Development of Solid Oxide Fuel Cell Electrodes with High Conductivity and Enhanced Redox Stability

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DEVELOPMENT OF SOLID OXIDE FUEL CELL ELECTRODES WITH HIGH
CONDUCTIVITY AND ENHANCED REDOX STABILITY

by

Brandon H. Smith

A Thesis

Presented to the Faculty of
Bucknell University
In Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemical Engineering

Approved:

Advisor

Department Chairperson

Engineering Thesis Committee Member

April 14, 2010
Date
I, Brandon Smith, do grant permission for my thesis to be photocopied.
Acknowledgements

Foremost I would like to thank Dr. Michael Gross, who has served as my advisor throughout the completion of this work. I am grateful for his excellent guidance, insight, and direction which have carried my research to a successful conclusion and for the friendship that has developed. I would also like to express my appreciation to the members of my thesis committee, Dr. Jeffrey Csernica and Dr. William Snyder, whose commitment to education has inspired and challenged me.

Several of my colleagues have also contributed to this body of research. I would like to thank Addison Yee, Brian Smith, Scott Schreiber, Billy Holler, Kristin Bretscher, and Jacob Pedder for all of their hard work over the past two years. It has been a pleasure working alongside and getting to know each of them. Additionally, many thanks are due to Diane Hall who was always willing to help me locate any supplies or information I needed.

Last, but certainly not least, I would like to thank my parents, Rodney and Tammy Smith, for their unwavering support and for always challenging me to excel to the best of my abilities. They are an endless reservoir of love and steadfast encouragement for me. I would also like to thank my sister, Brittany, for all of the fun times and good memories we have shared throughout the years.
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Abstract

Although significant advances in solid oxide fuel cell (SOFC) technology have been made, one limitation must be addressed before their benefits can be fully realized. SOFCs hold the promise of highly efficient electricity generation, low emissions, and fuel flexibility [1-3], yet the lack of toleration for oxidation and reduction cycles in the material currently used in SOFC anodes hinders the full-scale application of this technology. The material that is most widely incorporated in the anode of a SOFC is a ceramic-metallic (cermet) composite of Ni and yttria-stabilized zirconia (YSZ) [1, 4]. The Ni-YSZ cermet provides catalytic activity, ionic conductivity, and electronic conductivity [5, 6], but because Ni can be oxidized at high temperatures, it is intolerant to the oxidation cycles that are encountered during the SOFC startup procedure [7]. n-doped SrTiO$_3$ ceramic materials are a promising alternative for the Ni-based anodes [5] because ceramics are already in the oxidized state, and dopant materials can be added to provide the necessary electrical conductivity. Prior research in this area has focused on maximizing the electrical conductivity of ceramic materials without consideration for redox cycling encountered during fuel cell operation. The intent of this study was the development of new ceramic SOFC anode materials which possess electrical conductivity as well as redox stability.

In an effort to identify materials possessing the essential characteristics needed for use in SOFC anodes, the conductive properties of vanadium, tantalum, tungsten, and molybdenum-doped strontium titanates were investigated under realistic fuel cell
operating conditions and redox cycling. Minimum conductivity limits of 1 S/cm for bulk samples and 0.1 S/cm for porous composites obtained from the literature \([4, 8]\) were used to gauge if the novel ceramic exhibited a sufficiently high electrical conductivity. When \(\text{SrV}_x\text{Ti}_{1-x}\text{O}_3\) (SVT) was investigated for \(x = 0.01, 0.05, 0.1, \) and 0.2, the highest observed values for dense pellets reduced at 1400 °C did not satisfy the minimum bulk conductivity requirement. \(\text{SrTa}_x\text{Ti}_{1-x}\text{O}_3\) (STT) with \(x = 0.01, 0.05, 0.1, \) and 0.2 was found to exhibit reasonable conductivities after the samples were pre-reduced in \(\text{H}_2\) at 1400 °C, yet the only compositions which exhibited redox stability were \(x = 0.01\) and 0.05. Fuel cell tests indicated that reasonably good performance was achieved in humidified \(\text{H}_2\) for 1% Ta STT-YSZ anodes infiltrated with 3 wt% \(\text{CeO}_2\) and 1 wt% \(\text{Pd}\).

\(\text{SrW}_x\text{Ti}_{1-x}\text{O}_3\) (SWT) with \(x = 0.01\) and 0.2 was also investigated. Sufficient conductivity values were attained by the reduced pellets in humidified \(\text{H}_2\), but neither concentration of tungsten dopant maintained the enhanced conductivity obtained from the pre-reduction step after redox cycling. Following the investigation into SWT, samples were synthesized for \(\text{SrMo}_x\text{Ti}_{1-x}\text{O}_3\) (SMT) with \(x = 0.01, 0.2, 0.4, \) and 0.6. For the highly doped SMT samples, significant increases in conductivity of four orders of magnitude within the 750-800 °C temperature range suggested that the material reduces at SOFC operating temperatures, so it can be considered redox stable. However, an XRD analysis revealed that separate \(\text{SrTiO}_3\) and \(\text{SrMoO}_4\) phases formed at dopant concentrations where \(x \geq 0.2\).

Based on the results of the investigation of SMT, interest focused on \(\text{SrMoO}_4\) (SMO), but it was determined that SMO experiences a 40% increase in volume due to
thermal expansion. In order to overcome this obstacle, SMO was infiltrated into porous YSZ slabs to several target loadings as opposed to co-sintering SMO and YSZ. Thermal expansion experiments demonstrated that the maximum loadings which maintained expansion behavior similar to that of YSZ were 12.2 wt% SMO when a calcination temperature of 1000 °C was used and 20.6 wt% SMO when 1200 °C was used. Maximum conductivities of 15-20 S/cm were attained by samples infiltrated to roughly 20 wt% SMO for both calcination temperatures, but the slab at 20 wt% SMO which was calcined at 1200 °C exhibited the best electrical conductivity in addition to thermal compatibility with YSZ.

In the continuing search for materials which can replace problematic Ni-YSZ cermet anodes and eliminate several of the limitations hindering the widespread application of SOFCs, this study has sought to take steps in the direction of a practical solution. The results obtained from the body of work accumulated to this point support the claim that SrTa$_{0.01}$Ti$_{0.99}$-YSZ and 20 wt% SrMoO$_4$ infiltrated porous YSZ slabs calcined at 1200 °C are the optimal compositions which satisfactorily meet the anode requirements for high electrical conductivity and redox stability. As further research determines the conductive properties and redox stability of alternative materials for SOFC anode production, a wider understanding of the mechanisms at work within the electrodes will be gained. Once cheaper and more durable materials are found which can meet the necessary requirements for use in SOFC’s, the high costs currently hindering such power systems will decrease, enabling this “cleaner” method of electricity generation to compete with traditional fossil fuel-dependent systems [2, 9, 10].
Chapter 1  Introduction

1.1  Motivation

Throughout the 20th century, society has become increasingly dependent on fossil fuels as sources of energy to power industry, utilities, transportation, and a myriad of other sectors. Conventional methods of generating useful work from fossil fuels possess numerous innate disadvantages, including high levels of pollution, low efficiencies, and a lack of resource renewability [11]. The challenges associated with replacing an entire infrastructure designed around the utilization of petroleum, coal, and natural gas are too immense to be overcome all at once. However, the alternatives which have endured have been those which allow for a gradual transition from fossil fuels. Electrochemical fuel cells, and particularly solid oxide fuel cells (SOFCs), are promising alternative energy conversion devices which have the potential for implementing hydrocarbon fuels that are compatible with the current infrastructure, thereby allowing small steps to be taken towards a completely “green” fuel.

SOFCs have many advantages over internal combustion engines. Fuel cells can reduce air pollution emissions since they do not generate particulate matter or NO\textsubscript{x} and SO\textsubscript{x} aerosols [12], which are linked to smog and acid rain. They also operate in virtual silence, adding the potential for noise pollution reduction [13]. Compared to internal combustion engines, which are struggling to attain maximum efficiencies of slightly over 50\% [14], SOFCs can easily reach efficiencies greater than 80\% [15, 16]. These devices are more efficient than conventional power generation equipment because they have the
advantage of converting chemical energy from fuel directly to electrical energy without the need for turbines, boilers, and other pieces of equipment that have major energy losses associated with them [1].

SOFCs differ from most other categories of fuel cells in that they operate at very high temperatures, usually within the range of 600-1000 °C, to achieve reasonable ionic conductivity in the yttria-stabilized zirconia (YSZ) electrolyte (≈0.01 S/cm) [17, 18]. There are three advantages of such a high operating temperature. The first is fuel flexibility. The high operating temperature gives SOFCs the ability to directly utilize or internally reform hydrocarbon fuels, thereby making external fuel reforming equipment unnecessary [1, 16]. In principle, any oxidizable fuel can be used for SOFCs because O$^{2-}$ anions are transported across the electrolyte, which is not possible with most other types of fuel cells [19]. Second, high temperatures make SOFCs less sensitive to fuel impurities and catalyst poisons, such as sulfur and carbon monoxide [20]. Whereas CO acts as a poison to most fuel cells, SOFCs can operate with CO as a fuel [12, 21]. The third advantage of a high operating temperature is the potential for a cogeneration system or combined heat and power system (CHP). The waste heat derived from the electrochemical reaction can be harnessed to supply steam [1].

Figure 1-1 shows an example of a commercially available SOFC cogeneration system [22].
system which is capable of supplying the steam and hot water demands of a house or other small building in addition to electrical power. In order to generate sufficient power, most applications require fuel cell stacks that include hundreds of individual fuel cells, instead of a single SOFC [1]. Therefore, the system depicted in Figure 1-1 contains multiple SOFC stacks, as well as other subsidiary equipment required for operation which can be seen in the schematics of various SOFC systems included in Appendix A.

1.2 Operating Principles of SOFCs

There are many types of fuel cells, but all fuel cells generally consist of a layer of electrolyte sandwiched between an anode and a cathode [23]. Fuel cells are distinguished by the type of electrolyte membrane material they contain [20]. In SOFCs, the electrolyte is dense YSZ. Thus, SOFCs are named for the YSZ electrolyte, which is an oxide. Dense YSZ is the most common material of choice due to the fact that it possesses good ionic conductivity, negligible electrical conductivity, and stable performance in the presence of both oxidizing and reducing atmospheres [1]. These properties are essential since the electrolyte separates the air and fuel compartments of the cell.

The fuel, which is shown to be hydrogen in Figure 1-2, diffuses through the anode towards the anode-electrolyte interface where it reacts with O\(^2-\) anions according to the
reaction given in Equation 1-1 [25]. The reaction occurs within an active layer of the anode which is approximately 10-20 μm thick [12]. The cathode layer consists of a porous composite of YSZ with an electronically conductive catalyst that is active for the dissociation of oxygen to oxygen anions. During operation, oxygen is usually supplied to the system by simply exposing the cathode to air [20, 26]. Oxygen enters the cathode and is reduced by free electrons at active sites on the catalyst to form O^{2-} anions according to the reaction shown in Equation 1-2. The anions migrate through the cathode and across the dense YSZ electrolyte towards the interface between the electrolyte and the anode. The overall reaction of the system if hydrogen is used to fuel a SOFC is given in Equation 1-3 [25].

**Elementary and Overall Electrode Reactions for a SOFC Operating on H\textsubscript{2}**

Anode: \( \text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \) \hspace{1cm} (Equation 1-1)

Cathode: \( \text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-} \) \hspace{1cm} (Equation 1-2)

Overall: \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \) \hspace{1cm} (Equation 1-3)

If hydrocarbon fuels are used, the half reactions shown in Figure 1-3 describe the system, where “n” is the number of carbon atoms in the type of fuel being used. The overall reaction based on these half reactions can be found in Equation 1-4 [12].

\[ \text{C}_n\text{H}_{2n+2} + [(3n + 1)/2]\text{O}_2 \rightarrow \text{nCO}_2 + (n + 1)\text{H}_2\text{O} \ ] \hspace{1cm} (Equation 1-4)
The driving force for the transport of oxygen anions through the electrolyte is the difference between the oxygen chemical potential of the cathode and anode [27]. The oxidation reaction results in the release of electrons, which generate an electric current. The electrons are channeled through an external circuit to do work and then enter the cathode. Consequently, the electrolyte must be electrically insulating, otherwise the electrons will leak through the electrolyte to the cathode without accomplishing any useful work.

1.3 Anode Requirements

There are four primary requirements that any electrode material in a SOFC must exhibit. First, the material must be porous to enable the reactants to diffuse into each electrode and for products to diffuse out. Second, the material must possess electronic conductivity to transport electrons throughout the electrode and to or from an external...
circuit. Third, it must have ionic conductivity so that the $\text{O}_2^-$ anions are able to migrate throughout the electrode. Lastly, catalytic activity is necessary in order for the dissociation of oxygen and for the oxidation of fuel [2, 12, 28]. The region where the last three properties meet is often referred to as the Three Phase Boundary (TPB) [6, 29].

For the anode, the TPB exists in the approximately 10-20 μm thick active region near the anode-electrolyte interface [12]. It is at the TPB that the reaction occurs, as depicted in Figure 1-4. The ionically conductive electrolyte transports oxygen anions to the TPB of the anode where the anions encounter fuel which has diffused through the porous anode. At catalytically active sites within the TPB, the fuel and $\text{O}_2^-$ undergo the oxidation reaction which releases electrons [30]. Electronic conductivity is, therefore, also required to transport electrons away from the TPB to the external circuit. If any one of these critical properties is not present in sufficient levels within the anode, the anode will be inactive and suffer from poor electrochemical performance.

![Figure 1-4 Anode three phase boundary [12].](image)
Several other important considerations must also be made when selecting a material for use in SOFC anodes. The first is the coefficient of thermal expansion, also called the thermal expansion coefficient (CTE or TEC). The CTE of the anode material must be similar to that of the electrolyte and cathode, or the fuel cell will fail during sintering and while heating to normal SOFC operating temperatures because of the thermal mismatch [2].

Solid state reactions must also be avoided. An anode material should not react with the electrolyte or with other materials within the anode because other phases or compounds may form which do not meet the four primary anode requirements [31]. The presence of such additional phases would lead to decreased anode performance. Problems with solid state reactions are more prevalent when employing traditional processing and fabrication methods, since these methods require the anode and electrolyte components to be sintered together at temperatures as high as 1550 °C. Fabrication by tape casting and impregnation significantly lifts restrictions on anode material choices because most of the components can be infiltrated into a porous backbone and calcined at temperatures as low as 450 °C [12, 32].

Another consideration is the stability of the prospective material over the range of oxygen partial pressures (P_O2) encountered in the anode compartment. During startup and shutdown operations, fuel flow ceases, and the anode can experience a P_O2 of 10^{-15} to 10^{-25} atm. Ideal anode materials should be stable in the P_O2 range of 1 to 10^{-25} atm so that they will remain stable during these reduction-oxidation cycles, but the anodes which are most commonly incorporated into SOFCs fail during reduction-oxidation cycling [33].
1.4 Current Anode Limitations

Current state-of-the-art SOFC anodes, displayed in Figure 1-5, are produced from porous nickel and YSZ ceramic-metallic mixtures called cermets which fulfill all four primary anode requirements [1]. The Ni catalyzes the anode reaction and imparts electronic conductivity, and YSZ provides adequate ionic conductivity [34]. A large volume fraction of Ni is used in the anode to form a percolated phase, which is required for the transport of electrons from the anode-electrolyte interface to the external circuit or interconnect [1]. Considering that Ni is an excellent catalyst for steam reforming hydrocarbon fuels [35] and that the high SOFC operating temperature provides a source of heat for the reforming process, the appealing possibility of feeding hydrocarbons directly to the anode without the need for an external fuel reforming step becomes apparent [36]. Such direct utilization offers the potential for fuel flexibility and significantly increased efficiency for the system, since the losses associated with external reformers would be eliminated [37].

However, the primary obstacle preventing direct hydrocarbon utilization with Ni-YSZ anodes is that Ni is also a good catalyst for forming carbon fibers [37-39]. Ni-based anodes are, therefore, unstable in the presence of hydrocarbons unless large amounts of steam are also present [40]. While Ni-YSZ cermets are capable of outstanding performance in hydrogen or syngas (a mixture of H₂ and CO), Ni catalyzes the formation
of carbon filaments when operating with hydrocarbon fuels by deposition of carbon onto the surface of the Ni, dissolution of carbon into the bulk of the Ni, and precipitation of the carbon as a fiber [38]. In a process called “metal dusting,” the carbon fibers can physically lift Ni off the electrode surface and cause the anode to fracture due to the mechanical stresses induced by the fibers’ growth [41]. Although carbon fiber formation can be avoided in most cases if copious amounts of steam are provided to remove the carbon faster than it is deposited, the innate instability of the system and catastrophic consequences of fiber formation make any application of this approach impractical [12].

Ni-YSZ is also prone to sulfur poisoning [42, 43]. If desulfurization of the fuel is not performed, even low hydrogen sulfide concentrations in the fuel will deactivate the Ni catalyst. At 750 °C, a concentration of only 50 ppb H₂S in the feed stream results in strong poisoning of the anode, and at 1000 °C, a concentration of 1 ppm poisons the anode [20]. Intolerance for the reduction-oxidation cycles encountered during normal startup and shutdown operations is another limitation intrinsic to the Ni-YSZ based anode [15, 44, 45]. Ni is easily oxidized at high temperatures, and as oxidation occurs, the volume of the Ni phase increases and causes mechanical fracturing within a fuel cell [7].
Chapter 2  Background

2.1  Strategies for Addressing Ni-YSZ Anode Limitations

2.1.1  Ceramic Composite Anodes

In order to avoid the primary limitations innate to Ni-YSZ cermet anodes, much research has been performed in the search for replacement anode materials. Instead of focusing tremendous effort to find a single new material with properties matching those of Ni-YSZ cermet, a more practical strategy would be to develop a solution which could fulfill those primary anode requirements currently satisfied by the problem plagued Ni phase. Since Ni serves two functions, a promising alternative is the use of two separate materials independently optimized to achieve electrical conductivity and catalytic activity [5].

One approach to enhance the stability of SOFC anodes during reduction-oxidation cycles, a property referred to as redox stability, is to replace Ni with an electrically conductive ceramic [46-48]. Ceramic materials are dimensionally stable during redox cycles, offer excellent thermal stability, prevent carbon-fiber formation in the presence of hydrocarbon fuels, and depending on the particular ceramic that is used, can be sulfur tolerant [49]. Unfortunately, the electrochemical performance of most ceramic anodes has been modest compared to that achieved by cells incorporating Ni cermets. The modest performance of ceramic anodes is due to the difficulty of producing ceramics which have both high electronic and ionic conductivity at low P_{O2} while also possessing good surface reactivity with H_{2} and other fuels [28]. Typically, SOFCs with ceramic
anodes must be operated at higher temperatures to produce comparable power densities. Most studies with ceramic anodes have been carried out at temperatures above 900 °C, whereas good power densities (>500 mW/cm²) are routinely achieved on SOFCs with Ni-YSZ cerments at temperatures below 700 °C [50].

It has been argued that a minimum electrical conductivity of 1 S/cm is required for pure SOFC electrode materials [4, 8], and few oxides are capable of providing this at anode P\textsubscript{O2}. In addition, oxide conductivities are usually a strong function of P\textsubscript{O2}. While the P\textsubscript{O2} remains essentially 0.2 atm at an SOFC cathode, the P\textsubscript{O2} at the anode can vary by many orders of magnitude depending on the temperature and the H\textsubscript{2} to H\textsubscript{2}O ratio. Another challenge with ceramic anodes is that few oxides exhibit reasonable catalytic activity for oxidation. Obtaining good electronic conductivity and good catalytic activity in the same ceramic material has proven extremely difficult. Consequently, interest in electrically conductive ceramics containing separately added oxidation catalysts has grown in recent years.

2.1.2 \textit{n-doped Strontium Titanates}

One group of ceramics of great interest for use in SOFC anodes is \textit{n-doped} strontium titanates (Sr\textsubscript{X}TiO\textsubscript{3}, where “X” is the dopant), which have been shown to possess good electrical conductivity. Previous studies have observed values on the order of 10-100 S/cm with Sr\textsubscript{X}TiO\textsubscript{3} [2, 46, 51]. These materials also offer several other essential properties, including chemical inertness when sintered with YSZ and a CTE similar to that of YSZ, which is the main constituent of most SOFCs [52]. Negatively
doped SrXTiO$_3$ are ceramic materials which have had a portion of the strontium or titanium atoms replaced with other elements that contain a greater number of electrons. When Sr$^{2+}$ is doped with Y$^{3+}$ or La$^{3+}$ from the third column, the new material is called A-site doped SrXTiO$_3$. When Ti is doped with an element with a +5 or +6 charge, the material is referred to as B-site doped SrXTiO$_3$.

In order to achieve the high conductivities observed in the literature, most SrXTiO$_3$ ceramics must first be subjected to a pre-reduction step at a temperature much higher than SOFC operating temperatures [51]. For these materials, the reduced state exhibits conductivities which are two to three orders of magnitude greater than the oxidized state. One disadvantage of this approach is that the good electrical conductivity gained from the reduction step can be lost during the oxidation and reduction cycles encountered during operation, resulting in unacceptably high ohmic losses [2]. Oxidation usually occurs at a lower temperature than reduction, so the normal operating temperatures of SOFCs are often sufficient to partially or fully oxidize the pre-reduced SrXTiO$_3$. When the anode is exposed to fuel and a reducing atmosphere is reestablished, complete re-reduction does not occur at the lower temperature. The fact that a portion of the material remains in the oxidized state decreases the overall conductivity of the material. Therefore, determining whether or not the high extent of reduction can be maintained during exposure to redox cycles at fuel cell operating temperatures becomes a critical factor in deducing the applicability of a specific doped strontium titanate for supplanting Ni-YSZ anodes.
2.2 Preceding Studies

Due to the many favorable properties associated with $n$-type SrXTiO$_3$ ceramics, prior attempts have been made to determine which dopant materials engender high electrical conductivity. A-site lanthanum-doped La$_x$Sr$_{1-x}$TiO$_3$ (LST) and yttrium-doped Y$_x$Sr$_{1-x}$TiO$_3$ (YST) have been extensively studied for fuel cell applications [2, 46, 49, 53, 54], and more recently, B-site niobium-doped SrNb$_x$Ti$_{1-x}$O$_3$ (SNT) has been considered [2, 5, 55]. In a study conducted by Marina, Canfield, and Stevenson, the thermal, electrical, and electrocatalytic properties of LST were examined [46]. A maximum conductivity value of 16 S/cm was observed for samples sintered in air, and a conductivity of 360 S/cm was observed for samples reduced in H$_2$. While the authors claim that LST was found to be dimensionally and chemically stable when subjected to oxidation-reduction cycling and that the electrical conductivity was completely reversible after redox cycling at 1000 °C [46], further scrutiny shows that only dense samples were tested. However, dense samples do not represent the characteristics of a SOFC anode because the limited diffusion that occurs in a dense material does not equate to the porous microstructure required in actual anodes [5].

In a later study by Kolodiazhnyi and Petric, the defect chemistry model [56] was used to discuss two methods for doping SrTiO$_3$ to form $n$-doped SrXTiO$_3$ [2]. The first method produces vacancy-compensated single phase compounds of the type Sr$_{1-3x/2}$X$_x$TiO$_3$ which are sintered in air and reduced under SOFC anodic conditions. The contrasting method formulates the composition according to the electronic compensation regime of the type Sr$_{1-x}$X$_x$TiO$_3$ and requires sintering in air at high temperatures, which results in
multiphase compounds with partial electronic compensation of donors. When a vacancy-compensated material is sintered at low $P_{O_2}$, however, it is transformed to an electronically compensated compound with a strontium deficient second phase [2]. Both methods result in similar conductivities for compositions, but the authors chose to employ vacancy-compensated compounds when generating YST, SNT, and YSNT co-doped samples ($Y_xSr_{1.3x/2}TiO_3$, $Sr_{1-x/2}Nb_xTi_{1-x}O_3$, $Y_xSr_{1-(3x/2)-(y/2)}Nb_yTi_{1-y}$).

The investigation of YST and SNT revealed excellent conductivities of 340 and 100 S/cm for reduced samples of SNT and YST, respectively, at 800 °C in a low $P_{O_2}$ atmosphere. The authors measured the conductivity of reduced and oxidized samples at 800 °C in $P_{O_2}$ ranging from $10^{-20}$-$10^{-14}$ atm and observed that the reduced samples exhibited higher electrical conductivity. Reduced samples were sintered in air and then tested in $H_2$ in order to replicate redox cycling. After the oxidation step, the conductivities of the samples decreased to less than 10 S/cm. In contrast to heavily doped samples, such as $Sr_{0.9}Nb_{0.2}Ti_{0.8}O_3$, which exhibited a decline in conductivity from 339 to 0.12 S/cm upon oxidation, the electrical conductivities for lightly doped samples, such as $Sr_{0.995}Nb_{0.01}Ti_{0.99}O_3$, did not deviate significantly from its reduced value of 9.8 S/cm. This trend of increasing conductivity with decreasing dopant level in oxidized YST and SNT is interesting because highly reduced titanates tend to increase in conductivity with increasing dopant levels [5].

Using the work completed by Kolodiazhnyi and Petric as a springboard, further research into the properties of SNT has been performed by Gross, et al [5]. While the two previous studies investigated the conductivities of dense samples after redox cycling,
values obtained by testing dense pellets do not typically represent true equilibrium values due to very long equilibration times associated with the slow diffusion of strontium vacancies during oxidation [5]. To address this issue, Gross examined the conductive properties and redox stability of both bulk Sr$_{1-x}$Nb$_x$TiO$_3$ samples and porous SNT-YSZ composites for $x = 0.01, 0.05,$ and 0.2 under relevant SOFC operating conditions. The results can be seen in Figures 2-1 and 2-2.

Several definitive conclusions were drawn based on the recent SNT research. Foremost, it was determined that after redox cycling there is no benefit to using higher dopant concentrations. For $x = 0.01$ and 0.05, conductivities of approximately 1 S/cm were measured at 800 °C in humidified H$_2$, but for $x = 0.2$, the conductivity had decreased to 0.5 S/cm. Additionally, it was demonstrated that good fuel cell performance can be achieved with an SNT-YSZ anode infiltrated with an oxidation catalyst. Power densities of 415 and 640 mW/cm$^2$ were attained at 700 and 800 °C for H$_2$ fuel.

Figure 2-1 Conductivity of dense SrNb$_x$Ti$_{1-x}$O$_3$ pellets as a function of temperature in humidified H$_2$ for $x = 0.01$ (circles), 0.05 (diamonds), and 0.2 (triangles) [5].

Figure 2-2 Conductivity of sintered (open symbols) and reduced (solid symbols) porous SNT-YSZ composites as a function of temperature in H$_2$ for $x = 0.01$ (circles), 0.05 (diamonds), and 0.2 (triangles) [5].
2.3 Direction of Interest and Research Goals

Although many studies have been conducted to determine the properties of several $n$-doped SrXTiO$_3$ materials, the majority of previous research in this area has focused primarily on obtaining excellent electrical conductivity without considering the effect of redox cycling conditions, which are encountered during actual fuel cell operation. Thus, in a continuing effort to identify compounds with favorable properties, the research described hereafter sought to characterize the conductive properties of vanadium, tantalum, lanthanum, tungsten, and molybdenum-doped strontium titanates under fuel cell operating conditions and redox cycling to determine whether any of these materials could satisfy the requirements for SOFC anodes and serve as a replacement for Ni-YSZ based anodes. Rather than focusing on achieving the highest conductivity possible without considering redox stability, the goal of this research has been the development of redox stable materials which possess sufficient electrical conductivity and can maintain an adequate conductivity during redox cycling.

As a means of accomplishing the stated task, a procedure was employed which began with the production of a pure or bulk sample of the SrXTiO$_3$ being investigated from precursor reagents. From the bulk sample, dense pellets were formed and tested to determine if the material should be examined further. Considering the data presented in Table 2-1 for undoped SrTiO$_3$ as a baseline, it was possible to determine whether or not a particular dopant increased the electrical conductivity.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conductivity (S/cm)</th>
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<tbody>
<tr>
<td>600</td>
<td>0.002</td>
</tr>
<tr>
<td>650</td>
<td>0.003</td>
</tr>
<tr>
<td>700</td>
<td>0.005</td>
</tr>
<tr>
<td>750</td>
<td>0.010</td>
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<tr>
<td>800</td>
<td>0.024</td>
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<tr>
<td>850</td>
<td>0.048</td>
</tr>
<tr>
<td>900</td>
<td>0.091</td>
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to a practical level and maintained that conductivity through multiple oxidation cycles. If the redox stable conductivity of the dense pellets met the bulk conductivity minimum of 1 S/cm, porous SrXTiO$_3$-YSZ composites were fabricated and tested to better simulate an SOFC anode.

Electrically conductive ceramics which possess the desired qualities for use in SOFCs are not incorporated directly into an anode as a bulk material. The new ceramic is mixed with YSZ to form a composite material that displays excellent ionic conductivity imparted by the YSZ as well as electrical conductivity imparted by the novel ceramic. Pore formers are also added to make the composite porous, since fuel must diffuse through the anode. The diffusive processes in a porous composite occur much faster than in a dense sample of the bulk material because the length scale is much smaller. Whereas the length scale for diffusion in a dense sample is about 1 mm, the length scale for the composites used in fuel cells is approximately 1 μm. Diffusion time is proportional to $L^2/D$, where $L$ is the length scale for diffusion and $D$ is the diffusion coefficient, which means it would take six orders of magnitude longer in a dense pellet to achieve the same amount of diffusion as in a porous composite [5].

For this reason, the results obtained by testing porous composites are more indicative of equilibrium values than the dense pellet conductivity because they are representative of the microstructure in an SOFC anode. Electronic conductivity is expected to be approximately one order of magnitude lower in a composite than in a dense pellet because the composite is porous and because the SrXTiO$_3$ has been mixed with YSZ, which is an electronic insulator. This order of magnitude difference is clearly
visible when comparing the dense pellet data for SNT from Figure 2-1 with the porous composite data in Figure 2-2. Accordingly, the redox stable conductivity for a porous composite should be at least 0.1 S/cm to be considered sufficient for SOFC anodes.

If the redox stable conductivity of the porous composites exceeded 0.1 S/cm, actual fuel cells were fabricated with composite SrXTiO₃ anodes, and the performance of the cell was tested in hydrogen and methane. All SrXTiO₃ materials demonstrate poor catalytic activity, so an aqueous solution bearing a catalyst was added to promote the anodic reaction. Consequently, anodes incorporating separate electronic conductors and oxidation catalyst usually consist of two “regions,” as seen in Figure 2-3. The thin functional layer along the anode-electrolyte interface will have a heavy catalyst concentration due to the fact that the porous anode allows much of the aqueous catalyst bearing solution to seep down until the dense electrolyte prevents it from leaking through to the cathode. As a result, the anode functional layer is optimized for catalytic activity and becomes a 10-20 μm thick active region along the anode-electrolyte interface. The thicker conduction region on top of the functional layer contains less catalytic material and is optimized primarily for electrical conductivity to enable electrons freed by the oxidation reaction to reach the external circuit [12].

Conductivity and redox stability tests performed on dense pellets and porous composites provided insight into the electrical properties of the bulk material and

![Figure 2-3 Two regions within a ceramic anode](image)
SrXTiO$_3$-YSZ mixture, but subjecting the new anode material to further testing was imperative for demonstrating that it satisfied the other prerequisites for use in SOFCs. After favorable electrical conductivity values were obtained, the phase composition of the doped ceramic material was examined. Chemical and thermal compatibility with YSZ were also verified, after which, testing with fuel cells containing the new anode material was conducted. The results obtained from the fuel cell testing were used to gauge the electrochemical performance of the new anode. Consequently, tests were performed on cells which did not contain any separately added catalyst in order to determine the level of catalytic activity exhibited by the SrXTiO$_3$ anode and on cells with catalyst to measure the performance that can be expected from a system incorporating the new material. Only after the results from all of the experiments were collected could a final assessment be made to determine if V, Ta, La, W, and Mo-doped strontium titanates are feasible substitutes for Ni-YSZ anodes.
Chapter 3  Materials and Methods

3.1 Sample Preparation

3.1.1 Bulk Samples

3.1.1.1 Overview of Dense Pellet Production

In order to determine whether a new material possessed good electrical conductivity, bulk samples were synthesized by a solid state reaction method and tested. Production of these compounds began with meticulous measurements of the amounts of each precursor reagent required to achieve the desired level of doping for a 40 g batch. Stoichiometric mixtures were ball milled in ethanol for 24 hours, dried, and calcined in air at 1200 °C for 10 hours. The ball mill consisted of a 125 mL polyethylene bottle filled with about 200 g of 5 mm diameter spherical YSZ grinding media (5 mol% Y₂O₃, 95 mol% ZrO₂) which was placed on a device that rotated the bottle end over end. The rotating action and the movement of the YSZ beads thoroughly blended the reagents into a homogeneous slurry. After calcination, the powders were ball milled a second time in ethanol for 24 hours and dried. The resulting powder was then pressed into cylindrical 1 g pellets using a die and sintered at 1500 °C for 5 hours, resulting in dense pellets which were approximately 1.4 cm in diameter and 0.15 cm in thickness.

3.1.1.2 Calcination

During the calcination process, the dried mixture which was recovered from the ball mill was heated slowly (4 °C/min) to 1200 °C in air for 10 hours using a Zicar
Zirconia ZZI Hot Spot 110 furnace. The heat initiated a solid state reaction between each of the precursor reagents present within the homogenous mixture causing the oxides to undergo an atomic rearrangement to form a perovskite structure, which is depicted by Figures 3-1 and 3-2. The perovskite structure takes the form $\text{ABO}_x$, where “A” and “B” are cations of greatly differing size [49]. “A” has a larger atomic radius than “B”, and for this study, “A” was strontium, and “BO$_x$” was the titanate. In the unit cell, each titanium atom is octahedrally coordinated with six oxygen atoms, and a strontium atom is in the center. Depending on the type of $n$-doped perovskite, either the center A-site strontium atom or some of the B-site titanium atoms are replaced within the unit cells [8].

3.1.1.3 Sintering

Following the calcination process and second ball milling step, the sample was finely ground into a powder. In order to form a dense pellet for bulk conductivity testing, approximately 1 g of the powder was placed into a die between two pieces of Mylar film with hydrophobic coatings to prevent adhesion to the surface of the die. The die was then

![Figure 3-1 Octahedral coordination in perovskite [57, 58].](image1)

![Figure 3-2 The perovskite unit cell [59].](image2)
placed on a hydraulic press, and 1 metric ton of pressure was applied to compress the loose powder into a cylindrical disk-shaped pellet. At this point, the pellet was too fragile to undergo testing, so it was sintered at 1500 °C for 5 hours in air with a ramp speed of 2 °C/min. The high temperature sintered the pellet into a dense disk which was durable enough to withstand testing.

3.1.1.4 Pre-reduction

For many of the doped strontium titanate materials that were explored, a final high temperature pre-reduction step in a highly reducing dry hydrogen environment was required in order to attain the enhanced electrical conductivities reported in the literature [8, 60]. Those materials which did not necessitate the pre-reduction step were able to be reduced in a humidified H₂ atmosphere (3% H₂O) at lower temperatures (≈800 °C) encountered during the conductivity testing process. The high temperature pre-reduction step was performed using a Carbolite STF 15/180 tube furnace to heat the dense pellet to 1400 °C for 10 hours in dry H₂ at a ramp speed of 2 °C/min. Following the reduction process, the pellet was cleaned of any residual debris, and the diameter and thickness dimensions were measured.

3.1.2 Porous Composite Samples

In addition to dense pellets, porous composites, which were mixtures of 60 vol% of the doped strontium titanate bulk sample powder (SrXTiO₃) and 40 vol% YSZ by solids, and porous YSZ slabs were produced if the dense pellets exhibited sufficiently
high electrical conductivity and redox stability when tested. “Green” or unsintered composites were prepared by casting a slurry containing the calcined bulk sample powder, YSZ, and pore formers. YSZ slabs were prepared in the same manner, with the exception that no SrXTiO\textsubscript{3} powder was added. The slurry was prepared by first adding water and D3005 dispersant (Duramax 3005, Rohm and Haas) to a 150 mL beaker and magnetically stirring the contents for several minutes. Next, SrXTiO\textsubscript{3} and YSZ (TZ-8Y, Tosoh) powders were slowly added to the beaker with continuous stirring. After the slurry was well mixed, the graphite (99.9995%, 325 mesh, Alfa Aesar) and poly(styrene-co-divinylbenzene) (2% cross-linked, 200-400 mesh, Sigma-Aldrich) pore formers were slowly added to the beaker. The slurry was then allowed to stir at room temperature for 24 hours, after which, the HA-12 and B-1000 binders (Duramax, Rohm and Haas) were added. The amounts of each ingredient of the slurry required for both porous SrXTiO\textsubscript{3}-YSZ composites and porous YSZ slabs are given in Table 3-1.

<table>
<thead>
<tr>
<th>Table 3-1 Porous composite recipes.</th>
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<tbody>
<tr>
<td>Required Ingredients</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>D3005</td>
</tr>
<tr>
<td>SrXTiO\textsubscript{3}</td>
</tr>
<tr>
<td>YSZ</td>
</tr>
<tr>
<td>Graphite</td>
</tr>
<tr>
<td>Poly(styrene-co-divinylbenzene)</td>
</tr>
<tr>
<td>HA-12</td>
</tr>
<tr>
<td>B-1000</td>
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<td>Triton X-100</td>
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</tbody>
</table>
The slurry was stirred continuously and air dried for several days. A specific amount of evaporation has not been determined for this step, but a general rule of thumb is that an appropriate viscosity has been achieved when the slurry spreads evenly over Mylar film without beading up [12]. When it reached the appropriate viscosity, the slurry was poured into a small, rectangular alumina tray which was wrapped with aluminum foil and had a matching rectangular sheet of Mylar film resting in the bottom. The slurry was then dried, cut into uniform rectangular bars, and sintered at 1500 °C for 5 hours with intermediate 3 hour holds at 300 °C and 800 °C. The initial hold allowed the binders to burn off, and the second oxidized the pore formers. The sintered composites and slabs were 0.2 cm × 0.2 cm × 1.0 cm in size, and following the sintering process, composites incorporating SrXTiO3 materials requiring a pre-reduction step were reduced in dry H2 at 1400 °C for 10 hours. The porosity of the composites was calculated to be ≈40% by water up-take measurements when only graphite pore former was used and ≈60% when graphite and poly(styrene-co-divinylbenzene) were added.

3.1.3 Tape Casting

In preparation for fuel cell assembly, electrode and electrolyte films were fashioned by means of a tape casting method. SOFC electrolytes must be dense YSZ films capable of preventing diffusion between the fuel and oxygen compartments when the fuel cell is operating. In order to obtain a dense electrolyte film, a slurry of YSZ particles was prepared. The first step required water, D3005 dispersant, and YSZ to be added to a 125 mL polyethylene bottle containing about 200 g of spherical YSZ grinding
media and ball milled for 24 hours. When ball milling was complete, the slurry was transferred to a beaker, and HA-12 and B-1000 binders were added. The slurry was then magnetically stirred at room temperature and air dried until approximately 4 g were lost due to evaporation. The amount of each ingredient required for the electrolyte slurry can be found in Table 3-2.

<table>
<thead>
<tr>
<th>Required Ingredients</th>
<th>Required Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>18.01 g</td>
</tr>
<tr>
<td>D3005</td>
<td>1.09 g</td>
</tr>
<tr>
<td>YSZ</td>
<td>40.04 g</td>
</tr>
<tr>
<td>HA-12</td>
<td>6.86 g</td>
</tr>
<tr>
<td>B-1000</td>
<td>8.92 g</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>0.35 g</td>
</tr>
</tbody>
</table>

Once the slurry reached the correct viscosity, a 0.5 ft. × 3 ft. sheet of Mylar film was laid flush with a flat surface to serve as a carrier film for the tape. The slurry was then tape casted onto the Mylar film using a drawbar with designated height settings and a tapered edge to control the thickness of the tape. After tape casting was complete, the tape was allowed to thoroughly dry in air at room temperature.

Electrode films were tape casted in a process similar to that of the electrolyte, but instead of a dense film, SOFC electrodes require porous films to allow fuel and oxygen diffusion towards the electrolyte. Cathode tapes consist of a porous YSZ film, so the slurry recipe used to create the cathode tape was identical to the recipe given in Table 3-1 for porous YSZ slabs. However, instead of pouring the slurry into the alumina tray when
it reached the appropriate viscosity, the slurry was used to form a tape by employing the
tape casting method previously described to form the electrolyte tape.

Two distinct methods have been employed during this study to prepare “green”
anode tapes. The first was the co-fired method, and it included the same recipe in
Table 3-1 that was used to produce porous SrXTiO$_3$-YSZ composites. By this method,
the porous mixture of SrXTiO$_3$ and YSZ were fired together during the sintering step.
Like the cathode, it was tape casted as previously described. The second method was the
infiltration method, and it mimicked the process used to make the cathode tape. The
infiltration method required a porous YSZ film for both cathode and anode, and after the
film was sintered, an aqueous solution of SrXTiO$_3$ was infiltrated into the pores of the
YSZ framework in the anode using a procedure described in Section 3.1.4.2.

The tape casting process described to this point suggests that anode, cathode, and
electrolyte tapes must be casted separately and assembled to form the complete fuel cell,
but an alternative approach has also been employed. The other method is known as dual-
tape casting [12]. When the dual-tape casting method was used, the electrolyte was tape
casted, and then the cathode was tape casted directly overtop the electrolyte once it had
dried. The benefit of dual-tape casting is better adherence between the cathode and
electrolyte and the elimination of part of the assembly process. The disadvantage of this
method is the greater effort required when tape casting thinner electrolytes and the
increased difficulty in detecting portions of the tape which contained “pin holes.” Pin
holes are tiny holes in the tapes due to anomalies and raised points in the film caused by
the presence of dust particles between the film and the flat surface. The existence of any
such holes in the electrolyte presents a pathway for fuel and oxygen to meet and react through combustion rather than the desired electrochemical reaction. The dual-tape casting method is depicted in Figure 3-3.

### 3.1.4 SOFC Button Cells

#### 3.1.4.1 Fuel Cell Assembly

In the event that both dense pellets and porous composites of a given material demonstrated sufficiently high conductivity and redox stability, actual SOFC button cells incorporating the new anode material were constructed. Fuel cells were fabricated by stacking and compressing the anode, electrolyte, and cathode films. A 2.5 cm diameter punch allowed circular pieces to be cut from the electrolyte and cathode tapes. A smaller 1 cm diameter punch was employed to cut circular pieces from the anode tapes as well. Each electrode was then affixed to the electrolyte with a two step lamination process.

Lamination of the three components into a single SOFC button cell was accomplished by first stacking the electrolyte on top of the cathode. A hydraulic press with heated plates was then used to gently compress the two pieces together. Only a small amount of pressure was needed to compress the components, as excessive pressure
altered the thickness of the layers and resulted in deformation that caused stress fractures upon sintering. The pressure also had to be applied evenly at all points to maintain a uniform thickness in the electrolyte and electrodes. This was successfully achieved with the aid of two flat metal plates which were placed between the press and the fuel cell to distribute the pressure. After the electrolyte and cathode were laminated, the anode was attached near the center of the exposed face of the electrolyte in the same manner. The laminated components were then sintered in air at 1500 °C for 5 hours with 3 hour holds at 300 and 800 °C, followed by pre-reduction in dry H₂ at 1400 °C for 10 hours if required. The lamination process is displayed in Figure 3-4.

![Figure 3-4 Lamination of green tapes [12].](image)

### 3.1.4.2 Preparing the Anode

When anodes prepared using the co-fired method were included in the fuel cell, the SrXTiO₃ electronically conductive phase was already present in the anode as part of the composite. The use of a porous YSZ anode for the infiltration method, however,
requires the SrXTiO$_3$ to be added to the YSZ backbone after sintering. This was accomplished by incorporating the SrXTiO$_3$ into the porous anode by wet impregnation/infiltration of an aqueous solution of nitrate salts. The infiltration process began with the selection of water soluble nitrate salts which would transport the SrXTiO$_3$ to the anode pores. Using a syringe, the nitrate solutions were added drop-wise until the anode was saturated, and then the cell was heated to 450 °C to decompose the nitrates. These infiltration and heating steps were repeated until the target loading was reached, at which point, the cell was heated to 1200 °C in air for 10 hours to calcine the SrXTiO$_3$ and form the perovskite structure. A pre-reduction treatment would also follow if needed.

3.1.4.3 Preparing the Cathode

Once preparation of the anode was complete, the cathode was infiltrated with a compound which was active for the dissociation of oxygen to O$^2-$ anions. Two popular active perovskite cathode materials are La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) and La$_{0.8}$Sr$_{0.2}$FeO$_3$ (LSF) [11], and for this study, LSF was utilized. A 0.7 M aqueous solution of La, Sr, and Fe nitrate salts and citric acid with a La:Sr:Fe:citric acid molar ratio of 0.8:0.2:1:2 was prepared and added drop-wise until the cathode was saturated. The fuel cell was then heated to 450 °C, after which, the process was repeated until a final loading of 30 wt% LSF was attained. The active material loading must be greater than 15 vol%, which corresponds to approximately 30 wt% of the cathode, in order to achieve percolation [12]. Once the desired loading was reached, the LSF was calcined at 850 °C in air for 3 hours to form the perovskite structure.
3.1.4.4 Catalyst Infiltration

Because SrXTiO$_3$ perovskites lack significant electrocatalytic activity for the anode reaction, a Pd or CeO$_2$-Pd catalyst was added to increase the activity of the anode. The catalyst was infiltrated drop-wise into the porous anode of the sintered button cell from aqueous solutions of Ce(NO$_3$)$_3$·6 H$_2$O (99.99%, Alfa Aesar) and (NH$_3$)$_4$Pd(NO$_3$)$_2$ (99.9%, 5% max Pd, Alfa Aesar) to final loadings of 3 wt% CeO$_2$ and 1 wt% Pd with heat treatments at 400 °C between infiltrations. Although the electronically conductive phase must be impregnated to a loading greater than 15 vol% to achieve percolation or an interconnected network, catalytically active materials that are not relied upon for electronic conductivity can be incorporated at lower loadings [12].

3.2 Electrochemical Measurements

3.2.1 Dense Pellet and Porous Composite Conductivity Measurements

Achieving reasonable electronic conductivity in the anode and maintaining it throughout redox cycling was paramount for obtaining good performance from a fuel cell. In order to determine whether this primary anode requirement was fulfilled by a prospective SrXTiO$_3$ material, conductivity measurements were made on bulk samples and porous composites. Current was directly measured as a function of voltage, and conductivity was determined by calculating the ohmic resistance from the slope of the voltage-current (V-i) curve. Although electrical conductivity can also be calculated by measuring the total ohmic loss of an entire fuel cell and subtracting out the ohmic losses of the cathode and electrolyte, the additional time and effort required to prepare fuel cells
made it an impractical starting place. When little was known about the properties of the material, investigation of bulk samples enabled observation of the material with fewer complicating factors.

After production of a dense pellet was complete, the pellet was prepared for testing. Electrical contacts, consisting of silver wire and silver conductive ink (Alfa Aesar), were attached to both surfaces of the pellet for current collection. A standard dc four-probe method, depicted in Figure 3-5, was selected instead of a two probe version in order to compensate for the resistance associated with the testing apparatus. The contacts consisted of a three inch piece of low gauge silver wire which was twisted to form a loop near the middle of the strand. Silver paste was applied to one face of the pellet, after which the looped end of the wire was affixed to the pellet. When the paste was dry, the electrode was firmly bonded to the pellet. The process was then repeated for the other face of the pellet.

Each of the four wires was attached to a lead wire of the testing device. The testing apparatus consisted of a four-bore alumina tube which had an 80% Ni-20% Cr alloy wire running through each of the four passages. Ceramic sheathing was used to insulate any exposed wires to prevent short circuiting, and the apparatus was placed inside a larger ceramic tube which was sealed at both ends and positioned inside a heater with a programmable temperature controller.

Figure 3-5 Standard DC four-probe method.
Measurements were carried out in humidified H₂ using a Gamry Instruments Series G 750 potentiostat/galvanostat/ZRA in potentiostat mode to apply a voltage and measure the current passing through the sample. Maximum and minimum voltages were chosen which prevented the current from exceeding 0.7 A and the voltage from exceeding 10 V. The electrical conductivity of the sample was calculated using Equation 3-1, where \( \sigma \) is electrical conductivity, \( l \) is the conduction length, \( R \) is the ohmic resistance of the material, and \( A \) is the area of the pellet face [27]. The conduction length and area were determined from the dimensions of the sample, and the ohmic resistance was obtained from the slope of the V-i curve.

\[
\sigma = \frac{l}{RA} \quad \text{(Equation 3-1)}
\]

Dense pellet conductivity testing was divided into two parts: bulk conductivity and redox stability testing. During bulk conductivity testing, the ohmic resistance was obtained at 50 °C intervals for 600-900 °C to determine if the material exhibited an electrical conductivity greater than 1 S/cm. Redox stability testing was performed following bulk conductivity testing to establish whether the enhanced conductivity imparted by a high temperature pre-reduction step remained above 1 S/cm after multiple oxidation and reduction cycles. Redox stability was confirmed by obtaining steady state resistances at 700 and 800 °C in humidified H₂ after exposure to air for 3 hours, re-reduction in H₂ for 3 hours, re-oxidation in air for 3 additional hours, and a final re-reduction in H₂ for 3 hours. As shown in Figures 3-6 and 3-7, the conductivity of a sample which has undergone a pre-reduction step drops when oxidized at 700 or 800 °C,
but when the sample is re-reduced in H₂, the conductivity recovers to a fraction of its original value. If favorable results were obtained from the conductivity and redox stability tests for the dense pellet, porous composites or infiltrated slabs were prepared and tested in the same manner to determine whether a minimum conductivity of 0.1 S/cm and redox stability could be obtained.

![Figure 3-6 Electrical conductivity of a SrXTiO₃ sample at 800 °C in air.](image)

![Figure 3-7 Conductivity in humid H₂ at 800 °C after exposure to air for one (triangles) and two (squares) redox cycles.](image)

### 3.2.2 Fuel Cell Performance Measurements

#### 3.2.2.1 V-i and Power Curves

When dense pellets and porous composites containing a new material were found to display sufficient electrical conductivity, redox stability at high temperatures, and compatibility with other SOFC materials, actual SOFC button cells containing the new anodes were constructed. Two useful tools for gauging the electrochemical performance of the novel anodes were V-i and power density curves. In order to generate these curves, the V-i characteristics of a button cell were measured, and the P-i curve was calculated as a function of current density according to Equation 3-2.

\[
P = V \cdot i \tag{Equation 3-2}
\]
Preparation began with the addition of silver contacts to the anode and cathode of the fuel cell using the four-probe method. Silver wire and ink were selected because silver remains porous at SOFC operating conditions, unlike gold, which becomes dense and prevents diffusion of air to the cathode and fuel to the anode. Another important property of silver is that it is not a good oxidation catalyst, and therefore, does not mask the anode performance. Platinum is often used because it is stable at very high temperatures, but Pt is also an excellent oxidation catalyst that can easily convolute the performance being measured [12].

After the contacts were attached, the fuel cell was bonded to an alumina tube with a ceramic adhesive (Ceramabond 552-VFG, Aremco). The adhesive bound the fuel cell to the alumina tube and isolated the anode compartment. The tube was then fitted to a reactor which directed fuel towards the anode and carried unreacted fuel to the exhaust line. After the adhesive dried, silver extension wires insulated with ceramic sheathing were attached to the four probe wires to provide accessibility when the reactor was placed inside the heater. Oxygen was supplied to the cathode by exposing it to air. The completed assembly is shown in Figure 3-8.
The testing assembly was positioned inside a heater with a programmable temperature controller. In order to cure the adhesive, the testing assembly was heated to 93 and 260 °C and held at each temperature for 2 hours before continuing to the operating temperature. H₂ and methane were supplied to the anode from compressed cylinders according to the system shown in Figure 3-9. A water bubbler at room temperature was integrated into the fuel line to raise the humidity level of the fuel to approximately 3% H₂O. The fuel flow rate was regulated by a flow meter and maintained well above 20 mL/min at all times to ensure low conversion in the anode. Voltage was ramped from open circuit voltage (OCV ≤ 1.2 V) to zero voltage at a rate of 0.05 V/s and a frequency of 1 Hz. Measurements were taken between 650 and 900 °C at 50 °C intervals in both H₂ and CH₄. The data obtained from these measurements was used to generate a V-i plot and calculate the P-i curve. As shown in Figure 3-10, the deviation of the V-i curve from the OCV gives the total loss in the system, consisting of ohmic and non-ohmic losses. An example of a V-i and P-i plot is given in Figure 3-11.
Figure 3-9  Fuel line and experimental setup for SOFC button cell testing [12].

Figure 3-10  Voltage losses in a fuel cell [12].
3.2.2.2 Electrochemical Impedance Spectroscopy

As was seen in Figure 3-10, there are two types of losses that contribute to the total loss of voltage for a fuel cell at a given current density, ohmic and non-ohmic losses. Impedance spectroscopy can be employed to investigate each of these losses. Impedance spectroscopy imposes a sinusoidal current perturbation, $I(\omega)$, onto a working fuel cell and measures the frequency-dependent sinusoidal output [61]. For frequency-independent processes, the ratio of potential and current is a constant and the phase of the perturbation and the output are the same. The frequency-independent processes of a fuel cell are associated with the ohmic losses, i.e. the conductivity, of the electrodes and electrolyte, but frequency-dependent processes are associated with the non-ohmic losses, such as

Figure 3-11 V-i and P-i curves (solid symbols are power densities and open symbols are voltages).
losses due to the transport of gases through the porous electrodes and the reactions at the electrodes. Unlike the frequency-independent processes, the frequency-dependent processes exhibit a phase shift in the output. By varying the frequency of the current perturbation, \(\omega\), the frequency-dependent impedance spectrum can be presented as a Cole-Cole plot [61].

The ideal response of each frequency-dependent process would be a semi-circular impedance spectrum, which is mathematically equivalent to a single parallel R-C circuit with the value of the diameter of the semi-circle being R and the peak frequency being \(1/RC\). However, there are multiple processes occurring in a fuel cell with multiple overlapping arcs in the impedance spectra that make it difficult to completely separate the processes. While the peak frequency of arcs can point towards limiting processes in the fuel cell, the most definitive and important information that can obtain from an impedance spectra is the ohmic and non-ohmic losses associated with the fuel cell [12]. The impedance spectroscopy technique is demonstrated in Figure 3-12 and a Cole-Cole plot of an impedance spectrum is shown in Figure 3-13.
For this study, impedance spectra were collected with a Gamry Instruments Series G 750 potentiostat/galvanostat/ZRA in the galvanostatic mode. A frequency range of 0.1 Hz to 300 kHz and a 1 mA AC perturbation were imposed.

3.3 Thermomechanical Analysis

The thermal expansion of materials found to possess favorable conductivity and redox stability properties was examined in air between 35 and 950 °C with a TA Instruments 2940 Thermomechanical Analyzer (TMA) in dilatometer mode using a standard expansion probe. A temperature ramp rate of 5 °C/min was maintained when dense pellets were tested, and a ramp rate of 10 °C/min was used with porous composites and porous YSZ slabs. A force of 0.1 N was applied to the sample to prevent the probe from shifting during the testing process. When linear plots of \( \Delta L/L_0 \) as a function of temperature were obtained, the TEC was calculated from the slope and compared to the value for YSZ. Similar TEC values were indicative of thermal compatibility, a factor which prevents failure due to stresses in SOFCs at high temperatures caused by thermal mismatch.

3.4 Thermogravimetric Analysis

Thermogravimetric analysis was performed using a TA Instruments SDT Q600 Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC). A constant heating rate of 5 °C/min was used to heat bulk powder samples from room temperature to 800 °C, and then the samples were held at 800 °C for several hours.
200 mg samples were tested using small alumina crucibles, and the gas flow rate was set at 50 mL/min for all tests. Compressed air was supplied when an oxidizing environment was required, and a 5% H₂-95% Ar mixture was present when a reducing atmosphere was needed. In principle, the measured weight loss or gain for a sample made it possible to graphically determine the temperature at which the sample was oxidized or reduced. The weight change was due to loss or gain of oxygen atoms as they were either removed from or incorporated into the perovskite structure. Therefore, TGA provided the necessary information to assess whether the sample attained a fully oxidized or fully reduced state.

3.5 Phase and Microstructure

3.5.1 X-ray Diffraction

The phase compositions of bulk powders, dense pellets, and porous composites were determined by powder x-ray diffraction (XRD) analysis. A PANalytical X’pert PRO MPD Diffractometer was used to collected x-ray diffractograms within the range of $15^\circ \leq 2\theta \leq 80^\circ$ using Cu Kα radiation. Lattice parameters were determined with a computerized least-squares fit.

3.5.2 Scanning Electron Microscopy

The microstructure of finished electrodes was investigated by scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX). A Denton Vacuum Desk IV sputter coater was used to apply a gold coating to the surface of the sample to prevent charge accumulation, and a FEI Quanta 400 Scanning Electron Microscope was
used to generate micrographs and backscatter images of the sample. An example of a SEM micrograph of a SOFC is given in Figure 3-14.

Figure 3-14  SEM micrograph of a SOFC [12].
Chapter 4  Research Projects

4.1  Strontium Titanates

4.1.1  Vanadium-doped Strontium Titanate

In an effort to develop and characterize the properties of a conductive ceramic material with sufficient electrical conductivity and redox stability for use in SOFC anodes, the production and testing methods previously described were applied to several n-doped strontium titanate compounds. Each investigation began with the making of dense pellets from bulk powder samples. As a preliminary indication of the electrical properties of the specific material being analyzed, the conductivities of the dense pellets were measured under realistic SOFC operating conditions. If the dense samples displayed sufficiently high electrical conductivity in H₂, redox stability testing was performed on the pellets. Similarly, if the dense pellets maintained an acceptable conductivity after redox cycling, porous composites were generated, and the conductivities were measured in H₂ and after redox cycling. The porous composites more accurately represent the microstructure of a SOFC anode, so composite samples which demonstrate redox stability can be expected to maintain sufficient conductivity when incorporated as an anode. While the conductive properties of the material were being explored, various other tests were also performed for the purpose of confirming that the doped SrXTiO₃ was thermally and chemically compatible with YSZ. SrXTiO₃ ceramics which fulfilled all of the requirements for SOFC anodes were then identified as potential replacements for Ni-YSZ cermet.
In this manner, research into the properties of several SrXTiO$_3$ compounds commenced. Based on the promising results observed for Nb-doped strontium titanate [2, 5, 55], a B-site doped perovskite containing vanadium was explored. Bulk samples of SrV$_x$Ti$_{1-x}$O$_3$ (SVT) for $x = 0.01, 0.05, 0.1,$ and $0.2$ were synthesized from SrCO$_3$ (Aldrich, 99.9%), V$_2$O$_5$ (Alfa Aesar, 99.9%), and TiO$_2$ (Aldrich, 99.9%) precursors. Dense pellets were pressed from the bulk samples and pre-reduced at 1400 °C in dry H$_2$ for 10 hours. The conductivities of the SVT pellets were measured between 600 and 900 °C in humidified H$_2$, and the results are displayed in Figure 4-1.

![Figure 4-1](image_url)  Conductivity of pre-reduced dense SrV$_x$Ti$_{1-x}$O$_3$ pellets as a function of temperature in humidified H$_2$ for $x = 0.01$ (circles), 0.05 (diamonds), 0.1 (triangles), and 0.2 (squares).

For all samples, the conductivity increased with increasing temperature, but the minimum bulk conductivity requirement of 1 S/cm was not satisfied by any of the dopant
concentrations investigated. When compared to the conductivity of undoped SrTiO$_3$ given in Table 2-1, the SVT samples never achieved conductivities much greater than that of pure SrTiO$_3$. The highest observed value was 0.38 S/cm at 900 °C, which was only slightly higher than the undoped value of about 0.1 S/cm. Therefore, strontium vanadium titanate has been shown to exhibit poor electrical conductivity at SOFC operating temperatures and has been dismissed as a viable replacement for Ni-YSZ anodes.

4.1.2 Tantalum-doped Strontium Titanate

Following the elimination of SVT as a substitute material for SOFC anodes, interest focused on tantalum as a potential dopant for the development of an electrically conductive ceramic. Bulk samples of SrTa$_x$Ti$_{1-x}$O$_3$ (STT) with $x = 0.01$, 0.05, 0.1, and 0.2 were synthesized by a solid state reaction method from SrCO$_3$ (Aldrich, 99.9%), Ta$_2$O$_5$ (Alfa Aesar, 99.993%), and TiO$_2$ (Aldrich, 99.9%) precursors. XRD was employed to investigate the phase composition and morphology of bulk powders sintered in air at 1500 °C for 5 hours and reduced in dry H$_2$ at 1400 °C for 10 hours. The XRD patterns of the STT samples are provided in Figure 4-2 for $x = 0.01$, 0.05, and 0.10. All of the samples showed a single cubic perovskite structure, and the lattice parameter for each sample is shown in Figure 4-3.
Figure 4.2 XRD patterns of SrTa$_x$Ti$_{1-x}$O$_3$ for $x = 0.01$, 0.05, and 0.1. “Oxidized” corresponds to samples which were sintered at 1500 °C in air, and “Reduced” corresponds to samples which were reduced at 1400 °C in dry H$_2$.

Figure 4.3 Lattice parameters of SrTa$_x$Ti$_{1-x}$O$_3$ as a function of dopant concentration for samples sintered at 1500 °C in air (open symbols) and reduced at 1400 °C in H$_2$ (solid symbols).
The results suggest the lattice parameter is directly proportional to the dopant concentration for both oxidized and reduced samples within the dopant range investigated. For each composition, the lattice parameter of the reduced sample was higher than the oxidized sample. A previous study has shown that reducing SrNb$_x$Ti$_{1-x}$O$_3$ decreases the lattice oxygen stoichiometry of the perovskite structure resulting in the formation of Ti$^{3+}$ [55]. The larger ionic radius of Ti$^{3+}$ relative to Ti$^{4+}$ caused an increase in the lattice parameter, which is most likely the reason for the observed increase in the STT lattice parameter upon reduction. Additionally, the chemical compatibility of STT and YSZ was examined by comparing the XRD patterns of YSZ, STT, and STT-YSZ composite, as seen in Figure 4-4. No additional phases were detected for any of the composites, suggesting the composites are physical mixtures of STT and YSZ.

![Figure 4-4 XRD patterns of (a) SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ reduced at 1400 °C in H$_2$, (b) as received YSZ, and (c) SrTa$_{0.01}$Ti$_{0.99}$O$_3$ reduced at 1400 °C in H$_2$.](image)
In order to verify that STT was dimensionally stable at SOFC operating temperatures and thermally compatible with YSZ, the CTE values for each dopant concentration were calculated. TMA was employed to investigate the thermal expansion behavior of STT and YSZ pellets sintered in air at 1500 °C. An average CTE was calculated for the range between 50 and 950 °C. The average CTE calculated for YSZ was 10.5 ± 0.5 × 10⁻⁶ K⁻¹, which is in agreement with literature values [62]. For all STT samples, the average CTE was close to that of YSZ ranging from 11.3-11.8 × 10⁻⁶ K⁻¹. The similarity in values indicated thermal compatibility with other SOFC components, meaning that STT fulfills this rudimentary requirement for anode materials.

In order to characterize the electrical properties of STT, dense pellets were pressed from the bulk powders and pre-reduced at 1400 °C in dry H₂ for 10 hours. The conductivities of the pellets were measured between 600 and 900 °C in humidified H₂. As shown in Figure 4-5, conductivities were found to decrease as temperature increased for the samples with x = 0.01, 0.05, and 0.1. However, the opposite trend was observed for x = 0.2, which was incapable of meeting the minimum bulk conductivity limit. After testing at 900 °C was complete, the samples were cooled to 700 °C, and the measurement was repeated. For x = 0.01, the conductivity remained 9.6 S/cm when cooled, but for both x = 0.05 and 0.1, the conductivity decreased from approximately 17 S/cm to 7.3 S/cm and 2.5 S/cm, respectively. The P₀₂ of about 10⁻²⁰ atm established by the humidification of H₂ at 900 °C clearly resulted in decreased conductivity for higher Ta concentrations, suggesting that STT with x = 0.01 has the highest redox stability of the compositions investigated.
Since porous samples more accurately reflect the length scale of an anode and changes in conductivity upon redox cycling, co-fired porous STT-YSZ composites were generated for $x = 0.01, 0.05, \text{ and } 0.1$. The porous composites were prepared for testing by sintering all of the green samples in air at 1500 °C and pre-reducing half of the sintered composites in $H_2$ at 1400 °C. The conductivities of both sintered and pre-reduced STT-YSZ composites were measured in humidified $H_2$ between 600 and 900 °C, and the results are given in Figure 4-6. $d\sigma/dT$ was negative for all of the composites which were not pre-reduced, demonstrating non-metallic conductive behavior. In contrast to the results shown in Figure 4-5 for dense pellets, the conductivity of the $x = 0.1$ composite increased with increasing temperature. Such a distinct discrepancy between the dense and porous results demonstrates that dense samples do not represent equilibrium values that would be attained for an actual anode.

Figure 4-5 Conductivity of pre-reduced dense SrTa$_x$Ti$_{1-x}$O$_3$ pellets as a function of temperature in humidified $H_2$ for $x = 0.01$ (circles), 0.05 (diamonds), 0.1 (triangles), and 0.2 (squares).
For the $x = 0.01$ and 0.05 pre-reduced composites, metallic conductivity was observed, as $d\sigma/dT$ was negative. Similar behavior has been observed for SNT by previous studies, as shown in Figure 2-2. The conductivity of the STT-YSZ composite with $x = 0.01$ was 1.6 S/cm at 800 °C in humidified H$_2$, which was a factor of five lower than the corresponding dense pellet. Accounting for the fact that the composites were comprised of about 30 vol% STT, the difference in conductivity between dense pellets and porous composites was consistent with previous studies [5].

In order to determine if each of the STT samples exhibited redox stability, the conductivities of pre-reduced dense pellets and porous composites were measured in humidified H$_2$ after exposure to a high P$_{O2}$ oxidizing environment for 3 hours at 700 °C and a subsequent low P$_{O2}$ humidified H$_2$ reducing atmosphere for 3 hours at the same

![Figure 4-6](image_url)  
*Conductivity of sintered (open symbols) and pre-reduced (solid symbols) porous STT-YSZ composites as a function of temperature in humidified H$_2$ for $x = 0.01$ (circles), 0.05 (diamonds), 0.1 (squares).*
temperature. The redox cycle was repeated once more at 700 °C, and then the entire procedure was repeated at 800 °C, as depicted in Figure 4-7. The results of the redox tests for the STT pellets and STT-YSZ composites are listed in Table 4-1 for both temperatures.

![Figure 4-7](image)

**Figure 4-7** Variation in conductivity of a pre-reduced porous SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ composite as a function of time through two redox cycles in humidified H$_2$ and air at 700 and 800 °C.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>STT Pellet Conductivities (S/cm)</th>
<th>STT-YSZ Composite Conductivities (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Atmosphere</td>
<td>1% Ta</td>
</tr>
<tr>
<td>700 °C</td>
<td>Humid H$_2$</td>
<td>9.2</td>
</tr>
<tr>
<td>700 °C</td>
<td>H$_2$ after 3 h in Air</td>
<td>1.2</td>
</tr>
<tr>
<td>700 °C</td>
<td>H$_2$ after 6 h in Air</td>
<td>1.3</td>
</tr>
<tr>
<td>800 °C</td>
<td>H$_2$ after 3 h in Air</td>
<td>1.3</td>
</tr>
<tr>
<td>800 °C</td>
<td>H$_2$ after 6 h in Air</td>
<td>1.2</td>
</tr>
</tbody>
</table>
In addition to the redox cycling tests, the conductivities of pre-reduced composites were measured at 700 and 800 °C in humidified H₂ after 5 hour oxidation treatments at higher temperatures to determine the point at which the enhanced conductivity gained from the high temperature pre-reduction step was lost. The results for x = 0.01 and 0.05 are displayed in Figure 4-8. The dense SrTa₀.₁Ti₀.₉O₃ pellets did not possess a redox stable conductivity at 700 or 800 °C that surpassed the minimum bulk conductivity limit, so oxidation at higher temperatures was not pursued for this composition. For x = 0.01 and 0.05, conductivities of 0.86 and 0.37 S/cm were measured after oxidation at 1000 °C, which are sufficient for SOFC anode applications. However, sufficiently high conductivity was lost after oxidation at 1100 °C for both x = 0.01 and 0.05. At oxidation temperatures lower than 1100 °C, the conductivities for x = 0.01 were slightly higher than those of x = 0.05, but both remained above the minimum porous composite conductivity value of 0.1 S/cm.

![Figure 4-8 Conductivity of pre-reduced porous STT-YSZ composites in humidified H₂ at 700 °C (open symbols) and 800 °C (solid symbols) after oxidation at increasing temperatures for x = 0.01 (diamonds) and 0.05 (triangles).](image-url)
Two processes may have resulted in loss of conductivity upon oxidation. One reason for the loss of redox stability may have been due to the formation of Sr vacancies in the perovskite structure. SrO can form a second phase to compensate for the charge imbalance between the dopant and the Ti. The other possible explanation for the decrease in conductivity is that oxygen was incorporated back into the perovskite, causing Ti$^{3+}$ atoms to become Ti$^{4+}$. The increased positive charge would have resulted in a decrease in the number of electrons available to the Ti for conduction, and the net result would have been a decrease in the conductivity of the material [5].

Based on the favorable data obtained from all preceding experiments, it was concluded that SrTa$_{0.01}$Ti$_{0.99}$O$_3$ was the optimal composition. As such, SOFC button cells containing 1% Ta STT anodes were fabricated by laminating the cathode, electrolyte, and anode components. The resulting sintered cells consisted of 250 μm thick cathodes that had a porosity of 65%, 75 μm thick dense YSZ electrolytes, and 50, 100, or 200 μm thick anodes that were 40% porous. The cathodes were infiltrated with LSF to a target loading of 30 wt%, and the STT-YSZ anodes were infiltrated with catalyst to final loadings of about 3 wt% CeO$_2$ and approximately 1 wt% Pd. The electrolyte and cathode areas for the fuel cells were both calculated to be 1 cm$^2$, and the anode area was 0.35 cm$^2$, so an active area of 0.35 cm$^2$ was assumed for normalization of the performance calculations.

Electrochemical impedance and performance measurements were made for the fuel cells at 700, 750, and 800 °C in humidified H$_2$ and CH$_4$, and Voltage-current and Cole-Cole plots of the impedance spectra were generated. The results for SOFCs containing 50 μm thick 1% Ta STT-YSZ anodes impregnated with CeO$_2$-Pd catalyst and
The cells with the 50 μm anodes achieved the best performance of the three anode thicknesses investigated, generating maximum power densities slightly greater than 0.4 W·cm⁻². Thin anodes exhibit better performance because diffusion of fuel to the active region occurs faster and electrical resistance is not as great, since $RA$ decreases with $l$ in Equation 3-1. Thick anodes are normally avoided except when used as a source of structural stability for the cell, as in electrode supported cells [63]. All of the STT-YSZ cells produced by this study were cathode supported, so thick anodes offered no benefit. For comparison, the performance plots for 100 and 200 μm STT-YSZ anodes with and without catalyst in humidified H₂ and CH₄ have been included in Figures B-1 through B-8 in Appendix B. Attempts to optimize the anode performance were not made, but it is likely that performance could be improved.

Figure 4-9  V-i polarization curves for a fuel cell with a 50 μm thick SrTa₀.₀₁Ti₀.₉₉O₃-YSZ anode infiltrated with 3 wt% CeO₂ and 1 wt% Pd in humidified H₂ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares). Solid and open symbols are power densities and voltages, respectively.
Figure 4-10  Impedance spectra for a fuel cell with a 50 μm thick SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode infiltrated with 3 wt% CeO$_2$ and 1 wt% Pd in humidified H$_2$ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares).

Figure 4-11  V-i polarization curves for a fuel cell with a 50 μm thick SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode infiltrated with 3 wt% CeO$_2$ and 1 wt% Pd in humidified CH$_4$ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares). Solid and open symbols are power densities and voltages, respectively.
The total ohmic resistance, \((R_A\Omega)_{\text{Total}}\), was determined from the high frequency intercept using Equation 4-1 and the abscissa in the Cole-Cole plots, while the total non-ohmic resistance, \((R_{A\text{non-}\Omega})_{\text{Total}}\), was determined by subtracting the low frequency intercept from the high frequency intercept using Equation 4-2. \((Z_{\text{Real}})_{\text{High}}\) and \((Z_{\text{Real}})_{\text{Low}}\) are the high and low frequency intercepts, respectively, and \(A_{\text{Active}}\) is the active area assumed for the fuel cell anode.

\[
(R_A\Omega)_{\text{Total}} = (Z_{\text{Real}})_{\text{High}} \cdot A_{\text{Active}} \quad \text{ (Equation 4-1)}
\]

\[
(R_{A\text{non-}\Omega})_{\text{Total}} = [(Z_{\text{Real}})_{\text{Low}} \cdot A_{\text{Active}}] - [(Z_{\text{Real}})_{\text{High}} \cdot A_{\text{Active}}] \quad \text{ (Equation 4-2)}
\]

The total non-ohmic resistances at 700, 750, and 800 °C were 0.34, 0.21, and 0.10 \(\Omega\cdot\text{cm}^2\) based on Figure 4-10. Cathode non-ohmic losses for LSF-YSZ composites
have been reported to be approximately $0.1 \ \Omega\cdot\text{cm}^2$ at 700 °C [64], suggesting that the anode contributed around $0.24 \ \Omega\cdot\text{cm}^2$ to the total non-ohmic losses at this temperature.

In humidified H$_2$, the total ohmic resistance was more than half of the total cell resistance, but in humidified CH$_4$, the total ohmic resistance contributed a much smaller fraction of the total cell resistance because the non-ohmic losses were greater. The ohmic resistance attributed to the STT anode, $(RA_\Omega)_{\text{Anode}}$, was estimated from the impedance spectra by subtracting the electrolyte and cathode contributions, $(RA_\Omega)_{\text{Electrolyte}}$ and $(RA_\Omega)_{\text{Cathode}}$, from the total ohmic resistance, as seen in Equation 4-3. Previous studies have concluded that the ohmic resistance of a YSZ electrolyte ranges from $0.4 \ \Omega\cdot\text{cm}^2$ at 700 °C to $0.18 \ \Omega\cdot\text{cm}^2$ at 800 °C and the ohmic resistance of a LSF-YSZ cathode contributes approximately $0.04 \ \Omega\cdot\text{cm}^2$ [64]. It was assumed that CeO$_2$ and Pd did not contribute to the anode conductivity even though both CeO$_2$ and Pd are electronically conductive. This assumption was reasonable because the CeO$_2$ and Pd loadings correspond to filling only about 4 vol% of the anode pores, which is well below the percolation threshold required for conduction [5].

\[
(RA_\Omega)_{\text{Anode}} = (RA_\Omega)_{\text{Total}} - (RA_\Omega)_{\text{Electrolyte}} - (RA_\Omega)_{\text{Cathode}} \quad \text{(Equation 4-3)}
\]

Table 4-2 shows the anode ohmic resistances estimated from the impedance measurements of Figure 4-10. For comparison, theoretical ohmic resistances calculated from the four-probe conductivity measurements of porous STT composites shown in Figure 4-6 are included for reduced and non-reduced anodes. The theoretical anode ohmic resistances, $RA_\Omega^t$, were calculated using Equation 4-4, which is a rearrangement of
Equation 3-1. To account for the fact that the pre-reduced anodes had also been oxidized in air at 850 °C when the LSF in the fuel cell cathode was calcined, Equation 4-4 was used in conjunction with the conductivity values from Figure 4-8 for the SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ composite oxidized at 900 °C to estimate RA$_{\Omega}^b$. For all temperatures, the anode ohmic resistance of the fuel cell was higher than the theoretical quantities by approximately one order of magnitude. However, RA$_{\Omega}^b$ remained lower than RA$_{\Omega}^a$ for the “Not reduced” samples, which clearly indicates that the enhanced conductivity gained from the high temperature reduction step was maintained throughout the LSF calcination.

\begin{equation}
(RA_{\Omega})_{Anode} = \frac{l_{Anode}}{\sigma_{Porous \text{ Composite}}} \tag{Equation 4-4}
\end{equation}

| Table 4-2 Ohmic resistances of porous SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anodes as a function of temperature in humidified H$_2$. |
|---------------------------------|------------------|------------------|------------------|
| Reduced at 1400 °C in H$_2$ | RA$_{\Omega}^a$ ($\Omega \cdot$cm$^2$) | RA$_{\Omega}^b$ ($\Omega \cdot$cm$^2$) | RA$_{\Omega}^c$ ($\Omega \cdot$cm$^2$) |
| 700 °C | 0.0025 | 0.009 | 0.34 | 2.27 |
| 750 °C | 0.0029 | 0.006 | 0.18 | 1.09 |
| 800 °C | 0.0030 | 0.005 | 0.13 | 0.58 |

$^a$Theoretical RA$_{\Omega}$ from four-probe conductivity measurements (Fig. 4-6)
$^b$Theoretical RA$_{\Omega}$ from conductivity after oxidation at 900 °C (Fig. 4-8)
$^c$Calculated RA$_{\Omega}$ from fuel cell impedance measurements (Fig. 4-10)

The discrepancy between the theoretical and calculated anode ohmic resistance is most likely due to inaccuracies in the estimation of the electrolyte contribution. While the electrolyte ohmic resistance was calculated from a bulk YSZ conductivity literature value, it has been shown that the electrolyte resistance in a fuel cell is typically higher than the theoretical value [3]. The difference between measured and theoretical values can be large enough to explain the discrepancy observed in Table 4-2.
SEM was also employed to investigate the microstructure of porous STT-YSZ. Figure 4-13 is a micrograph of the cross section of a SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode and Figure 4-14 provides a magnified view showing the inside of a pore. Figure 4-15 is a micrograph of the anode surface taken in backscatter mode, which depicts heavier compounds as lighter shades and lower atomic number compounds as darker shades. Consequently, the 1% Ta STT (atomic number of Sr is 87 and that of Ti is 47) appears as the darker colored grains and YSZ (atomic number of Y is 89 and that of Zr is 91) as the lighter grains. The STT and YSZ particles appear well dispersed and the average grain size is roughly 3 μm.

![SEM micrograph of a porous SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ SOFC anode.](image)
Upon completion of the analysis of the thermal, electrical, and redox stable properties of STT, it was concluded that SrTa$_x$Ti$_{1-x}$O$_3$ with $x = 0.01$ and $0.05$ possess sufficiently high redox stable conductivities to fulfill the role of an electrically conductive ceramic within SOFC anodes. Lower dopant concentrations were found to exhibit higher redox stability, and the enhanced conductivity imparted by the high temperature reduction step was maintained after oxidation at 1000 °C. SrTa$_{0.01}$Ti$_{0.99}$O$_3$ achieved the highest redox stable conductivity, and was, therefore, the optimum STT composition.

Figure 4-14  SEM micrograph of the inside of a SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode pore.

Figure 4-15  Backscatter image of the surface of a SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ SOFC anode.
4.1.3 Tungsten-doped Strontium Titanate

Following the successful identification of SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ as a feasible electrically conductive ceramic for use in SOFC anodes, work ensued on the investigation into the properties of B-site doped SrXTiO$_3$ containing tungsten (W$^{6+}$). Bulk samples of SrW$_x$Ti$_{1-x}$O$_3$ (SWT) for $x = 0.01$ and 0.2 were prepared from SrCO$_3$ (Aldrich, 99.9%), WO$_3$ (Alfa Aesar, 99.99%), and TiO$_2$ (Aldrich, 99.9%) precursors. Dense pellets were pressed from the bulk samples and pre-reduced at 1400 °C in dry H$_2$ for 10 hours. The conductivities of the SWT pellets were measured between 600 and 900 °C in humidified H$_2$, and the results are displayed in Figure 4-16.

![Figure 4-16 Conductivity of sintered (open symbols) and pre-reduced (solid symbols) dense SrW$_x$Ti$_{1-x}$O$_3$ pellets as a function of temperature in humidified H$_2$ for $x = 0.01$ (circles) and 0.2 (diamonds).]
The conductivities were generally higher as temperature increased, but the values for both of the sintered samples peaked around 800 °C. For the reduced dense pellet where \( x = 0.01 \), the measured conductivities remained fairly constant, just barely above the minimum required bulk conductivity limit. In contrast, the conductivity of the sample with \( x = 0.2 \) increased sevenfold from 0.47 S/cm at 600 °C to 3.49 S/cm at 900 °C. Since both compositions successfully surpassed the minimum conductivity, redox stability testing was performed on the dense pellets, and the results are listed in Table 4-3 [65].

<table>
<thead>
<tr>
<th>Conditions</th>
<th>SWT Pellet Conductivities (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1% W</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td><strong>Atmosphere</strong></td>
</tr>
<tr>
<td>700 °C</td>
<td>Humid H(_2)</td>
</tr>
<tr>
<td>700 °C</td>
<td>H(_2) after 3 h in Air</td>
</tr>
<tr>
<td>700 °C</td>
<td>H(_2) after 6 h in Air</td>
</tr>
<tr>
<td>800 °C</td>
<td>H(_2) after 3 h in Air</td>
</tr>
<tr>
<td>800 °C</td>
<td>H(_2) after 6 h in Air</td>
</tr>
</tbody>
</table>

Although sufficient values were attained by the reduced pellets in humidified H\(_2\), neither concentration of tungsten dopant maintained the enhanced conductivity obtained from the pre-reduction step after redox cycling. The conductivity of SWT with \( x = 0.2 \) plummeted, but the conductivity for \( x = 0.01 \) remained much higher than its corresponding sintered values in Figure 4-16, indicating that complete oxidation did not occur or partial re-reduction occurred during the 3 hour periods in H\(_2\). However, the low conductivities observed after redox cycling demonstrated that strontium tungsten titanate is not redox stable at SOFC operating temperatures, so SWT has been dismissed as a viable material for use in SOFC anodes.
4.1.4 Molybdenum-doped Strontium Titanate

After SWT was dismissed as a substitute material, interest shifted to molybdenum-doped strontium titanate (SMT). In order to explore the conductive properties of SrMo$_x$Ti$_{1-x}$O$_3$, bulk samples were synthesized for $x = 0.01, 0.2, 0.4$, and $0.6$ from SrCO$_3$ (Aldrich, 99.9%), MoO$_3$ (Alfa Aesar, 99.95%), and TiO$_2$ (Aldrich, 99.9%) precursor reagents. Dense pellets were pressed from the bulk powders, sintered in air at 1500 °C, and pre-reduced at 1400 °C in dry H$_2$ for 10 hours. The conductivities of the SMT pellets were measured between 600 and 900 °C in humidified H$_2$, and the results are displayed in Figure 4-17.

Figure 4-17 Conductivity of sintered (open symbols) and pre-reduced (solid symbols) dense SrMo$_x$Ti$_{1-x}$O$_3$ pellets as a function of temperature in humidified H$_2$ for $x = 0.01$ (circles), 0.2 (diamonds), and 0.4 (triangles).
The conductivities of each of the compositions increased with increasing temperature and dopant concentration. As expected, the pre-reduced samples exhibited higher conductivities than those which were not pre-reduced at high temperatures, but a close examination of Figure 4-17 reveals that good electrical conductivities were achieved with the sintered SMT when x = 0.2 and 0.4. Large increases in the measured conductivities of four orders of magnitude are visible around 750-800 °C for these two sintered samples, suggesting that the material was reduced by the low P_{O2} humidified H_2 atmosphere at the lower temperatures encountered during the conductivity testing process. The fact that a high temperature pre-reduction step was not needed to attain sufficient conductivities for highly doped SMT is significant because it means the material will reduce at SOFC operating temperatures and will be naturally redox stable.

When XRD was used to analyze oxidized samples of the bulk SMT powders, it revealed that multiple phases formed at dopant concentrations where x ≥ 0.2. The XRD patterns for all of the compositions are shown in Figure 4-18. In the patterns for x ≥ 0.2, new peaks appeared at 2θ = 27, 30, 46, 52, and 57, and the signal strengths of the new peaks increased as the concentration of molybdenum increased. As such, the additional peaks are likely due to separate SrTiO_3 and SrMoO_4 phases which formed when the material was subjected to high temperatures during the preparation process. Consequently, highly doped SMT possessed sufficiently high redox stable conductivities at 800 °C but failed to meet the critical single phase requirement, so strontium molybdenum titanate has been dismissed as a viable option for use in SOFC anodes.
Interest in strontium molybdate (SMO) emerged from the conclusions reached during the investigation of SMT. SMT was shown to possess acceptable electrical conductivity and innate redox stability at SOFC operating temperatures [66-68], but the discovery of multiple phases in the material negated the possibility of incorporating it as a replacement for Ni-YSZ anodes. It was noted that while both SrTiO$_3$ and SrMoO$_4$ phases formed, SrMoO$_4$ was the only compound contributing to the high conductivity because undoped SrTiO$_3$ displays poor electrical conductivity, as exemplified by Table 2-1. For this reason, the decision to deviate from doped strontium titanate materials and pursue strontium molybdate was made. However, a similar study exploring SrVO$_3$ reported issues with dimensional stability at high temperatures due a 40% increase.

Figure 4-18 XRD patterns for SMT with x = 0.01, 0.2, 0.4, and 0.6 and standard patterns for SrTiO$_3$ (JCPDS 89-4934) and SrMoO$_4$ (JCPDS 85-0586).
in volume upon oxidation to SrVO$_4$ [69]. When calculations were performed analyzing the oxidation of SrMoO$_3$ to SrMoO$_4$, a 40% volume expansion was also obtained, which makes SMO incompatible with common SOFC components. In order to circumvent this obstacle, porous YSZ slabs were prepared and infiltrated with SMO, instead of co-firing SMO and YSZ to form porous composites [70]. Infiltrating the SMO into the pores of the sintered slab and onto the YSZ infrastructure provided the SMO adequate space for expansion inside the pore without compromising the integrity of the YSZ substructure.

Consequently, porous YSZ slabs were prepared and sintered at 1500 °C for 5 hours, and the porosity of the slabs was determined to be roughly 60% by water uptake measurements. The SMO target loadings selected for analysis are listed in Table 4-4. Due to the fact that SMO is insoluble in water [71, 72], the infiltration process required the addition of equal volumes of two separate aqueous solutions containing the necessary precursor reagents, namely 0.35 M Sr(NO$_3$)$_2$ and (NH$_4$)$_2$Mo$_7$O$_{24}$. Each infiltration cycle was followed by a heat treatment at 450 °C in air to decompose the nitrate and ammonium and deposit strontium and molybdenum within the pores of the YSZ slab. A calcination step at 1000 or 1200 °C was also required once the loadings were reached.

<table>
<thead>
<tr>
<th>Percent of Total Pore Space Containing SMO (vol%)</th>
<th>Percent of Solids (vol%)</th>
<th>SMO Weight Percent (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>7.0</td>
</tr>
<tr>
<td>8</td>
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<td>10</td>
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<tr>
<td>12</td>
<td>18</td>
<td>14.5</td>
</tr>
<tr>
<td>16</td>
<td>24</td>
<td>19.5</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>24.8</td>
</tr>
</tbody>
</table>
For the purpose of phase analysis, bulk SrMoO\textsubscript{4} powder was synthesized by a solid state reaction method from SrCO\textsubscript{3} (Aldrich, 99.9\%) and MoO\textsubscript{3} (Alfa Aesar, 99.95\%) precursors. XRD was employed to investigate the phase composition and morphology of powder samples calcined in air at 1200 °C for 5 hours and reduced in dry H\textsubscript{2} at 800 °C for 24 hours. The XRD patterns of the bulk SMO samples are provided in Figure 4-19. In addition, the chemical compatibility of SMO and YSZ was examined by comparing the XRD patterns of YSZ powder, bulk SMO calcined at 1200 °C, and a YSZ slab infiltrated to a target loading of 19.5 wt% SMO, as seen in Figure 4-20. No additional phases were detected in the infiltrated slab, implying that only SMO and YSZ were present [73].

Figure 4-19 XRD patterns for a SMO powder sample which was (a) oxidized to SrMoO\textsubscript{4} at 1200 °C in air, (b) reduced to SrMoO\textsubscript{3} at 800 °C in dry H\textsubscript{2}, (c) re-oxidized to SrMoO\textsubscript{4}, and (d) re-reduced to SrMoO\textsubscript{3}, and standard patterns for (e) SrMoO\textsubscript{4} (JCPDS 85-0586) and (f) SrMoO\textsubscript{3} (JCPDS 81-0640).
In order to determine the effect of different calcination temperatures on the particle sizes of the SMO, half of the infiltrated slabs were calcined at 1000 °C and the remaining half were calcined at 1200 °C. It was speculated that a lower calcination temperature resulted in a larger quantity of smaller particles, whereas a higher temperature generated fewer but larger particles. SEM was employed to investigate this effect. Figures 4-21 and 4-22 depict the microstructure of the porous YSZ backbone before any SMO was added. Figures 4-23 and 4-24 show oxidized and reduced slabs which have been infiltrated to approximately 20 wt% SMO and calcined at 1000 °C. For comparison, Figures 4-25 and 4-26 illustrate oxidized and reduced slabs which have similar loadings and were calcined at 1200 °C. The effect of the calcination temperature is evident in the differences in average particle diameter, where slabs heated to 1000 °C formed 1-2 μm particles, and those calcined at 1200 °C produced 3-7 μm particles.
Figure 4-21 SEM micrograph of a blank (0 wt% SMO) porous YSZ slab.

Figure 4-22 SEM micrograph of the inside of a pore of a blank (0 wt% SMO) YSZ slab.

Figure 4-23 SEM micrograph of a YSZ slab infiltrated with 19.0 wt% SMO and calcined at 1000 °C.

Figure 4-24 SEM micrograph of a YSZ slab infiltrated with 19.0 wt% SMO, calcined at 1000 °C, and reduced at 800 °C.

Figure 4-25 SEM micrograph of a YSZ slab infiltrated with 20.5 wt% SMO and calcined at 1200 °C.

Figure 4-26 SEM micrograph of a YSZ slab infiltrated with 20.5 wt% SMO, calcined at 1200 °C, and reduced at 800 °C.
TMA was employed to investigate the thermal expansion behavior of the SMO infiltrated YSZ slabs to verify that dimensional stability was maintained at SOFC operating temperatures, and the resulting curves are given in Figures 4-27 and 4-28 for each calcination temperature. The CTE values could not be calculated for the slabs, as a linear slope was not observed; however, a similar study has concluded that thermal strains ensuing from an expansion 0.19-0.21% greater than that of YSZ must not be exceeded to avoid internal fracturing [74]. This range was based on calculations applied from a study which developed a model for the elastic deformation of multiple layers [75]. For our study, the calculations were verified under the same assumptions [76] and used to analyze the TMA data for the SMO infiltrated YSZ slabs to identify unacceptably large deviations from the blank YSZ slab (0 wt% SMO). Consequently, the highest permissible strains observed in Table 4-5 for each calcination temperature corresponds to loadings of 12.2 and 20.6 wt% SMO.

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Infiltrated Loading (wt% SMO)</th>
<th>Measured Temperature (°C)</th>
<th>Measured (ΔL/L₀)Max (%)</th>
<th>Equivalent (ΔL/L₀)YSZ (%)</th>
<th>Percent Difference (%)</th>
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<td>665</td>
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<td>1.20</td>
</tr>
</tbody>
</table>
Figure 4-27 Thermal expansion as a function of temperature for SMO infiltrated YSZ slabs which were calcined at 1000 °C.

Figure 4-28 Thermal expansion as a function of temperature for SMO infiltrated YSZ slabs which were calcined at 1200 °C.
TGA was used to determine the reduction temperature at which a bulk powder sample of SrMoO$_4$ was reduced to SrMoO$_3$ and the oxidation temperature where SrMoO$_3$ was oxidized to SrMoO$_4$. The weight changes shown in Figure 4-29 were due to loss or gain of oxygen atoms as they were either removed from or reincorporated into the SMO depending on the type of environment the samples were immersed in. Reduction of SrMoO$_4$ began near 750 °C and continued for about 4 hours. Likewise, oxidation of SrMoO$_3$ commenced at 350 °C and attained complete oxidation after 1 hour.

![Figure 4-29 Thermogravimetric analysis of bulk SMO powders calcined at 1200 °C.](image)

The results obtained in Figure 4-29 reinforced the hypothesis that SMO can be considered a redox stable material, since reduction is possible under normal SOFC operating conditions. Accordingly, a high temperature pre-reduction was not necessary to achieve good conductivity with SMO, so redox cycling was not performed during the
conductivity testing process. Electrical conductivity of the SMO infiltrated porous YSZ slabs was measured in humidified H$_2$ between 600 and 900 °C for samples calcined at 1000 and 1200 °C infiltrated to each of the target loadings. The results displayed in Figure 4-30 seem to indicate that a well defined range of loadings exist between 8 and 13 vol% SMO, above which the conductivity is consistently high and below which poor conductivity is exhibited. The variability of values measured within this region demonstrates that percolation to form an interconnected SMO network is sensitive at these loadings. The maximum conductivity attained for both series of samples was on the order of 15-20 S/cm for loadings near 17 vol% SMO (≈20 wt% SMO).

![Figure 4-30 Conductivity of SMO infiltrated porous YSZ slabs calcined at 1000 (solid symbols) and 1200 °C (open symbols) as a function of loading following a 24 hour equilibration period at 800 °C in humidified H$_2$.](image)

A dense pellet was also pressed from the bulk SMO powder which had been calcined at 1200 °C and tested to acquire the bulk conductivity of SMO as a baseline. During the course of preparing the dense pellet, the temperature at which SMO
decomposes was discovered to be near 1500 °C. As such, the dense pellet was sintered at 1400 °C instead of the customary 1500 °C to prevent decomposition, but densification was still achieved. Since the roughly 20 wt% SMO loading calcined at 1200 °C demonstrated the highest electrical conductivity at 800 °C in addition to thermal compatibility with YSZ, it was selected as the optimum loading. In Figure 4-31, the conductivity of a 20.2 wt% SMO infiltrated porous YSZ slab is shown as a function of temperature, and the conductivities of a dense SMO pellet and blank YSZ slab are included for comparison. The fact that the infiltrated slab possessed the conductivity of YSZ at temperatures below 800 °C and assumed that of pure SMO at temperatures above 800 °C becomes readily apparent from the trends.

Figure 4-31  Conductivity of a blank porous YSZ slab (triangles), dense SMO pellet (diamonds), and 20.2 wt% SMO infiltrated YSZ slab (squares) as a function of temperature in humidified H₂.
Upon completion of the investigation into the properties of SMO, it was concluded that incorporating SMO into porous YSZ slabs through a multistep infiltration process overcame the innate difficulties associated with expansion for loadings less than 12 or 20 wt% SMO depending on the calcination temperature. Analysis of an infiltrated slab with XRD also confirmed that no additional phases formed upon calcination, and a comparison of average particle sizes performed from SEM micrographs demonstrated that larger particles are formed as the calcination temperature increases. For bulk SMO and infiltrated slabs, the characteristic exponential increase in conductivity observed at 800 °C in H₂ after an equilibration period of several hours strongly correlates with the reduction features of SMO ascertained from the TGA results. Slabs infiltrated to 20 wt% SMO exhibited the best electrical conductivity well in excess of the minimum requirement, and 20 wt% SMO samples calcined at 1200 °C demonstrated thermal compatibility with YSZ. Therefore, 20 wt% SMO infiltrated porous YSZ slabs calcined at 1200 °C have been established as the optimum loading for use in SOFC anodes.
Chapter 5  Conclusions and Recommendations

5.1  Summary of Objectives

The primary goal of this work was the identification and development of ceramic materials which possessed the characteristics needed for use in SOFC anodes. Ceramic materials offer solutions to several of the limitations of Ni-YSZ cermet anodes, but in order for any new material to be considered for utilization, it must exhibit porosity, electronic conductivity, ionic conductivity, catalytic activity, and thermal and chemical compatibility with YSZ. Porosity was achieved without great difficulty by adding pore forming substances, and ionic conductivity was attained by mixing the novel ceramic material with $O^2-$ conductive YSZ. However, most ceramic materials are not electrically conductive and catalytically active, so satisfying these requirements was accomplished by incorporating two separate materials, one being an electrically conductive ceramic and the other a catalyst for the oxidation reaction.

Several excellent oxidation catalysts have been thoroughly explored for SOFC applications, so the focus of this study centered upon the identification and characterization of the properties of electrically conductive ceramic materials. Distinction between sufficiently and insufficiently conductive materials was made on the basis of minimum conductivity limits of 1 S/cm for bulk samples and 0.1 S/cm for porous composites obtained from the literature. Redox stability was also a major concern, since the anode would be subjected to both oxidizing and reducing conditions during operation. As such, it was essential that the conductivity of the ceramic remained above the
minimum limit after redox cycling. Additionally, if a high temperature pre-reduction step was required to achieve acceptable conductivities, this study sought to ascertain whether the high conductivity imparted by the pre-reduction process was maintained after redox cycling.

5.2 Conclusions

With the stated objectives in mind, interest focused on $n$-doped SrXTiO$_3$ materials, which were reported to demonstrate good electrical conductivity [2, 5]. However, instead of attempting to achieve the highest conductivity possible, SrXTiO$_3$ materials were developed with the aim of achieving redox stability. Anodes which only exhibit excellent conductivity when consistently maintained in a H$_2$ environment are not practical, considering the many opportunities for oxidation during operation. Therefore, the conductive properties of vanadium, tantalum, tungsten, and molybdenum-doped strontium titanates were investigated under realistic fuel cell operating conditions and redox cycling.

Following the research into vanadium, tungsten, and molybdenum-doped SrXTiO$_3$, each compound was found to be deficient in an essential area. SVT was discarded because the minimum bulk conductivity limit was not met for any of the dopant concentrations explored. Although pre-reduced SWT possessed sufficient conductivity prior to redox cycling, the enhanced conductivity obtained from the pre-reduction step was not maintained after redox testing. The low conductivities observed after redox
cycling demonstrated that SWT was not redox stable at SOFC operating temperatures, so it was also rejected as a viable material for use in SOFC anodes.

In contrast to SVT and SWT, pre-reduced molybdenum-doped SrXTiO$_3$ exhibited excellent conductivity of about 20 S/cm for pre-reduced SMT with $x = 0.2$. The conductivities of each of the compositions increased with increasing temperature and dopant concentration. Good electrical conductivities on the order of 3 and 60 S/cm were also achieved with $x = 0.2$ and 0.4 SMT samples which had not been pre-reduced. For the highly doped SMT samples, significant increases in conductivity of four orders of magnitude within the 750-800 °C temperature range suggested that the material will reduce at SOFC operating temperatures and can thus be considered redox stable. However, an XRD analysis revealed that multiple phases formed at high dopant concentrations, and the additional peaks in the XRD patterns were identified as separate SrTiO$_3$ and SrMoO$_4$ phases. Consequently, highly doped SMT possessed sufficiently high redox stable conductivities at 800 °C but failed to meet the critical single phase requirement, so SMT was dismissed as a viable option for use in SOFC anodes.

The investigation into tantalum-doped strontium titanate successfully demonstrated that sufficient redox stable conductivity can be achieved with porous SrTa$_x$Ti$_{1-x}$O$_3$ samples for $x = 0.01$ and 0.05. An XRD analysis proved that STT-YSZ was a chemically compatible physical mixture of STT and YSZ, and the similarity in CTE values obtained from the TMA between bulk STT and YSZ verified thermal compatibility. Although STT samples with $x = 0.1$ and 0.2 were also prepared, the composition with $x = 0.2$ was eliminated because it failed to meet the minimum bulk
conductivity requirement. For $x = 0.1$, redox stability was lost after oxidation at 800 °C, thereby rendering the material impractical for use in SOFC anodes. Lower dopant concentrations were found to exhibit higher redox stability, and the enhanced conductivity imparted by the high temperature reduction step was maintained after oxidation at 1000 °C for STT samples with $x = 0.01$ and 0.05. Conductivities of 0.86 and 0.37 S/cm were observed for $x = 0.01$ and 0.05 following oxidation at 1000 °C, but redox stability was lost upon oxidation at 1100 °C for both compositions.

Since $\text{SrTa}_{0.01}\text{Ti}_{0.99}\text{O}_3$ was identified as the best composition, SOFC button cells containing 50, 100, and 200 μm $\text{SrTa}_{0.01}\text{Ti}_{0.99}\text{O}_3$-YSZ anodes were assembled and tested. SEM was employed to analyze the cells to show that the STT and YSZ particles were well dispersed and that the average grain size was roughly 3 μm. Reasonably good electrochemical performance was achieved when the STT-YSZ anodes were infiltrated with 3 wt% CeO$_2$ and 1 wt% Pd. Fuel cells with 50 μm anodes generated maximum power densities slightly greater than 0.4 W/cm$^2$, performing better than the cells containing either of the thicker anodes. The theoretical ohmic resistances of the STT-YSZ anodes were calculated from the four-probe conductivity measurements obtained after oxidation at 900 °C to account for the calcination of the LSF in the cathode. The resultant values were then compared to the ohmic resistances calculated from the impedance spectra high frequency intercepts. Theoretical resistances remained lower than the values calculated based on the conductivities of unreduced composites, demonstrating that the enhanced conductivity gained from the high temperature pre-reduction step was maintained through the LSF calcination.
Therefore, upon completion of the analysis of the thermal, electrical, and redox stable properties of STT, it was concluded that SrTa$_x$Ti$_{1-x}$O$_3$ with x = 0.01 and 0.05 successfully fulfilled all of the chemical and thermal compatibility prerequisites for use in SOFC anodes and possessed sufficiently high redox stable conductivities to fulfill the role of an electrically conductive ceramic. However, because 1% Ta STT achieved the highest redox stable conductivity, the assessment of this study was that SrTa$_{0.01}$Ti$_{0.99}$O$_3$ proved to be the optimum composition and a feasible replacement for Ni-YSZ anodes.

Based on the identification of separate SrMoO$_4$ and SrTiO$_3$ phases within the highly conductive SMT samples, the conclusion was reached that SrMoO$_4$ was the only species contributing to the excellent electrical conductivity. Removal of the SrTiO$_3$ insulating phase was theorized to further increase the observed conductivity, so an investigation into the properties of SMO was launched. However, previous research indicated that SMO was dimensionally unstable at high temperatures due to a 40% expansion upon oxidation. In order to overcome this problem, porous YSZ slabs were prepared and infiltrated with SMO, and an XRD analysis performed on the infiltrated slabs detected no additional phases, confirming that only SMO and YSZ were present.

The effect of calcination temperature on SMO was also studied based on SEM images depicting larger average particle diameters for samples calcined at 1200 °C and smaller grains for samples calcined at 1000 °C. Further research is needed to clearly identify the effects on the properties of SMO associated with the different particle sizes, but certain potential correlations have been eliminated during the course of this study. For instance, the empirical results obtained from the conductivity testing process exclude
the possibility of any significant influence on conductivity, since similar values were achieved for samples prepared at both calcination temperatures for a given loading. On the contrary, a connection between thermal expansion and particle size may be evident. Thermal expansion was limited to 0.19-0.21% above that of YSZ, so experiments employing the TMA demonstrated that the maximum loading which remained below this range was 20.6 wt% SMO when calcined at 1200 °C but a drastically lower 12.2 wt% SMO when calcined at 1000 °C.

According to the data collected by the TGA, reduction of minimally conductive SrMoO₄ to highly conductive SrMoO₃ began near 750 °C and required 4 hours to complete. Similar observations were made during the conductivity testing process, where an equilibration period of several hours at 800 °C was required before stable conductivity values could be recorded. As a result, the testing procedure was modified to include a step which held the samples at 800 °C for 24 hours within a humidified H₂ atmosphere to facilitate accurate measurements. The implication of such a low reduction temperature suggests that SMO can be reduced under typical SOFC operating conditions and should be considered a redox stable material. Consequently, the conductivities of various loadings of SMO infiltrated into porous YSZ slabs were measured after the equilibration period at 800 °C in humidified H₂, and a comparison was made which served to identify the optimum loading. The maximum conductivities selected from the evaluation were found to be 15-20 S/cm, which were attained by the samples infiltrated to 20 wt% SMO for both calcination temperatures.
Upon completion of the investigation into the properties of SMO, it was concluded that incorporating SMO into porous YSZ slabs through a multistep infiltration process overcame the innate difficulties associated with thermal expansion for loadings less than or equal to roughly 12 or 20 wt% SMO when calcined at 1000 and 1200 °C, respectively. Slabs infiltrated to 20 wt% SMO and calcined at 1200 °C exhibited the best electrical conductivity in addition to thermal compatibility with YSZ. Therefore, 20 wt% SMO infiltrated porous YSZ slabs calcined at 1200 °C have been established as the optimum loading for use in SOFC anodes.

5.3 Recommendations for Future Research

Although the results produced by this study have successfully identified 1 and 5% Ta-doped SrXTiO₃ and 12 wt% SMO calcined at 1000 °C and 20 wt% SMO calcined at 1200 °C infiltrated porous YSZ slabs as potential replacements for Ni-YSZ anodes, further research opportunities remain. Great strides have been made in characterizing the chemical, thermal, electrical, and redox stability properties of several n-doped strontium titanate materials, but additional work is needed before a definite conclusion can be drawn concerning the applicability of lanthanum-doped strontium titanate (LST), yttrium-doped strontium titanate (YST), and SMO. As a preliminary indication, the dense pellet results reported by other studies for LST appear to satisfy all of the requirements for SOFC anodes, but extending the investigation to porous LST-YSZ composites would provide the necessary information to determine if LST is actually redox stable.
If any compositions are able to maintain sufficient conductivity after redox cycling when incorporated as a composite, the next step would be to assemble and test SOFC button cells containing LST-YSZ anodes. The cells should contain anodes which are 50 μm thick and a thin electrolyte in order to achieve good performance, and the cathode should be infiltrated with LSF to a loading of approximately 30 wt%. Likewise, button cells should be prepared with and without CeO$_2$-Pd catalyst to gauge the activity of LST. Following the completion of the LST research, similar work should commence with YST, since prior studies with YST have investigated dense samples but have also failed to consider porous composites.

Due to the fact that several loadings of SMO infiltrated YSZ slabs proved to possess reasonable electrical conductivity and thermal compatibility with YSZ, fuel cells should be assembled to test the actual performance of SMO anodes. The cells should contain 20 wt% SMO infiltrated YSZ anodes calcined at 1200 °C which are 50 μm thick, an electrolyte which as thin as is practical, and a cathode which contains LSF to foster the formation of O$_2^-$ anions. Additionally, half of the fuel cells should be infiltrated with CeO$_2$-Pd catalyst, and the other half should be prepared without catalyst to gauge the activity of the SMO. The results obtained from these tests will enable a final decision to be made for the feasibility of SMO infiltrated anode application.

In the continuing search for materials which can replace problematic Ni-YSZ cermet anodes and ameliorate several of the limitations hindering the widespread application of SOFCs, this study has sought to take steps in the direction of a practical solution. The results obtained from the body of work accumulated to this point support
the claim that SrTa$_{0.01}$Ti$_{0.99}$-YSZ and 20 wt% SrMoO$_4$ infiltrated porous YSZ slabs calcined at 1200 °C are the best compositions which satisfactorily meet the anode requirements for high electrical conductivity and redox stability. As further research determines the conductive properties and redox stability of alternative materials for SOFC anode production, a wider understanding of the mechanisms at work within the electrodes will be gained. Once cheaper and more durable materials are found which can meet the necessary requirements for use in SOFC’s, the high costs currently hindering such power systems will decrease, enabling this “cleaner” method of electricity generation to compete with traditional fossil fuel-dependent systems [2, 9, 10].
References


Figure A-1 Diagram of a possible SOFC and steam turbine combined cycle with approximate temperatures of the fluids indicated in degrees Celsius at the different stages of the process [20].
Figure A-2  Schematic for a 4.5 MW natural gas fueled pressurized SOFC system [20].

Figure A-3  Schematic for a 500 MW coal fueled pressurized SOFC system [20].
Appendix B  SrTa$_{0.01}$Ti$_{0.99}$O$_3$ Fuel Cell Performance Curves

Figure B-1  V-i polarization curves for a fuel cell with a 100 μm thick SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode infiltrated with approximately 30 wt% Pd in humidified H$_2$ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares). Solid and open symbols are power densities and voltages, respectively.

Figure B-2  Impedance spectra for a fuel cell with a 100 μm thick SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode infiltrated with approximately 30 wt% Pd in humidified H$_2$ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares).
Figure B-3  V-i polarization curves for a fuel cell with a 100 μm thick SrTa₀.₀₁Ti₀.₉₉O₃₋YSZ anode infiltrated with approximately 30 wt% Pd in humidified CH₄ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares). Solid and open symbols are power densities and voltages, respectively.

Figure B-4  Impedance spectra for a fuel cell with a 100 μm thick SrTa₀.₀₁Ti₀.₉₉O₃₋YSZ anode infiltrated with approximately 30 wt% Pd in humidified CH₄ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares).
Figure B-5 V-i polarization curves for a fuel cell with a 200 μm thick SrTa<sub>0.01</sub>Ti<sub>0.99</sub>O<sub>3</sub>-YSZ anode infiltrated with 3 wt% CeO<sub>2</sub> and 1 wt% Pd in humidified H<sub>2</sub> for 700 °C (circles), 750 °C (triangles), and 800 °C (squares). Solid and open symbols are power densities and voltages, respectively.

Figure B-6 Impedance spectra for a fuel cell with a 200 μm thick SrTa<sub>0.01</sub>Ti<sub>0.99</sub>O<sub>3</sub>-YSZ anode infiltrated with 3 wt% CeO<sub>2</sub> and 1 wt% Pd in humidified H<sub>2</sub> for 700 °C (circles), 750 °C (triangles), and 800 °C (squares).
Figure B-7  V-i polarization curves for a fuel cell with a 200 μm thick SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode without catalyst in humidified H$_2$ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares). Solid and open symbols are power densities and voltages, respectively.

Figure B-8  Impedance spectra for a fuel cell with a 200 μm thick SrTa$_{0.01}$Ti$_{0.99}$O$_3$-YSZ anode without catalyst in humidified H$_2$ for 700 °C (circles), 750 °C (triangles), and 800 °C (squares).
Appendix C  Thesis Defense Presentation Slides

Development of SOFC Electrodes with High Conductivity and Enhanced Redox Stability

Thesis Defense
Brandon Smith
Chemical Engineering Department
April 14, 2010

Introduction

• Disadvantages associated with conventional fossil fuel based power generation methods:
  ▫ Generate CO₂, CO, NOₓ, SOₓ, and other pollutants
  ▫ Consume non-renewable resources
  ▫ Low efficiencies

• Electrochemical fuel cells, and particularly solid oxide fuel cells (SOFCs), are promising alternative energy conversion devices for a multitude of applications

SOFC Advantages

• Reduced air pollution
  ▫ Eliminate NOₓ, SOₓ, and CO emissions
  ▫ Eliminate CO₂ emissions when operating on H₂

• Noise pollution reduction

• High efficiency (≥ 60%)

• Mechanical simplicity and scalability

• High operating temperature (600 – 1000 °C)
  ▫ Fuel flexibility
  ▫ Increased resistance to catalyst poisoning
  ▫ Potential for cogeneration systems
SOFC Operating Principles

- Oxygen enters the cathode and reacts with free electrons at active sites on the catalyst to form $O^2-$.
- The anions migrate through the cathode and across the electrolyte to the interface between the electrolyte and the anode.
- Fuel enters and diffuses through the anode towards the anode-electrolyte interface where it reacts with $O^2-$ anions.

Hydrogen Fueled SOFCs

**Elementary and Overall Electrode Reactions for a SOFC Operating on $H_2$**

**Anode:** $H_2 + O^{2-} \rightarrow H_2O + 2e^-$  \hspace{1cm} (1)

**Cathode:** $\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$  \hspace{1cm} (2)

**Overall:** $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$  \hspace{1cm} (3)
Hydrocarbon Fueled SOFCs

Overall Reaction

\[ C_nH_{2n} + 2 + \left[ \frac{(3n + 1)}{2} \right] O_2 \rightarrow nCO_2 + (n + 1)H_2O \]

SOFC Anode Requirements

- **Porosity** to enable the fuel to diffuse into the anode and for products to diffuse out
- **Electronic conductivity** to transport electrons to the external circuit
- **Ionic conductivity** so that the \( O^{2-} \) anions are able to migrate throughout the anode
- **Catalytic activity** for the oxidation of fuel

Three Phase Boundary (TPB)

- The region of the anode where the primary anode requirements meet is often referred to as the TPB
- It exists within the 10-20 \( \mu m \) thick active region along the anode-electrolyte interface
Current SOFC Anodes

- Porous Ni-YSZ cermets are used in SOFC anodes because they meet the four primary electrode requirements
  - Ni provides catalytic activity and electrical conductivity
  - YSZ contributes ionic conductivity

Limitations of Ni-YSZ Anodes

- When operating with hydrocarbon fuels, Ni catalyzes the formation of carbon filaments which lift Ni off the electrode surface and cause fracturing within the anode
- Ni-YSZ is also prone to sulfur poisoning
- Ni-YSZ anodes are intolerant of oxidation cycles due to the resulting volume expansion when Ni is oxidized

Replacement Anode Materials

- One possible solution is to replace the Ni-YSZ with an electrically conductive ceramic and a catalyst
- $n$-doped SrTiO$_3$ has been shown to possess good electrical conductivity on the order of 10-100 S/cm
- SrTiO$_3$ has a perovskite structure, and perovskites take the form ABO$_3$, where “A” is strontium and “B” is the titanium
- $n$-doped SrTiO$_3$ are ceramic materials which have had a portion of the strontium or titanium atoms replaced with other elements
A and B-site Doped Perovskites

Redox Stability

- The doped perovskites must usually be subjected to a high temperature pre-reduction step to achieve the good conductivities which have been observed in the literature.
- The high electrical conductivity achieved from the pre-reduction step can be lost during the oxidation and reduction cycles encountered during SOFC operation.

Preceding Studies

- Prior attempts have been made to determine which dopant materials result in high electrical conductivity.
- A-site doped SrTiO₃:
  - LaₓSr₁₋ₓTiO₃ (LST) has been explored in a study conducted by Marina, Canfield, and Stevenson, in which maximum conductivities of 16 and 360 S/cm were observed at 1000 °C for samples sintered in air and H₂, respectively.
  - YₓSr₁₋ₓTiO₃ (YST) has been explored by Kolodiazhny and Petric, and a maximum conductivity of 100 S/cm was observed for pre-reduced samples at 800 °C.
### Preceding Studies

- **B-site doped SrTiO$_3$**
  - Kolodiazhnyi and Petric have also investigated the conductive properties of SrNb$_x$Ti$_{1-x}$O$_3$ (SNT) and observed a maximum conductivity of 340 S/cm for pre-reduced samples at 800 °C.
- Previous studies have investigated the conductivity of dense samples after redox cycling, but values obtained from dense samples do not typically represent equilibrium values.
- To address this issue, the redox stability of both dense SNT samples and porous SNT-YSZ composites were examined in a study performed by Gross, et al.

### Dense Samples vs. Porous Composites

- Diffusion time is proportional to $L^2/D$.
  - “L” is the length scale for diffusion.
  - “D” is the diffusion coefficient.
- Length scales for dense samples and porous composites used in SOFC anodes are **1 mm** and **1 μm**, respectively.
  - The length scale of a dense sample is about 3 orders of magnitude larger than that of a porous composite.
  - Diffusion time will be six orders of magnitude longer.
- A diffusion time of **1 minute** in a porous composite corresponds to a diffusion time of approximately **700 days** in a dense sample.

### Research Goals

- Most prior research in this area has focused on achieving maximum conductivity without considering the effect of redox cycling conditions.
- Instead of focusing primarily on high conductivity, the goal of this research was the development of redox stable materials which possess and maintain **sufficient** electrical conductivities.
- This research sought to characterize the conductive properties of V, Ta, W, and Mo-doped SrTiO$_3$ materials under fuel cell operating conditions and redox cycling to determine if these materials satisfy the requirements for SOFC anodes.
Overview of Investigation Techniques

- Bulk Conductivity & Redox Stability Testing
- XRD Analysis
- Composite Conductivity & Redox Stability Testing
- TMA
- TGA
- SEM
- Fuel Cell Performance Testing

Electrical Conductivity Limits

- New materials must have a bulk conductivity of at least 1 S/cm to be an acceptable electron conductor.
- For a porous composite, the redox stable conductivity should be at least 0.1 S/cm to be considered sufficient for SOFC anodes.
- Comparing the bulk conductivity of a novel ceramic to that of undoped SrTiO$_3$ in humidified H$_2$ provided a method for ascertaining the effectiveness of a particular dopant.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>0.003</td>
</tr>
<tr>
<td>650</td>
<td>0.003</td>
</tr>
<tr>
<td>700</td>
<td>0.010</td>
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<td>750</td>
<td>0.024</td>
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<td>800</td>
<td>0.043</td>
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<tr>
<td>850</td>
<td>0.091</td>
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</table>

Redox Stability Testing

- Redox stability testing was performed to establish whether the conductivity remained sufficient after redox cycling.
- Testing consisted of two oxidation-reduction cycles in air and humidified H$_2$ at 700 °C and 800 °C.
Fuel Cell Fabrication

- Anodes, electrolytes, and cathodes were prepared by tape casting slurries
- Components were punched out of the resulting films
- Lamination was employed for component assembly

SEM Microstructure Analysis

Scanning electron microscopy (SEM) micrographs of the cross section of a SOFC button cell, anode, and cathode

Fuel Cell Testing Assembly

- Electrical contacts were added to the anode and cathode
- The completed button cell was attached to the end of an alumina tube with a ceramic adhesive
- The exposed end of the ceramic tube was then fitted over a quartz reactor which directed fuel toward the anode
Experimental Setup

- The testing assembly was positioned inside a furnace with a programmable temperature controller
- \( \text{H}_2 \) and \( \text{CH}_4 \) were supplied from compressed cylinders
- A water bubbler was added to the fuel line to raise the humidity of the fuel to approximately 3% \( \text{H}_2\text{O} \)

Impedance Spectroscopy

- Electrochemical impedance spectroscopy was used to distinguish ohmic and non-ohmic losses in the fuel cells
- A sinusoidal current perturbation is imposed on the operating fuel cell, and the frequency-dependent sinusoidal voltage response is measured

V-doped SrTiO\(_3\) (SVT)

Conductivity of pre-reduced dense Sr\(_x\)V\(_{1-x}\)Ti\(_3\)O\(_9\) pellets as a function of temperature in humidified \( \text{H}_2 \) for \( x = 0.01 \) (circles), 0.05 (diamonds), 0.1 (triangles), and 0.2 (squares)
Ta-doped SrTiO$_3$ (STT)

Conductivity of pre-reduced dense Sr$_{1-x}$Ta$_x$TiO$_3$ pellets as a function of temperature in humidified H$_2$ for $x = 0.01$ (circles), 0.05 (diamonds), 0.1 (triangles), and 0.2 (squares)

STT XRD Analysis

STT-YSZ Composite Conductivity

Conductivity of sintered (open symbols) and pre-reduced (solid symbols) porous STT-YSZ composites in humidified H$_2$ for $x = 0.01$ (circles), 0.05 (diamonds), 0.1 (squares)
STT Redox Stability

Conductivity of dense STT pellets and porous STT-YSZ composites as a function of temperature in humidified H₂ after redox cycling at 700 °C and 800 °C.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>STT Pellet Conductivities (S/cm)</th>
<th>STT-YSZ Composite Conductivities (S/cm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1% Ta 5% Ta 10% Ta</td>
<td>1% Ta 5% Ta</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Humid H₂</td>
<td>9.2 7.3 2.6</td>
<td>1.2 1.3</td>
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<td>700 °C H₂ after 3 h in Air</td>
<td>1.2 4.8 0.83</td>
<td>0.63 0.48</td>
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<tr>
<td>700 °C H₂ after 6 h in Air</td>
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<td>0.71 0.57</td>
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<td>800 °C H₂ after 3 h in Air</td>
<td>1.3 1.3 0.24</td>
<td>1.1 1.0</td>
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<td>800 °C H₂ after 6 h in Air</td>
<td>1.2 1.1 0.16</td>
<td>1.2 0.98</td>
</tr>
</tbody>
</table>

STT Oxidation Temperature

Conductivity of pre-reduced porous STT-YSZ composites at 700 °C (open symbols) and 800 °C (solid symbols) after oxidation for x = 0.01 (diamonds) and 0.05 (triangles).

SEM Analysis

SEM micrograph of the inside of a SrTa₀.01Ti₀.99O₃⁻ YSZ anode pore

Backscatter image of the surface of a SrTa₀.05Ti₀.95O₃⁻ YSZ anode
STT-YSZ Anode Performance

V-i curves for a fuel cell with a 50 μm thick SrTa<sub>0.01</sub>Ti<sub>0.99</sub>O<sub>3</sub>-YSZ anode infiltrated with 3 wt% CeO<sub>2</sub> and 1 wt% Pd in humidified H<sub>2</sub> for 700 °C (circles), 750 °C (triangles), and 800 °C (squares).

Success!

- Results from the investigation of pre-reduced 1 and 5% Ta-doped STT-YSZ composites indicate that both materials possess the necessary requirements for use in SOFCs.
- SrTa<sub>0.01</sub>Ti<sub>0.99</sub>O<sub>3</sub>-YSZ composites demonstrated the highest redox stable conductivity, on the order of 1.2 S/cm, so 1% Ta-doped STT was selected as the optimum STT composition and a feasible replacement for Ni-YSZ.
- Fuel cell tests confirmed that reasonably good performance can be achieved in humidified H<sub>2</sub> for SrTa<sub>0.01</sub>Ti<sub>0.99</sub>O<sub>3</sub>-YSZ anodes infiltrated with 3 wt% CeO<sub>2</sub> and 1 wt% Pd.

**W-doped SrTiO$_3$ (SWT)**

Conductivity of sintered (open symbols) and pre-reduced (solid symbols) dense SrW$_x$Ti$_{1-x}$O$_3$ pellets in humidified H$_2$ for $x = 0.01$ (circles) and 0.2 (diamonds)

![Graph](image)

**SWT Redox Stability**

Conductivity of dense SWT pellets as a function of temperature in humidified H$_2$ after redox cycling at 700 °C and 800 °C

<table>
<thead>
<tr>
<th>Conditions</th>
<th>SWT Pellet Conductivities (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1% W</td>
</tr>
<tr>
<td>700 °C</td>
<td>Humid H$_2$</td>
</tr>
<tr>
<td>700 °C</td>
<td>H$_2$ after 3 h in Air</td>
</tr>
<tr>
<td>700 °C</td>
<td>H$_2$ after 6 h in Air</td>
</tr>
<tr>
<td>800 °C</td>
<td>H$_2$ after 3 h in Air</td>
</tr>
<tr>
<td>800 °C</td>
<td>H$_2$ after 6 h in Air</td>
</tr>
</tbody>
</table>

**Mo-doped SrTiO$_3$ (SMT)**

Conductivity of sintered (open symbols) and pre-reduced (solid symbols) dense SrMo$_x$Ti$_{1-x}$O$_3$ pellets in humidified H$_2$ for $x = 0.01$ (circles), 0.2 (diamonds), and 0.4 (triangles)

![Graph](image)
SMT XRD Analysis

XRD patterns for SMT with x = 0.01, 0.2, 0.4, and 0.6 and standard patterns for SrTiO$_3$ and SrMoO$_4$.

SrMoO$_4$ (SMO)

- SrMoO$_4$ was the only phase contributing to the high conductivity of the SMT samples so an investigation of SMO was performed.
- A study exploring SrVO$_3$ reported a 40% increase in volume upon oxidation to SrVO$_4$.
- Calculations for the oxidation of SrMoO$_3$ to SrMoO$_4$ also revealed a 40% increase in volume, which is incompatible with other SOFC components.
- Infiltration of SMO into porous YSZ slabs was employed to circumvent this obstacle.
- Infiltrating SMO into the pores of a sintered slab and onto the YSZ infrastructure provided adequate space for expansion inside the pore without compromising the integrity of the substructure.

SMO Infiltrated Porous YSZ Slabs

Composite fabrication by impregnation (Gross, et al. 2007)
SMO Infiltrated Porous YSZ Slabs

Target loadings for SMO infiltrated porous YSZ slabs

<table>
<thead>
<tr>
<th>Percent of Total Pore Space Containing SMO (vol%)</th>
<th>Percent of Solids (vol%)</th>
<th>SMO Weight Percent (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>7.0</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>9.5</td>
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<tr>
<td>10</td>
<td>15</td>
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</tr>
<tr>
<td>12</td>
<td>18</td>
<td>14.5</td>
</tr>
<tr>
<td>16</td>
<td>24</td>
<td>19.5</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>24.0</td>
</tr>
</tbody>
</table>

SMO XRD Analysis

- SMO oxidized to SrMoO$_4$
- SMO reduced to SrMoO$_3$
- SMO re-oxidized to SrMoO$_4$
- SMO re-reduced to SrMoO$_3$

Standard SrMoO$_4$ pattern
Standard SrMoO$_3$ pattern

SMO XRD Analysis

- YSZ slab infiltrated with ≈20 wt% SMO
- YSZ
- Bulk SrMoO$_4$ powder

Intensity (a.u.) vs. 2θ (deg.)
SEM Particle Size Analysis

SEM micrograph of a YSZ slab infiltrated with 19.0 wt% SMO, calcined at 1000 °C, and reduced at 800 °C

SEM micrograph of a YSZ slab infiltrated with 20.5 wt% SMO, calcined at 1200 °C, and reduced at 800 °C

Thermomechanical Analysis (TMA)

Thermal expansion as a function of temperature for SMO infiltrated YSZ slabs which were calcined at 1000 °C

TMA

Thermal expansion as a function of temperature for SMO infiltrated YSZ slabs which were calcined at 1200 °C
**Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis of bulk SMO powders calcined at 1200 °C

![Graph showing Thermogravimetric Analysis](image)

**SMO Conductivity**

Conductivity of SMO infiltrated porous YSZ slabs calcined at 1000 °C (solid symbols) and 1200 °C (open symbols) following a 24 hour equilibration period at 800 °C in humidified H₂

![Graph showing SMO Conductivity](image)

**SMO Conductivity**

Dense SMO pellet (diamonds)
20.2 wt% SMO infiltrated YSZ slab (squares)
Blank porous YSZ slab (triangles)
Success!

- 12 and 20 wt% SMO infiltrated YSZ slabs exhibited good electrical conductivity, redox stability, and thermal and chemical compatibility with other SOFC components.
- Results from the investigation of SMO infiltrated porous YSZ slabs suggest that 20 wt% SMO calcined at 1200 °C is the optimum loading which possesses the necessary requirements for use in SOFCs.
- Additional research is needed to reinforce this conclusion by producing button cells with SMO infiltrated anodes for performance testing.

Summary

- Specified the advantages of SOFC technology over conventional power generation methods.
- Explained the operating principles behind SOFCs.
- Described the drawbacks of the current material used in SOFC anodes.
- Summarized the results of previous studies investigating doped SrTiO$_3$ ceramic materials as a solution.
- Listed the goals of this research and described the techniques employed to produce and test samples.

Summary

- Eliminated SVT, SWT, and SMT as potential materials for use in SOFC anodes, proving that each was deficient in a critical requirement.
- Presented results to support the claim that 1% Ta-doped STT-YSZ anodes and 20 wt% SMO infiltrated YSZ slabs calcined at 1200 °C satisfactorily meet the anode requirements for sufficient electrical conductivity and redox stability.
- STT-YSZ and SMO infiltrated YSZ anodes can, therefore, be considered as replacement materials for Ni-YSZ cermets.
Acknowledgements

• Professor Gross
• Professor Csernica
• Professor Snyder
• Diane Hall
• Addison Yee
• Brian Smith
• Scott Schreiber
• Billy Holler
• Kristin Bretscher
• Jacob Pedder