¹ [1,7,12,13,18,20,25,27-30], which demonstrates the importance of being certain of the CTE for each specific material. The values calculated in this work would subsequently be used in cell and stack simulations to prove design reliability for NexTech Materials.

2.2. Apparatus Design

The experimental setup designed to measure CTE is shown in Figure 13. The apparatus is in the form of a pushrod dilatometer, and its name comes from the crucial alumina pushrod which can be seen in Figure 13 making contact with the specimen. The apparatus was designed based on the specifications and guidelines provided in ASTM standard E228 – 06 [31]. The specimen is supported between two holding blocks. The alumina rod extends well outside the furnace and is coupled to a linear variable
differential transformer (LVDT) core. As the LVDT core moves in and out of the LVDT housing, the output voltage from the coils within the LVDT varies.

The LVDT used was a Schaevitz 125-HPA AC LVDT. The signal from the LVDT was sent for conditioning to a Schaevitz ATA-101 Analog Transducer Amplifier, the output of which is directly proportional to the LVDT core displacement. For the high resolution LVDT to operate well it was important to keep it out of any high temperature air near the furnace. To accomplish this, the long alumina pushrod was employed, as well as several pieces of insulation.

The material of interest was 3 mol\% Y\textsubscript{2}O\textsubscript{3} stabilized ZrO\textsubscript{2}. Samples which were 45 x 13 x 1.9 mm\textsuperscript{3} were obtained for characterization. The other material which was obtained
for device calibration was 99.999% pure elemental aluminum. The description of the calibration process is described in the next section.

2.3. Method of Calculation

ASTM E228 – 06 provided the calibration techniques, CTE definitions, and CTE calculation equations which were used in this work [31]. It was first necessary to compute the calibration curve for the experimental apparatus as a function of temperature. This curve is determined in order to be able to account for extraneous apparatus expansion including that of the alumina rod and furnace base as well as any other unknown parts of the setup. It is calculated by taking the difference between the measured expansion of a reference material and its known expansion over the desired temperature range. The formula used is shown in Equation 5, where $A_{Ti}$ is the calibration value at temperature $T_i$, $\left(\frac{\Delta L}{L_0}\right)_t$ is the change in length over original length for $t$, the true reference expansion from the standard and $m$, the measured expansion. As was mentioned, the reference material chosen in this work was aluminum, whose true reference expansion is provided in the standard.

$$A_{Ti} = \left[\left(\frac{\Delta L}{L_0}\right)_t - \left(\frac{\Delta L}{L_0}\right)_m\right]_{T_i}$$ (5)
Figure 14: Plot of true and measured reference aluminum expansion for apparatus calibration

An example of the measured aluminum expansion versus its true reference expansion is shown in Figure 14. Taking the difference between the two curves shown provides the calibration curve, as calculated by Equation 5. After calculating the calibration curve over the desired temperature range several times for statistically averaged reliability, the apparatus was used to measure the expansion of the 3YSZ. Expansions of the electrolyte specimens were calculated using Equation 6, which employs the calibration curve $A_{T_i}$.

\[
\left[ \frac{\Delta L}{L_0} \right]_{T_i} = \left[ \left( \frac{\Delta L}{L_0} \right)_m + A \right]_{T_i}
\]  

(6)
Each $\frac{\Delta L}{L_0}_{T_i}$, which is a change in length over original length of the YSZ specimen with all apparent apparatus expansions removed is then used in Equation 7 to calculate the CTE, $\alpha_{RT-T_i}$, which is the average CTE between room temperature and the temperature $T_i$.

$$\alpha_{RT-T_i} = \frac{1}{T_i-RT} \left[ \frac{\Delta L}{L_0} \right] _{T_i}$$  \hspace{1cm} (7)

2.4. CTE Results and Discussion

The CTE calculations were performed for 3YSZ over the temperature range 150° - 650°C, and the results are shown in Figure 15. For this range, the average CTE varies between about 9 and 11.5 µm·m⁻¹·°C⁻¹. Depicted in Figure 16 are the results of the current measurements shown in blue and overlaid on results from the works of: (a) Hayashi et al. [29] and (b) Radovic et al. [30]. In Figure 16a it can be seen that there is a direct comparison against the 3 mol% results. The two results match well at higher temperatures with some divergence below about 475 K (~250°C). Figure 16a also demonstrates the expectation that CTE will increase with decreasing mol% yttria. This information can be used to verify the extent to which the values from this work match those in Figure 16b, and indeed the 3YSZ values from this work are slightly higher than the 4.5YSZ values from Radovic et al.
Figure 15: Average CTE, $\alpha$, the change in specimen length from room temperature to the temperature at each data point, normalized by the room temperature length and $\Delta T$ from room temperature to the temperature at each data point, for 3YSZ.
Figure 16: The results from this thesis (data points) overlaid on those of, (a) Hayashi et al. [29] and (b) Radovic et al. [30]

Having seen good agreement between the experimentally measured values of this work, and those from the literature, it was decided that the values measured herein could be used for future finite element analysis. These values will be used in subsequent FEA in this work and future stack models.

2.5. Conclusions

Thermal expansion in SOFCs can be a major cause of stress and failure. As a result, it is critical that the CTE of all SOFC materials be well characterized. In an electrolyte supported cell such as that created by NexTech Materials, the thermal expansion of the electrolyte will drive the stresses in the other layers of the PEN structure. A measurement apparatus was assembled and calibrated according to ASTM standard E228
– 06, in order to measure the CTE of 3YSZ used in NexTech Materials’ fuel cells. The measurements made using this apparatus were in good agreement with those seen in literature. It is recommended that new CTE measurements be made whenever changes are made in the company’s electrolyte materials.
Chapter 3: Temperature Induced Deflection

3.1. Introduction

Zirconia ceramics, specifically yttria doped zirconia (Y$_2$O$_3$–ZrO$_2$), have been used as oxygen sensors [32], oxygen pumps [33], thermal barrier coatings [34], and electrolytes in solid oxide fuel cells [35]. By itself ZrO$_2$ forms a monoclinic phase at temperatures less than 1170°C. Yttria can stabilize zirconia into more useful phases and these ceramics are typically called yttria stabilized zirconia (YSZ). YSZ is useful in such a wide variety of applications as a result of their highly favorable material properties. YSZ can have low thermal conductivity [34], relatively high fracture toughness, high bending strength, thermodynamic stability at high temperatures, and excellent ionic conductivity [36]. However, these properties vary with yttria content; for instance, 8 mol% YSZ (8YSZ) is reported to have high conductivity and thermodynamic stability at high temperatures but suffers from poor thermal shock resistance and low fracture toughness [36]. On the other hand, 2YSZ can offer much greater toughness but compared to 8YSZ, has 3x lower conductivity [37]. YSZ material properties are further reported to vary as a result of phase changes, even at constant Y$_2$O$_3$ levels [38]. In light of applications that involve chemical, mechanical, and thermal conditions, the evolution of material
properties in terms of both composition and phase of YSZ creates new opportunities for research.

The undertaking of understanding YSZ has been, as of yet, widely varying. In studying the $Y_2O_3 - ZrO_2$ system one finds that there are inconsistencies, metastabilities, and confusions [37,39,40]. In 1988 Yoshimura compiled the phase diagrams of seven different authors; the overlapping of these diagrams is shown in Figure 17 [40].

![Figure 17: Compilation of phase diagrams of Y$_2$O$_3$-ZrO$_2$ system by [40]](image-url)
As can be seen in Figure 17, crucial divisions between phases, both in terms of mol% Y₂O₃ and temperature have proven difficult to define. This is caused, in large part, by the fact that metastable phase boundaries are more often observed experimentally than equilibrium phase boundaries [40]. More recently, a phase diagram that includes the metastable phase lines was created using experimental and computational studies [41]. This phase diagram explains some of the discrepancies seen previously and is shown in Figure 18 including solid equilibrium boundary lines which separate the cubic phase (C), tetragonal phase (T), and monoclinic phase (M) regions. The dashed lines T₀(T/M) and T₀(C/T) are metastable phase boundaries which, if taken into consideration, can be used to clear up many of the confusions and inconsistencies that researchers in previous decades had encountered. For instance, without the T₀(T/M) line, it would be expected that below the T₀(T/M) line, in the green shaded region in Figure 18, YSZ would exist in the equilibrium monoclinic phase. However, it has been found that commonly, a metastable tetragonal phase exists in the mol fraction and temperature ranges shown.
Figure 18: Y$_2$O$_3$ phase diagram depicting equilibrium regions of cubic (C), tetragonal (T), and monoclinic (M) phase as well as metastable phase lines $T_d(C/T)$ and $T_d(T/M)$ from [41]

3.2. Samples

Samples containing 70 wt% 3YSZ and 30 wt% 8YSZ, which is a commonly used electrolyte material for SOFCs, were studied in thermal deflection experiments and modeled using finite element analysis (FEA). The purpose of this work was to quantify and explain unexpected thermal deformation of the YSZ samples. It is proposed that the unexpected result is related to the phase state and stability of the constituent YSZ
concentrations. In particular, it is believed that the metastable phase boundary described in the previous paragraph has been encountered with the samples under investigation. Chevalier et al. in [41] analyzed YSZ sintered at a similar temperature and for a similar length of time as that used in this work. According to their analysis of the metastable phase diagram, the 3YSZ portion of the samples used in this work is likely a mixture of 2.4 mol% Y₂O₃ metastable tetragonal phase and 7.5 mol% Y₂O₃ cubic phase. Based on literature [37,39], the 8YSZ portion of the samples should be fully stabilized cubic phase. For the remainder of this work, it is assumed that the as-received samples contain some mixture of tetragonal and cubic phase particles. This will help to understand the subsequent experiments and results and the description of a plausible mechanism causing these unexpected results.

Samples with dimensions shown in Figure 19 were provided in both patterned and unpatterned varieties. The samples had been prepared by layering and laminating green, tape cast sheets of YSZ with the desired composition up to the desired thickness. The green laminates were then cold isostatically pressed, followed by sintering at 1450°C for 2 hours. A forging sinter under a 9 pound load was then carried out at 1450°C for an additional 2 hours in order to remove any bumps or raised portions of the samples.

Figure 20a shows the unpatterned strip and Figure 20b shows the patterned strip, with hexagonal cutouts covering roughly the middle third of the patterned specimen. As was described previously, the thin areas created by these cutouts provide active ion transport regions in the SOFC electrolyte. The unpatterned samples were measured to be an
average of 181 µm thick, whereas the patterned samples were measured to be an average of 262 µm thick in the support regions.

Figure 19: Dimensioned drawing of an unpatterned sample (dimensions in mm)

Figure 20: (a) Unpatterned and (b) patterned samples
3.3. Experimental Procedure

An experiment was designed to repeatably study two interesting and unexpected phenomena associated with localized heating with a propane torch. First, unexpectedly large out-of-plane deflections of the YSZ strips were observed. Secondly, the deflection had a directional nature. It was necessary to construct simple fixtures on which the samples would be held and heated with the propane torch, so that this phenomenon could be studied with consistent experiments. The experimental setup that was used is shown in Figure 21, and it includes the YSZ sample, ceramic support blocks, propane torch, camera, and darkened backdrop. The C-clamp shown does not constrain the out-of-plane deflection or deformation of the strip; it is only in place to help maintain a stable supporting block.
The experiment consisted of placing the YSZ strip upon the ceramic support blocks and then bringing in the already lit propane torch. The torch was placed a distance of 10 cm away from the sample with its heat directed toward the center of the strip. The torch was left in place for 1 minute and 30 seconds and then removed. The strip was then left in place and for another 30 seconds. The camera was used to take digital photos of the sample in 10 second increments during each two minute long experiment. A sample photo is shown in Figure 22. A digital photo before each experiment was used to provide a flat alignment reference. A graphical schematic of the experiment is shown in Figure 23, with representations of the torch placement, snapshots, and calculated deflections.
Figure 22: Photo taken during torch experiment which shows both the deformed shape of the strip and the flame height
Important information was collected from each photograph including the torch flame height and the sample deflection. In order to objectively analyze the data in the digital images, two MATLAB codes were written. The first code was used to extract the height of the inner blue flame from the image. This inner blue flame is shown in Figure 24 and is easier to detect than the larger, lighter flame. The height in pixels of each inner blue flame was checked before experiments began, and tracked throughout each experiment to ensure that consistent flames were being applied to each sample. The propane control knob made it easy to control the inner blue flame height. Thermocouple measurements
of temperatures on various points of the sample, in the flame, and in the air surrounding the sample were taken during initial experiments. Also, a Raytek® Miniature Infrared Sensor was used to capture the temperature profile along the length of the torch heated sample.

![Propane torch flame depiction](image)

**Figure 24**: Propane torch flame depicting inner blue flame and larger, lighter flame

The second MATLAB code was written to determine the out-of-plane deflection experienced by each sample. For each sample, a conversion between pixels and mm was calculated based on the initial specimen length. Next, the sample was isolated by filtering out the dark background, leaving the white sample and its associated pixels in place. This information was then compared against similar information from before the torch was introduced, giving the deflection of each sample in pixels. Sample images associated with this filtering and comparison process are shown in Figure 25.
Figure 25: MATLAB figures depicting various steps in the deflection code, (1) the as captured photo, (2) converted to black and white, and (3) filtering out the background for (A), a flat sample and (B), a deflected sample.

Directional heating experiments were performed on samples that were as-received or samples that underwent one of three treatments: deadweight bending, heating at 800°C,
or a combination of the bending and heating. Deadweight bending, which is shown in Figure 26, was employed because the tetragonal to monoclinic phase transformation is promoted in the presence of tensile stress [41,42]. In the case of the experiments in this work, a small, furnace ready, ceramic block was chosen as the weight. It had a mass of 27.5 g and caused a specimen deflection which was on the order of that caused by torch heating. An 800°C heat-treatment was chosen because Swain demonstrated phase transformations and associated “shape memory” type effects in zirconia ceramics at 800°C over lengths of time as short as 2 hours [43]. The heating cycle for the treatment in this work was a ramp up at 13 °C·min⁻¹ to 800 °C, followed by a 3 hour dwell period and a 13 °C·min⁻¹ ramp back down to room temperature.
3.4. Finite Element Models

In order to attempt to replicate experimental results, two separate 2D thermal-structural models were constructed in ANSYS™. In each model an area representing half of the specimen cross-section was created. At one end of this area, the model was constrained in the out-of-plane direction and a symmetry constraint was applied to the other end of the area. Also shared between the two models are the material properties listed in Table 2. The only material property that was not the same between the two
models was the coefficient of thermal expansion, which was the property of interest in
the FEA.

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>E, elastic modulus</td>
<td>200 GPa</td>
</tr>
<tr>
<td>k, thermal conductivity</td>
<td>2 W-m(^{-1})-K(^{-1})</td>
</tr>
<tr>
<td>h, convective heat transfer</td>
<td>5 W-m(^{-2})-K(^{-1})</td>
</tr>
</tbody>
</table>

The two models differed in the way that the CTE varied through the thickness of the
sample. Variation in CTE was chosen as it was a likely cause of deflection
experimentally. It was likely because CTE variation can be seen to cause layered
material deflection with thermal loading, as is often seen in SOFC Positive electrode-
Electrolyte-Negative electrode structures. It was also likely because CTE change could
accompany a phase change between metastable tetragonal YSZ and monoclinic YSZ. In
the first model, the CTE varied as a pseudo-continuous gradient through the thickness,
with a variable number of layers existing through the thickness. Each layer in the model
had an incrementally different value of CTE. A representation of this CTE gradient
model is given in Figure 27 with each color in the figure representing a material model
with different CTE.
The second model was designed to simulate a sample in which there is an abrupt change in CTE near one of the surfaces. Such a bimaterial model was sure to exhibit deflection upon heating. This model was warranted because the literature shows that in dense YSZ, a tetragonal to monoclinic transformation can occur only on a thin surface layer [44,45]. Badwal and Nardella in [44] report that the tetragonal to monoclinic transformation occurs in a 10 to 20 µm surface layer and not in the bulk of dense YSZ samples. Furthermore, they found experimentally that the maximum transformation takes place in the first 3 to 4.5 µm of this surface layer. The model was programmed to allow the percentage of transformed thickness to be varied. As transformed thickness was varied, the FEA deflection results could then be matched with experimental ones. Figure
28 shows a sample of what the cross-section of this bimaterial model looked like in the simulated environment.

To ensure temperature matching between the experiment and model, several iterations of varying the heat flux in the model were performed until the experimental temperature profile was sufficiently replicated. Representations of the thermal boundary conditions applied in the model are shown in Figure 29, and they include a small area of heat flux into the sample from the torch, as well as free convection above and below the sample. The free convection ambient temperatures were based on thermocouple measurements made around the sample. Once thermal boundary conditions were applied,
the model calculated nodal temperatures using PLANE55 elements. Contour plots of the nodal temperatures calculated are shown in the series of screenshots in Figure 30.

Figure 29: Representations of thermal boundary conditions applied in FEA
Figure 30: Contour plot of model temperature changes in degrees Celsius, offset by 20°C for (a) the whole model, with breakouts of (b), (c), and (d)

With boundary conditions described earlier and the nodal temperatures for the just described thermal analysis, structural analysis was performed. The element PLANE182 was used for the structural portion of the analysis. Outputs from this, the final step in the FEA, will be discussed in Section 3.5.5.
3.5. Results and Discussion

3.5.1. Directionally Preferred Deflection

When the directional dependence on heat-induced deflection was first discovered, it was thought to be a property inherent to the sample. The expectation was that the fabrication process resulted in residual stresses or varying material properties within each sample. The initial observations were that the deflection went in the same direction relative to the sample face regardless of its orientation or the direction from which it was heated. However, upon investigation with fresh samples and more consistent experiments, it was found that the directional preference was induced during the first heating.

Four possible sample orientations are given in Table 3. Regardless of the initial sample orientation (A being face up and B being face down), as shown in Table 3, the sample always deflected toward the torch during the first heating experiment. Table 3 shows that for subsequent heating experiments, the first heating experiment orientation was so to speak ‘locked-in’ with the associated first heating experiment deflection direction. For instance, Sample 2 was placed in orientation B (face down) during its first heating experiment and heated from below. Since it was heated from below, it deflected down toward the torch. Sample 2 was then placed in orientation A (face up) during its second heating experiment and it deflected up. In order to show that the downward deflection of Sample 2 was ‘locked-in’, it was flipped back over and heated in orientation
B, and once again it exhibited the same downward deflection it had during the first heating. To prove that the directional dependence was not the result of always heating from below, Sample 4 in Table 3 was initially heated from above. Despite heating from above, the directional dependence in Sample 4 was consistent with the other samples.

Table 3: Unpatterned sample deflection direction depending on sample orientation during first heating experiment. (Downward deflections are highlighted in grey along with their associated orientations for a given sample)

<table>
<thead>
<tr>
<th>Sample</th>
<th>First Heating Experiment</th>
<th>Subsequent Heating Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Orientation (1 or 2)</td>
<td>Deflection Direction</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
<td>Down</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>Down</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>Down</td>
</tr>
<tr>
<td>4†</td>
<td>A</td>
<td>Up</td>
</tr>
</tbody>
</table>

† It is important to note that Sample 4 was heated from above during its first heating experiment while the other three Samples were heated from below during their first heating experiments

Table 4: Patterned sample deflection direction depending on sample orientation. (Downward deflections are highlighted in grey along with their associated orientations for a given sample)

<table>
<thead>
<tr>
<th>Sample</th>
<th>First Heating Experiment</th>
<th>Subsequent Heating Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Orientation (1 or 2)</td>
<td>Deflection Direction</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
<td>Down</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>Up</td>
</tr>
</tbody>
</table>

At first glance, the patterned samples seemed to contain an inherent directional preference prior to the first heating experiment. This apparent effect is demonstrated in Table 4, which shows that patterned samples deflected away from the cutouts during all heating experiments. In other words, unlike the unpatterned samples, it did not matter which side was heated first. However, with the aid of Figure 31, it was determined that the same induced directional preference ideas applied to the patterned samples.
Figure 31: (a) Picture of patterned sample showing cross-section that is analyzed in, (b) showing it heated in orientation A, and (c) showing it heated in orientation B.
Figure 31a shows a patterned specimen with A-A cross-section. Figure 31b and Figure 31c show the cross-sectional schematics for the patterned sample being heated in orientations A and B, respectively. Included in the two schematics are representations of the torch flame coming from below the sample, the primary heating area, and the neutral axis. Operating under the assumption that the schematics shown are of a first heating experiment, the argument goes as follows. The sample in orientation A, heated from below in Figure 31b deflects down as was seen experimentally in all such oriented samples in Table 4. This makes sense, as the primary heating area is on the continuous bottom surface of the sample which is below the neutral axis. As such, the phenomenon is induced just as it is on an unpatterned sample heated from below and the directional preference for the sample in Figure 31b is now to deflect away from the cutouts.

On the other hand, the sample in orientation B, heated from below in Figure 31c deflects up as was seen experimentally in all such oriented samples in Table 4. It can be seen that since the majority of the area of the patterned sample is filled with cutouts, most of the heat reaches the bottom surface at the base of the cutout section. Since the base of the cutouts is above the neutral axis, the majority of the material that gets heated in this orientation is above the neutral axis. The result is that this reacts very much like an unpatterned sample heated from above (see Table 3, Sample 4) and thus it deflects upward. Now, for the sample in Figure 31c, the directional preference is to deflect away from the cutouts.

Since the difference between the unpatterned and patterned specimens was consistent with simple analysis of the heated plane and neutral axis, it was possible to move forward
with identifying the mechanisms for the large, directionally induced deflection from just
the unpatterned samples. Of particular interest are the following observations: First, the
magnitudes of the deflections were relatively large and could not be explained by mere
thermal expansion under through-thickness temperature gradients. Secondly, there
existed great curiosity as to why this mechanism was inducing a directional preference.
It was thought that if heating the specimen in orientation A with a torch was causing a
material change on that side of the sample, then that same change would also take place
on the other side when the specimen was flipped and heated in orientation B. Equal
changes to first side A and then side B would negate any directional dependence.

3.5.2. Treatments to Induce Directionally Preferred Deflection

It was demonstrated that the observed phenomenon of the directionally preferred
deflection was being induced by the torch heating experiments. In an effort to understand
how and why there was directional dependence occurring, observations of other
treatments were made. The results presented up until this section have all been from as-
received samples. The purpose of this section is to consider the results from the treated
specimens, those that had been bent, heated, or bent while being heated, in order to
determine the mechanism by which the torch was inducing said phenomenon.

As was previously stated, there was precedent from the literature to consider applying
tensile stress and strain in order to induce the tetragonal to monoclinic phase
transformation which was thought to be a possible operating mechanism in this work. It
was desired that the deflection resulting from bending be on the same order of magnitude of the torch deflection so that the strains experienced by the sample would be on the same order. If then, the mechanism of inducing the directional preference was via a certain strain field, this would be replicated in deadweight loading experiments. Thus, it was hypothesized that there would be an induced preference in bent samples which would not be overcome by the first heating experiment. Table 5 displays the results from heating experiments performed on two deadweight bent samples.

Table 5: Samples which were loaded with the deadweight and subsequently torch heated

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experiment</th>
<th>Orientation</th>
<th>Deflection Direction</th>
<th>Deflection Magnitude (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Deadweight A</td>
<td>Down</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>First Heating B</td>
<td>Down</td>
<td>1.7 ± 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Second Heating A</td>
<td>Up</td>
<td>2.2 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Deadweight B</td>
<td>Down</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>First Heating B</td>
<td>Down</td>
<td>1.5 ± 0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Second Heating A</td>
<td>Up</td>
<td>2.0 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from the results in the table, the deadweight loading treatment had no effect on the torch heating response of the samples. One sample was bent in orientation A while the other sample was bent in orientation B. In bending one of each sample in either direction, this treatment exposed a different face to tensile strain in either sample. They were then each placed in orientation B for their first heating experiment to see if one of them would have experienced a stress/strain field which would have pre-induced them to deflect up away from the torch on first heating rather than down toward it. The results showed that this was not the case. Both samples deflected downward on first
heating in orientation B and then upon being flipped over and heated in orientation A they deflected upward. The magnitudes of the deflections for each sample were close enough to each other so that it could not be said whether some transformation had caused increased deflection in one direction rather than the other.

The next treatment of samples considered was a uniform heating at 800°C for 3 hours. This was done in an attempt to bump the metastable tetragonal YSZ into an equilibrium phase of monoclinic YSZ. If it were possible to transform the tetragonal to monoclinic prior to torch heating, then this transformation mechanism would not be available during the torch heating experiment and thus the large, directionally preferred deflections would not be possible. It was shown though, after the uniform heating treatment at 800°C that the phenomenon was still occurring. The sample still deflected down on the first torch heating. Furthermore, over six cycles, the sample deflected 2.1 mm on average, which was similar in magnitude to the deflection of as-received specimens. The next possible recourse, since both bending and heating alone had had no effect, was to combine the two.

It was thought that, since the torch heating experiment involved both deflection and heating of the sample, that a treatment which included both of these characteristics might induce the directional preference prior to the torch heating experiment. Yet again, however, the directional preference induced by the torch experiments could not be avoided. The sample which was bent using the ceramic deadweight and heated using the previously described heating regimen was then put through six alternating torch heating experiments. The magnitude of the deflection experienced by the sample is shown in
Figure 32 and was not noticeably affected by the heat treatment and bending. As-received samples in general, deflected about 2.0 mm which is similar in magnitude to the deflections seen in the figure. It should be noted that although the first cycle seems to have caused a larger than usual deflection, which could possibly indicate an alteration due to the pre-treatment, it was observed that the sample came out of the furnace with some permanent deformation. As a result of the bending at 800°C there was a bow to the sample which was calculated by the MATLAB code to be 0.6 mm. After adjusting this cycle’s deflection by 0.6 mm, its deflection falls right in line with that of the other cycles.

Figure 32: Magnitude of deflection experienced by heat-treated and bent sample
This bending while heating at 800 °C was the third of three treatments used in an attempt to induce the directional preference prior to torch heating experiments. The other two treatments, which were simply bending and heating at 800°C by themselves, also failed to induce the phenomenon. While the directional dependence had yet to be explained, there were still other interesting results to be analyzed.

3.5.3. Other Notable Results

Having moved past the basics which defined the proposed theory, and having attempted to replicate it with several treatments, other results which may help understand the mechanism involved were analyzed. One such result is that the induced directional preference remains, even with up and down cycling. Figure 33 shows that for a given sample, cycled 10 times, the magnitude of the deflection remains relatively constant at around 2.0 mm deflection. Every odd point in Figure 33 is a downward deflection, while every even point is an upward deflection. This means that the sample was exposed to 5 downward and 5 upward cycles in an alternating fashion, without demonstrating any diminishing deflection. Another sample was put through a similar cycling regimen, and it also demonstrated a highly consistent set of deflection magnitudes with thermal cycles.
The next result of interest is that the induced directional preference of the deflection is effectively permanent in time, with all other variables held the same. Three sets of samples were put through the thermal deflection experiment on the same day. One set was then cycled the next day, with the induced directionality still in place. The other two sets were cycled 10 days and 1 month later; the deflection and/or directionality did not diminish. This result would seem to indicate that without adjusting the sample in any way between experiments, the induced directional preference remained. There have been studies which have shown metastable phase transformations in YSZ during aging of...
between 2 and 9000 hours at temperatures from room temperature up to about 400°C [36,38,46]. This is the type of transformation which is thought to be the cause of the induced directional preference in this work. Since this work only performed aging of roughly 700 hours (1 month), longer aging times may still be of interest.

Regardless of time between experiments, it was shown that in unpatterned samples and for the same heating, upward deflection was slightly greater in magnitude than downward deflection. This effect can be seen in Figure 34, however it must be noted that this is thought to be a geometric artifact in the experiment rather than an inherent property of the material. In looking closely at the support blocks, it can be seen that there is an initial overlap area at each end of the specimen that rests on each supporting block. Figure 35 shows a schematic representation of this overlap area and its effect on deflection. One can see that as a sample deflects up, the point which makes contact with the support block will move out to the edge of the specimen. This allows for the curvature of the entire sample to contribute to the deflection magnitude. On the other hand, when a sample deflects down, the point which makes contact with the support block will move in to the corner of the support block. This means that there will be a portion of the sample, namely the portion outside these support points, whose curvature does not contribute to the magnitude of deflection detected by the MATLAB program. This effect was minor and, given the error bars in Figure 34, was nearly undetectable; however it was important to the author to point out this possible experimental artifact.
Figure 34: Upward deflection magnitude compared with downward deflection magnitude for the same heating
Another interesting result is the observation that each specimen underwent additional deflection immediately upon removal of the torch. The additional deflection was observed visibly in every experiment and captured using photographs and the MATLAB code during one particular experiment. The transient cooling effect on deflection is shown in Figure 36, and one can see that for about 3 – 4 seconds after torch removal, the specimen underwent additional upward deflection. The magnitude of this deflection was about 0.6 mm, which, considering that the steady-state deflection during torch heating was 2.4 mm, is substantial.
No single result provides a direct identification and confirmation of the mechanism which caused the large out-of-plane deflection and directional preference thereof. However, one can examine the entire body of results and compare them against the results from the finite element model in order to come to a sufficient understanding of a plausible mechanism.
3.5.4. XRD Results

Since the directionality of the deflection was locked into the sample after the first heating, there is presumably a permanent change to the material’s microstructure. Scanning Electron Microscopy was inconclusive. Phase analysis was then performed with X-ray diffraction (XRD). A low angle (2θ = 27.5° - 32.5°) XRD scan was performed on the bottom surface of a sample. This surface was one that was initially heated by the torch during this sample’s first heating experiment. The results are shown in Figure 37 and they demonstrate in Figure 37a the existence of the tetragonal phase and in Figure 37b the existence of the monoclinic phase. The tetragonal phase peak is expected based on the literature analysis provided in Section 3.2. The literature also predicted the existence of the cubic phase in these samples. Although not shown in this thesis, several fast scans which encompassed much larger ranges of 2θ angles captured both the cubic and tetragonal phase peaks. The interesting result from Figure 37 is the existence of the monoclinic phase peaks. Per the analysis in Section 3.2, it was assumed that there would not be any monoclinic phase present in the samples. With these XRD results in hand, it is believed that the experiments have induced some phase change which produced monoclinic phase particles. Further discussion of such a transformation and its possible implications are covered in the following sections.
Figure 37: XRD scan results showing: (a) a large tetragonal peak and the red box which shows the window viewed in (b) which shows two definitive monoclinic peaks at 28.2° and 31.5°.
3.5.5. FEA Results

With the experimental results having been presented and discussed, a framework was created, within which the finite element results can be examined. The first way that this is done is by demonstrating that the deflections seen experimentally are drastically larger than are predicted by the FEA with constant CTE throughout the specimen. For constant CTE, thermally induced deflection would be solely the result of through-thickness thermal gradients. However, for constant CTE, the FEA model predicted a deflection of only 15 µm, which is two orders of magnitude smaller than the 2 mm deflections seen experimentally. This would seem to indicate that the CTE is not constant through the thickness and that something must be changing with regard to CTE. Additional FEA was used to investigate possible CTE variations.

For the first model, the result of interest is the CTE gradient at which the FEA results match the experimental results. Rather than referring to a given model output as coming from a given CTE gradient (\( \nabla \text{CTE} \)), the output shall be referred to as coming from a given difference in CTE (\( \Delta \text{CTE} \)). Because of the way that the CTE gradient is defined within the model, since the thickness always remains the same, \( \nabla \text{CTE} \) only changes as \( \Delta \text{CTE} \).

It was then important to establish whether or not the magnitude of the initial CTE from which a change was made mattered. For instance the \( \Delta \text{CTE} \) for both 6.5 – 6 µm·m\(^{-1} \cdot \circ C^{-1} \) and 10.5 – 10 µm·m\(^{-1} \cdot \circ C^{-1} \) is 0.5 µm·m\(^{-1} \cdot \circ C^{-1} \), but do they provide the same
deflection for the same temperature profile? It was found that the deflection only varied as a function \( \Delta \text{CTE} \) rather than the overall magnitude of CTE values and \( \Delta \text{CTE} \). This, along with the results presented in Chapter 2 which measured the CTE of bulk 3YSZ, made pinpointing the CTE profiles of interest considerably more simple.

The deflection magnitude calculated by the CTE gradient FEA model is shown in Figure 38 for several values of \( \Delta \text{CTE} \). The figure indicates that a \( \Delta \text{CTE} \) through the thickness of between 0.4 and 0.5 \( \mu \text{m} \cdot \text{m}^{-1} \cdot \text{oC}^{-1} \) would provide the experimentally determined torch heating deflections of around 2 mm. A screenshot from the FEA model showing the true deflection at \( \Delta \text{CTE} = 0.4 \mu \text{m} \cdot \text{m}^{-1} \cdot \text{oC}^{-1} \) is shown in Figure 39a and it is compared against an experimental photo of a sample with the same deflection in Figure 39b. A white line is superimposed on both images for the purposes of comparing them to horizontal. The deflection profiles from both the FEA model and experimental photo are visibly very close to one another and the maximum magnitude of deflection for both is equal to within the resolution of the experimental measurement. This demonstrates that the CTE gradient model possesses the capability to match what was observed experimentally.
Figure 38: CTE gradient model FEA results

Figure 39: Comparison of deflections seen, (a) in the FEA results and (b) experimentally
For the second model, two variables were examined, both $\Delta$CTE and transformed layer thickness. Figure 40 shows the results for varying transformed layer thicknesses of 4 to 20 $\mu$m. This range was based on values seen in the literature [44]. Depending on the portion of the sample that is transformed, causing the change in CTE, the $\Delta$CTE would have to be between 4.3 and 1.0 $\mu$m·m$^{-1}$·°C$^{-1}$ for a layer thickness of between 4 and 20 $\mu$m, respectively. For the bimaterial model then, as well as the gradient model, it can be seen that experimental deflections can be replicated. Further discussion of these models will be presented in the Conclusions section, as they are compared against the experiments and literature as a means of verification.
3.6. Conclusions

For decades considerable ambiguity and confusion has surrounded the phase state of yttria stabilized zirconia. In fact, Suresh et al. report that “Indeed, researchers synthesizing zirconia and other materials in very fine particulate form routinely find that the phase of the material they have generated is not the expected phase at room temperature and pressure” [47]. There have been many explanations of this notion, ranging from phase metastabilities [40] to surface energy difference between polymorphs.
At present, this work has no new information to add to these arguments, however it seems that it experienced something similar to what “researchers … routinely find”, that is, unexpected phases.

Experiments showed that there was a directionally preferred thermal deflection being induced in 70 wt% 3YSZ + 30 wt% 8YSZ samples. This phenomenon was accompanied by deflections upon torch heating of around 2 mm. The following three treatments were used to try to induce this phenomenon besides torch heating: bending, heating at 800°C, and heating and bending simultaneously. None of the three treatments successfully changed the samples in such a way that the directional dependence of deflection was not then induced by the torch heating experiments.

X-ray diffraction results pointed to a plausible mechanism which could be causing the preferred deflection. The monoclinic phase, unexpected in the as-received samples, was shown to exist on the bottom of an experimented-on sample. It is proposed that these monoclinic particles were created by the transformation of some of the metastable tetragonal phase expected to exist in the as-received samples. The cause of this transformation can be explained in relation to Figure 41. One can see that in the deflected state, the bottom portion of the sample is in a tensile strain region whereas the top of the sample is in a compressive strain region. It has been demonstrated in the literature that the tetragonal to monoclinic phase transformation is promoted in a tensile stress/strain field [41,42]. As such, it is proposed that the initial influence of the torch heating is to cause a strain state that initiates the t – m transformation. The literature states that this t – m transformation is accompanied by a 3 – 6% volume expansion.
Such an expansion occurring in the bottom of the sample would cause further downward deflection of the sample.

It is also proposed that the monoclinic phase has a CTE which is greater than that of the tetragonal phase. A larger CTE for the monoclinic phase could possibly prevent further transformation with thermal cycles. It causes the untransformed side in Figure 41 to be in a compressive region, which tends to impede t – m transformation. FEA results demonstrated that without the existence of a change in CTE through the thickness of the sample, the thermal deflection would only be on the order of 15 µm. Two models, one with a pseudo-continuous CTE gradient through the thickness and one with an abrupt change in CTE on a thin surface layer were capable of predicting deflections which were similar in magnitude to those seen experimentally. Either model seems plausible, in that the metastable phase transformation could be occurring gradually through the thickness, thus causing a gradient in CTE through the thickness; or it could be occurring just near
the surface, making the bimaterial model seem more likely. The observations that the directional preference is maintained for at least 1 month and with thermal cycles in which the sample orientation is flipped indicate that the mechanism which is occurring is permanent.
Chapter 4: Conclusions and Future Work

This thesis has presented results whose focus is on the thermal expansion of the solid oxide fuel cell material yttria stabilized zirconia. SOFCs, being high temperature devices, have complex issues relating to thermal expansion. In light of these problems, this work built an apparatus and measured the coefficient of thermal expansion of a specific electrolyte material. The CTE calculations were performed for 3YSZ over the temperature range 150° - 650°C. For this range, the average CTE varies between about 9 and 11.5 µm·m⁻¹·°C⁻¹. These values are in good agreement with the values seen in literature.

Future work related to the measurement of CTE values of bulk YSZ include enhancing the apparatus and employing a more controllable furnace. It should be made clear that future variations in SOFC electrolyte composition should be followed by new CTE measurements.

This thesis also includes investigations of unexpected thermal deflections of thin electrolyte membrane specimens. Two finite element models with varying CTE configurations were created in order to help understand and explain the deflection observations and measurements. Using the experimental results, X-ray diffraction analysis, FEA results, and literature, it was shown that a phase transformation between
the metastable tetragonal and monoclinic phases of YSZ is occurring and could be causing the CTE variations.

Future work to further understand the directionally preferred deflection includes measuring the values of CTE for the various phases of YSZ. Knowing the values of CTE for the various phases of YSZ would allow for better FEA models to be created. This knowledge, paired with high resolution TEM imaging of experimental samples both before and after torch heating would serve to confirm the hypothesis that phase change through the thickness of each sample is occurring. It would also be of interest to attempt to anneal out the directionally preferred deflection phenomenon. Heat treatments of various temperatures and lengths of time could be attempted to remove a given sample’s preference to deflecting in a given direction and thereby help in understanding the underlying mechanisms. As the aging experiments in this work only went up to 1 month in duration, longer aging of samples could be attempted to see if the directional preference still exists.

Understanding each of these different thermal aspects of the SOFC electrolyte material will allow for designers and researchers to improve on current technologies. CTE values, phase stability information, and robust FEA can help to create SOFCs which are able to operate and be thermally cycled in ways that will make them more commercially viable. Commercially viable SOFCs represent one of many bright hopes for the future of world energy production.
References


