

$\text{Sr}_{2-x}\text{VMoO}_{6-y}$ DOUBLE PEROVSKITES: A NEW GENERATION OF
SOLID OXIDE FUEL CELL ANODES

by

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of the requirements for the degree

of

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ABSTRACT

Fuel cells are an attractive power source due to their ability to efficiently convert chemical energy stored in fuel directly into electricity. The ability of Solid Oxide Fuel Cells (SOFCs) to reform hydrocarbons at the anode provides for fuel flexibility, an advantage over other types of fuel cell technologies. The primary goals of this dissertation were to investigate the limitations of the currently used anode cermet material, synthesize a double perovskite material ($\text{Sr}_{2-x}\text{VMoO}_{6-y}$) without these limitations and investigate the electrical conduction properties of this mixed ionic and electronic conductor (MEIC) in a SOFC anode environment.

The electronic current density limitation of a Ni-YSZ anode was determined through the development of a computer simulation and use of experimental data. The electronic current density distribution for nickel particles in a Ni-YSZ anode was calculated via a Monte-Carlo percolation model. Experiments were performed to determine the failure current densities of thin nickel wires in a SOFC anode environment. The results show a current density limitation of Ni-YSZ anodes that is not expected with MEIC anodes.

A MEIC anode material, $\text{Sr}_{2-x}\text{VMoO}_{6-y}$, was synthesized and characterized using a variety of techniques. The expected MEIC nature of this perovskite material eliminates a potential anode limitation, while adding other benefits over Ni-YSZ. X-ray diffraction (XRD) was used to verify crystal structure. In contrast to the trace amounts of secondary insulating phases found through XRD, XPS shows a high percentage (85-90%) of these secondary phases at the surface.

The electrical conductivity of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ was found to exceed that reported for Ni-YSZ anodes in a typical SOFC anode environment. Polycrystalline $\text{Sr}_{1.9}\text{VMoO}_{6-y}$ samples exhibited higher electrical conductivity than that reported for SrMoO_3 polycrystalline samples, making it a candidate for being the highest electrical conducting oxide known. These conduction values were only measured after specific thermal treatments in a reducing atmosphere. These treatments reduced secondary surface phases, $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 , into their more conducting counterparts, SrVO_3 and SrMoO_3 . Vanadium and molybdenum valence state XPS fitting parameters for primary and secondary phases are reported.

CHAPTER ONE

INTRODUCTION TO DISSERTATION

Fuel cells are an attractive power source due to their ability to cleanly and efficiently convert chemical energy stored in fuel directly into electricity. The ability of Solid Oxide Fuel Cells (SOFCs) to reform hydrocarbons at the anode [1] provides for fuel flexibility, an advantage over other types of fuel cell technologies.

One of the most prevalent SOFC anode materials is a cermet in which the metal and ceramic phases provide distinct properties to the overall electrode function [2,3]. These cermets consist of a composite of nickel, selected for its catalytic and electronic conductivity properties, and an oxygen ion conductor, such as yttrium stabilized zirconium oxide (YSZ). Cermet anode performance relies on percolating networks of nickel particles, YSZ particles and open pores to provide electronic conduction/catalytic activity, oxygen ion transport and gas transport respectively. The anode reaction is confined to the spatial sites, called triple phase boundaries (TPB), where these three phases are in contact. The reliance on a TPB is a fundamental limitation of a composite anode.

Ni-YSZ anodes experience performance degradation over time due to the migration and agglomeration of nickel particles during SOFC operation [4,5]. The result is a decrease in the length of the TPB, a measure of the active anode region, as well as an increase in ohmic resistivity due to loss of connectivity in percolating nickel networks. An image of a nickel fuel electrode before and after high temperature exposure to

hydrogen is seen in Fig. 1. The overall impact of agglomeration and migration is a decrease in performance and lifetime of the SOFC anode.

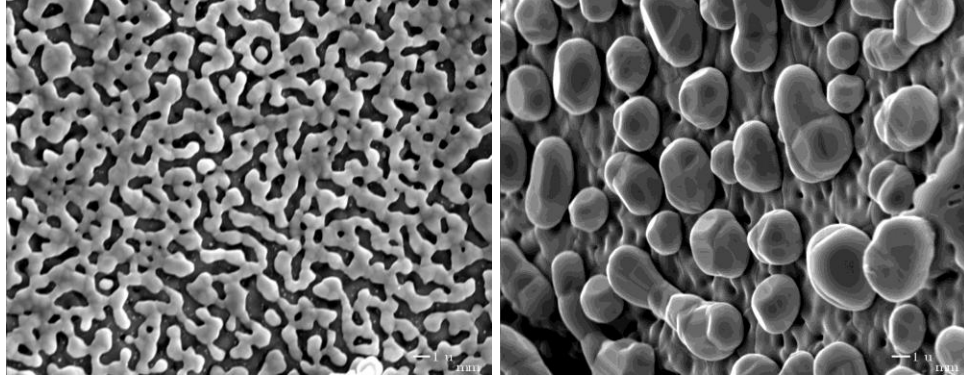


Fig. 1. Left: As prepared percolating networks of Ni metal in a fuel electrode. Right: Discontinuous and agglomerated Ni metal in a fuel electrode after 5 hrs in hydrogen at 850 °C

The mechanism for nickel migration and agglomeration is not fully understood [6], but may be partially associated with joule heating from electronic current in the percolated nickel networks within the anode. In order to investigate this degradation mechanism a three dimensional percolation model was developed to simulate a Ni-YSZ anode. The model was used to calculate the current density distribution for nickel particles in the anode. Experiments with thin nickel wires in a SOFC anode environment were performed to determine the current density that would cause failure of connectivity due to melting. The calculation and experiment combine to define an upper limit on Ni-YSZ anode current density. This investigation is presented in Ch. 3 and as a publication in the journal Fuel Cells, titled “Electronic Current Distribution Calculation for a Ni-YSZ Solid Oxide Fuel Cell Anode”.

The confinement of anode active area to the TPB, the upper limit of anode current density and fragile nature of nickel networks are consequences of the use of two solid phases in the anode, one for electron transport and one for oxygen transport. A material capable of both electron and ion transport could replace the traditional cermet structure [7,8], eliminating these fundamental limitations of composite anodes. Replacing cermet with a single phase MEIC in a porous anode creates an active anode region over a dual phase boundary (DPB), established over the entire surface of the MEIC instead of localizing it to the TPB. Fig. 2 depicts the active regions of a TPB and DPB. A typical Ni-YSZ anode (35% Ni 35% YSZ 30% porosity) restricts electronic current to the fragile nickel networks occupying only 35% of the anode volume. A MEIC anode with the same porosity would allow electronic current to flow through 70% of the anode volume, reducing solid phase current density while increasing the robustness of conduction networks.

Double perovskite structured materials (Fig. 3) have been MEICs of recent focus in SOFC fuel cell research due to their ability to achieve high mixed ionic and electronic conduction, while exhibiting high catalytic activity [9,10,11].

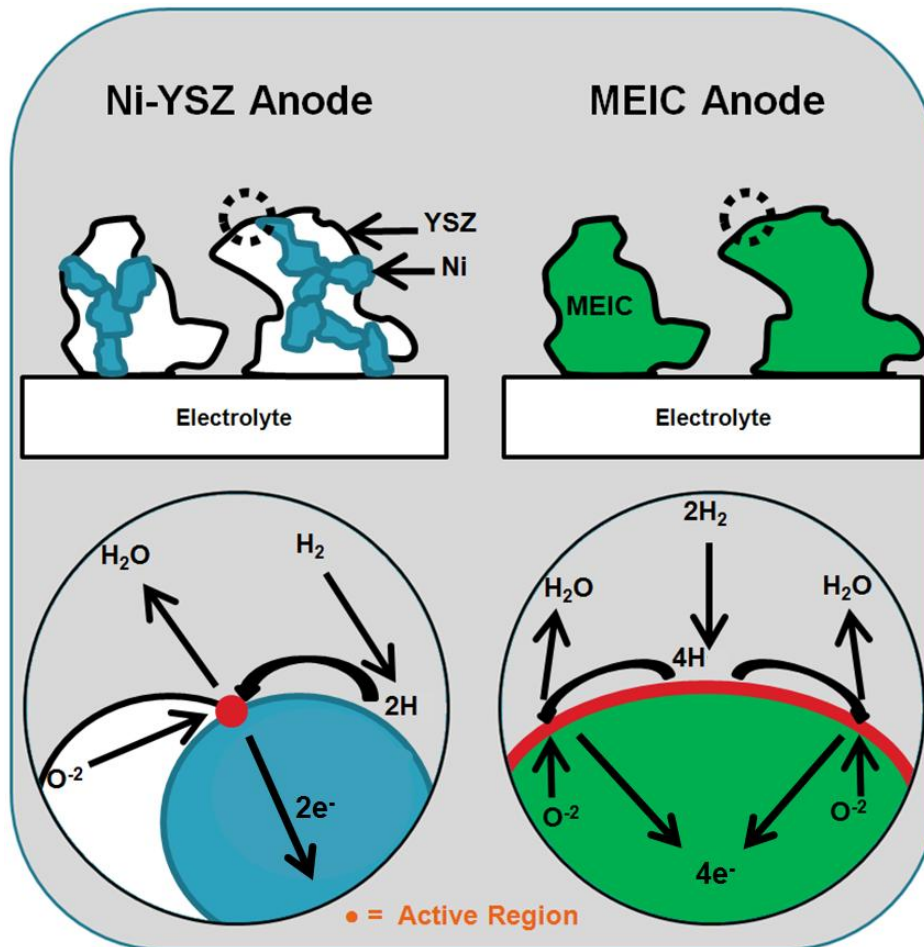


Fig. 2. A comparison of active regions for Ni-YSZ (left) and an MEIC (right)

The class of double perovskites with A-site strontium and one of the B sites occupied by molybdenum (Sr_2MMoO_6 $M'=V, Fe, Mn, Mg, Cr, Co, Ni$) have exhibited high electrical conductivity values in SOFC anode environments. Table 1 [10,12-23] summarizes the reported electrical conductivity values of Sr_2MMoO_6 and other relevant materials. Traditional Ni-YSZ fuel electrodes have exhibited conductivities of 0.1 S/cm, 40 S/cm, and 989 S/cm for nickel contents of 15, 30, and 50 solids volume percent at 800 °C in hydrogen [23]. Sr_2VMO_6 has the highest reported electrical conductivity of these

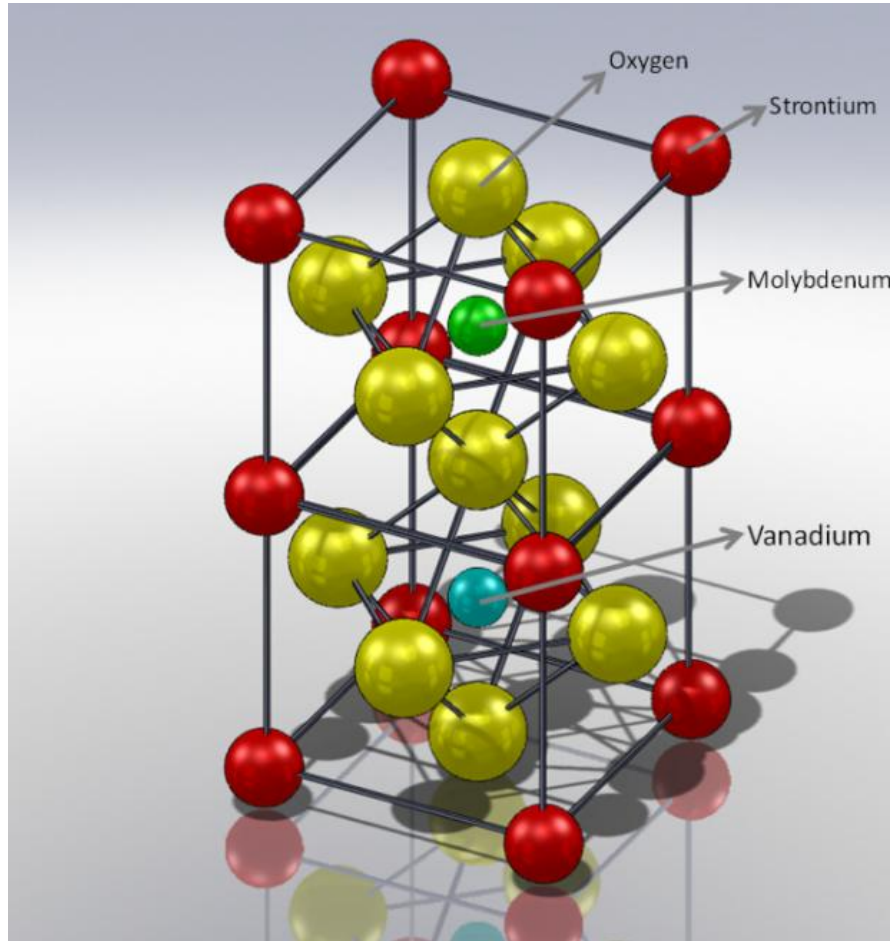


Figure 3: Representation of Sr_2VMoO_6 double perovskite structure

Sr_2MMoO_6 materials, with a value of 280 S/cm at 900 C in a reducing atmosphere. Electron band structure calculations for this material predict metallic like conduction [24]. Polycrystalline SrVO_3 and SrMoO_3 samples have reported room temperature electrical conductivities of 400 S/cm [22] and 10,000 S/cm [21] respectively, with single crystal SrMoO_3 conductivity reported at 200,000 S/cm [20]. These factors make the $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ double perovskite material interesting as a highly electrically conductive oxide material.

Table 1. Reported electrical conductivities of Sr_2MMoO_6 and other relevant materials

Composition	Conductivity (S/cm)	Temperature ($^{\circ}\text{C}$)	Environment	Reference
Sr_2VMoO_6	12000	25	Air	Karen 2006
Sr_2VMoO_6	280	900	10% H_2/N_2	Aguadero 2011
Sr_2VMoO_6	256*	800	vacuum after reduction	Fortiev 1987
$\text{Sr}_2\text{FeMoO}_6$	222*	800	H_2	Zhang 2010
$\text{Sr}_2\text{MnMoO}_6$	~ 10	800	H_2	Huang 2006
$\text{Sr}_2\text{MgMoO}_6$	~ 10	800	H_2	Huang 2006
$\text{Sr}_2\text{MgMoO}_6$	7.7*	800	5% H_2/Ar	Vasala 2010
$\text{Sr}_2\text{CrMoO}_6$	2.54*	800	5% H_2/Ar	Yin 2011
$\text{Sr}_2\text{CoMoO}_6$	1.7*	800	5% H_2/Ar	Huang 2009
$\text{Sr}_2\text{CoMoO}_6$	4.0*	800	H_2	Huang 2009
$\text{Sr}_2\text{CoMoO}_6$	0.013	800	5% H_2/N_2	Viola 2002
$\text{Sr}_2\text{CoMoO}_6$	0.08	800	15% H_2	Viola 2002
$\text{Sr}_2\text{NiMoO}_6$	0.07*	800	5% H_2/Ar	Huang 2009
$\text{Sr}_2\text{NiMoO}_6$	0.45*	800	H_2	Huang 2009
Ni-YSZ(15vol%Ni)	0.103	900	H_2	Aruna 1998
Ni-YSZ(30vol%Ni)	40	900	H_2	Aruna 1998
Ni-YSZ(50vol%Ni)	989	900	H_2	Aruna 1998
SrVO_3	100*	577	H_2/Ar mixture	Giannakopoulou 1994
SrMoO_3	10000*	27	cryostat	Hayashi 1979
SrMoO_3 (single crystal)	196000	27	Not reported	Nagai 2005

* Read from published graph

$\text{Sr}_{2-x}\text{VMoO}_{6-y}$ ($x = 0.0, 0.1, 0.2$) double perovskite materials were processed and characterized. A-site deficiency was investigated to induce oxygen vacancies and increase oxygen ion conduction. Analysis and characterization of the processing and sintering of the $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ powders/samples was performed utilizing dilatometry, X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA), Field Emission Scanning Electronic Microscopy (FESEM), micro-hardness testing, and DC conductivity testing. In general there is a lack of published material pertaining to the material structure

and properties resulting from fabrication and variations in stoichiometry. In this manner, a focus of this research was to identify the means by which these materials can be repeatedly fabricated and to understand how variations in stoichiometry and sintering temperature impact chemical phase, elemental concentration and valence states, which in turn govern important fuel electrode properties such as microstructure, coefficient of thermal expansion, mechanical strength, and electrical conductivity. This investigation is presented in Ch. 4 and as a publication in the journal Materials Chemistry and Physics, titled “Processing and Characterization of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites”.

Initial room temperature conductivity measurements for $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ ($x = 0.0, 0.1, 0.2$) double perovskite materials subsequent to sintering were much lower than expected, less than 10 S/cm compared to the 12,000 S/cm reported by Karen et al. [19]. When these materials were heated and cooled in a reducing atmosphere subsequent to sintering, a significant increase in electrical conduction was noted. XPS was used to determine elemental valence states before and after electrical conductivity measurements. XPS was also conducted before and after 30 minute anneals in 10^{-6} torr H_2 at temperatures ranging from 200-700 $^{\circ}\text{C}$. Thermal gravimetric analysis (TGA) was utilized to measure the weight loss as a function of temperature due to reduction of the $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples, in a dry reducing atmosphere (5% H_2 and 95% N_2), from room temperature to 800 $^{\circ}\text{C}$ then cooled back to room temperature. XRD was used to verify crystal structure in $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples before and after conductivity tests. The purpose of the XPS, XRD and TGA measurements was to understand the electrical conductivity behavior during thermal cycling in a reducing atmosphere. This investigation is presented

in Ch. 5 and as submitted manuscript to the Journal of Applied Physics, titled “Electrical Conductivity of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ ($x=0.0, 0.1, 0.2$) Double Perovskites”.

As mentioned this dissertation contains three main sections (Ch. 3, 4, 5) related to the limitations of current SOFC anode technology, the synthesis of a material without these limitations and understanding the electrical conductivity of this material. In Ch. 3 the electronic current density limitation of a Ni-YSZ anode was determined through the development of a computer simulation and use of data experimental data. Chapter 4 contains information on the synthesis and characterization of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$. Chapter 5 is an investigation of the electrical conductivity behavior of this material upon reduction. Definitions and descriptions of relevant terms and techniques are presented in chapter two. The conclusions from this compilation of work are discussed in Ch. 6.

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CHAPTER TWO

METHODS AND TECHNIQUES

Percolation Theory

In 1956 S.R. Broadbent and J.M. Hammersley submitted a paper regarding the study of how the random properties of a medium influence the percolation of a fluid through it. The medium and fluid discussed bear general interpretations; solute diffusing through solvent, electrons migrating over atomic lattices, molecules penetrating a porous solid, disease infecting a community, etc. Since then percolation models have been used to understand the properties of various materials.

The movement of a fluid through a lattice is determined by the space in which it is allowed to and not allowed to propagate. A lattice partially filled with randomly placed allowed spaces (site percolation model) or path lengths (bond percolation model) will develop connected clusters of various sizes. Figure 1 contrasts the two models.

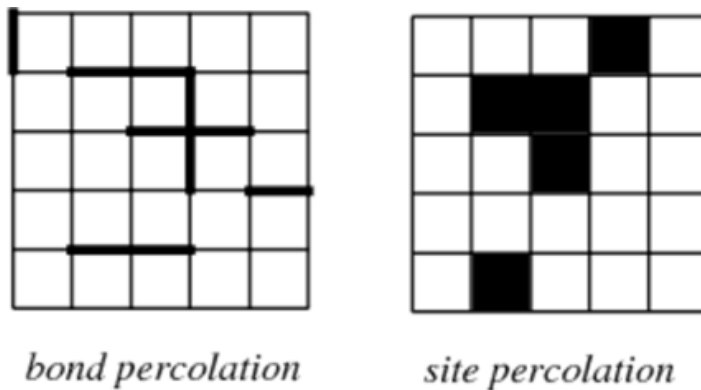


Fig. 1. Bond and site percolation models [1].

If a cluster of sites or bonds spans the volume, the cluster is said to percolate through the volume. Percolation models are used to investigate the physical properties of the randomly developed clusters. These properties are dependent on the lattice geometry as well as the occupational probability, p . The occupation probability is defined as the probability that a lattice site or bond is occupied. The variation in cluster size developed as a function of the occupation probability in a two dimensional site percolation model is presented in Fig. 2.

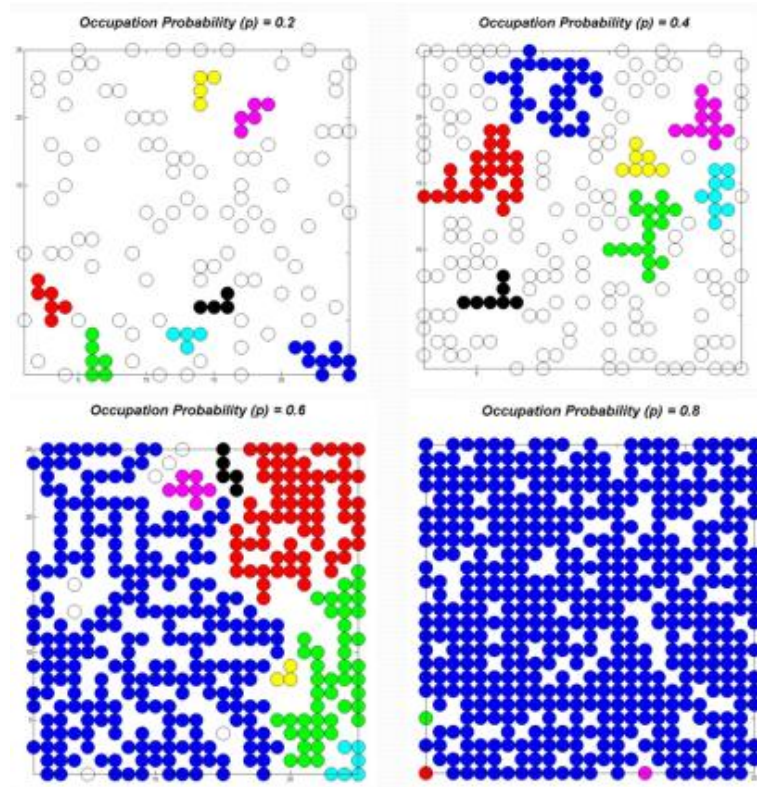


Fig. 2. Two dimensional square lattices randomly filled with different occupation probabilities (clockwise from top left $p = 0.2$, 0.4 , 0.6 and 0.8). Connected clusters have been colored. Note the increase in cluster size as occupation probability is increased.

As p is increased the average cluster size developed increases. Note that a percolating cluster, one that spans the lattice, is developed only in the $p = 0.6$ and 0.8 cases. As the lattice size tends towards infinite a critical occupational probability value, called the percolation threshold, can be identified. At an occupational probability equal to the percolation threshold, p_c , a percolating cluster will always form. Below the percolation threshold, $p < p_c$, no clusters will be found to span the lattice. The behavior of the probability for a percolating cluster to develop, percolation percent, as a function of occupation probability and lattice size can be seen in Fig. 3. For infinite lattices, the percolation threshold varies with lattice geometry and dimension as can be seen in Table 1.

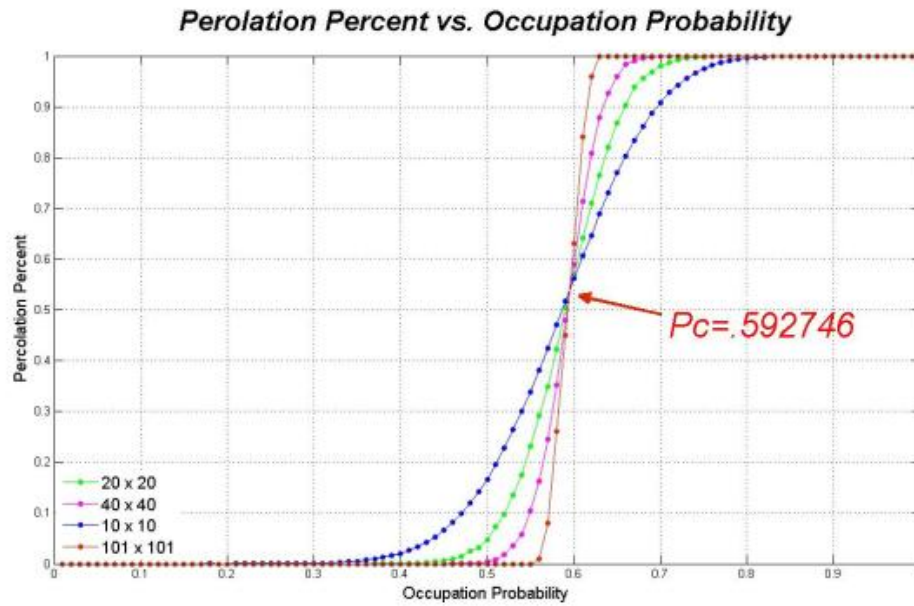


Fig. 3. Percolation percentage vs. occupational probability for different lattice sizes.

Lattice	Site	Bond
Honeycomb (2d)	0.6962	0.6527
Square (2d)	0.5927	0.5000
Triangular (2d)	0.5000	0.3473
Simple Cubic (3d)	0.3116	0.2488
Body Centered Cubic (3d)	0.2460	0.1803
Face Centered Cubic (3d)	0.1993	0.1202

Table 2. Site and bond percolation threshold values for different lattice geometries and dimensions.

A percolation threshold that is dependent on occupational probability indicates that a system is behaving in a manner consistent with percolation theory. Figure 4 shows Ni-YSZ electrical conductivity values exhibiting a threshold as a function of nickel solids loading [1]. An increase of electrical conductivity of four orders of magnitude occurs at approximately 30% solids loading of nickel in a Ni-YSZ anode. This increase in conductivity is due to the development of percolating clusters of nickel across the anode.

A site percolation model was developed representing a Ni-YSZ anode. A comparison of a two dimensional structure developed by the model and that developed for a nickel fuel electrode are shown in Fig. 5.

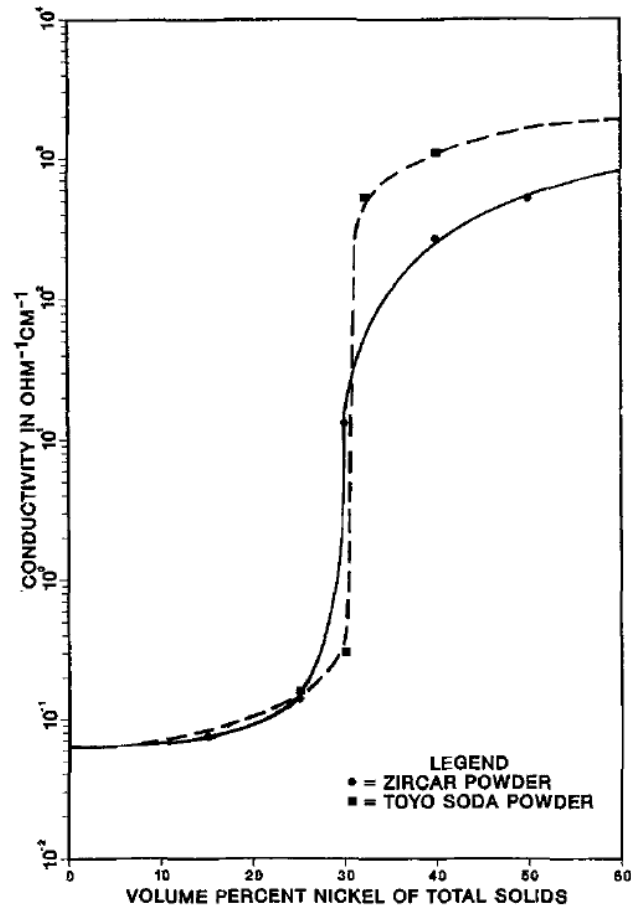


Fig. 4. Electrical conductivity vs. nickel content. Conductivity exhibits a threshold near 30% nickel solids loading [2].

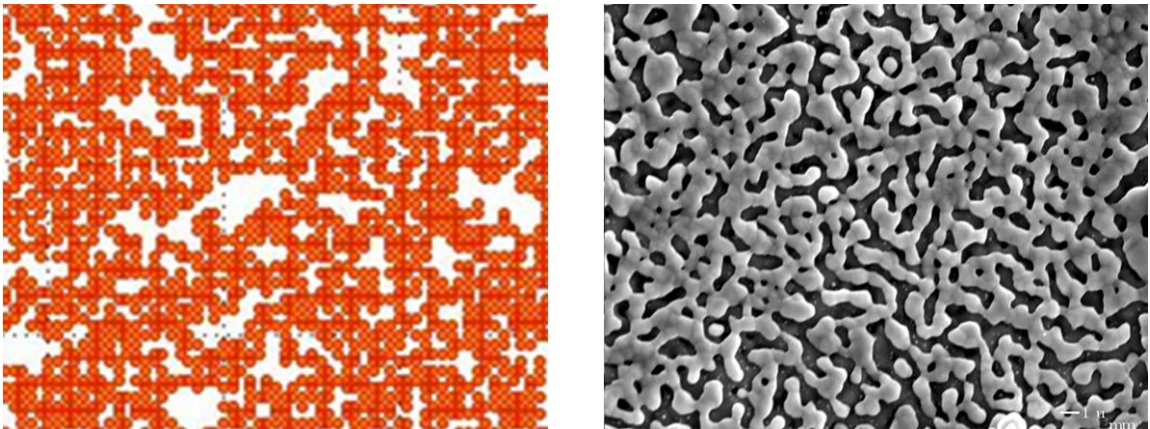


Fig. 5. Comparison of a two dimensional simulated nickel structure (left) to an actual nickel fuel electrode (right). Only percolating structures are shown on the left.

The model established a porous medium of nickel and YSZ. The bonds between percolating clusters of two million or more nickel sites were considered to be equal valued resistors. A voltage was applied to the developed nickel networks and current flow through each nickel site was calculated through the relaxation of a node voltage equation:

$$V_i = \frac{\sum_{n=1}^N V_n}{N} \quad (Eq. 1)$$

where the node or site voltage, V_i , is equal to the average of the number of occupied neighbor site, N , voltages, V_n . The conversion from nickel sites to bonds of resistors and subsequent application of an electric potential is depicted in Fig. 6.

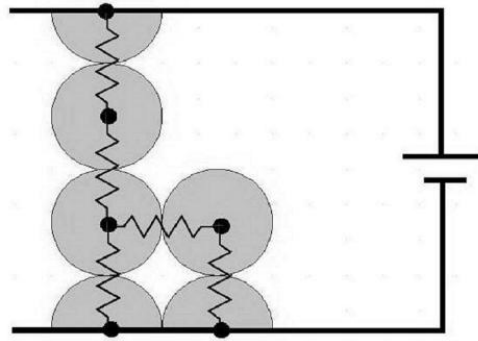


Fig. 6. Conversion of nickel sites to resistor bonds

The distribution of current density values within connected nickel particles was investigated for different modeled areas, Ni/YSZ volume ratios and anode porosities. A thin nickel wire experiment in a SOFC anode atmosphere was performed to determine current densities that cause the wire to fail due to melting. The model and experiment combine to give an upper limit on Ni-YSZ anode current density.

X-ray Photoelectron Spectroscopy

The photoelectric effect was discovered by Heinrich Hertz in 1887 and explained by Albert Einstein in 1905. Electron Spectroscopy for Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS) was later developed as an analytical tool, winning Kai Siegbahn the Nobel Prize in 1981.

The process in which an x-ray is incident on a sample and a photoelectron is emitted is depicted in Fig. 7.

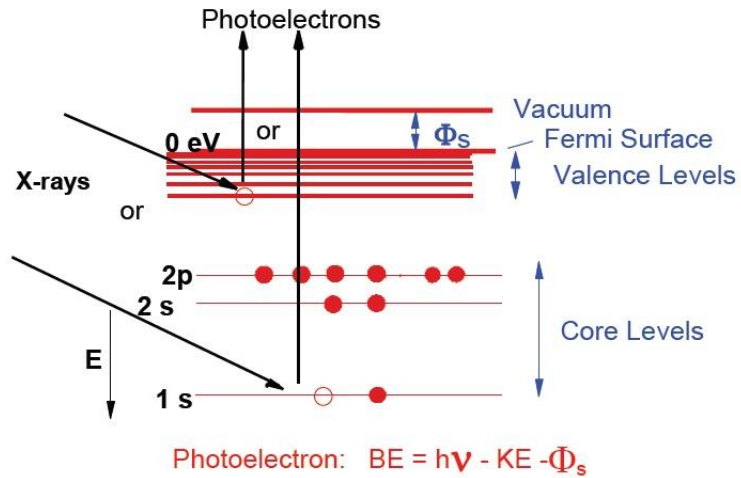


Fig. 7. X-ray stimulation of photoelectrons [4]

The binding energy (BE) of the electron can be determined from the x-ray energy ($h\nu$), electron kinetic energy (KE) and the work function of the sample (ϕ_s):

$$BE = h\nu - KE - \phi_s \quad (Eq. 2)$$

The binding energy of the electron defines the element and atomic level from which it emanated. The core level electron binding energies for U and corresponding XPS spectrum is shown in Fig. 8.

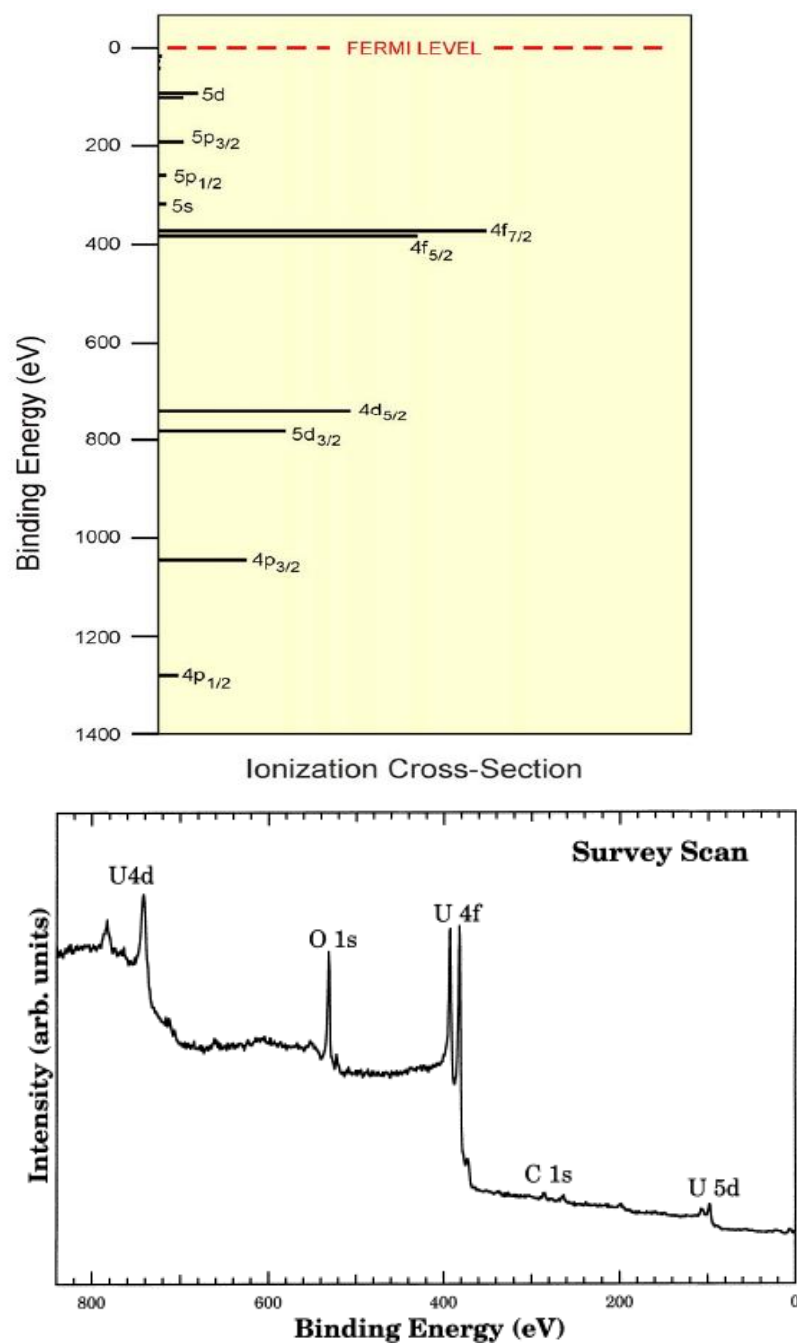


Fig. 8. Top – Core level electron binding energies for uranium are indicated on the y axis. The ionization cross section, x axis, provides relative signal strengths for the emission levels. Bottom – A XPS survey of uranium, oxygen and carbon are also present on the surface [4].

The core level signals are superimposed on a background of inelastically scattered electrons. The number of electrons that can escape from a solid without undergoing an inelastic collision decreases with the depth, x , as $\exp(-x/\lambda)$, where λ is the mean free path. Approximately 95% of the analyzed signal originates from the first 3λ , typically on the order of few nanometers.

(XPS can be used for quantitative surface analysis. This is accomplished through the use of signal area ratios and empirically developed relative sensitivity factors RSF).

The composition fraction of an element can be calculated:

$$C_x = \frac{\frac{A_x}{S_x}}{\sum_i \frac{A_i}{S_i}} \quad (Eq. 3)$$

where A_x is the signal area, S_x is the RSF for the corresponding signal region, while A_i and S_i are the signal areas and RSFs from the other elements present in the spectrum. An example of compositional analysis of a XPS spectrum is presented in Fig. 9.

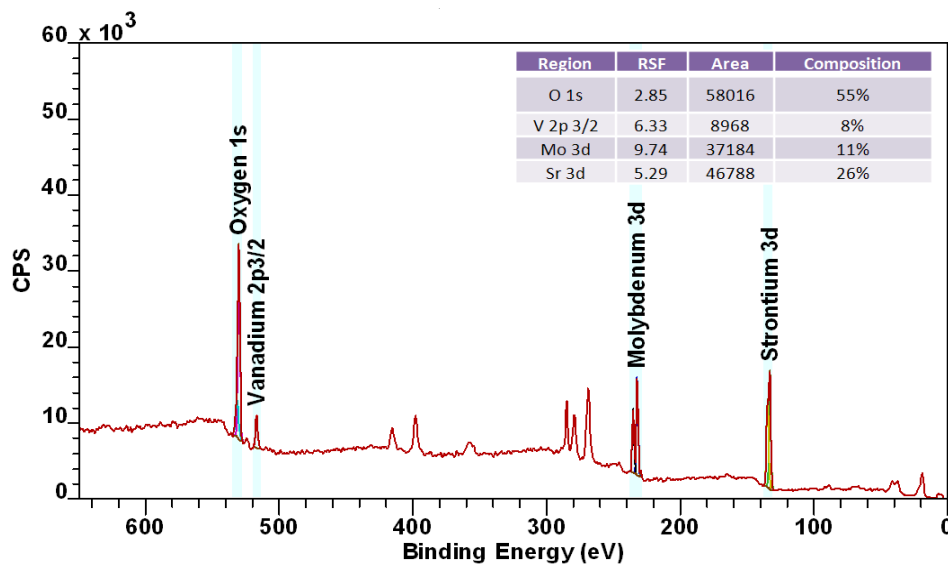


Fig. 9. Compositional analysis of a $\text{Sr}_2\text{VMoO}_{6-y}$ sample

Chemical shifts or alterations in electron binding energies occur due to changes in the valence shell contribution to the potential as a result of outer electron chemical bonding. Chemical shifts can be used to distinguish between electrons emanating from different elemental valence states. During chemical bonding, valence electrons are either drawn away or toward the nucleus depending on the type of bond, changing the potential experienced by emitted electrons. Elements that have electrons drawn away during bonding have a more positive effective potential from the nucleus, resulting in higher binding energy values. Binding energies for electrons emitted from the $3d_{5/2}$ core level for Mo, MoO_2 and MoO_3 are 227.8 eV, 230.0 eV, 232.5 eV respectively measured relative to the Fermi energy. The deconvolution of a Mo 3 d core level region spectrum into different valence contributions is presented in Fig. 10.

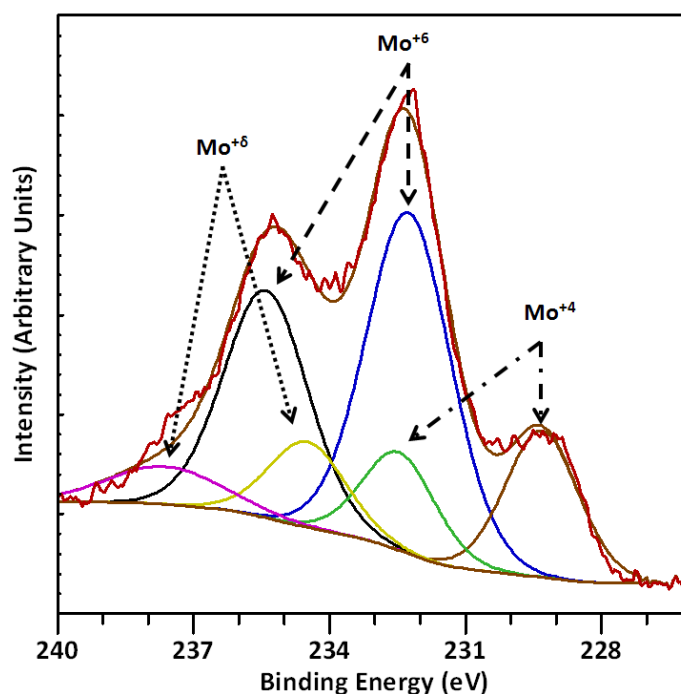


Fig. 10. Chemical analysis of a $\text{Sr}_2\text{VMoO}_{6-y}$ sample. Three separate contributions to the spectrum are identified.

Two spectral features are present for electrons originating from orbitals with orbital angular momentum, ℓ , values greater than zero. These features, called spin orbit split pairs, represent two total angular momentum quantum numbers, j . Spin orbit split pairs arise from an interaction between electron spin ($s=\pm 1/2$) and orbital angular momentum, $j = |\ell \pm s|$. The spin orbit split separation between Mo $3d_{5/2}$ and Mo $3d_{3/2}$ core lines is 3.15 eV. The number of electrons with total angular momentum, j , is equal to $2j+1$, providing for a known area ratio between the spin orbit split pairs. Mo $3d_{5/2}$ and Mo $3d_{3/2}$ signals will have an area ratio of 3:2.

In this work XPS was used to determine the surface composition and elemental valence states of $\text{Sr}_{2-x}\text{VMoO}_6$ materials. All published XPS work was conducted at Pacific Northwest National Laboratory (PNNL) in the ion beam facility. The XPS system at PNNL was desirable for a variety of features; sample heating, gas exposure system, rapid sample cooling, rapid sample loading and high signal rate. The experimental details relevant to XPS are discussed in Ch. 4 and 5.

Rutherford Backscattering Spectroscopy and Nuclear Reaction Analysis

In 1911 Rutherford's backscattering experiments with alpha particles and gold foil established the nuclear model of the atom. In 1957 Rutherford Backscattering Spectroscopy (RBS) and Nuclear Reaction Analysis (NRA) were established as materials analysis methods.

RBS is a commonly used, non-destructive analysis tool capable of providing quantitative compositional analysis of materials. The technique is simple in nature. A

beam of energetic ions is directed at the surface of a sample. The ions within the beam undergo classical elastic collisions with the atoms in the sample. A solid state detector is used to count the number of backscattered ions according to their energy. From the backscattered ion spectrum, sample composition and thickness can be determined. For an incident ion of mass, M_1 , and energy, E_0 , the backscattered ion energy, E_s , from an element of mass, M_2 , is dependent only on the scattering angle. The backscattering angle is defined as the angle between the incident ion beam direction and the detector. The backscattered ion energy is related to its incident energy by the kinematic factor, K , where $E_s = KE_0$. and K is given by:

$$K = \left[\frac{M_1 \cos \theta + (M_2^2 - M_1^2 \sin^2 \theta)^{1/2}}{M_1 + M_2} \right]^2 \quad (Eq. 4)$$

RBS spectra of uniform thick samples will exhibit edges from elastic collisions with atoms near the surface. Ions scattered from atoms below the surface will experience energy loss as they pass through the sample, ingoing and outgoing. This energy loss as a function of path length within the sample results in a background signal extending towards lower energies and originating from the step in signal formed by collisions at the surface.

The scattering cross section or probability of a backscattering event is proportional to the sample nucleus charge squared, making the RBS technique sensitive to heavy elements (Mo, Sr, V) and less sensitive to lighter elements (C and O) Fig. 11.

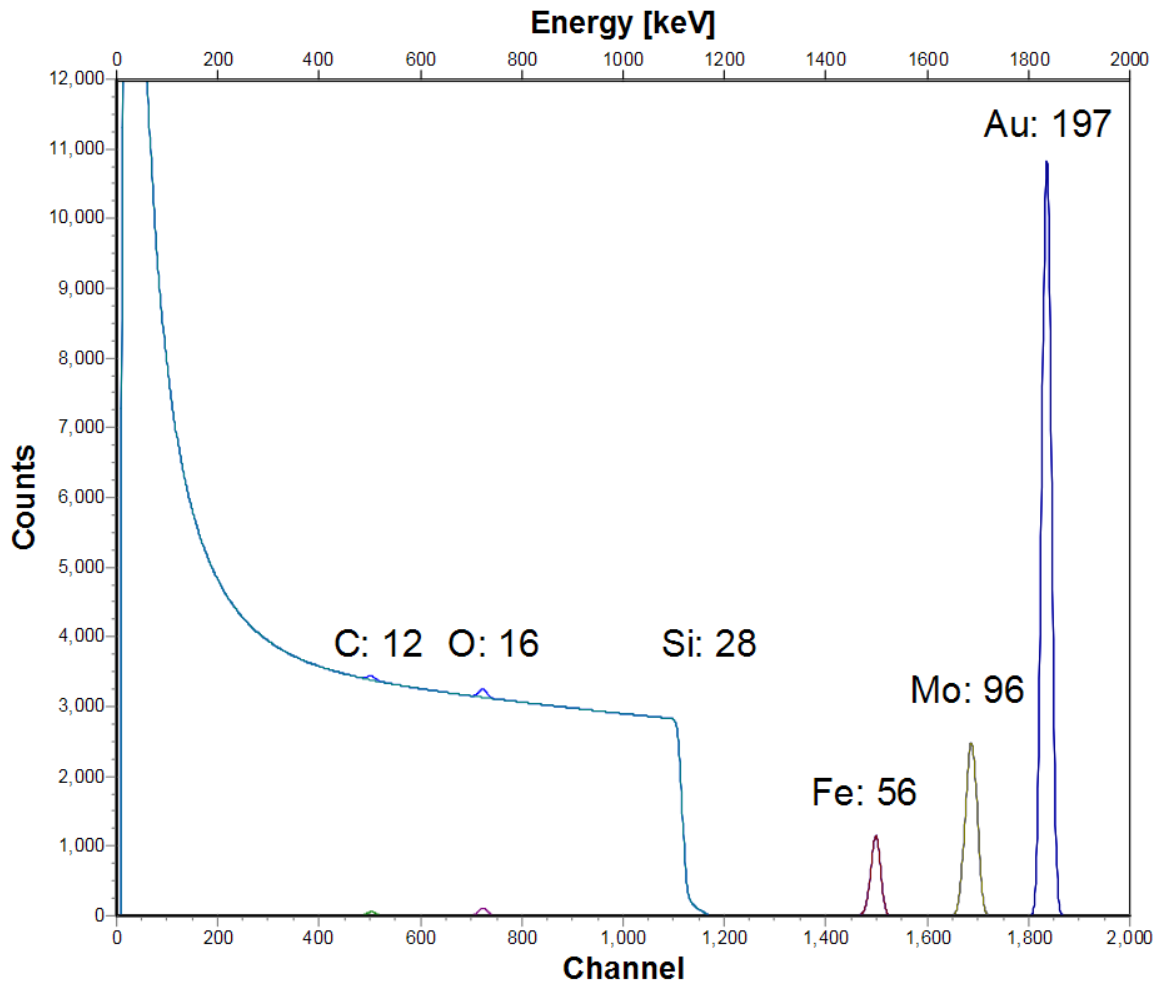


Fig. 11. The mass sensitivity of RBS can be seen in a backscattering spectrum for equal amounts, 3×10^{16} Atoms/cm², of C, O, Fe, Mo, Au on a Si substrate [5].

For detection of these lighter elements, such as carbon and oxygen, a nuclear reaction between the incident ion and target nucleus can be used. This technique is referred to as Nuclear Reaction Analysis (NRA). Unlike RBS, due to the nuclear reaction between the incident ion and nucleus, the detected energy is typically higher than the incident ion beam. This separates the signal from the RBS spectrum and associated accumulated background. Beam energies and ion species can be selected to take advantage of resonances in the nuclear reaction cross section to increase signal. Figure 12

is a region of a NRA spectrum taken with a 0.9 MeV deuterium beam. The only signal present in this region is from the $^{12}\text{C}(\text{d},\text{p})^{13}\text{C}$ nuclear reaction at about 3 MeV.

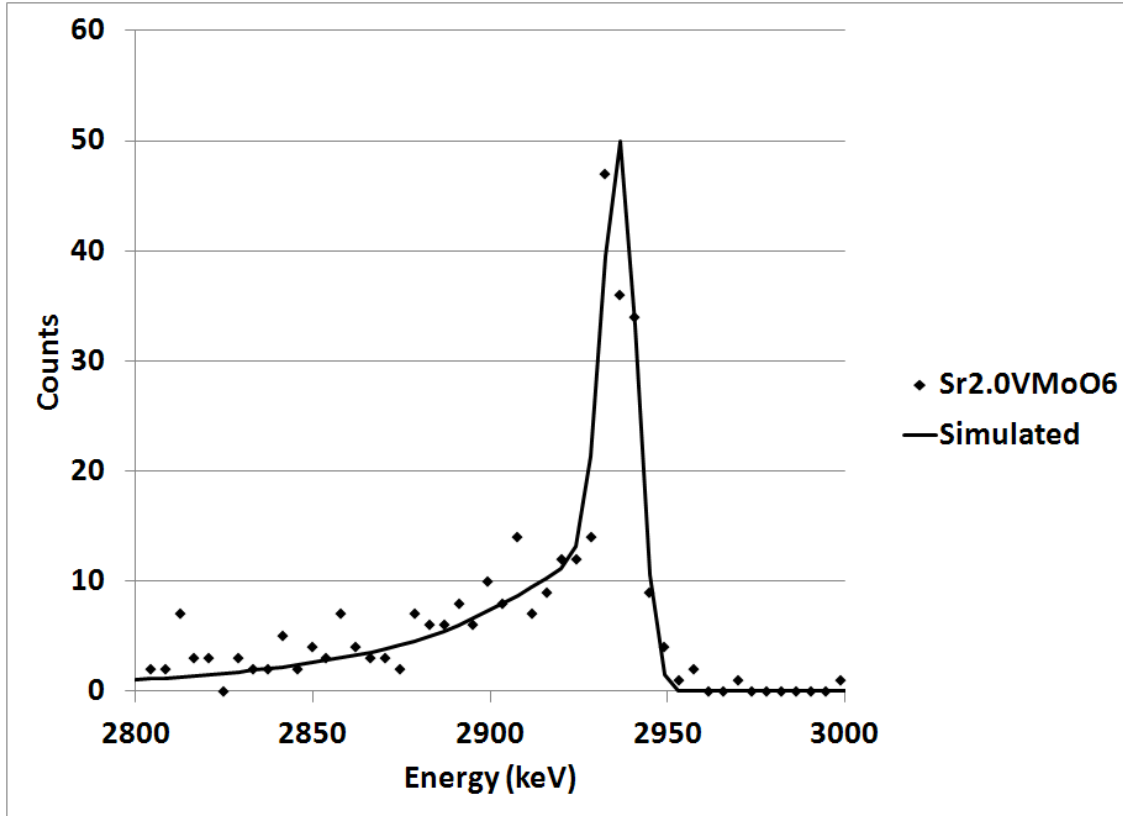


Fig. 12. 0.9 MeV D⁺ NRA spectrum of a $\text{Sr}_{2.0}\text{VMoO}_{6-\delta}$ sample sintered at 1300 °C. The spectrum indicates a 0.1 μm carbon surface layer with less than 1% carbon content in the bulk.

RBS was used to determine vanadium content while NRA was used to determine carbon content in $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples. The experimental details and procedures are discussed in Ch. 4.

X-ray Diffraction

In 1895 Wilhelm Rontgen is credited for his systematic study of x-rays. In 1914 Max von Laue was awarded the Nobel Prize in Physics for his discovery of the diffraction of x-rays by crystals. X-ray diffractometers are now commonly used to determine the crystal structure of materials.

X-ray diffractometers are based on Bragg's law:

$$2d \sin \theta = n\lambda \quad (\text{Eq. 5})$$

where n is an integer, λ is the incident x-ray wavelength, d is the spacing between lattice planes and θ is the angle between the incident ray and scattering plane. When the path length difference of two scattered waves is an integer value of the wavelength constructive interference occurs and a maximum in the diffraction pattern is observed as depicted in Fig. 13.

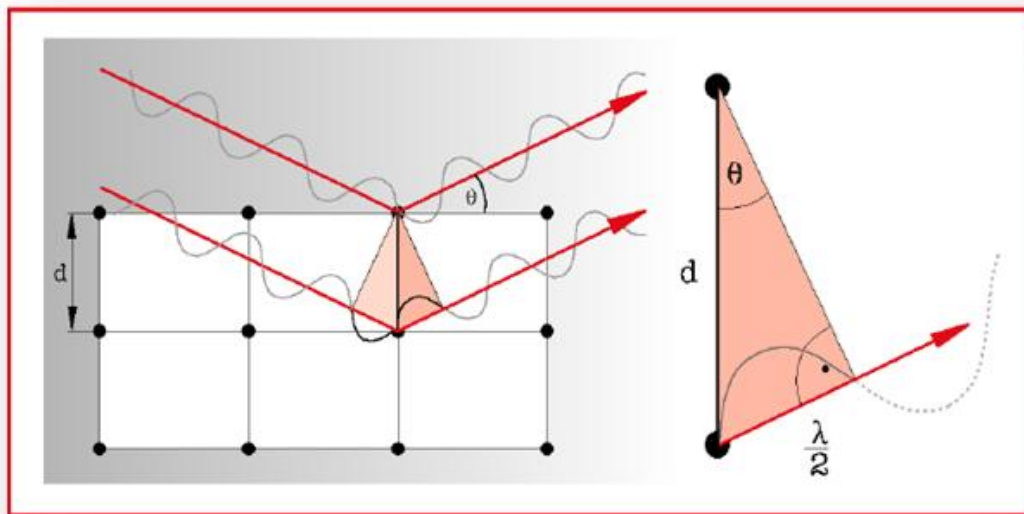


Fig. 13. Bragg diffraction conditions [6].

For a given lattice structure multiple scattering planes can be identified. Figure 14 shows a few possible d values for scattering planes in a simple cubic lattice. X-ray diffraction patterns can be used to determine crystal structure and lattice parameters of materials.

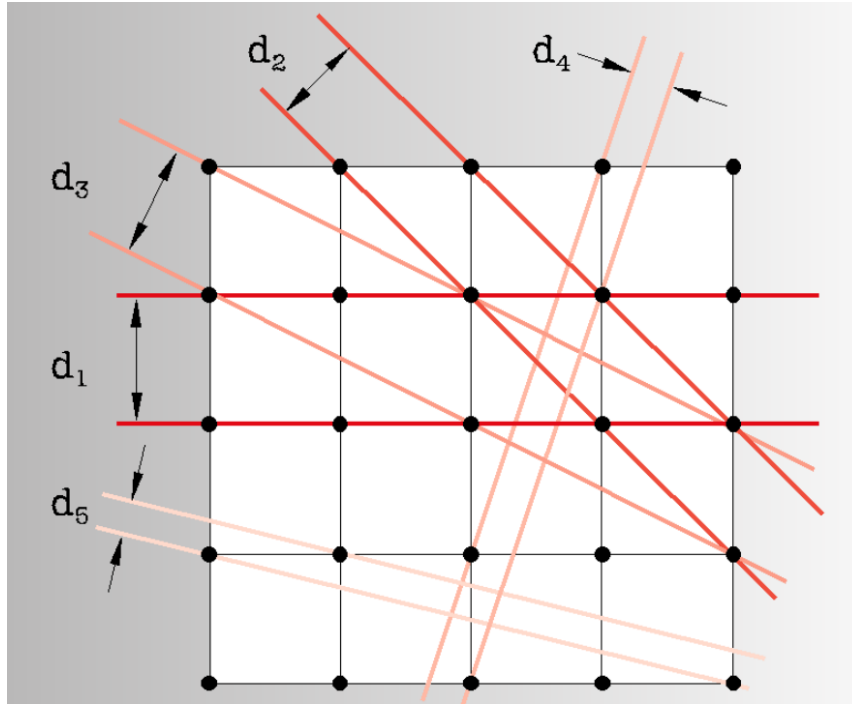


Fig. 14. d spacings for different scattering planes within a simple cubic lattice [6].

X-ray diffraction was performed on $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples and powders to identify main and secondary crystal phases. The experimental procedures and conditions are discussed in Ch. 4 and 5.

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CHAPTER THREE

ELECTRONIC CURRENT DISTRIBUTION CALCULATION FOR A NI-YSZ SOLID
OXIDE FUEL CELL ANODE

Contribution of Authors and Co-Authors

Manuscript in Chapter 3

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Contributions: Developed the model, software simulation, analyzed the resulting data, and wrote the manuscript.

Co-Author: Cameron Law

Contributions: Conducted the nickel wire experiments

Co-Author: Richard Smith

Contributions: Obtained funding for the project, assisted in interpreting the nickel wire experiment results, contributed to the writing and editing of the manuscript.

Co-Author: Stephen Sofie

Contributions: Obtained funding for the project, contributed to the editing of the manuscript, thesis advisor for Cameron Law

Co-Author: Camas Key

Contributions: Provided useful discussions related to the model and experiment and contributed to the editing of the manuscript.

Co-Author: Michael Kopczyk

Contributions: Provided useful discussions related to the model development.

Co-Author: Michael Lerch

Contributions: Provided programming assistance and useful discussions related to the model.

Manuscript Information Page

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ABSTRACT

A simulation of a nickel-yttrium stabilized zirconium oxide (Ni-YSZ) solid oxide fuel cell cermet anode was used to determine the electronic current distribution within the percolating networks of nickel particles distributed in the electrode. The anode is simulated via a Monte-Carlo percolation model and current distribution is calculated via a relaxation algorithm. Nickel particle current densities are reported as a ratio to the total anode current density allowing results to be applied to any anode current density. Calculated current distributions were drastically affected by the volume percent of nickel as well as anode porosity. Experiments were performed to determine failure current densities of thin nickel wires to establish the relationship between critical current densities and surface area or volume of the wires. Both reducing and oxidizing environments were used for these measurements over a temperature range up to 800 °C.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are a promising power generation solution due to their high efficiency and low emissions. One of the most prevalent anode materials is a cermet in which the metal and ceramic phases provide distinct properties to the overall electrode function [1, 2]. These cermets consist of a composite of nickel, selected for its catalytic and electronic conductivity properties, and an oxygen ion conductor, such as yttrium stabilized zirconium oxide (YSZ). Anode performance relies on percolating networks of nickel particles, YSZ particles and open pores to create triple phase

boundaries (TPBs) within the anode. The nickel, YSZ and pores provide transport of electrons, oxygen ions and fuel gas respectively.

A common problem with these composite anodes is the migration and agglomeration of the nickel particles during SOFC operation [3, 4]. This results in a decrease in the length of the TPB as well as an increase in ohmic resistivity as nickel metal coarsens at SOFC operating temperatures from 750 to 1000 °C [5]. The overall impact is a decreased performance and lifetime of the SOFC. The mechanism for nickel migration and agglomeration is not fully understood [6], but may be partially associated with joule heating from electronic current in the percolated nickel networks within the anode.

To investigate the possible contribution of joule heating to Ni agglomeration, we carried out a calculation of current densities for nickel particles in a composite anode via a percolation model [7]. Experiments in oxidizing and reducing environments were also performed to determine failure limits of nickel wires at elevated temperatures for several different wire diameters.

2. Model

A simple cubic matrix is developed, in similar fashion to Kawashima and Hishinuma [8], from $1\ \mu\text{m}^3$ blocks to create a volume representing a 50 μm thick anode with an area of $40000\ \mu\text{m}^2$ (200 μm x 200 μm). Typical particle diameters for nickel and YSZ in cermet anodes are 1 μm and 5 μm respectively [9]. This matrix is randomly filled with $125\ \mu\text{m}^3$ cubic YSZ particles until the desired volume percentage of YSZ has been

achieved (35-65 Ni/YSZ %). The YSZ particles are allowed to overlap to facilitate generation of irregularly structured YSZ networks. Overlapping volumes were not counted twice. The matrix is then randomly filled with $1 \mu\text{m}^3$ nickel particles until the proper volume percentage of nickel has been achieved (35-65 Ni/YSZ %). Larger size Ni particles are developed when neighboring sites are occupied by Ni. The volume percentage of porosity is achieved from the remaining unfilled space. For the simple cubic nickel lattice established within the space not occupied by YSZ, the occupational probability for nickel exceeded the percolation threshold in all cases reported. It is important to note that this is treated in a site percolation model fashion [10]. After a percolated nickel network is found, the nickel particles are converted into sites connected by resistors, or a bond percolation model [11]. This is necessary due to the fact that the nickel particles can have current going to more than one neighbor. Figure 1 is a two dimensional representation of nickel particles (circles) and the resistor network subsequently developed. The current distribution calculation presented in this paper is for a three dimensional percolation model.

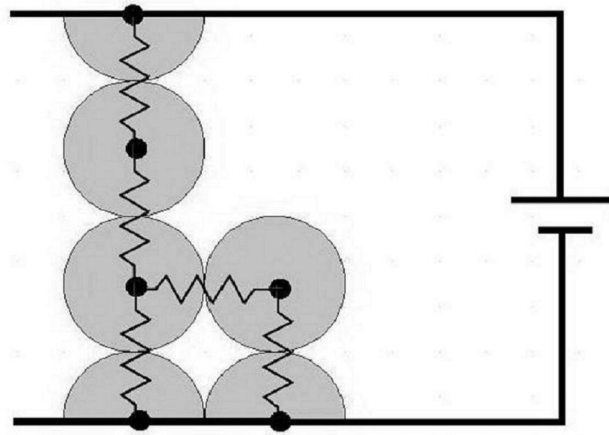


Figure 1: A resistor network developed from percolating nickel sites (circles). A potential is applied over the resulting circuit and electronic current through each site is calculated.

A voltage is applied to the nickel network(s) and node voltages are solved by an iterative relaxation of the node voltage equation:

$$V_i = \frac{\sum_{n=1}^N V_n}{N} \quad (Eq. 1)$$

where the node voltage, V_i is the average of nearest connected neighbor voltages, V_n and N is the total number of nearest neighbors. Iterations were continued until changes in all node voltages were less than 0.001 % of the anode voltage. After a sufficiently stable solution is achieved, the currents of each resistor in the bond scheme are determined by calculating voltage differences over each resistor. These currents are then appropriately scaled by setting the total current density through the model equal to unity. The current density through each node, or nickel particle, is then calculated. Values reported are a ratio of nickel particle current density, J_{ni} , to anode current density, J_a , so that the data are useful for any anode current density. A ratio of 100 would mean that nickel particles are experiencing 100 times the current density of the anode as a whole. Each time the simulation is run a unique structure of Ni, YSZ and pores is developed. Simulations were repeated and the resulting distributions averaged over multiple runs for each variable investigated: modeled area, porosity and Ni/YSZ volume ratio. This process was continued until each point in the averaged distribution changed by less than 0.001 % upon subsequent cycles. Typical simulations contained more than 2 million nickel particles.

Percolation theory has been effective for investigating electrical conduction in cermet [8]. However some key differences between the simulation and a SOFC anode should be mentioned. The simulation assumes that all current density is electronic in

nature. Computer simulations and studies of the TPB within SOFC anodes suggest that the contribution of ionic conduction to current density is minimal away from the electrolyte [12, 13]. A visual representation of current contributions in a 49.6 μm thick Ni-YSZ anode reconstructed by a focused ion beam scanning electron microscope was published by Kanno et al. [14] and shows the majority of the anode dominated by electronic conduction. In order to calculate nickel particle current densities an area is required. This area was chosen to be 1 μm^2 , the size of simulated nickel particles. The actual cross sectional area for current flow may vary from much smaller, associated with necking in spherical particles, to larger, associated with agglomerated structures in nickel networks. Nearest neighbors are identified in our calculations via a simple cubic structure; the actual packing structure may be different within a pre-conditioned and operating anode. Dees et al. report Ni-YSZ anode material becoming electronically conductive with nickel content above 21.1% of the total anode volume (32/68 Ni/YSZ, 34% porosity) [15]. Percolation theory predicts this threshold to be 31.2%, 24.8% and 20.0% for simple cubic, body center cubic and face center cubic structures respectively [16]. Our simple cubic calculation agrees with the 31.2% threshold prediction when run with the same conditions as traditional percolation simulations (Ni particles and pores of the same size, no YSZ). However the introduction of larger irregular shaped YSZ particles in the model shifts this threshold to between 21.0% (35/65 Ni/YSZ, 40% porosity) and 24.5% (35/65 Ni/YSZ, 30% porosity).

3. Experimental

To determine the maximum current for which the particles of nickel in the modeled nickel network could conduct prior to failure due to melting, specimens of nickel wire were first placed in a quartz tube of a tube furnace and brought up to temperatures of 400, 600 and 800 °C. The current was increased until failure for all examined temperatures in both oxidizing and reducing atmospheres. The reducing and oxidizing atmospheres allowed the comparison of pure nickel metal wire and nickel metal wire with an oxidized coating.

The min/max function of a multimeter, connected to the two ends of the wire, was used to record the maximum current carried prior to failure. For the tests in a reducing atmosphere, a reducing gas (5% H_2 /95% N_2) at standard conditions was introduced at a flow rate of 2 to 4 liters per hour for a minimum of 15 minutes prior to testing. For the samples to be tested at temperatures other than room temperature, the tube furnace was set to the temperature of interest which was achieved within a few minutes. The current was increased linearly at a rate of approximately 200 mA/min. This allowed an increasing current to pass through the specimen until the current dropped to zero, indicating that the nickel wire specimen failed and the circuit was no longer continuous. This method was used by Durkan et al. when studying electromigration in gold nanowires [17]. Five diameters of wire were tested: 10, 25, 50, 127 and 250 μm .

4. Results and discussion

4.1. Modeled Area Dependence

In order to ensure scaling of the model to typical anode areas the current distribution as a function of modeled area was analyzed. A range of areas was selected for simulation on a 50 μm thick anode near the percolation threshold (40 % porosity and 35/65 Ni/YSZ %). The dependence of the current density distribution on area modeled becomes larger as the percolation threshold is approached. Figure 2 shows the calculated percentage of Ni particles at each current density for several modeled anode areas as indicated in the figure. The y axis for the types of distribution plots presented can be interpreted as the percentage of total nickel particles experiencing a particular current density. For example, the 10000 μm^2 case has less than 0.4 % of nickel particles in the anode experience a current density that is exactly 10 times higher than that of the anode as a whole ($\log(J_{\text{Ni}}=J_a) = 1$). The other modeled areas have greater than 0.4 % of nickel particles experiencing current densities higher than exactly 10 times the anode as a whole. These plots give the reader information on how the distribution changes as a function of simulated parameters. The percent difference between 40000 μm^2 and 62500 μm^2 area simulations at the distribution maximum was about 1 %. For 62500 μm^2 versus 90000 μm^2 this difference was reduced to 0.6 %. This difference will continue to become smaller as modeled area increases, therefore a 40000 μm^2 model area is sufficient to allow scaling to typical anode areas. Calculations presented were performed using this area.

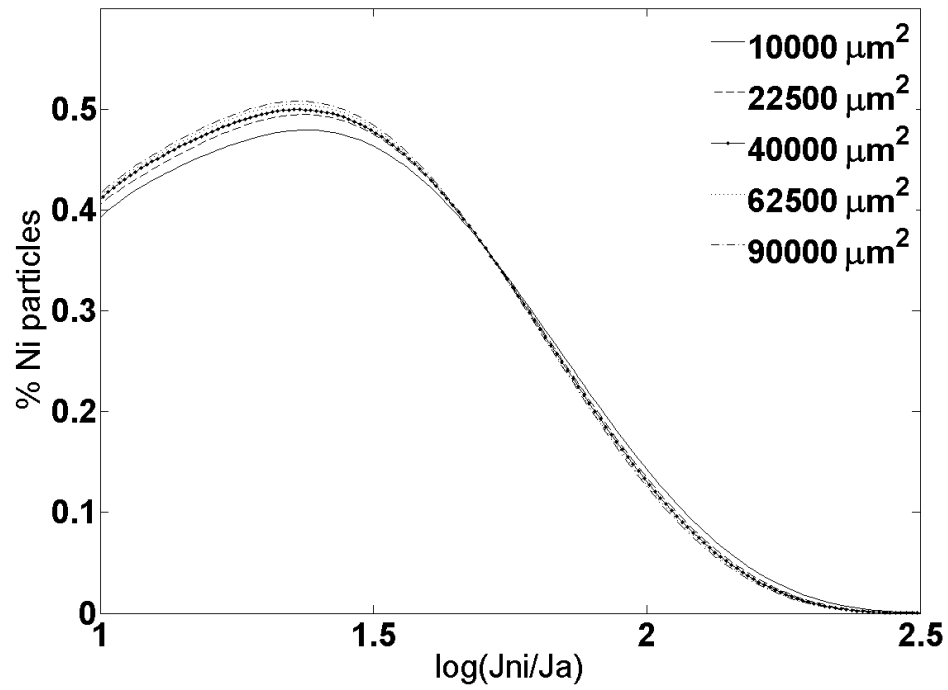


Figure 2: Percent of nickel particles at a particular current density for a 50 μm thick anode with 40% porosity and 35/65 Ni/YSZ %. $J_{ni}=J_a$ is the ratio of the nickel particle current density to the anode current density. Results are shown for several modeled areas as indicated.

4.2. Nickel/YSZ Volume Percentage Dependence

Nickel volume percentage has a large effect on the current distribution within the anode. Figure 3 shows the current distribution for Ni particles as a function of nickel content for an anode with 30% porosity.

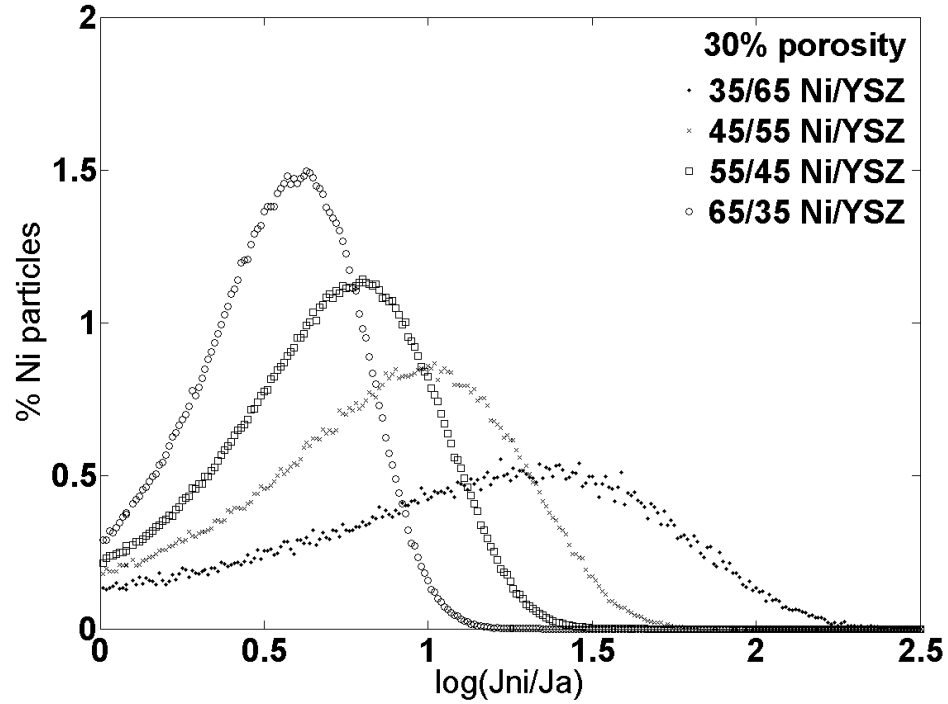


Figure 3: Percent of nickel particles at a particular current density for a 50 μm thick anode with 30% porosity. $J_{ni}=J_a$ is the ratio of the nickel particle current density to the anode current density. Results are shown for several Ni/YSZ ratios as indicated. For the 65/35 Ni/YSZ simulation, 0.13 % of nickel particles in the anode experience a current density 100 times higher than that of the anode as a whole.

Lowering nickel content from 65% to 35% causes the distribution maximum to shift from a ratio of approximately 4 to over 25 times that of the anode as a whole. The distribution also becomes wider as nickel content decreases. For the case of 35/65 Ni/YSZ with 40% porosity (not shown in Fig. 3), some nickel particles were experiencing over four orders of magnitude higher current densities than that reported for the anode as a whole. These simulation parameters placed the nickel occupation probability near the percolation threshold, and some simulations generated anodes without a percolating network of nickel across the anode. Higher nickel content of 45/55 Ni/YSZ, 40% porosity, or lower porosity of 30%, 35/65 Ni/YSZ, always produced a percolated network or networks of

nickel. In all simulations, once above the percolation threshold, the fraction of Ni particles belonging to the percolating network or networks increases with higher nickel content or lower porosity. These two simulations had nickel particles with current densities of over 250 times that reported for the anode. It was also found that large percentages, 10-40 %, of nickel particles are expected to have current densities below that of the anode as a whole. Results from a variety of parameters are summarized in Table 1.

Table 1. Percent of nickel particles above and below a multiple of the anode current density

Ni/YSZ ratio	$\frac{I_{ni}}{J_a} < 1$	$\frac{I_{ni}}{J_a} > 10$	$\frac{I_{ni}}{J_a} > 100$	$\frac{I_{ni}}{J_a} > 200$
20% Porosity				
35/65	17.61%	29.46%	0.00%	0.00%
45/55	12.35%	12.35%	0.00%	0.00%
55/45	10.39%	1.87%	0.00%	0.00%
65/35	10.00%	0.06%	0.00%	0.00%
30% Porosity				
35/65	32.00%	42.64%	1.78%	0.07%
45/55	20.67%	30.67%	0.00%	0.00%
55/45	15.24%	13.03%	0.00%	0.00%
65/35	11.25%	1.03%	0.00%	0.00%
40% Porosity				
35/65	NA	NA	NA	NA
45/55	39.10%	40.34%	2.97%	0.21%
55/45	25.09%	33.88%	0.00%	0.00%
65/35	18.96%	20.44%	0.00%	0.00%

The power generated from Joule heating can be calculated:

$$P = \frac{I^2 L \rho(T)}{A} \quad (Eq. 2)$$

where I is current, L is length, A is the cross sectional area and μ is the temperature dependent resistivity. Resistivity for metals increases with temperature. Consequently

Joule heating in nickel particles is increased with larger currents, higher temperatures and reduced cross sectional area. The inability for nickel to rapidly dissipate heat from Joule heating could contribute to nickel agglomeration.

4.3. Porosity Dependence

Porosities of 20%, 30% and 40% were analyzed for the 45/55 Ni/YSZ anode. The effect of porosity is very similar to variation of the Ni/YSZ volume percentage ratios. Due to the size difference between YSZ and nickel or pore sites the developed geometries in this section are different from the previous section causing the distributions for the same total volume fraction of nickel to be unique in each case. Figure 4 shows the current distribution as a function of porosity for an anode with 45% nickel content. Increasing porosity from 20% to 40% causes the distribution maximum to shift from a current density ratio of approximately 6 to over 30 times that of the anode as a whole. The distribution also becomes wider as porosity increases. Porosity essentially affects the total anode nickel volume percent, and thus the nickel occupation probability, in the same way as the starting Ni/YSZ material ratio. An anode with 40 % porosity, 45/55 Ni/YSZ % and a current density of 1 A/cm^2 would have 0.21 % of nickel particles experiencing current densities greater than 200 A/cm^2 .

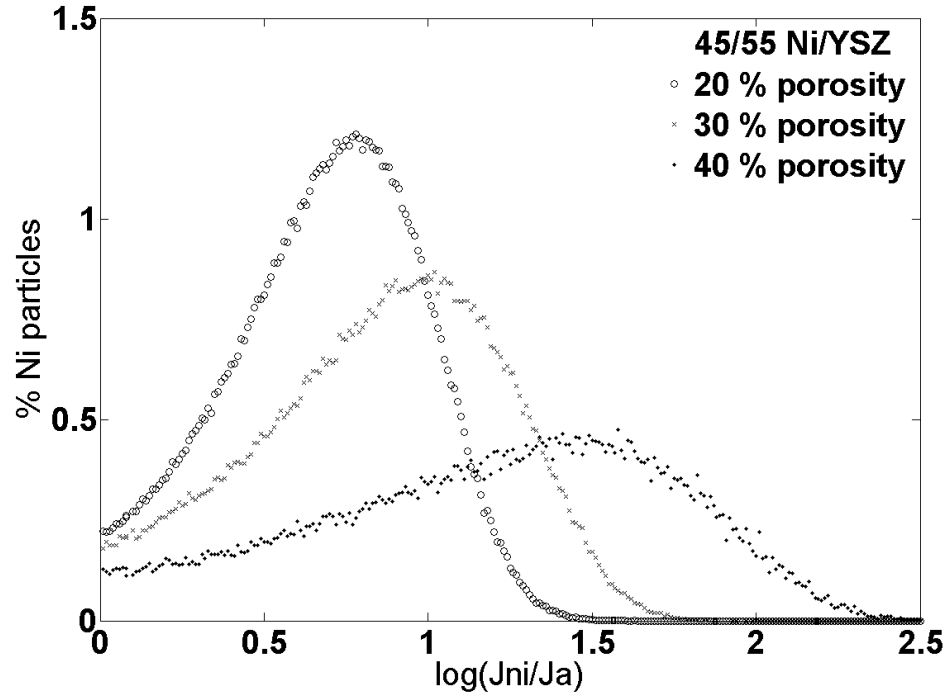


Figure 4: Percent of nickel particles at a particular current density for a 50 μm thick 45/55 Ni/YSZ anode. $J_{ni}=J_a$ is the ratio of the nickel particle current density to the anode current density. Results are shown for several porosities as indicated. For the 40 % porosity simulation, 0.16 % of nickel particles in the anode experience a current density 100 times higher than that of the anode as a whole.

4.4. Experimental Results

Three trials were conducted at each temperature for a 25 μm wire in air and in a reducing environment. The averaged results are shown in Figure 5. The critical current density (CCD) in air for this size wire decreases to 75% of the initial value with increasing temperature to 800 $^{\circ}\text{C}$. The CCD is consistently about 30% higher in the reducing environment. This is an expected result since oxidation will reduce the available

metal cross section for electron conduction. A reduction of the metallic cross section would lead to an increase in the current density within the non-oxidized nickel.

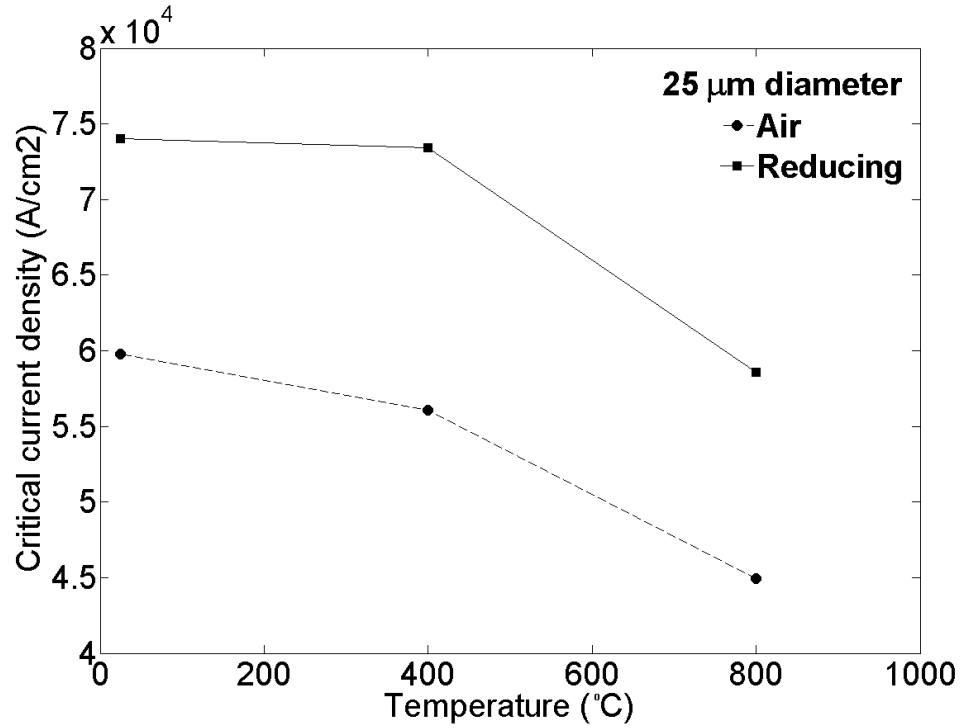


Figure 5: Temperature dependence of critical current density in reducing and oxidizing environments for 25 µm diameter nickel wire.

Figure 6 shows the measured CCD for several Ni wire diameters at different temperatures in air and in the reducing atmosphere. The CCD in air for a 10 µm wire decreased to 65% of initial value while increasing temperature from 25 °C to 800 °C with average values ranging from 88000 to 136000 A/cm². A substantially lower CCD is measured for the 25 µm wire for all temperatures studied. Further, the separation between oxidized and reduced nickel is smaller for 25 µm versus 10 µm diameter wires. The oxide thickness should not vary significantly with wire diameter and has a larger influence for the smaller diameter wires.

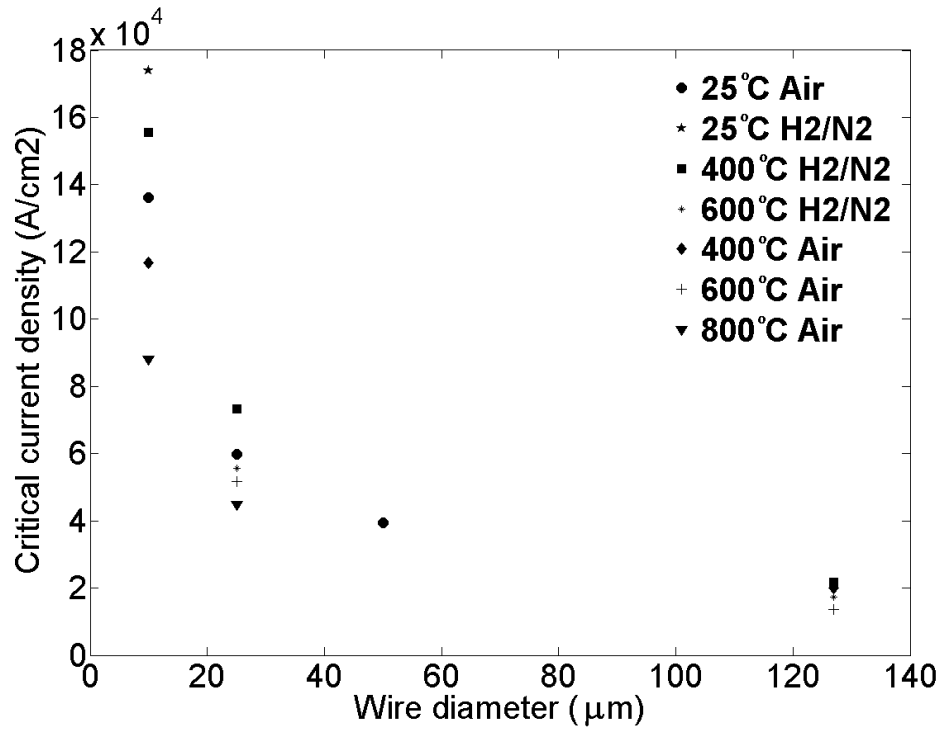


Figure 6: Critical current density as a function of wire diameter in oxidizing and reducing atmospheres for temperatures ranging from 25 to 800 °C as indicated.

A trend in decreasing CCD as a function of increasing diameter is also seen in Figure 6. One explanation for this trend could be that heat is dissipated to the gaseous environment through the surface of the wire. A large surface-to-volume ratio means that the surface area for a unit length can provide much better heat transfer by convection and radiation than a unit length with significantly less surface area [17, 18]. The surface to volume ratio increases as diameter decreases providing higher CCDs for the small diameter wires.

5. Conclusions

A percolation model of the current density distribution within a Ni-YSZ anode was analyzed for modeled area, nickel volume percentage and porosity dependence. It was found that an area of $40000 \mu\text{m}^2$ is a sufficient modeling area that ensures accurate scaling to typical anode sizes. Both nickel volume percentage and porosity had significant effects on the current distribution within the modeled anode. Low nickel content and high porosities produced anodes with nickel particles experiencing high current densities compared to the anode current density. There is a wide distribution of current densities seen by nickel particles in an anode. A large percentage of the nickel particles experience current densities below that reported for the anode.

Small percentages of nickel particles are seeing high current densities compared to the overall anode. Even though the percentages are low, the impact to anode resistance from disconnecting these particles is drastic and can lead to increased ohmic resistance and possible anode failure. The results from this calculation are not dependent on the resistive properties of nickel as can be seen from the node voltage equation (Eq. 1). Thus the results are valid for any anode made up of an electronic conductor, ionic conductor and porous networks.

The experimental study provided an average CCD of 58600 A/cm^2 for $25 \mu\text{m}$ nickel wire in a typical SOFC environment (reducing and 800°C). For typical nickel particle sizes in anodes this value should increase due to surface to volume ratios. Results from wire experiments in gaseous environments may differ from nickel embedded in a porous YSZ structure, where heat transfer to the surrounding environment will be

inhibited by the YSZ. Using the results listed in Table 1, and assuming a high current density of 10 A/cm^2 , very few nickel particles are expected to see the CCDs shown in Figure 6. Joule heating may assist nickel migration, however this experiment and calculation suggests that it is not the primary driving mechanism for nickel migration or failure of cells.

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CHAPTER FOUR

PROCESSING AND CHARACTERIZATION OF $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ DOUBLE
PEROVSKITESContribution of Authors and Co-Authors

Manuscript in Chapter 4

Author: Adam Weisenstein

Contributions: Synthesized double perovskite powders and pellets. Performed dilatometry, microhardness, and resistivity measurements. Drafted initial manuscript.

Co-Author: Nick Childs

Contributions: Performed RBS and XPS analysis. Collaborated on the drafting of the manuscript.

Co-Author: Roberta Amendola

Contributions: Assisted in performing initial XPS and collaborated on the drafting of the manuscript.

Co-Author: David Driscoll

Contributions: Performed XRD and collaborated on the drafting of the manuscript.

Co-Author: Stephen Sofie

Contributions: Collaborated on the conception and design of the investigation and provided important intellectual content to the manuscript.

Co-Author: Paul Gannon

Contributions: Collaborated on the conception and design of the investigation and provided important intellectual content to the manuscript.

Co-Author: Richard Smith

Contributions: Collaborated on the conception and design of the investigation and provided important intellectual content to the manuscript.

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ABSTRACT

In this study, the analysis and characterization of the processing and sintering of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ perovskites, where $x=0.0, 0.1$ and 0.2 , was investigated with application potential in high temperature fuel cell electrodes and electro-catalysts. $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ substrates were sintered in a reducing ($5\%\text{H}_2$ $95\%\text{N}_2$) atmosphere at 1100°C , 1200°C , and 1300°C . The x-ray diffraction patterns indicate that the double perovskite is the primary phase for $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets sintered at 1200°C and 1300°C for 20 hours; however, these pellets show a secondary phase of $\text{SrMoO}_{4-\delta}$. X-ray photoelectron spectroscopy revealed a deficiency of vanadium on the pellet surfaces, in which samples yielded surface vanadium concentrations of less than 5%. The vanadium inhomogeneity can be explained by the formation of the $\text{SrMoO}_{4-\delta}$ scheelite phase (ABO_4) due to oxygen exposure on the surface of the pellets, which indicates inward vanadium migration to the bulk, and was exhibited in redox cycling. $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets sintered at 1300°C showed the lowest resistivity at both SOFC operating temperature (800°C) and room temperature. The resistivity tests also show a semiconductor to metallic transition for all double perovskites, from heating up to 800°C to cooling down to room temperature in a reducing atmosphere, related to the reduction of Mo^{6+} to Mo^{4+} .

1. Introduction

Solid Oxide Fuel Cells (SOFCs) have demonstrated an ability to be a viable source of energy production because of the associated high efficiencies and their unique fuel flexibility, which allows the use of dirty hydrocarbons. However, SOFCs typically

utilize fuel electrodes composed of nickel and yttria-stabilized zirconia (YSZ), which contribute to many short comings. These short comings include nickel metal coarsening that leads to agglomeration and extreme sensitivity to fuel impurities. Metal catalysts operating at high temperatures, including nickel, coarsen resulting in the loss of continuous electronic pathways at SOFC operating temperatures. This can lead to a reduced triple phase boundary length, which can be detrimental to the longevity and performance of the fuel cell [1,3]. Further, studies have shown sulfur, a contaminant in most fossil fuels, to irreversibly poison the nickel catalyst [4]. To address these challenges, new materials have been sought after to replace the mixed metal and ceramic two-phase Ni/YSZ fuel electrode.

One proposed solution is to utilize a single phase Mixed Ionic Electronic Conductor (MIEC) to replace the traditional cermet structure [5,6]. Normally, current collection is limited to the nickel network being continuous throughout the fuel electrode and degrades over time with nickel metal coarsening [1]. However, the continuous pathway problem could be solved with the use of a single phase MIEC ceramic as a fuel electrode. The MIEC structure can also extend the triple phase boundary through the fuel electrode such that any exposed gas surface will facilitate electrochemical operation. This study is focused on examining the double perovskite structure, as shown in Fig. 1, because of the potential to engineer mixed ionic and electronic conduction, thermal and chemical stability, high tolerance to sulfur, and good single-cell performance in hydrogen and methane [7,8].

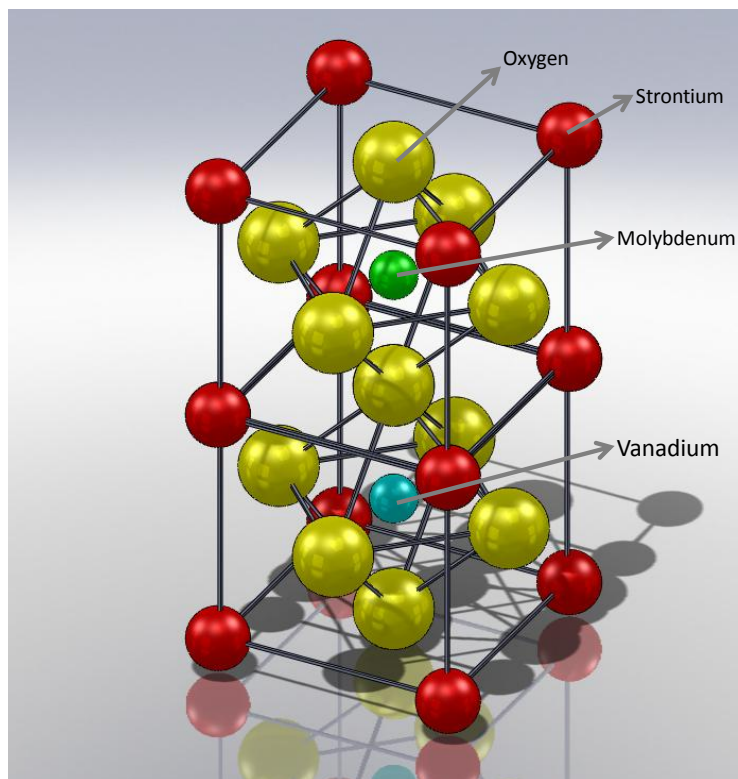


Fig. 1. Representation of $\text{Sr}_2\text{VMoO}_{6-\delta}$ double perovskite

The double perovskite structure allows the engineering of two discrete unit cells to modify properties, because its structure consists of long range repeating layers of two discrete single perovskites. In some manner this structure acts as a composite that is ordered at the atomic level. A limited number of double perovskites have been researched and utilized as fuel electrodes; such as $\text{Sr}_2\text{MnMoO}_6$, $\text{Sr}_2\text{Mg}_{1-x}\text{MnMoO}_6$, and, $\text{Sr}_2\text{Fe}_{4/3}\text{Mo}_{2/3}\text{O}_6$ and have shown electrical conductivities in the 450 S/cm, 10 S/cm, and 16 S/cm range, respectively [7,9]. The double perovskites A_2VMoO_6 , where $\text{A}=\text{Ca}$ and Sr , have also been investigated and have shown conductivities as high as 3,600 S/cm and 12,000 S/cm, respectively [10]. Traditional Ni/YSZ fuel electrodes have exhibited

conductivities of 0.1 S/cm, 40 S/cm, and 989 S/cm for nickel contents of 15, 30, and 50 volume percent [11], which is substantially less than the bulk nickel reported conductivity of 25,906 S/cm at 900°K [12]. This indicates that a double perovskite can provide adequate to exceptional electrical conductivity for a SOFC, providing that electro catalysis can also be facilitated.

$\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ perovskites, where $x=0.0, 0.1$ and 0.2 , were selected for investigation due to the significant conductivity observed in initial testing and reported catalytic activity of molybdenum and vanadium oxides [13,14]. Several multivalent double perovskites were also initially investigated (e.g. $\text{Sr}_2\text{B}^{\text{I}}\text{B}^{\text{II}}\text{O}_6$, where B^{I} represents Ni, Ti, W, Mn, and V and B^{II} represents Mo, V, and W); however the resulting conductivities were lower than 100 S/cm and as such were not further examined in this study. Analysis and characterization of the processing and sintering of the $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ powders/pellets utilizing: dilatometry, X-Ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA), Field Emission Scanning Electronic Microscopy (FESEM), micro-hardness testing, and DC conductivity testing was investigated due to the relative novelty of the double perovskite materials and the lack of published material pertaining to the material structure and properties resulting from fabrication and variations in stoichiometry. In this manner, the focus of this research is to identify the means by which these materials can be repeatedly fabricated and to understand how variations in stoichiometry and sintering temperature impact chemical phase, elemental concentration

and valence states, which in turn govern important fuel electrode properties such as microstructure, coefficient of thermal expansion, mechanical strength, and resistivity.

2. Experimental procedure

As received Alfa Aesar $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ precursor powders (SrCO_3 Stock#14343, VO_2 Stock#22957, and MoO_2 Stock#48117 at 58.3, 16.4, 25.3 weight%, respectively), were combined with 40g of deionized water, ball milled for 24 hours, and then flash frozen with liquid nitrogen. The frozen slurry was then placed into a Virtis Advantage vacuum freeze dryer, for at least 96 hours, where the liquid was sublimed from the slurry, producing well homogenized powders without agglomeration and precursor separation through traditional drying processes. The powders were then calcined in a box furnace at 1000°C for 6 hours at a heating rate of $5^\circ\text{C}/\text{min}$ and a cooling rate of $10^\circ\text{C}/\text{min}$ and then ground by hand with a mortar and pestle. Pellets for sintering in the dilatometer were fabricated by pressing the thermally treated powders in a 6.35mm (1/4in) die at 250 MPa. $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ disks were also prepared, for valence state and chemical shift analysis by XPS, by utilizing the tape casting method at a solids loading of 30%, where 25.4mm (1 in) disks were subsequently punched out of the green tapes for sintering.

Pressed pellets and tape cast disks were sintered in a reducing ($5\%\text{H}_2$ $95\%\text{N}_2$) atmosphere at 1100°C , 1200°C , and 1300°C in both a Linseis dilatometer L75 and a atmosphere controlled tube furnace (MTI, GSL 1500X), respectively, at a heating/cooling rate of $10^\circ\text{C}/\text{min}$ for 20 hours. The three sintering temperatures were determined from initial dilatometer tests performed on all of the investigated double perovskites, indicating

that the highest rate of densification occurred between 1100°C and 1300°C, which corresponds to sintering temperatures reported by Karen et al [10].

Phase characterization of the dilatometer sintered pellets was performed by X-Ray Diffraction (XRD) (Scintag X1, $\text{CuK}\alpha_1=1.5406\text{\AA}$) where an aluminum bracket was fabricated to hold the 6.35mm (1/4in) pellets for analysis. X-ray Photoelectron Spectroscopy (XPS, Physical Electronics 5600) was utilized on the same sintered pellets to determine the elemental percentages from a depth of up to 3 nanometers and to identify chemical shifts and valence states of the elemental species. The C 1s, O 1s, V 2p, Sr 2p and Mo 3d core-level regions of the XPS spectrum were recorded. The spectrometer energies were calibrated to the O 1s (530.0 eV) peak for the V 2p region and to the C 1s (284.8 eV) peak for the Sr 2p and Mo 3d regions of the spectrum. XPS was performed with a magnesium X-ray source ($\text{Mg K}\alpha = 1253.6\text{ eV}$) operated at 15 kV and 15 mA. A Shirley background was used during peak fitting and a Marquardt-Levenberg optimization algorithm was used to deconvolute peaks into various charge state contributions [15]. RBS with 2.5 MeV H^+ and 1.2 MeV He^+ ion beams was used to determine bulk compositional analysis of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ samples sintered at 1300°C. NRA with a 0.9 MeV D^+ beam was used to determine carbon content through the $^{12}\text{C}(\text{d,p})^{13}\text{C}$ nuclear reaction. The H^+ and D^+ beams were incident on the samples at 7° from normal with a scattering angle of 150°, and the He^+ was incident normal to the sample with a scattering angle of 165°. The integrated charge for the H^+ , He^+ and D^+ spectra was 80 μC , 48 μC and 40 μC respectively. Simulation of measured spectra was performed with the software program SIMNRA [16].

Scanning electron microscopy (FE-SEM Zeiss SUPRA 55VP) was utilized at 1000x for each pellet and these microstructures were then analyzed in binary image processing software ImageJ, where the pictures were converted to a binary color scheme and porosity was evaluated. Dilatometer tests were performed on all of the $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets sintered from 1100°C to 1300°C to determine the double perovskite sintering characteristics. $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets sintered at 1300°C were also redox tested in a Linseis dilatometer L75 to observe the ability of the double perovskites to reduce and oxidize at 800°C in three different oxygen partial pressures. The redox cycle testing consisted of alternating between forming gas (95% N_2 /5% H_2), nitrogen, and air at one hour intervals. SEM was used to investigate the microstructure of the redox cycled double perovskites.

A LECO microhardness tester with a test load of 200 gram-f was used to conduct Vickers hardness tests on the sintered pellets to identify the relative strength of the materials relative to the sintering process. Multiple measurements were made on the surface of the pellets and then the theoretical yield strength was estimated and averaged. DC conductivity tests were performed on the double perovskite sintered pellets by connecting silver wire leads to sintered pellets via silver paste using a 4-probe measurement technique utilizing an Agilent 34420A Nano Volt Meter. The samples were then clamped into a stainless steel fixture with electrical insulating alumina plates and placed inside a tube furnace for which a controlled atmosphere could be introduced. Resistivity tests were then performed on all sintered pellets, heating from 20°C to 800°C and then cooling to room temperature, in a reducing environment (5% H_2 and 95% N_2).

The non-invasive XRD, XPS, RBS, hardness testing, and resistivity tests were performed on the dilatometer sintered pellets, prior to the invasive investigation of the microstructure.

3. Experimental results

3.1 X-Ray Diffraction (XRD)

The XRD patterns for the double perovskites are shown in Figs. 2, 3, and 4. The XRD patterns in Fig. 2 indicate that the double perovskite is the main phase for $\text{Sr}_2\text{VMoO}_{6-\delta}$ pellets sintered at 1200°C and 1300°C for 20 hours; however these pellets show a scheelite-type secondary phase of ABO_4 , where A represents Sr and B represents V or Mo. The XRD pattern for $\text{Sr}_2\text{VMoO}_{6-\delta}$ pellets sintered at 1100°C for 20 hours indicates that the ABO_4 structure is the primary phase, while showing a double perovskite secondary phase. As shown in Figures 3 and 4, $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ and $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ also exhibit the double perovskite as the main phase for the pellets sintered at 1200°C and 1300°C for 20 hours, with a secondary scheelite phase. Also, $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ sintered at 1200°C shows a phase pure double perovskite. These tests indicate that the scheelite phase is reduced and the desired double perovskite $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ structure is formed as the sintering temperature increases. The presence of SrMoO_4 prompted investigation into the electrical conductivity of the phase, as described in the DC Conductivity section, where it was found to have low conductivity when compared to the double perovskite structure.

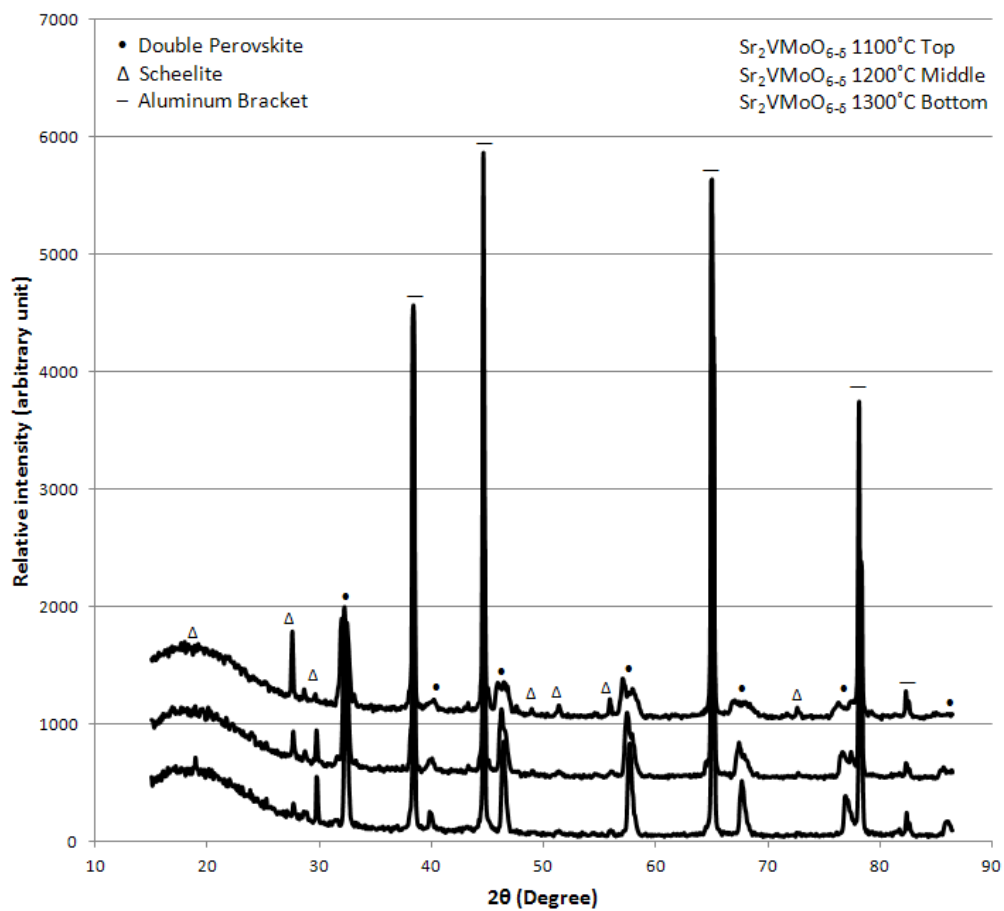


Fig. 2. XRD pattern for $\text{Sr}_2\text{VMoO}_{6-\delta}$ sintered at 1300°C, 1200°C and 1100°C for 20 hours

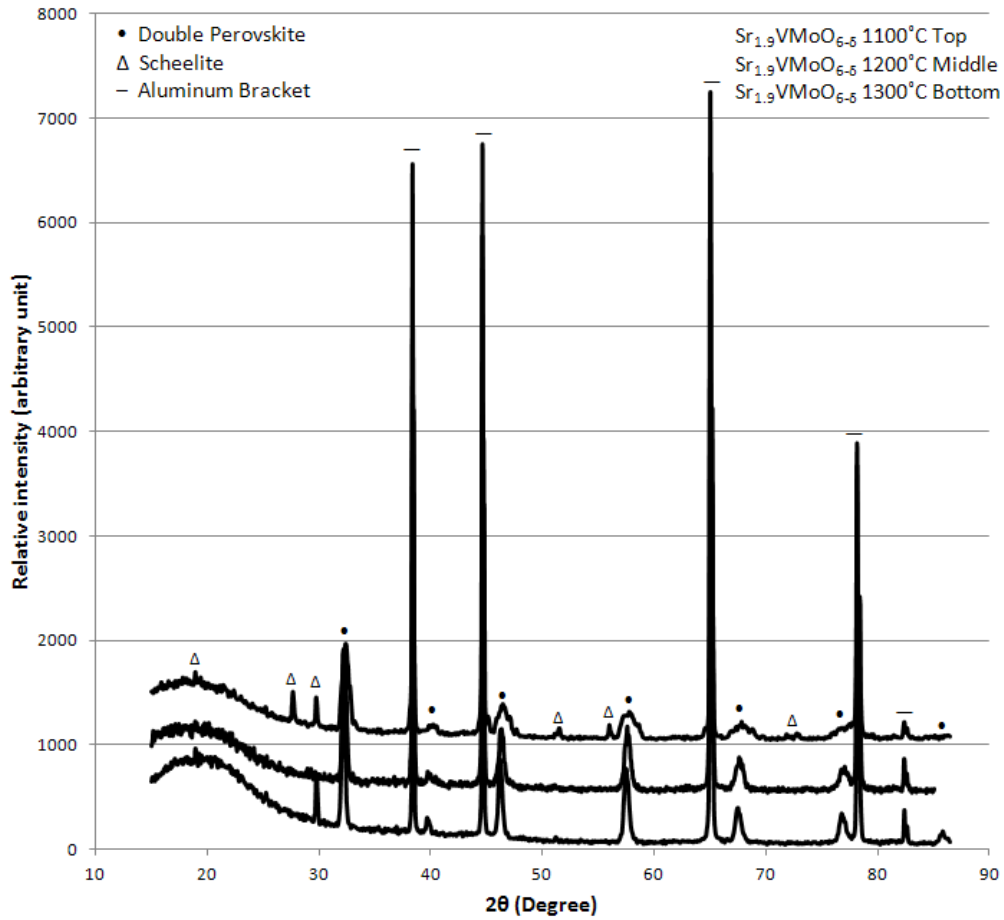


Fig. 3. XRD pattern for $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ sintered at 1300°C, 1200°C and 1100°C for 20 hours

3.2 X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS)

XPS was utilized on the sintered pellets to determine the elemental percentages at a depth of up to 3 nanometers. Figure 5 represents an XPS survey spectrum used for this compositional analysis. XPS revealed a deficiency of vanadium on the pellet surfaces, as shown in Table 1, as 8 out of 9 samples had surface vanadium elemental contents of less than 5%. The average elemental composition over all samples analyzed was found to be 24.8%, 4.2%, 11.8%, and 59.2% for Sr, V, Mo, and O, respectively.

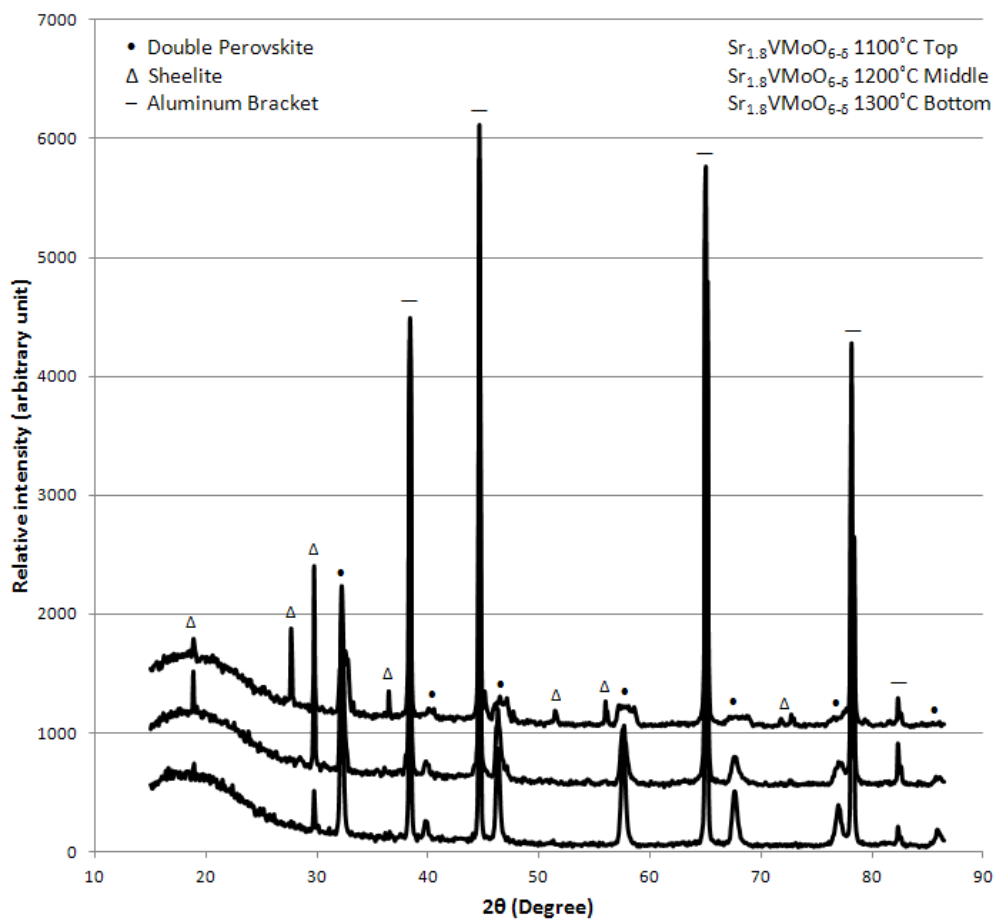


Fig. 4. XRD pattern for $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ sintered at 1300°C, 1200°C and 1100°C for 20 hours

No significant trends were identified with different starting compositions or with different sintering temperatures; however it is important to note that up to 10% error can be expected in compositional analysis via XPS.

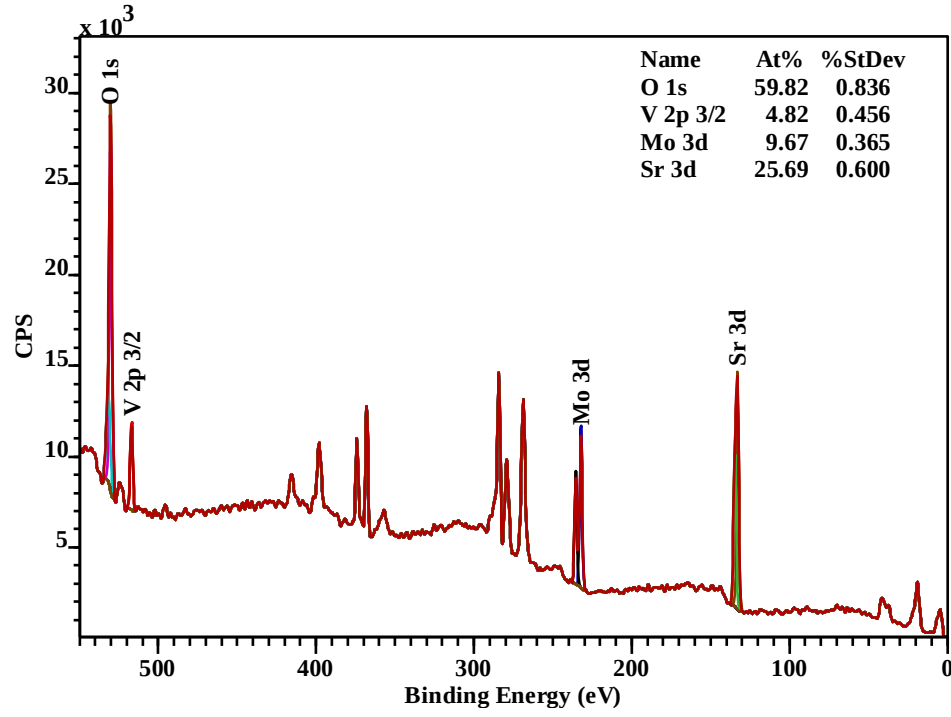


Fig. 5. XPS spectrum for $\text{Sr}_2\text{VMO}_{6-\delta}$ sintered at 1300°C 20 hours

Table 1. Elemental percentages at the surface of $\text{Sr}_{2-x}\text{VMO}_{6-\delta}$ sintered pellets as determined by XPS

$\text{Sr}_{2.0}\text{VMO}_6$	Sintering Temperature ($^{\circ}\text{C}$)	Sr(%)	Mo(%)	V(%)	O(%)
	1300	25.6	9.6	4.8	60.0
	1200	28.1	12.2	3.8	56.0
	1100	24.7	12.1	3.1	60.1
$\text{Sr}_{1.9}\text{VMO}_6$	Sintering Temperature ($^{\circ}\text{C}$)	Sr(%)	Mo(%)	V(%)	O(%)
	1300	22.2	15.4	2.7	59.7
	1200	24.4	10.4	4.5	60.8
	1100	24.7	12.9	2.4	60.1
$\text{Sr}_{1.8}\text{VMO}_6$	Sintering Temperature ($^{\circ}\text{C}$)	Sr(%)	Mo(%)	V(%)	O(%)
	1300	25.7	10.9	8.5	54.9
	1200	23.7	11.0	4.3	61.0
	1100	23.7	11.9	4.0	60.4

XPS was also used to analyze the chemical shifts and valence states of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ tape cast samples. The Sr 2p region of the 1100°C sample exhibits two phases, thought to be strontium carbonate and strontium in a perovskite-like phase, as shown in Figure 6.

The percent composition of these phases, determined by fitted area ratios of the Sr 2p_{3/2} region, is 27% and 73% for the carbonate-like and perovskite-like phases, respectively. The Sr 2p region of the 1300°C sample exhibits a main phase, 91% of the 2p_{3/2} peak, consistent with a perovskite-like phase, with the remaining assumed to be the carbonate phase [17,18]. The Mo 3d regions of both samples exhibit a mix of valence states, ranging from Mo(VI) to Mo(0). The Mo valence states for the 1300°C sintered sample are dominated by Mo(VI) and Mo(IV), 76.9% and 18.5% respectively.

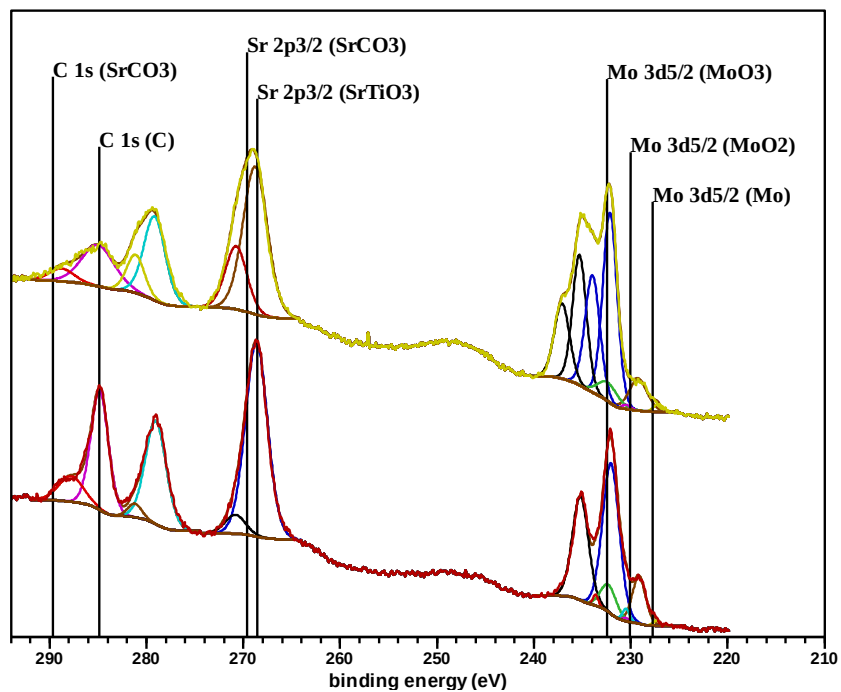


Fig. 6. Carbon 1s, Strontium 2p and Molybdenum 3d regions for $\text{Sr}_{2.0}\text{VMoO}_{6-\delta}$ tape casted samples sintered at 1100 °C (top) and 1300 °C (bottom) in a reducing atmosphere (5% H_2 /95% N_2)

The 1100°C sintered sample is also dominated by the same Mo(VI)/Mo(IV) valence states (87.7%/11.2%). The Mo(VI) state in the 1100°C samples exhibits two chemical components, one $3d_{5/2}$ component at a binding energy (BE) of 232.1 eV and another at a BE of 233.9 eV making up 53.5% and 34.2% of the total Mo $3d_{5/2}$ signal respectively [19]. At this time the authors are unable to find a similar reference to a Mo $3d_{5/2}$ peak at this higher BE and attribute it to localized sample charging. This higher BE Mo(VI) state is not present in the 1300°C sintered sample. The O1s peak for the 1100°C sintered sample was broader than the 1300°C sample, consisting of 47% at 530.0 eV and 53% at 531.8 eV. The 1300°C sample O 1s region was split between 63% at 530.0 eV and 37% at 531.8 eV. The binding energy for O 1s in perovskite oxides has been reported to be between 529.8 eV and 530.2 [20]. The 1100°C vanadium region was fit to two charge state $2p_{3/2}$ contributions, one with a BE of 517.0 eV and another with a BE of 519.0 eV, as shown in Figure 7. These are thought to be vanadium in a V(V) state (69%) and V(IV) state (31%). The 1300°C vanadium region was fit to two charge state $2p_{3/2}$ contributions, one with a BE of 516.9 eV and another with a BE of 514.0 eV. These are thought to be vanadium in a V(IV) state (90%) and V(III) state (10%) [21].

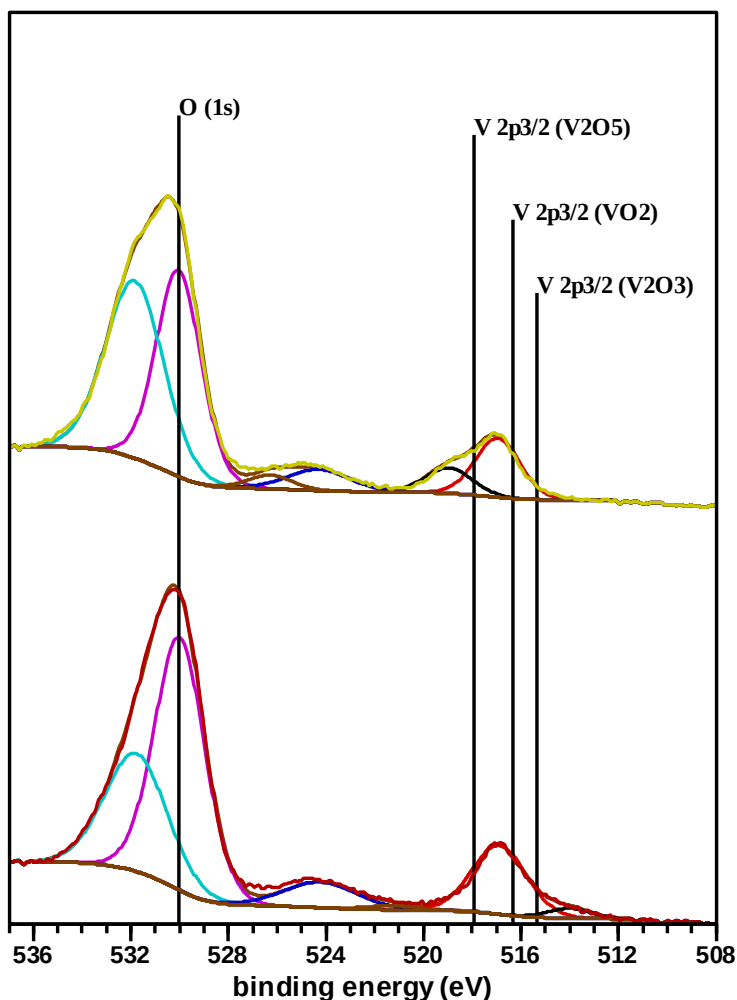


Fig. 7. Oxygen 1s and vanadium 2p regions for $\text{Sr}_{2.0}\text{VMoO}_{6-\delta}$ tape casted samples sintered at 1100 °C (top) and 1300 °C (bottom) in a reducing atmosphere (5% H_2 /95% N_2)

As shown in Table 2, RBS confirmed the bulk elemental compositions of samples were close to the starting ratios of Sr/Mo/V with the remainder being 60-60.4% O. Simulated bulk stoichiometries of $\text{Sr}_{2.0}\text{VMoO}_6$, $\text{Sr}_{1.9}\text{VMoO}_{5.9}$ and $\text{Sr}_{1.8}\text{VMoO}_{5.8}$ for SR20, SR19 and SR18 samples were in agreement with data from both H^+ and He^+ spectra. For the He^+ beam, Sr and Mo kinematic factors are 0.836 and 0.849 (0.958/0.962 for H^+ beam) respectively, making resolution between Sr and Mo concentrations difficult. A

simulated spectrum for $\text{Sr}_{2.0}\text{VMoO}_6$ along with the SR20 He^+ RBS spectrum is shown in Figure 8. The non-Rutherford O cross section for the H^+ beam is much larger than that of the Rutherford cross section of He^+ , providing a higher signal in the proton spectrum. However, simulations between 58% and 60% oxygen volume contents are within the noise of the spectrum making these contents indistinguishable. A simulated stoichiometry of $\text{Sr}_{2.0}\text{VMoO}_6$ placed on the SR20 He^+ RBS spectrum is shown in Figure 9. A large amount of pile-up is noted above the Sr/Mo edge in the H^+ spectrum due to a high beam current, but this is unlikely to affect composition simulations drastically. A simulated spectrum with a carbon content of 3.5% for the first 0.05-0.1 μm on the SR20 NRA spectrum is shown in Figure 10. The carbon content falls off to less than 1% in the bulk. The only signal present in this region comes from the $^{12}\text{C}(\text{d},\text{p})^{13}\text{C}$ nuclear reaction. SR19 and SR18 spectra showed similar surface and bulk carbon contents.

Table 2. Elemental percentages at the surface of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ sintered pellets as determined by RBS

Sample	Strontium	Molybdenum	Vanadium	Oxygen
$\text{Sr}_{2.0}\text{VMoO}_{6-\delta}$	20%	10%	10%	60%
$\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$	19.4%	10.2%	10.2%	60.2%
$\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$	18.8%	10.4%	10.4%	60.4%

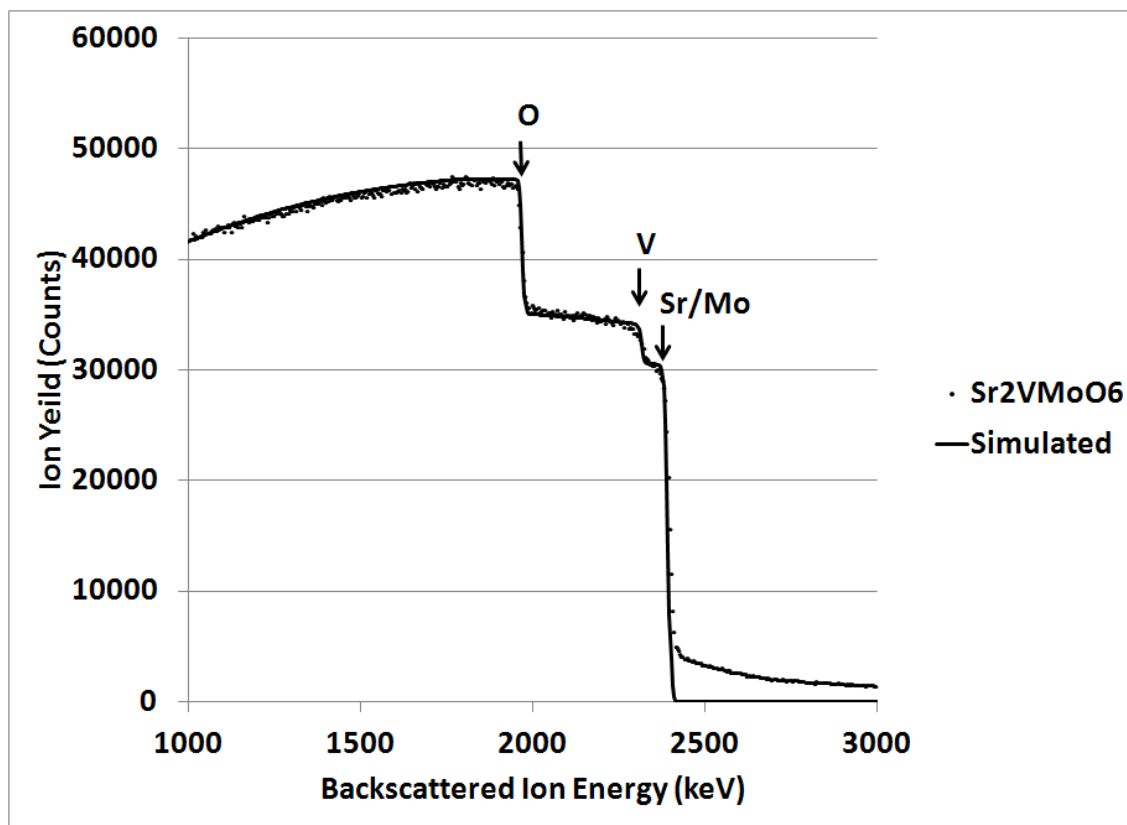


Fig. 8. 2.5 MeV H⁺ RBS spectrum of a Sr_{2.0}VMoO_{6-δ} tape cast disc sample sintered at 1300 °C. SIMNRA software was used to simulate a composition of 20% Sr, 10% V, 10% Mo and 60% O

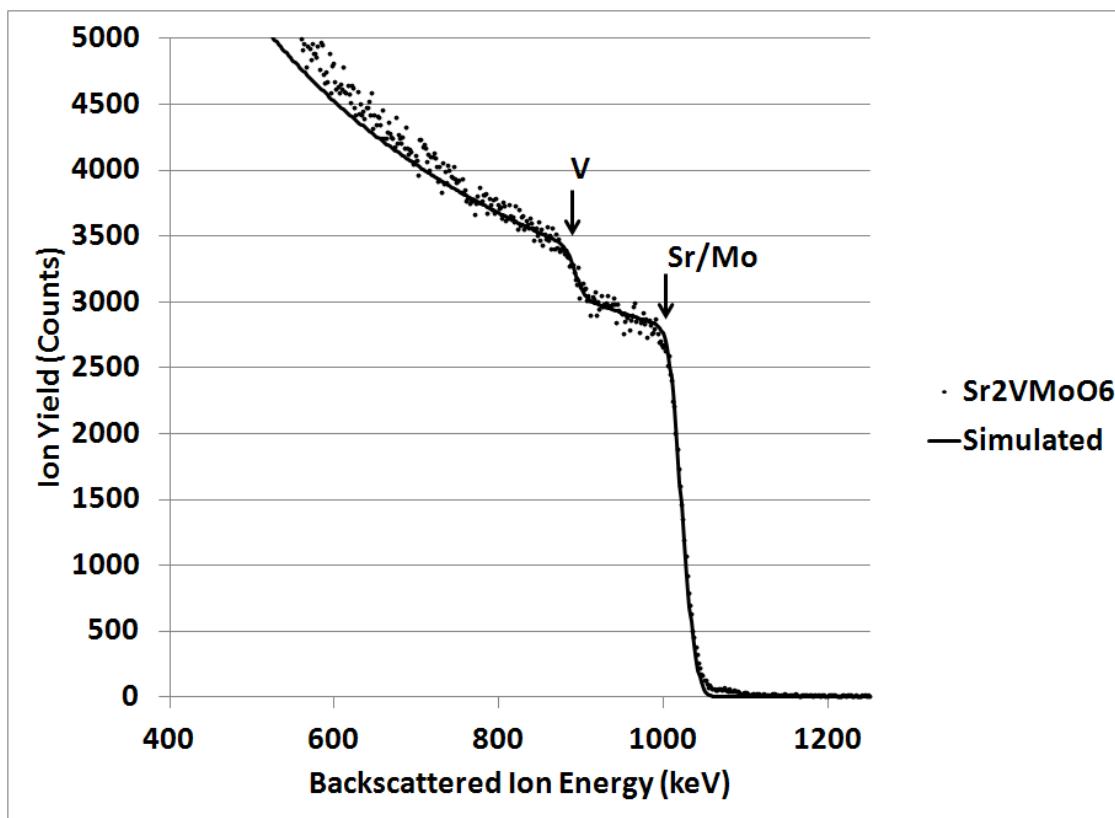


Fig. 9. 1.2 MeV He^+ RBS spectrum of a $\text{Sr}_{2.0-x}\text{VMoO}_{6-\delta}$ pressed pellet sample sintered at 1300°C . SIMNRA software was used to simulate a composition of 20% Sr, 10% V, 10% Mo and 60% O

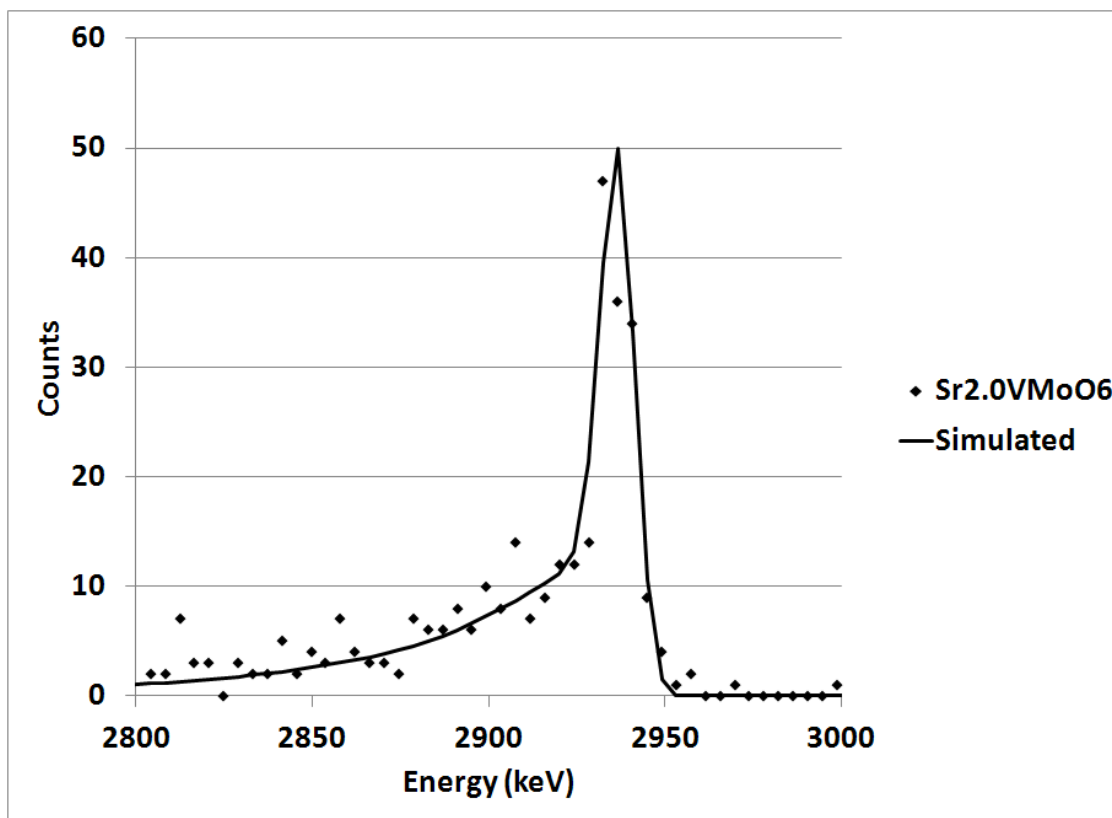


Fig. 10. 0.9 MeV D⁺ NRA spectrum of a Sr_{2.0}VMoO_{6-δ} sample sintered at 1300 °C. The spectra indicates a 0.5-0.1 μm carbon surface layer with less than 1% carbon content in the bulk

3.3 Redox Cycling

The redox cycled Sr_{2-x}VMoO_{6-δ} pellets were cross-sectioned and then analyzed in a FESEM to investigate the change in microstructure due to the cycling of oxygen partial pressures. The original (upper left) microstructure and photo (upper right) of the redox tested pellet and resulting microstructure of Sr_{1.9}VMoO_{6-δ} is shown in Fig. 11. A JEOL JSM-6100 Scanning Electron Microscope (SEM) was used for elemental mapping of the Sr_{1.9}VMoO_{6-δ} cross-section, as shown in Fig. 12. The microstructure indicates that two different layers form during the redox testing of the Sr_{1.9}VMoO_{6-δ} pellet. The

microstructure of the black colored middle section of the pellet resembles the original microstructure (bottom right); however the white colored outside section shows a high level of coarsening (bottom left). The elemental mapping of the $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ pellet indicates a vanadium rich area at the boundary of the two layers and suggests that vanadium is migrating throughout the pellet. The change in oxygen partial pressure is not a concern if the fuel cell is run in alternating power and electrolysis modes and is properly sealed, but it could affect the double perovskite adversely if exposed to air at fuel cell operating temperature, which could happen if the fuel supply is not sufficient for high fuel cell power demands [22].

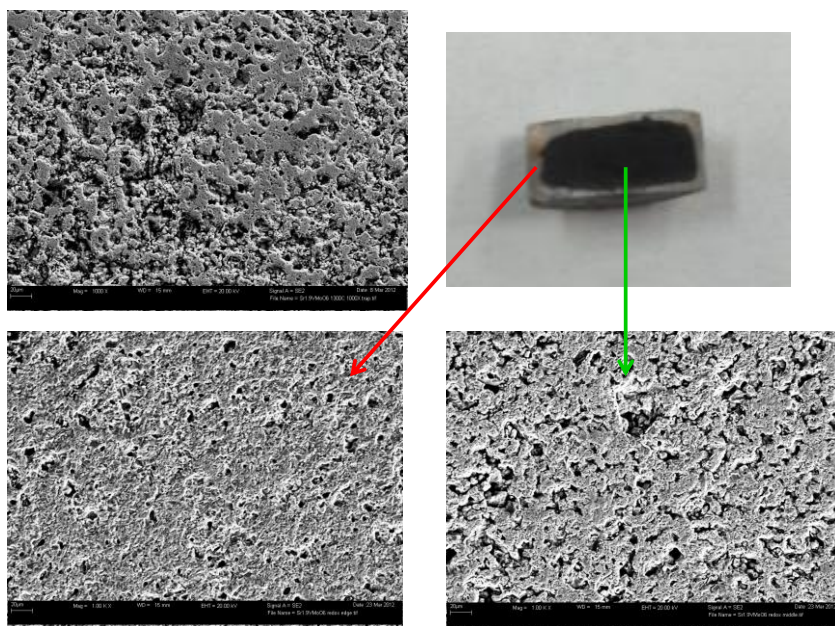


Fig. 11. FESEM microstructure images of an original sintered $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ pellet (upper left) and a redox tested $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ pellet (bottom two images). Arrows indicate outside and inside sections of the pellets to the corresponding microstructure

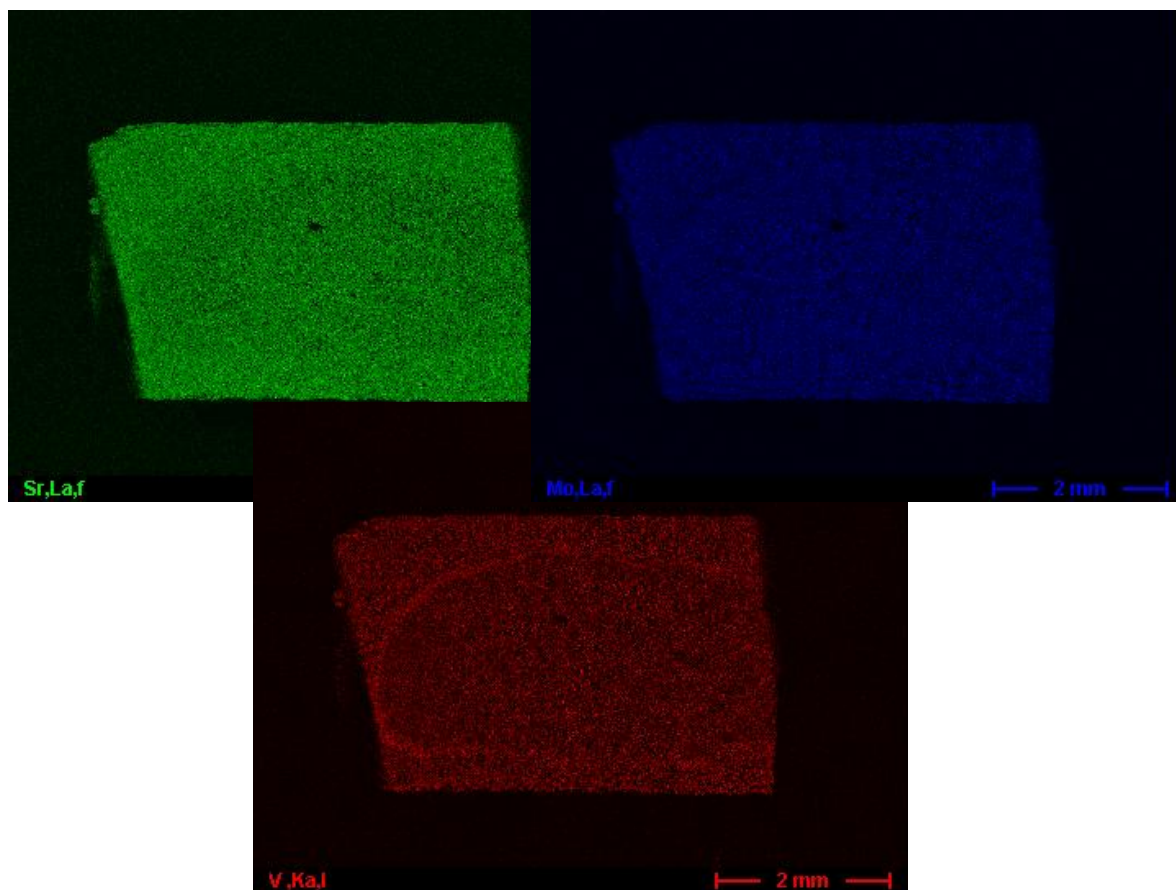


Fig. 12. SEM elemental imaging of a $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ redox tested pellet, where top left, top right, and bottom pictures represent Sr, Mo, and V, respectively

3.4 Microstructure and Micro-Hardness Testing

FESEM images of the microstructure of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets at a magnification of 1000X are shown in Figs. 13, 14, and 15. $\text{Sr}_2\text{VMoO}_{6-\delta}$ pellets sintered at 1200°C and 1100°C for 20 hours have very similar microstructures and very similar amounts of porosity, as shown in Table 3. However, the $\text{Sr}_2\text{VMoO}_{6-\delta}$ pellet sintered at 1300°C for 20 hours exhibits much more densification with reduction in porosity. The $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ sintered pellets showed a much different microstructure than the $\text{Sr}_2\text{VMoO}_{6-\delta}$ sintered

pellets. Further, the $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ pellet sintered at 1200°C has a much different microstructure and porosity than the pellets sintered at the two other temperatures, which could correspond to the apparent elimination of the spinel structure observed by XRD analysis. The microstructure of the $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ sintered pellets is similar to the $\text{Sr}_2\text{VMoO}_{6-\delta}$ sintered pellets and also exhibited higher densification at the higher sintering temperatures. As shown in Table 3, $\text{Sr}_2\text{VMoO}_{6-\delta}$ showed the highest yield strength for all of the tested pellets when sintered at 1300°C , however exhibits a drastic drop in yield strength for the 1200°C and 1100°C sintered pellets.

Table 3. Yield strength and porosity of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ sintered pellets

Sintering Temp ($^\circ\text{C}$)	Compound	Yield Strength (Mpa)	Porosity (%)
1300	$\text{Sr}_2\text{VMoO}_{6-\delta}$	391	35.3
	$\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$	365	44.8
	$\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$	259.2	45.8
1200	$\text{Sr}_2\text{VMoO}_{6-\delta}$	206.6	41.8
	$\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$	332.4	35.0
	$\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$	217.9	38.1
1100	$\text{Sr}_2\text{VMoO}_{6-\delta}$	205.2	41.7
	$\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$	166.6	47.9
	$\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$	203	33.2

This is not the same phenomena observed for $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$, where the pellets sintered at 1300°C and 1200°C exhibit similar yield strength and are much greater than the 1100°C sintered pellet; however the $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ pellets show a steady decline in strength at the sintering temperature is decreased. The average yield strength of 260.8 MPa, with an average porosity of 40.4%, for all of the $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets corresponds favorably to

published values of 61.5-88.5 MPa, with a porosity of 26.3-43.0%, of traditional Ni/YSZ cermets [23]. The high strength of the $\text{Sr}_2\text{VMoO}_{6-\delta}$ sintered pellets observed during hardness testing indicates that the double perovskite would be more effective when utilized in a fuel electrode supported SOFC.

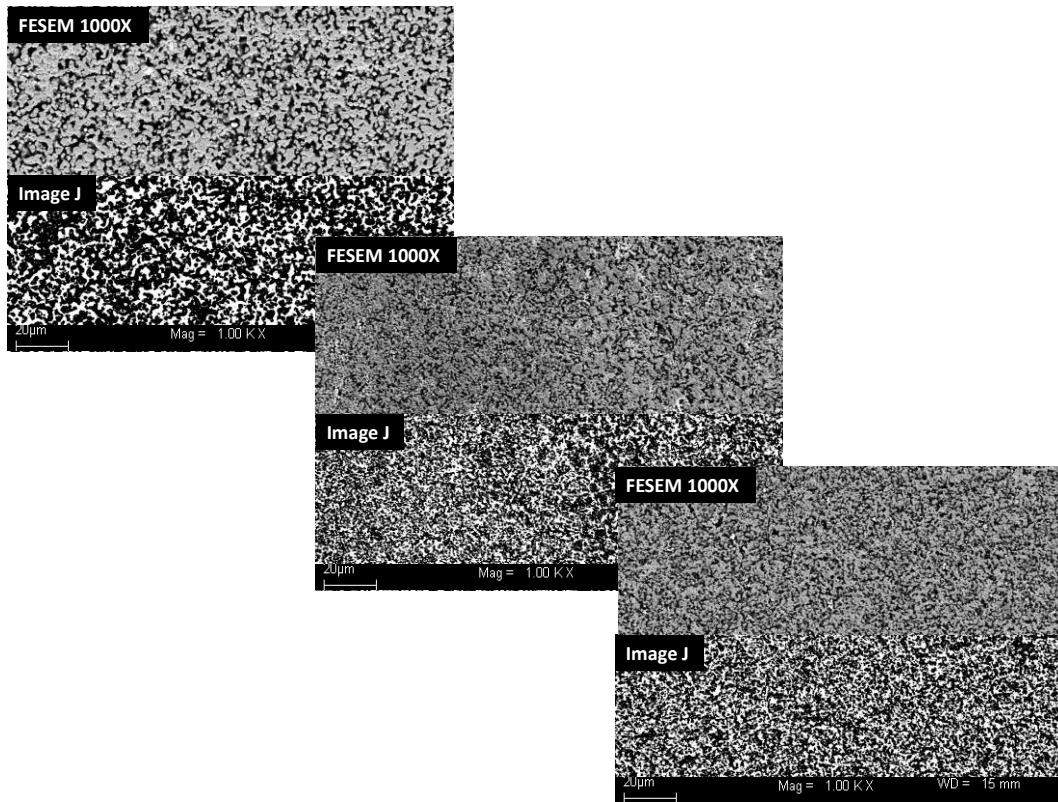


Fig. 13. FESEM/ ImageJ Binary microstructure image of the 1300°C, 1200°C, and 1100°C (top left to bottom right) sintered $\text{Sr}_2\text{VMoO}_{6-\delta}$ pellets

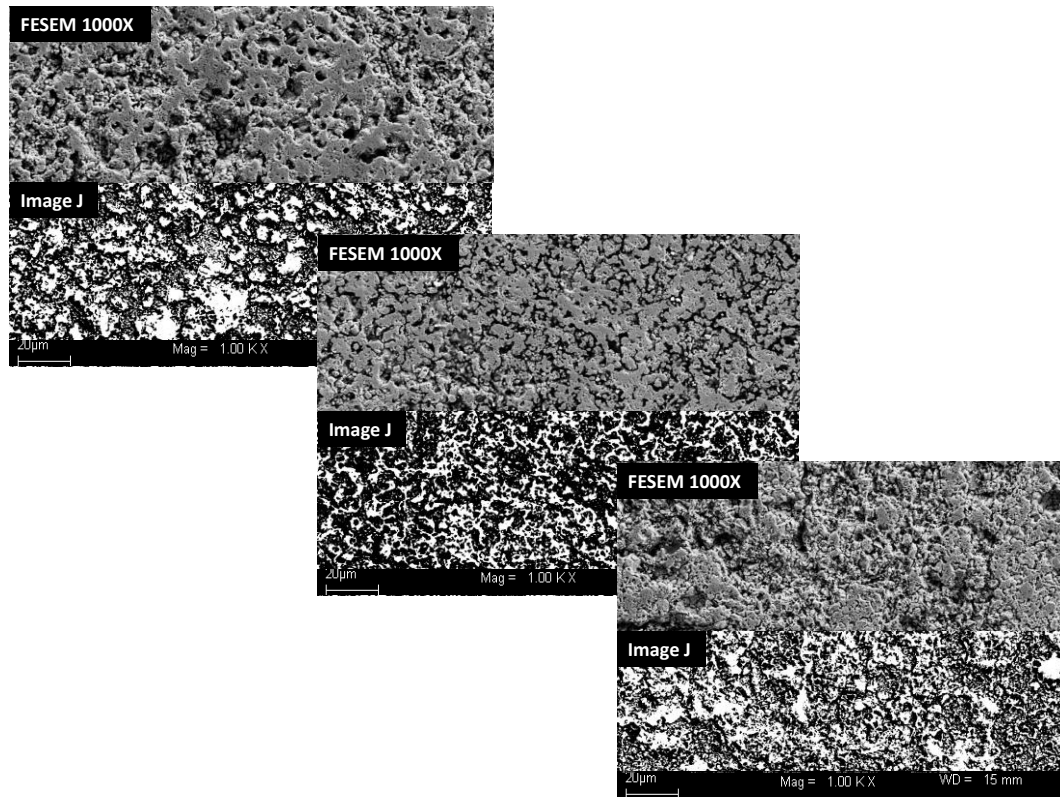


Fig. 14. FESEM/ ImageJ Binary microstructure image of the 1300°C, 1200°C, and 1100°C (top left to bottom right) sintered $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ pellets

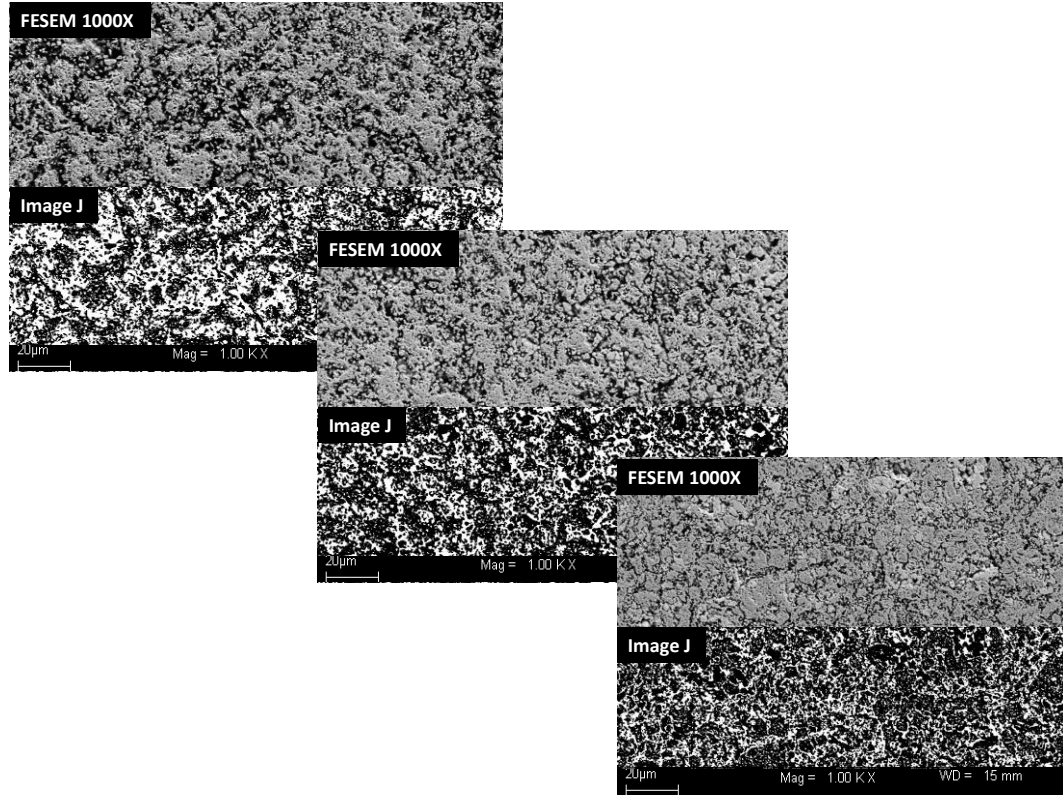


Fig. 15. FESEM/ ImageJ Binary microstructure image of the 1300°C, 1200°C, and 1100°C (top left to bottom right) sintered $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ pellets

3.5 DC Resistivity Testing

As shown in Figures 16, 17, and 18, $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets sintered at 1300°C showed the lowest resistivity at both Solid Oxide Fuel Cell (SOFC) operating temperature (800°C) and room temperature after cooling from 800°C. The minimum resistivity for $\text{Sr}_2\text{VMoO}_{6-\delta}$ was $7.965 \times 10^{-7} \Omega \cdot \text{m}$. The minimum resistivity for $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ was $6.124 \times 10^{-7} \Omega \cdot \text{m}$ and the minimum resistivity for $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ was $4.439 \times 10^{-7} \Omega \cdot \text{m}$. These resistivity values correspond well to the values published by Karen et al. [10], where the maximum conductivity for $\text{Sr}_2\text{VMoO}_{6-\delta}$ differs by 4% from the published room temperature values. The $\text{Sr}_2\text{VMoO}_{6-\delta}$ pellets show a significant

difference in resistivity at 800°C between all three sintering temperatures. This can be attributed to a reduction in porosity and the reduction of the scheelite structure associated with change in sintering temperature. The $\text{Sr}_{1.9}\text{VMoO}_{6-\delta}$ pellets exhibit very similar resistivities for 1300°C and 1200°C sintering temperatures, which also can be explained from formation of the double perovskite phase.

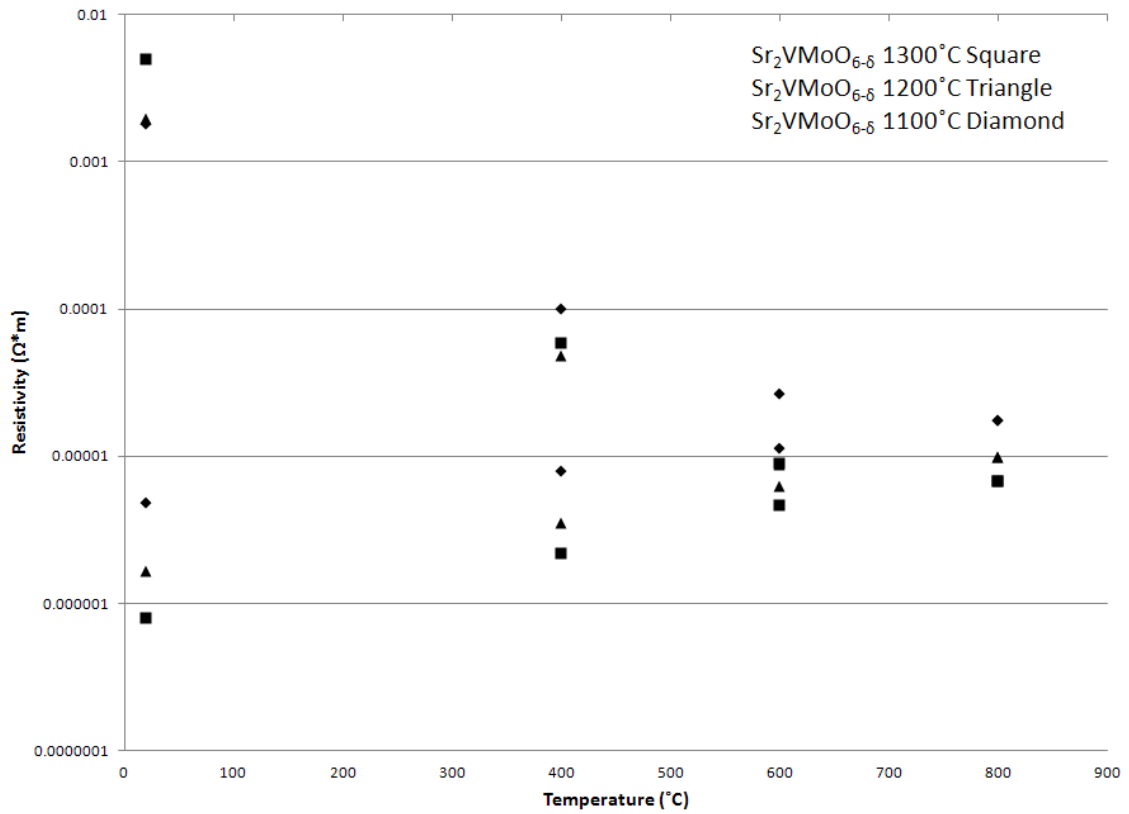


Fig. 16. Resistivity vs. Temperature for sintered $\text{Sr}_2\text{VMoO}_{6-\delta}$ pellets

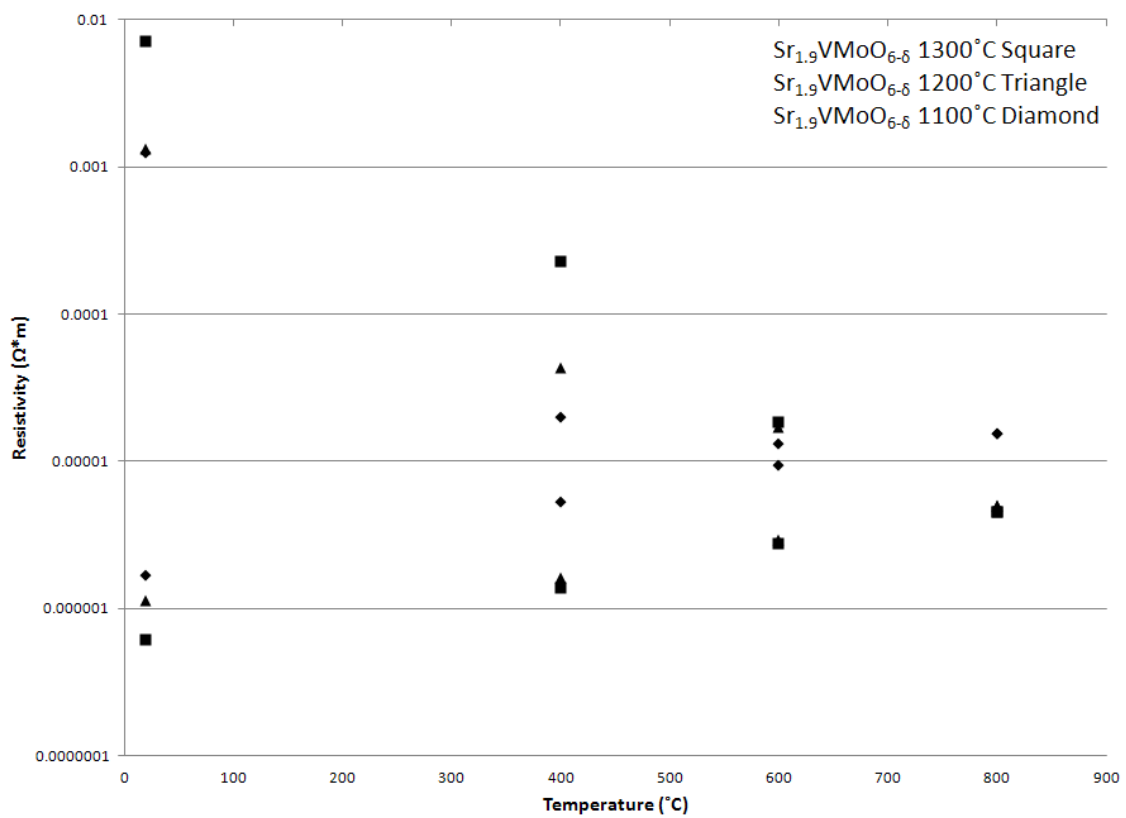


Fig. 17. Resistivity vs. Temperature for sintered $Sr_{1.9}VMoO_{6-\delta}$ pellets

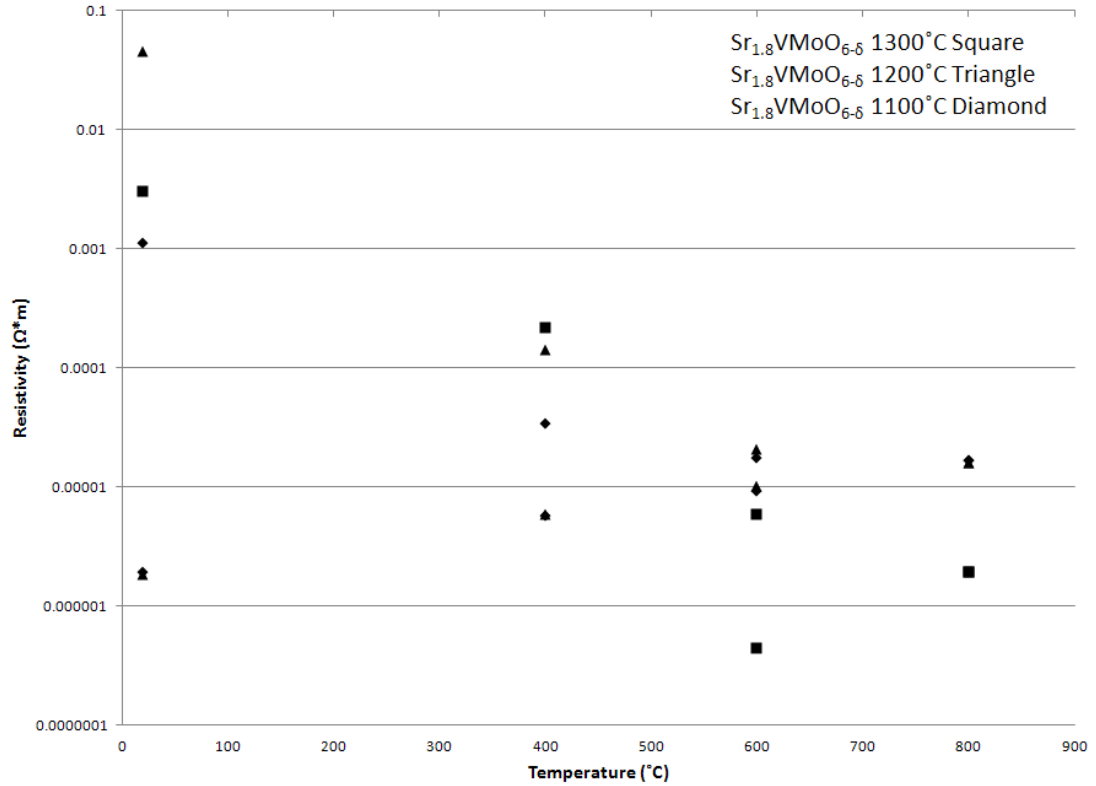


Fig. 18. Resistivity vs. Temperature for sintered $\text{Sr}_{1.8}\text{VMoO}_{6-\delta}$ pellets

4. Discussion

4.1 Formation of the Double Perovskite Structure

The observed amounts of Mo(IV), Mo(VI), V(IV), and V(V) valence states from XPS, for the b-site cation species, provides some understanding on the formation of the Scheelite and double perovskite structures. The corresponding ionic radii are 0.58 Å, 0.59 Å, 0.65 Å, and 0.54 Å, for Mo(IV), Mo(VI), V(IV), and V(V) valence states, respectively. This would indicate that both Mo(IV) and Mo(VI) could substitute into the SrVO_3 B-site. However, the b-site cations in the double perovskite structure have a total charge of 8^+ , which is only achievable with Mo(IV) and V(IV) out of the valence states

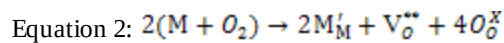
observed during XPS analysis. These valence states would correspond to a Goldschmidt tolerance factor (Equation 1) of .994, which is acceptable for a cubic structure; however the low elemental percentage of V and high amount Mo(IV) at the surface of the material would indicate that a low amount of double perovskite exists at the surface of the pellet.

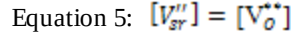
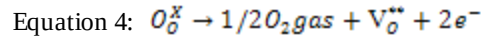
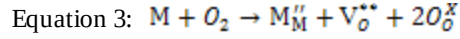
$$\text{Equation 1: } (R_A + R_O)/\sqrt{2}(R_B + R_O) \text{ [24]}$$

With R_A =A-site ionic radii, R_O =Oxygen ionic radii, and R_B =Average B-site ionic radii. The low amount of the perovskite phase at the surface and higher amount in the bulk of the material can be explained from the slow reduction of Mo(VI) to Mo(IV) and the rapid oxidation of Mo(IV) to Mo(VI), therefore forming the scheelite phase rapidly at the surface of the pellet [13]. The formation of $\text{SrMoO}_{4-\delta}$ at the surface could lead to the decomposition of $\text{Sr}_2\text{VMoO}_{6-\delta}$ and therefore lead to vanadium migration towards the bulk of the material. This migration corresponds to the low elemental percentage found from surface sensitive XPS and the concentrated vanadium layer in the bulk of the material caused by high temperature oxidation during redox cycling. Kuepper et al. [25] also found that $\text{Sr}_2\text{FeMoO}_{6-\delta}$ decomposes in air to $\text{SrMoO}_{4-\delta}$ at the surface and $\text{SrFeO}_{3-\delta}$ at the lower levels, resulting in a Fe deficiency at the surface of the material. The reduction of Mo(VI) to the Mo(IV) valence state is the driving factor for the substitution of molybdenum on the vanadium site in the already formed perovskite, which indicates that a reducing atmosphere, high temperature, and long dwell time is needed to fully develop the double perovskite structure. This corresponds to the finding of Fang et al. [26] and Aguadero et al. [27], where SrMoO_4 was found during processing of $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{CoMoO}_6$, respectively. Further, Fang et al. [26] were able to form more of the double perovskite phase at higher sintering temperatures in a reducing atmosphere.

4.2 Resistivity of $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites

The total electrical conductivity of the $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ double perovskites including both ionic and electronic contributions is driven by defects associated with attaining charge neutrality through both dopant additions as well as oxygen concentration. This in turn yields anion vacancies that facilitate oxygen ion transport, changes in cation oxidation that yield both polarons and free electrons. Polaron hopping occurs when the negatively charged polaron on the multivalent cation M^{4+} site jumps to the M^{3+} site, where M represents V or Mo for $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$. This process continues throughout the material as long as multiple oxidation states are present. Electronic conductivity produced by charge neutrality is further demonstrated by Equations 2 through 4, where the reduction of the b-site cations (V or Mo in this study) is shown in Kroger-Vink notation. Equations 2 and 3 represent the reduction of vanadium with a 4^+ oxidation state to 3^+ and 2^+ oxidation states, therefore producing one and two oxygen vacancies, respectively. These vacancies can generate ionic conduction and also, through charge neutrality, produce free electrons as shown in Equation 4. Equations 2 and 3 represent the possible defect scenarios of the b-site reduction, however based on the results of this study and the findings of Fotiev et al. [28], the vanadium and molybdenum 4^+ states are more conductive than the vanadium 3^+ and molybdenum 5^+ combination. The oxygen vacancies are not limited to the reduction of b-site cations and can be produced in much of the same way by reducing the amount of a-site cations. The sub-stoichiometry would lead to oxygen vacancies, due to charge neutrality as shown in Equations 5.





With $M = V, \text{ and } Mo, V = \text{Vacancy}$, ' = negative charge, * = positive charge, and x = neutral charge. The resistivity tests performed in a reducing atmosphere exhibit semiconductor behavior when the double perovskite is heated up to 800°C; however metallic behavior is observed when the pellets are cooled to room temperature from 800°C. The small resistance at lower temperatures in a reducing environment was reported by both Karen et al. [10] and Aguadero et al. [29], however the resulting conductivity was much higher than the results found by Aguadero et al [29]. This can also be explained through the reduction of Mo^{6+} to Mo^{4+} in the reducing atmosphere during the resistivity testing. As found by Katrib et al. [13], molybdenum trioxide (MoO_3) will start to reduce to molybdenum dioxide in an hour of exposure to a reducing environment at 350°C which will contribute to free Mo 4d and Mo5s electrons that can exhibit metallic conductivity. This is further validated by the XRD and conductivity tests, where $Sr_{2-x}VMoO_{6-\delta}$ pellets sintered at 1300°C for 20 hours exhibit the lowest resistivity and shows the double perovskite as its main phase. This suggests that the greatest conductivity can only be achieved by extending the sintering time and temperature parameters to try and facilitate the desired double perovskite structure.

5. Conclusions

The XRD patterns indicate that the double perovskite is the primary phase for $Sr_{2-x}VMoO_{6-\delta}$ pellets sintered at 1200°C and 1300°C for 20 hours; however, these pellets

show a secondary phase of $\text{SrMoO}_{4-\delta}$. These tests indicate that the phase pure double perovskite $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ structure can only be achieved in a reducing atmosphere at high temperatures (1300°C) and the $\text{SrBO}_{4-\delta}$ scheelite phase is the main phase at lower temperatures and oxidizing atmospheres. Thus studies evaluating this or other double perovskites that utilize molybdenum must be cautious of processing conditions that are insufficient to yield phase pure materials. XPS revealed a deficiency of vanadium on the pellet surfaces, as 8 out of 9 samples had surface vanadium contents of less than 5% and the average composition over all samples analyzed was found to be 24.8%, 4.2%, 11.8%, 59.2% for Sr, V, Mo, O, respectively. The low vanadium concentration can be explained by the formation of the $\text{SrMoO}_{4-\delta}$ scheelite phase due to oxygen exposure on the surface of the pellets, which indicates vanadium migration to the bulk, and was exhibited in redox cycling. RBS confirmed the bulk elemental compositions of samples were close to the starting ratios of Sr/Mo/V with the remainder being 58-64% O.

$\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets exhibited an average yield strength of 260.8 MPa, which corresponds favorably to published values of 61.5-88.5 MPa of traditional Ni/YSZ cermets [23]. The high strength of the $\text{Sr}_2\text{VMoO}_{6-\delta}$ sintered pellets observed during hardness testing indicates that the double perovskite should be sufficiently strong for the fabrication of fuel electrode supported SOFC. $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets sintered at 1300°C showed the lowest resistivity at both SOFC operating temperature (800°C) and room temperature after cooling from 800°C . This can be attributed to a reduction in porosity and the reduction of the insulating scheelite structure associated with change in sintering temperature. The resistivity tests also show a semiconductor to metallic transition for all

double perovskites from heating up to 800°C to cooling down to room temperature in a reducing atmosphere. The metallic transition is indicated to be a result of the reduction of Mo^{6+} to Mo^{4+} in the reducing atmosphere during the resistivity testing, therefore liberating Mo 4d and Mo5s electrons.

Future efforts will consist of investigating the mechanisms of conductivity by utilizing temperature segmented conductivity testing, thermal gravimetric analysis, and temperature controlled in-situ XPS to further demonstrate the temperature at which reduction occurs as well as how cation oxidation states influence the observed conductivity.

Acknowledgments

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CHAPTER FIVE

ELECTRICAL CONDUCTIVITY OF $\text{Sr}_{2-X}\text{VMoO}_{6-Y}$ ($X = 0.0, 0.1, 0.2$) DOUBLE
PEROVSKITESContribution of Authors and Co-Authors

Manuscript in Chapter 5

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Contributions: Synthesized double perovskite powders and pellets. Performed conductivity and TGA measurements. Collaborated on the drafting of the manuscript.

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Contributions: Provided useful discussions related to the experiment and contributed to the editing of the manuscript.

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ABSTRACT

Electrical conductivity of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ ($x=0.0, 0.1, 0.2$) double perovskites has been investigated in a reducing atmosphere at temperatures up to 800°C . This material has a key application in solid oxide fuel cell anodes as a mixed ion and electron conductor. A solid state synthesis technique was used to fabricate materials and crystal structure was verified through x-ray diffraction. Subsequent to conventional sintering in a reducing environment, elemental valence states were identified through x-ray photoelectron spectroscopy on the double perovskite material before and after annealing in a hydrogen environment. Samples exhibited metallic like conduction with electrical conductivities of 1250 S/cm ($\text{Sr}_2\text{VMoO}_{6-y'}$), 2530 S/cm ($\text{Sr}_{1.8}\text{VMoO}_{6-y''}$) and 3610 S/cm ($\text{Sr}_{1.9}\text{VMoO}_{6-y'''}$) at 800°C in 5% H_2 /95% N_2 , with a substantial increase in conductivity upon cooling to room temperature. Room temperature electrical conductivity values for $\text{Sr}_{1.9}\text{VMoO}_{6-y'''}$ make it a candidate as the highest electrically conductive oxide known. Highly insulating secondary surface phases, $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 , begin to reduce at 400°C in a hydrogen environment, as confirmed by X-ray photoelectron and thermal gravimetric analysis. This reduction, from V^{5+} and Mo^{6+} to lower valence states, leads to a large increase in sample electrical conductivity.

1. Introduction

Fuel cells are an attractive energy conversion technology due to their ability to efficiently convert chemical energy stored in fuel directly into electricity bypassing traditional combustion processes. The potential to reform hydrocarbons at the anode and

the use of carbon monoxide as a fuel instead of a poison¹, are advantages Solid Oxide Fuel Cells (SOFCs) have over other types of fuel cell technologies.

Current state-of-the-art SOFC technology utilizes a porous cermet anode consisting of nickel and yttria-stabilized zirconia (YSZ). Percolated networks of nickel, YSZ and pores allow for transport of electrons, oxygen ions and gases within the anode. The junction of these three phases (Ni, YSZ, pore) form a triple phase boundary (TPB). Anode reactions are localized to the TPB in this system, limiting the active area of the anode. Additional well known problems exist with Ni-YSZ anode materials such as agglomeration of nickel particles^{2,3}, irreversible degradation due to sulfur poisoning⁴ susceptibility to coke formation⁵ and limited reported electrical conductivity values of 989 S/cm in hydrogen at 900 °C⁶.

Perovskite type materials are of interest as an anode material in part due to their potential as a mixed electronic and ionic conductor (MEIC). Replacing Ni and YSZ with a MEIC in a porous anode establishes the active anode region over a dual phase boundary (DPB) established at the surface of the MEIC instead of localizing it to a TPB. Additionally the perovskite type materials have shown stability in high temperature reducing environments⁷, catalytic ability to oxidize hydrogen^{8,9} and methane⁹, tolerance to sulfur poisoning¹⁰ and resistance to coke formation¹¹.

Electrical conductivity, a critical electrode property, has been reported for a variety of Sr_2MMoO_6 (M= V, Fe, Mn, Mg, Cr, Co, Ni) double perovskite materials. A summary of the reported electrical conductivities of these and other relevant materials is presented in Table I¹²⁻²⁴. Sr_2VMoO_6 has the highest reported electrical conductivity of these

Sr_2MMoO_6 materials, with a value of 280 S/cm at 900 C in a reducing atmosphere.

Electron band structure calculations for this material predict metallic like conduction²⁵.

Polycrystalline SrVO_3 and SrMoO_3 samples have reported room temperature electrical conductivities of 400 S/cm²³ and 10,000 S/cm²² respectively, with single crystal SrMoO_3 conductivity reported at 200,000 S/cm²¹. These factors make the $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ double perovskite material interesting as a highly electrically conductive oxide material.

Table I. Reported electrical conductivities of Sr_2MMoO_6 and other relevant materials

Composition	Conductivity (S/cm)	Temperature ($^{\circ}\text{C}$)	Environment	Reference
Sr_2VMoO_6	12000	25	Air	Karen 2006
Sr_2VMoO_6	280	900	10% H_2/N_2	Aguadero 2011
Sr_2VMoO_6	256*	800	vacuum after reduction	Fortiev 1987
$\text{Sr}_2\text{FeMoO}_6$	222*	800	H_2	Zhang 2010
$\text{Sr}_2\text{MnMoO}_6$	~10	800	H_2	Huang 2006
$\text{Sr}_2\text{MgMoO}_6$	~10	800	H_2	Huang 2006
$\text{Sr}_2\text{MgMoO}_6$	7.7*	800	5% H_2/Ar	Vasala 2010
$\text{Sr}_2\text{CrMoO}_6$	2.54*	800	5% H_2/Ar	Yin 2011
$\text{Sr}_2\text{CoMoO}_6$	1.7*	800	5% H_2/Ar	Huang 2009
$\text{Sr}_2\text{CoMoO}_6$	4.0*	800	H_2	Huang 2009
$\text{Sr}_2\text{CoMoO}_6$	0.013	800	5% H_2/N_2	Viola 2002
$\text{Sr}_2\text{CoMoO}_6$	0.08	800	15% H_2	Viola 2002
$\text{Sr}_2\text{NiMoO}_6$	0.07*	800	5% H_2/Ar	Huang 2009
$\text{Sr}_2\text{NiMoO}_6$	0.45*	800	H_2	Huang 2009
Ni-YSZ(15vol%Ni)	0.103	900	H_2	Aruna 1998
Ni-YSZ(30vol%Ni)	40	900	H_2	Aruna 1998
Ni-YSZ(50vol%Ni)	989	900	H_2	Aruna 1998
SrVO_3	100*	577	H_2/Ar mixture	Giannakopoulou 1994
SrMoO_3	10000*	27	cryostat	Hayashi 1979
SrMoO_3 (single crystal)	196000	27	Not reported	Nagai 2005

* Read from published graph

2. Experimental

2.1 Synthesis

$\text{Sr}_{2-x}\text{VMoO}_{6-y}$ powder was fabricated by solid state synthesis utilizing SrCO_3 , VO_2 and MoO_2 precursor powders as described elsewhere²⁶. This powder was mechanically homogenized by ball milling then calcined at 1000°C for 6 hours under ambient conditions. The calcined powder was uniaxially pressed at 250MPa to form 6.35 mm diameter, 3 mm thick pellets for conductivity measurements. In order to achieve the desired temperatures in an ultra-high vacuum environment, thin discs were formed utilizing a tape-cast technique. A suspension was prepared at 30% solids loading utilizing a polyvinyl butyral binder system and xylene/ethanol solvent mixture. The suspension was tape cast onto a Mylar carrier through a doctor blade with a 1 mm gap setting. The ceramic tape was dried and 25.4 mm diameter, 0.8 mm thick disks were punched out of the green tapes in preparation for sintering and testing. The double perovskite structure was formed by thermally treating the green tape disks and pellets in a reducing wet ($5\%\text{H}_2$ $95\%\text{N}_2$) atmosphere ($\sim 10^{-11}\text{pO}_2$) at 1300°C for 20 hours in a tube furnace. Uniaxially pressed pellets exhibited higher green density (3.0g/cc), than the tape cast disks (2.63g/cc) which is partially attributed to the addition of the polymeric additives. The changes in A-site amounts also contributed to variations in the microstructure and porosity (Fig. 1). $\text{Sr}_{2.0}\text{VMoO}_{6-y}$ (SR20), $\text{Sr}_{1.9}\text{VMoO}_{6-y}$ (SR19), $\text{Sr}_{1.8}\text{VMoO}_{6-y}$ (SR18) sample porosities, calculated from image analysis, were 35.3%, 44.8% and 45.8% respectively.

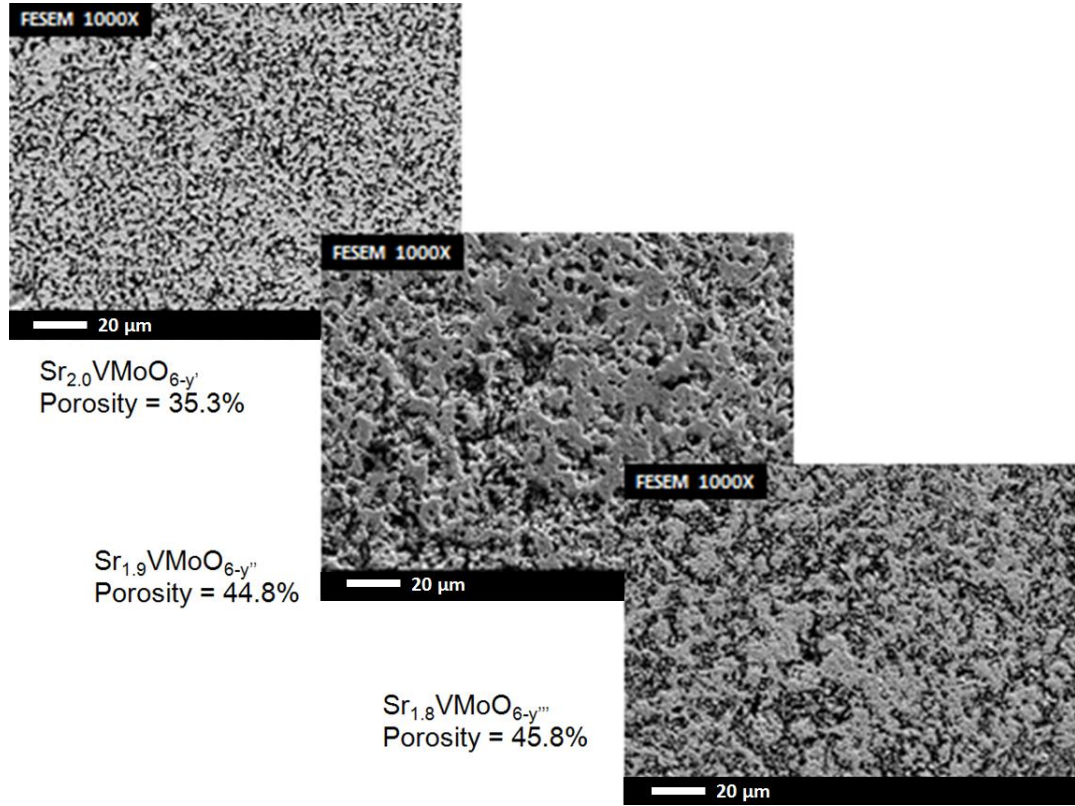


Fig. 1. Microstructure and porosity of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ double perovskite pressed pellets sintered at 1300°C

2.2 X-ray Powder Diffraction

X-ray powder diffraction (XRD) was used to verify the double perovskite crystal structure in $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples. Powder for XRD was ground from samples after the sintering process and from samples placed in the furnace during conductivity measurements. A Cu $K\alpha$ source was used over an angular range of $25-60^\circ 2\theta$ with a step size of 0.01° . Measurements were taken at room temperature in air.

2.3 Electrical Conductivity

DC conductivity tests were performed on sintered $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ double perovskite pressed pellets using a modified 4-probe measurement technique, utilizing an Agilent 34420A nanovolt meter. The conductivity tests were set up by attaching two silver wire leads to the top and two to the bottom of the double perovskite pellets. Silver electrodes were painted on the top and the bottom of the samples to create a uniform conducting layer across the face of the double perovskite pellets. The silver wire/electrode assembly was then clamped between electrically insulating alumina plates by a stainless steel fixture to provide mechanical stability for the wire contacts. The conductivity tests were conducted inside a tube furnace (Lindberg/Blue TF55035A-1) for which a controlled wet reducing atmosphere (2.9% H_2O , 4.9% H_2 and 92.2% N_2) could be introduced. Temperature segmented tests from room temperature to 200°C, 400°C, 600°C, and 850°C at a heating rate of 2°C/min were performed on the sintered $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ double perovskite pressed pellets to further demonstrate the effects of temperature and reduction on conductivity. These tests were continuous; samples were cycled in a wet reducing environment from room temperature $\uparrow 200^\circ\text{C} \downarrow 50^\circ\text{C} \uparrow 400^\circ\text{C} \downarrow 50^\circ\text{C} \uparrow 600^\circ\text{C} \downarrow 50^\circ\text{C} \uparrow 850^\circ\text{C} \downarrow 50^\circ\text{C}$. Conductivity measurements were made once per minute during this cycle. The error in calculated conductivity is dominated by the sample geometry measurement at low conductivities (± 0.5 S/cm at 10 S/cm) and by the resistance measurement at high conductivities (± 872 S/cm at 10,000 S/cm).

2.4 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) was utilized to measure the weight loss as a function of temperature due to reduction of the $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples, in a dry reducing atmosphere (5% H_2 and 95% N_2), from room temperature to 800°C then cooled back to room temperature. This was done with a heating and cooling rate of 2°C/min.

2.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to determine elemental valence states before and after electrical conductivity measurements. XPS was also conducted before and after 30 minute anneals in 10^{-6} torr H_2 at temperatures ranging from 200-700 °C. The tape casting technique produced much thinner samples than the pressed pellets (0.8 mm vs 3.0 mm). The heating characteristics for the thinner more porous samples allowed for the investigation of the effects of annealing at higher temperatures and thus were used. These annealing runs were performed in a ultra-high vacuum chamber by raising the base chamber pressure of less than 10^{-9} Torr to a pressure of 10^{-6} Torr by introducing research grade H_2 (99.9999% purity). The sample was then heated to the desired temperature and held for 30 minutes. The sample temperature was brought to room temperature in less than 10 minutes by flowing liquid nitrogen through the sample holder. Once the sample temperature was below room temperature the H_2 flow was stopped and a chamber pressure of less than 10^{-9} torr was obtained before XPS was performed.

A magnesium X-ray source (Mg K α = 1253.6 eV, 0.7 eV FWHM) operated at 15 kV and 15 mA was used to stimulate electron emission. Spectra were recorded with a pass energy of 25 eV (energy resolution $\sim \pm 0.3$ eV) at a step size of 0.05 eV. With these conditions approximately 95% of the collected signal comes from the first 3 nm of the material surface. The C 1s, O 1s, V 2p, Sr 2p and Mo 3d photoelectron emission regions were recorded. Binding energies (BE) were calibrated relative to the O 1s (530.0 eV) peak for the V 2p region and the C 1s (284.8 eV) peak was used for the Sr 2p and Mo 3d regions.

A Shirley background was used during XPS peak fitting and a Marquardt-Levenberg²⁷ optimization algorithm was implemented by the CasaXPS software program to deconvolute emission peaks into different valence contributions. The vanadium 2p main and satellite peaks were allowed to vary within ± 0.2 eV of the BE values reported for vanadium oxidation states by Silversmit et al.²⁸. FWHM values were allowed to vary between 1.7 ± 0.1 eV for the V⁵⁺ and V⁴⁺ states and 2.0 ± 0.1 eV for the V³⁺, V^{2+/1+} and V ^{β +} valence states. A separation of 7.33 eV and area ratio of 2:1 was used for the V 2p_{3/2}/V 2p_{1/2} spin-orbit split pair. Mo 3d main peaks were allowed to vary within ± 0.2 eV of an average of BE values reported for molybdenum oxides²⁹⁻³⁴. FWHM values were allowed to vary between 1.7 ± 0.1 eV for Mo⁵⁺, 1.8 ± 0.2 eV for Mo⁴⁺ and 2.0 ± 0.1 eV for the Mo⁶⁺ and Mo ^{δ +} valence states. A separation of 3.15 eV and area ratio of 3:2 was used for the Mo 2p_{5/2}/Mo 2p_{3/2} spin-orbit split pair. The fit parameters described here for the O 1s-V 2p and Mo 3d regions provided adequate simulations for the 11 separate data sets in each of the two regions.

3. Results

3.1 X-ray Powder Diffraction

The majority phase for powders ground from both pressed pellets and tape cast discs was found to be in agreement with reflections based on the crystal information provided by Karen et. al. for the double perovskite $\text{Sr}_2\text{VMoO}_{6.0}$ (space group Pm-3m, $a = b = c = 3.916 \text{ \AA}$)²⁰. Throughout the study the main secondary phases found were $\text{Sr}_3\text{V}_2\text{O}_8$ (space group R-3m $a=b=5.619 \text{ \AA}$ $c=20.100 \text{ \AA}$)³⁵ and scheelite structured SrMoO_4 (space group $I4_1/a$ $a=b=5.394$ and $c = 12.010 \text{ \AA}$)³⁶. These secondary phases were found in varying amounts and were not present in all samples. No significant changes were noted in the crystal structure or the amounts of secondary phases when comparing powders ground before and after thermal cycling in a wet reducing atmosphere. XRD patterns from powders ground from samples after the sintering process are presented in Fig 2.

3.2 Electrical Conductivity

Initial room temperature conductivity measurements subsequent to sintering for SR20, SR19 and SR18 pellets were 3.2 S/cm, 4.6 S/cm and 9.4 S/cm respectively. Conductivities measured during and after cycling from RT $\uparrow 200 \text{ }^\circ\text{C}$ $\downarrow 50 \text{ }^\circ\text{C}$ showed no significant changes. Measured electrical conductivity for the three tested stoichiometries on the cycle from $50 \text{ }^\circ\text{C}$ $\uparrow 400 \text{ }^\circ\text{C}$ $\downarrow 50 \text{ }^\circ\text{C}$ is shown in Fig. 3.

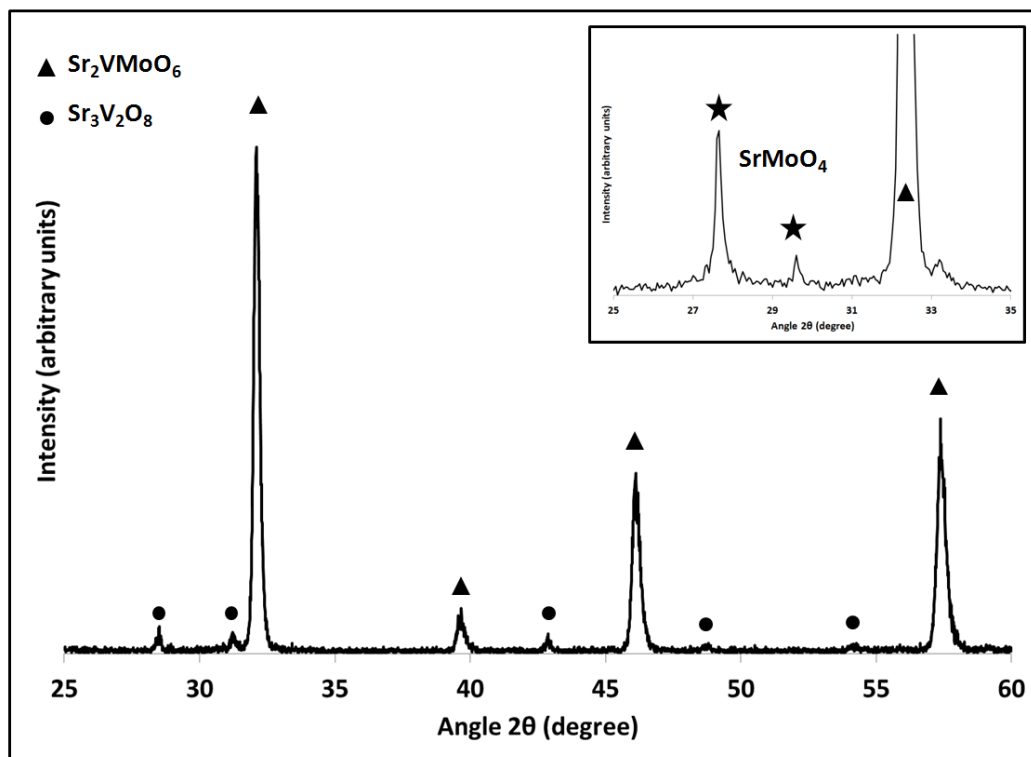


Fig. 2. XRD pattern of a Sr_2VMoO_6 sample at room temperature in air. This sample exhibits a contaminate phase of $\text{Sr}_3\text{V}_2\text{O}_8$, noted with circles. Inset: XRD pattern of a different Sr_2VMoO_6 sample. A contaminate phase of SrMoO_4 , noted with stars, is present.

Semiconductor like conduction (increasing conductivity with increasing temperature) is shown throughout the cycle; however a significant increase in conduction at 50°C was observed at the end of the heating cycle. Upon heating the average conductivity of the three samples increased from 11 S/cm to 435 S/cm. After cooling from 400°C to 50°C the measured conductivities were 159 S/cm, 219 S/cm and 265 S/cm for the SR20, SR19 and SR18 pellets.

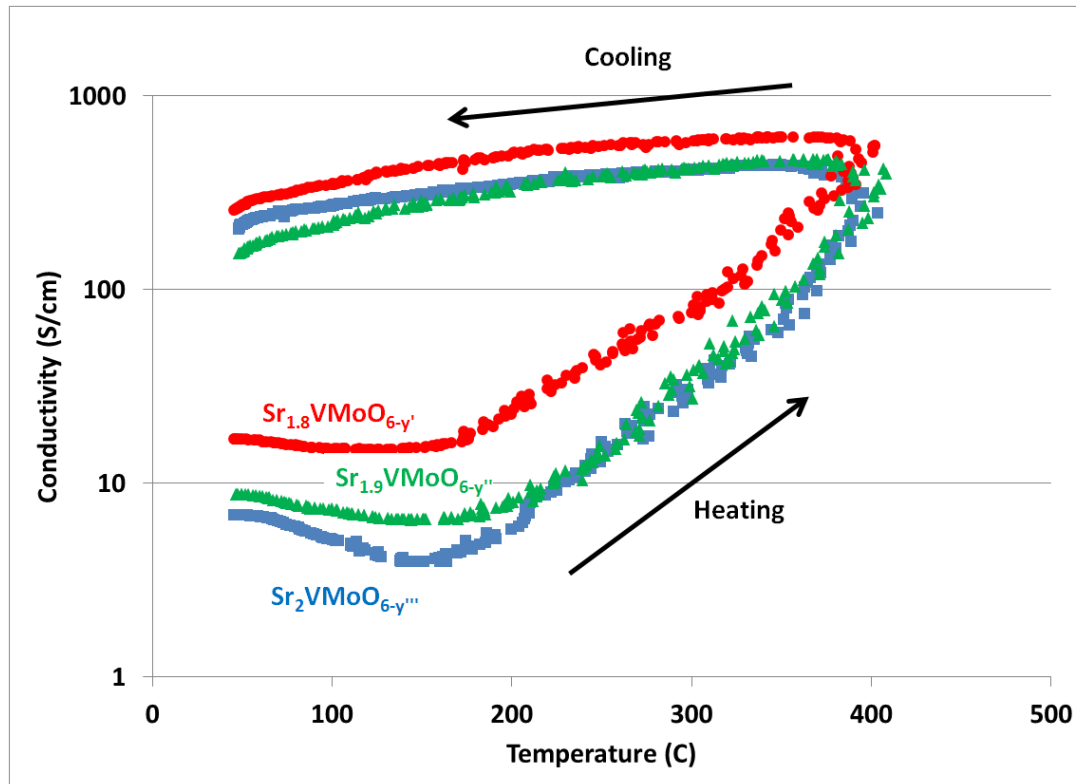


Fig. 3. Electrical conductivity of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ pressed pellets vs. temperature upon heating to and cooling from 400 °C in a nitrogen environment with 2.9% H_2O /4.9% H_2 content.

Heating to 600 °C from 50 °C resulted in an increase of conductivity to an average of 1423 S/cm for the three samples at 600 °C. After cooling, conductivities returned to the approximate values found after the 400 °C cycle. The final heating from 50 °C $\uparrow$ 850 °C resulted in conductivities of SR20 = 1250 S/cm, SR18 = 1800 S/cm and SR19 = 3000 S/cm at 800 °C in a wet reducing atmosphere (Fig. 4). When cooled from 850 °C all samples exhibited metallic conduction (increasing conductivity with decreasing temperature). Final 50 °C conductivities for the SR20 and SR18 samples were 9300 S/cm and 18000 S/cm respectively. The SR19 electrical conductivity was superior to other stoichiometries and reached the limits of the measurement system as can be seen by the

scatter as the sample approaches 50 °C. A linear extrapolation on the calculated slope during cooling from 850 °C to 600 °C results in a conservative conductivity estimate of ~30,000 S/cm at 50 °C for the SR19 sample. Upon room temperature exposure to air all sample conductivities showed degradation over time.

3.3 Thermal Gravimetric Analysis

TGA was utilized to determine the total weight loss due to reduction of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ sintered powders on a cycle from room temperature to 850 °C and back to room temperature in a reducing atmosphere. The total weight loss for the three samples averaged over three separate runs was 0.223%, 0.087% and 0.124% for the SR20, SR19 and SR18 powders.

3.4 X-ray Photoelectron Spectroscopy

XPS analysis was performed on SR20, SR19 and SR18 pressed pellets and tape cast discs. Comparison of XPS spectra from the two preparation techniques, tape cast and pressed pellets, as prepared and after annealing yielded no significant chemical differences. The tape cast discs are much thinner (0.8 mm vs 3.0 mm) than the pellets. The heating characteristics for the thinner more porous samples allowed for the investigation of the effects of annealing at higher temperatures utilizing in-situ methods and thus are reported.

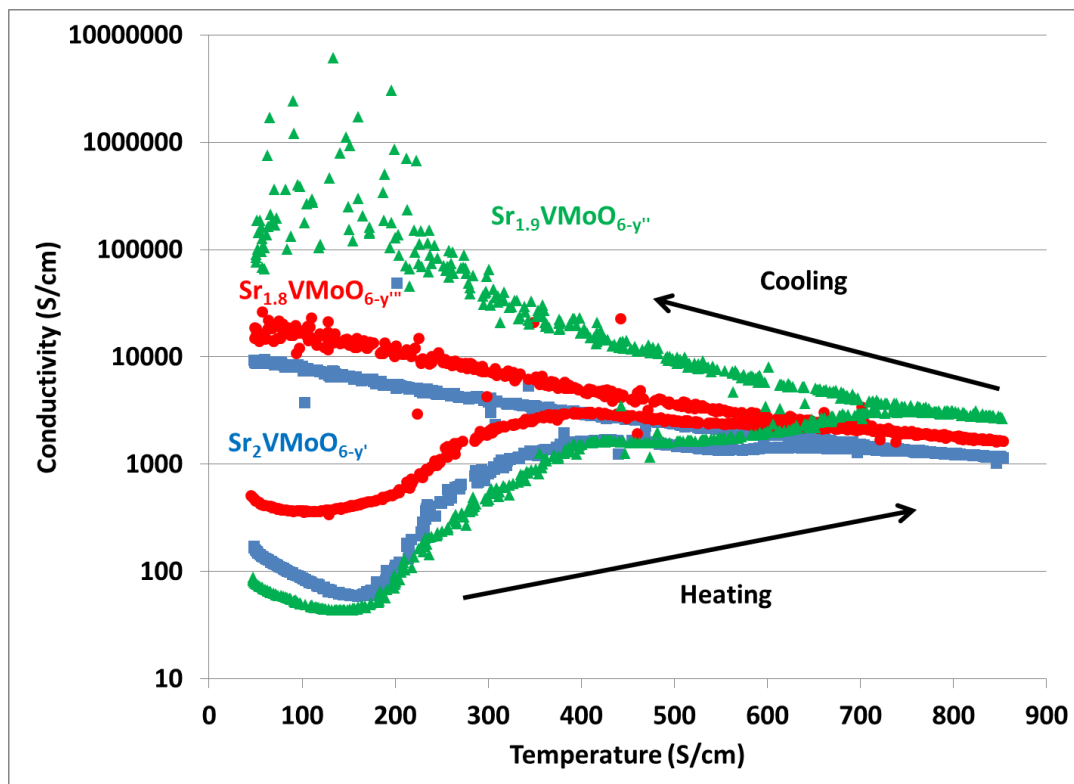


Fig. 4. Electrical conductivity of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ pressed pellets vs. temperature upon heating to and cooling from 850 °C in a nitrogen environment with 2.9% H_2O /4.9% H_2 content. The scatter in data as the $\text{Sr}_{1.9}\text{VMoO}_{6-y''}$ cools below 300 °C is due to instrument limitation in measuring such high conductivity.

Figs. 5 and 6 represent valence deconvolutions of Mo 3d and V 2p spectral regions measured on a SR20 tape cast disc after anneals up to 700 °C in 10^{-6} Torr H_2 .

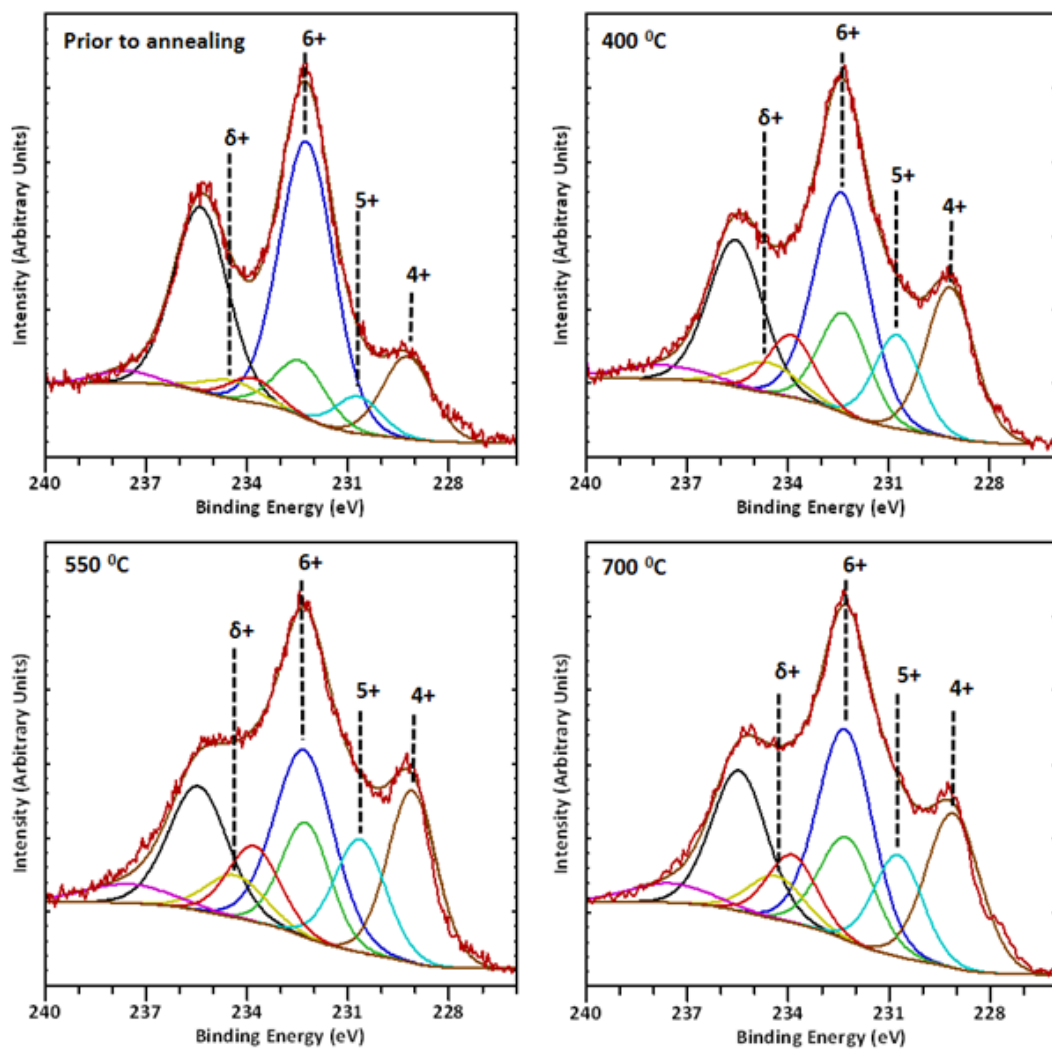


Fig. 5. Mo 3d core-level region XPS spectra of a $\text{Sr}_{2.0}\text{VMoO}_{6-y'}$ tape cast disc, prior to annealing and after 30 minute annealings at 400 C, 550 C and 700 C in 10^{-6} Torr H_2 .

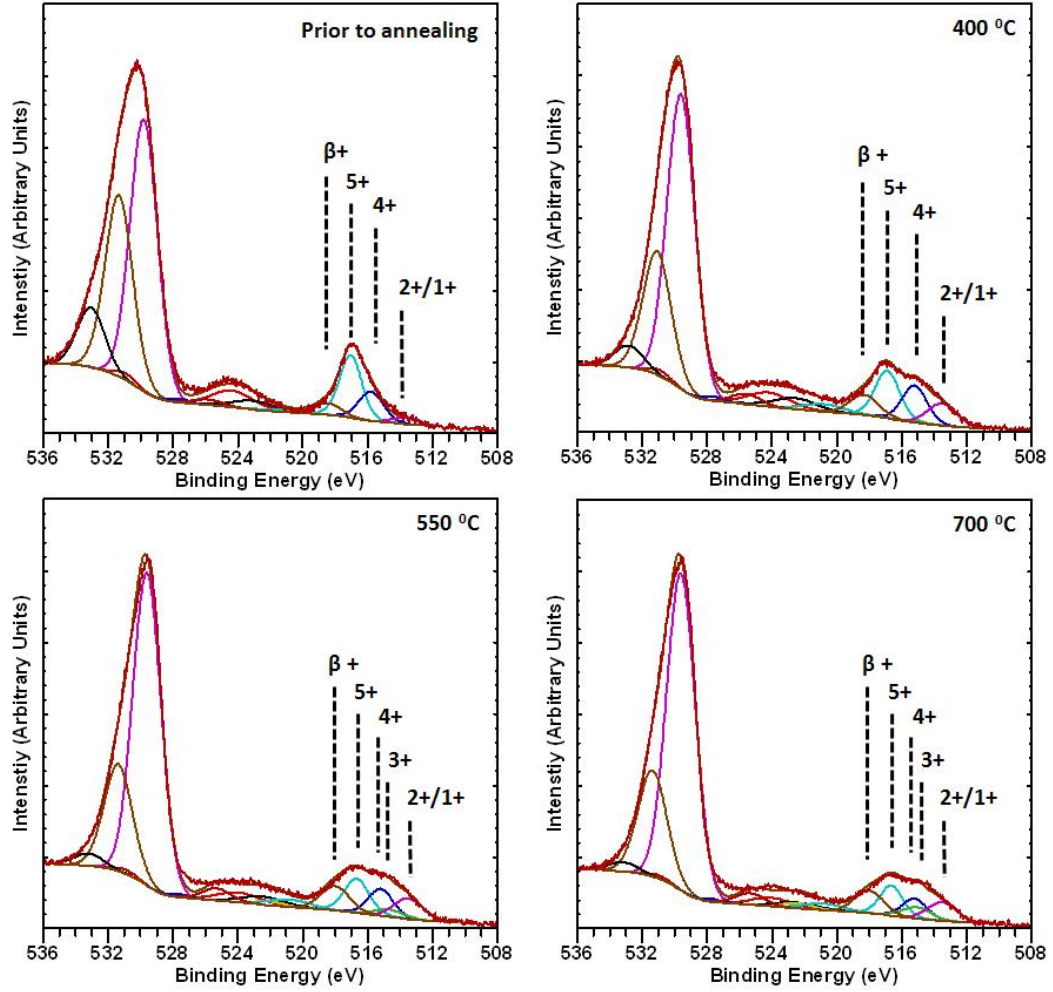


Fig. 6. O 1s and V 2p core-level region XPS spectra of a $\text{Sr}_{2.0}\text{VMoO}_6$ tape cast disc, prior to annealing and after 30 minute annealings at 400 C, 550 C and 700 C in 10^{-6} Torr H_2 .

A plot of the simulated valence distributions through the progression of these thermal treatments for V and Mo is presented in Fig 7. A summary of SR20, SR19 and SR18 valence distribution results can be found in Table II. Measured binding energies and signal FWHMs is presented in Table III.

Table II. Average of XPS fit parameters for $\text{Sr}_{2-x}\text{VMoO}_{6-y}$

Core Line	Binding Energy (eV)	FWHM (eV)
V $\beta+$ 2p _{3/2}	518.6	2.1(0)
V 5+ 2p _{3/2}	517.2	1.7(1)
V 4+ 2p _{3/2}	515.7	1.8(0)
V 3+ 2p _{3/2}	515.2	2.1(0)
V 2+/1+ 2p _{3/2}	513.8	2.0(1)
Mo $\delta+$ 3d _{5/2}	234.7	1.9(8)
Mo 6+ 3d _{5/2}	232.6	1.9(7)
Mo 5+ 3d _{5/2}	230.9	1.7(1)
Mo 4+ 3d _{5/2}	229.6	1.7(3)

Table III. XPS V and Mo valence distributions for $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples as prepared and after annealing in a hydrogen environment

		Valence Distribution (%)								
Sample	Condition	V β +	V 5+	V 4+	V 3+	V 2+/1+	Mo δ +	Mo 6+	Mo 5+	Mo 4+
SR20	Prior to Annealing	12	54	28	0	6	5	69	8	19
SR19		16	42	31	0	11	5	45	21	29
SR18		23	48	21	0	8	14	48	16	22
Average		17	48	26	0	9	8	54	15	23

SR20	400 C	16	35	27	3	19	7	47	17	29
SR19		17	31	24	11	18	9	31	20	40
SR18		19	37	20	9	15	10	52	12	25
Average		17	34	24	8	17	9	44	16	31

SR20	550 C	20	30	27	4	19	9	40	21	30
SR19		19	21	22	23	16	9	25	27	40
SR18		22	30	12	22	13	10	46	14	29
Average		20	27	20	16	16	9	37	21	33

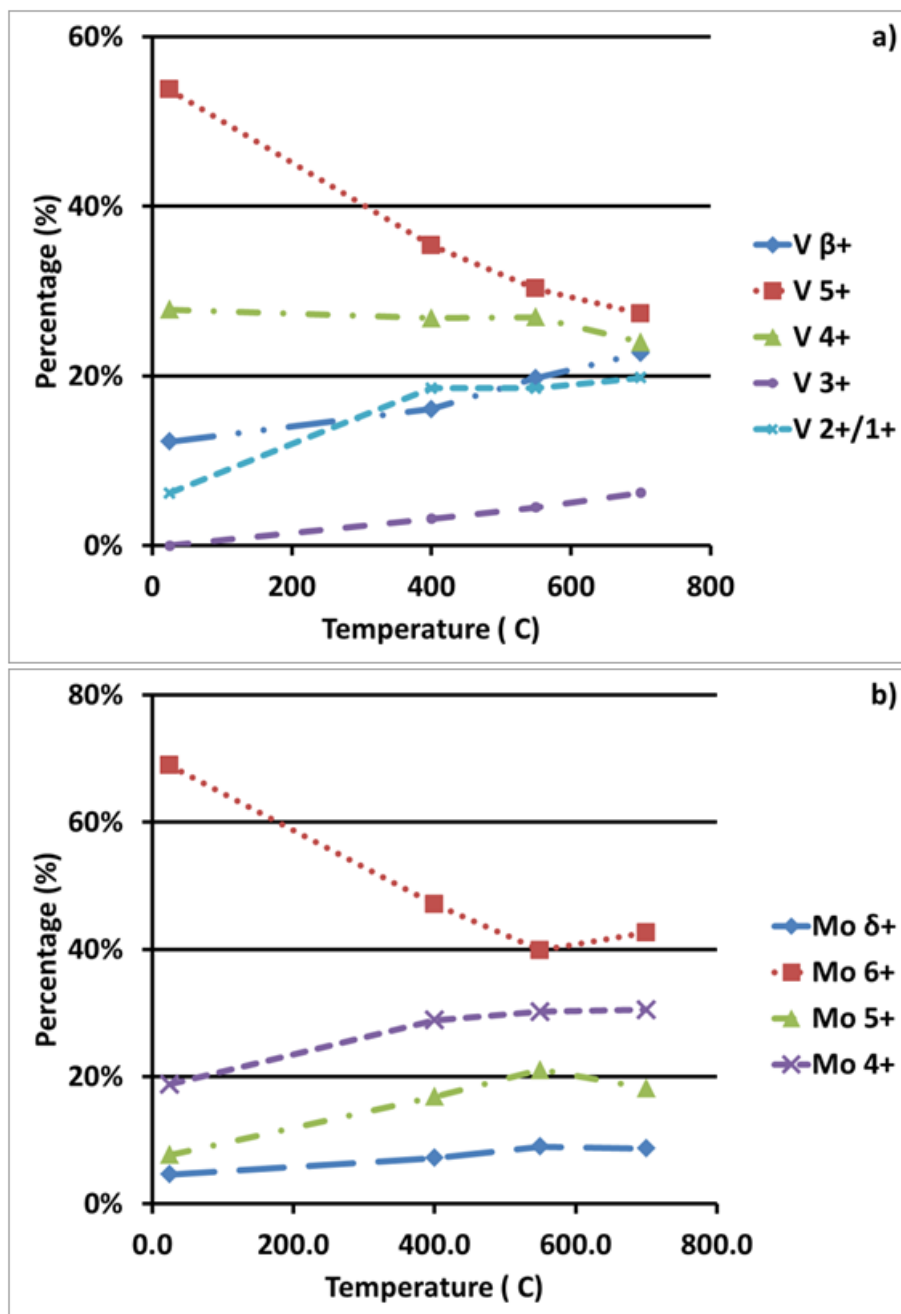


Fig. 7. Evolution of different a) vanadium and b) molybdenum valence states as a function of annealing temperatures up to 700°C for a $\text{Sr}_{2.0}\text{VMoO}_{6-y'}$ tape cast disc.

Both the vanadium 2p and molybdenum 3d regions exhibited spectral contributions that have not been reported in other M_aO_b ($M=V,Mo$) materials. The analyzed vanadium region had a V 2p_{3/2} contribution at a BE 1.4 eV higher than BEs typically reported for the V^{5+} state ($V^{\beta+}$ 2p_{3/2} core line at BE = 518.6 eV, FWHM = 2.1 eV). The analyzed molybdenum region had a Mo 3d_{5/2} contribution at a BE 2.1 eV higher than BEs typically reported for the Mo^{6+} state ($Mo^{\delta+}$ 3d_{5/2} core line at BE = 234.7 eV, FWHM = 2.0 eV). The necessity of including the $V^{\beta+}$ and $Mo^{\delta+}$ phases can be seen in Fig. 8, showing fits performed with and without the $V^{\beta+}$ and $Mo^{\delta+}$ states.

As prepared samples exhibited a vanadium valence state dominated by V^{5+} with the remainder in the $V^{\beta+}$, V^{+4} and $V^{2+/1+}$ states. The average V valence distribution over the three samples was 48% V^{5+} , 17% $V^{\beta+}$, 26% V^{+4} , and 9% $V^{2+/1+}$. The molybdenum valence state in the as prepared samples was dominated by the Mo^{+6} state while the remainder consisted of $Mo^{\delta+}$, Mo^{5+} and Mo^{4+} phases. The average Mo valence distribution over the three samples was 54% Mo^{6+} , 8% $Mo^{\delta+}$, 15% Mo^{5+} , 23% Mo^{4+} . The strontium and oxygen had valence states of Sr^{2+} and O^{2-} , respectively, as expected and did not change state throughout the experiment.

Additional 30 minute thermal treatments at 400 °C, 550 °C and 700 °C in 10^{-6} Torr H_2 resulted in continued reduction of both the vanadium and molybdenum valence states in the SR20 and SR19 samples. Due to heater limitations, the 700 °C anneal with the SR18 sample was not conducted. The average vanadium and molybdenum valence distribution for the SR20 and SR19 samples after the 700 °C anneal were 22% $V^{\beta+}$ /26% V^{5+} /23% V^{4+} /11% V^{3+} /18% $V^{2+/1+}$ and 9% $Mo^{\delta+}$ /36% Mo^{6+} /18% Mo^{5+} /36% Mo^{4+} , respectively.

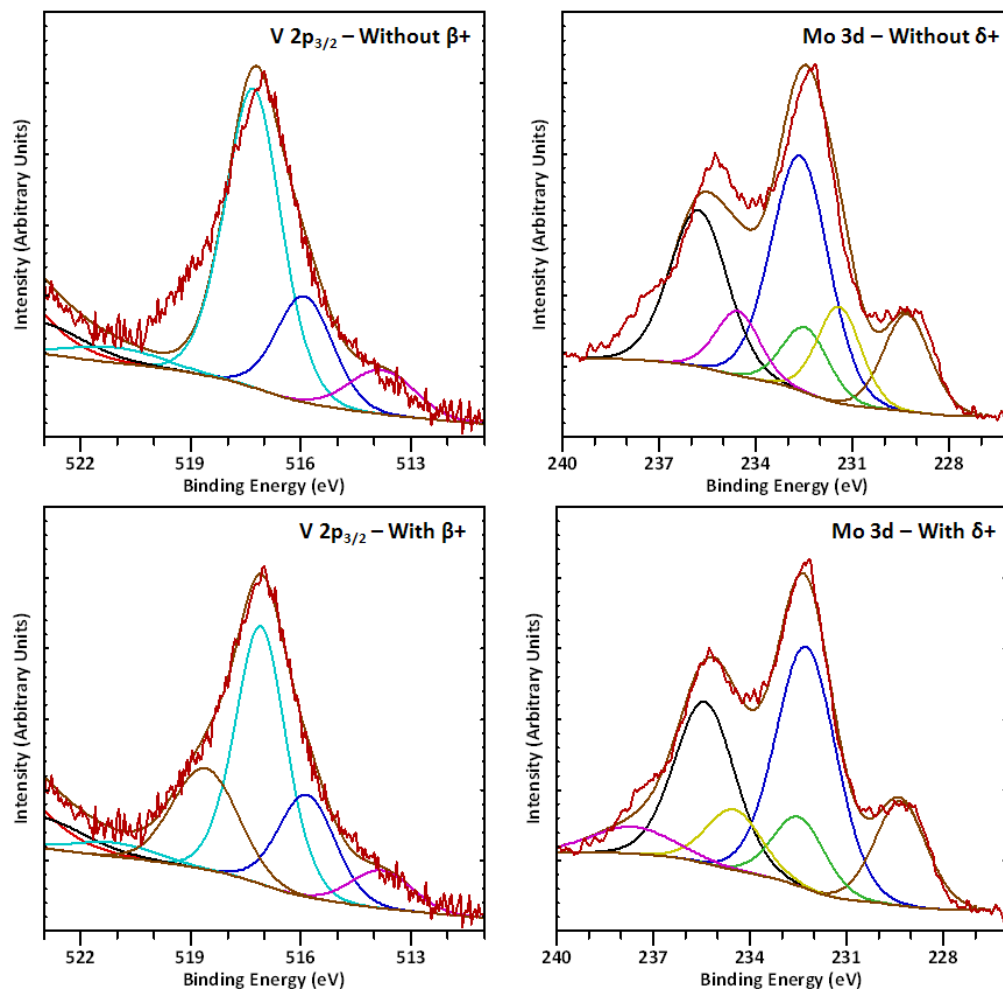


Fig. 8. V $2p_{3/2}$ region (left column) and Mo 3d region (right column) core-level region XPS spectra of a SR18 tape cast disc prior to annealing. Top row: Spectral fits conducted without the reported higher BE phases, V β^+ and Mo δ^+ . Bottom row: Spectral fits conducted with the reported higher BE phases, V β^+ and Mo δ^+ .

Upon exposure to stagnant air at room temperature the, partial re-oxidation of the sample surface was noted in as little time as 40 minutes using XPS.

4. Discussion

Solid state synthesis of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples exhibited high (1250-3000 S/cm @ 800 °C) metallic like conduction after thermal cycling in a wet reducing atmosphere (2.9% H_2O / 4.9% H_2 /92.2% N_2). After thermal cycling the conductivity values measured agree best with those reported at room temperature by Karen et. al. as opposed to other referenced conductivities.

XRD of powders ground from samples before and after being subjected to the same conditions as conductivity tests indicate minor contributions from the $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 secondary phases in the bulk of the $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples. However XPS spectra of the surface of these samples prior to any additional treatment after sintering revealed a high (85-90%) content of the V^{5+} and Mo^{6+} valence states. These valence states are consistent with the presence of the highly insulating $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 phases. These valence states were found to be reduced upon annealing in hydrogen at temperatures ranging between 400-700 °C. For vanadium during reduction the increase of the V^{4+} is consistent with the SrVO_3 phase as well as the oxidation-state couple $\text{V}^{4+}/\text{Mo}^{4+}$ in $\text{Sr}_{2.0}\text{VMoO}_{6.0}$; the increase of V^{3+} is consistent with the oxidation-state couple $\text{V}^{3+}/\text{Mo}^{5+}$ in $\text{Sr}_{2.0}\text{VMoO}_{6.0}$. For molybdenum during reduction the increase of Mo^{4+} is consistent with the SrMoO_3 phase as well as the oxidation-state couple $\text{V}^{4+}/\text{Mo}^{4+}$ in $\text{Sr}_{2.0}\text{VMoO}_{6.0}$, while the increase of Mo^{5+} is consistent only with the oxidation-state couple $\text{V}^{3+}/\text{Mo}^{5+}$ in $\text{Sr}_{2.0}\text{VMoO}_{6.0}$. The DC electrical conductivities of $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 are semiconductor like, while SrVO_3 and SrMoO_3 exhibit metallic conduction with values many orders of magnitude higher than their oxidized counterparts.

The presence of an unusual Mo 3d_{5/2} core line, similar to the Mo^{β+} phase reported in this study, has been reported in other studies of double perovskite materials with B site Mo³⁷⁻³⁹. Sarma et al. suggest this spectral feature is due to a complex Mo 3 d core state while Santiso et al. suggest this may be due to charging effects. The expected insulating valence states, V⁵⁺ and Mo⁶⁺, are reduced by annealing in a hydrogen environment. The reported V^{β+} and Mo^{δ+} states remain constant and are not reduced upon annealing.

During the thermal cycle from 50 °C ↑ 400 °C ↓ 50 °C we observe a transition in the trend of conductivity values. All samples exhibited semiconductor like conduction, however settle to an average value 40 times higher than at the start of the cycle. This temperature region is similar with the temperature region reported for the reduction of SrMoO₄ to SrMoO₃⁴⁰ and Sr₃V₂O₈ to SrVO₃⁴¹ in reducing environments. During the thermal cycle from 50 °C ↑ 850 °C ↓ 50 °C all samples exhibited semiconductor like conduction upon heating and metallic like conduction upon cooling. TGA measurements confirm that samples reduce in weight over a cycle from room temperature to 800 °C and back to room temperature. It is unclear if this final change is due to a reduction of a different phase and/or a continuation of the reduction seen in lower temperature cycles. It is important to note that the partial pressure of oxygen ranges from ~10⁻³³ to ~10⁻¹⁹ bar between 400 °C and 850 °C. The electrical conductivity values were dependent on the rate in which the samples were heated and cooled, and thus the time spent in the range of oxygen partial pressure. A thermal cycling rate of 10 °C/min produced lower final conductivity values than when performed with the slower reported rate of 2 °C/min. A single thermal cycle at 2 °C/min from 50 °C ↑ 850 °C ↓ 50 °C produced lower final

conductivity values than when all cycles were performed (room temperature $\uparrow$ 200 °C $\downarrow$ 50 °C $\uparrow$ 400 °C $\downarrow$ 50 °C $\uparrow$ 600 °C $\downarrow$ 50 °C $\uparrow$ 850 °C $\downarrow$ 50 °C). Due to reaction kinetics and environmental oxygen partial pressure values, both the thermal cycling rate and temperature cycles are critical experimental factors. Upon room temperature exposure to air after reduction, XPS confirmed surface oxidation of both V and Mo valence states, while conductivity values were also observed to degrade.

XRD, XPS, TGA and referenced publications^{12,19,20} are consistent with the conclusion that reduction of highly insulating secondary phases in $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ materials synthesized by methods described here leads to a metallic like material with high conductivity. XRD patterns in this study did not always contain measureable amounts of secondary phase; however given the phase detection limits of XRD in the 3-5% range this is not unexpected. In contrast, XPS confirmed a surface valence state distribution dominated by the V^{5+} and Mo^{6+} states in all samples studied. In other studies of Sr_2MMoO_6 double perovskite materials where the expected state of molybdenum is Mo^{6+} , it is difficult to distinguish between Mo in a double perovskite phase and Mo in SrMoO_4 through XPS and possibly is unnoticed in XRD patterns. The variability in reported conductivities for these materials may be due to the presence of these contaminant phases arising from differences in processing techniques and the environmental conditions of the conductivity tests.

The electrical conductivity of $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ materials at 800 °C in a 2.9% H_2O /4.9% H_2 /92.2% N_2 environment exceeds that reported for state of the art Ni-YSZ anodes by a factor between 1.25 and 3 at the same temperature in similar environments. The

metallic like conduction is the result of highly delocalized d-electrons, an undistorted metal-oxygen bond angle and a bond length that allows for overlapping of the metal t_{2g} and oxygen p_{π} electron orbitals^{12,20,22}. Polycrystalline $\text{Sr}_{1.9}\text{VMoO}_{6-y}$ samples exhibited higher room temperature electrical conductivity than that reported for SrMoO_3 polycrystalline samples ($\text{SR19} > 30,000 \text{ S/cm}$). A fully dense, single crystal sample of $\text{Sr}_{1.9}\text{VMoO}_{6-y}$ would be a candidate for exhibiting the highest electrically conducting oxide known.

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CHAPTER 6

SUMMARY OF DISSERTATION

The primary goals for this dissertation were to investigate the limitations of the currently used anode cermet material, synthesize and characterize a double perovskite material ($\text{Sr}_{2-x}\text{VMoO}_{6-y}$) without these limitations and to investigate the electrical conduction properties of this mixed ionic and electronic conductor (MEIC) in a SOFC anode environment. Each of these goals was accomplished. The unique contributions to the scientific community are summarized in three manuscripts (Chapters 3-5).

Limitations of Current SOFC Anode Technology

In order to investigate nickel network current densities a computer simulation of percolating nickel networks in a Ni-YSZ anode was developed. Using a percolation model we were able to calculate the current density distribution within connected nickel particles in a simulated Ni-YSZ anode. The model was analyzed for modeled area, nickel volume percentage and porosity dependence. Both nickel volume percentage and porosity had significant effects on the current distribution within the modeled anode. Low nickel content and high porosities produced anodes with nickel particles experiencing high current densities compared to the anode current density. There is a wide distribution of current densities seen by nickel particles in an anode. A large percentage of the nickel particles experience current densities below that reported for the anode. Small percentages of nickel particles experience high current densities compared to the overall

anode. Even though the percentages are low, the impact to anode resistance from disconnecting these particles is drastic and will lead to increased ohmic resistance and possible anode failure. The results from this calculation are not dependent on the resistive properties of nickel. Thus the results are valid for any anode made up of an electronic conductor, ionic conductor and porous networks.

The experimental study provided an average critical current density of 58600 A/cm² for 25 μ m nickel wire in a typical SOFC environment (reducing and 800 °C). For typical nickel particle sizes in anodes this value should increase due to surface to volume ratios. Results from wire experiments in gaseous environments may differ from nickel embedded in a porous YSZ structure, where heat transfer to the surrounding environment will be inhibited by the YSZ. Very few nickel particles are expected to see the critical current densities measured in this investigation during normal fuel cell operation. Joule heating may assist nickel migration, however this experiment and calculation suggests that it is not the primary driving mechanism for nickel migration or failure of cells.

Creating a Materials Solution

XRD patterns indicate that the double perovskite is the primary phase for Sr_{2-x}VMoO_{6- δ} pellets sintered at 1300°C for 20 hours in hydrogen; however, these pellets show a secondary phase of SrMoO_{4- δ} . Thus studies evaluating this or other double perovskites that utilize molybdenum must be cautious of processing conditions that are insufficient to yield phase pure materials. XPS revealed a deficiency of vanadium on the pellet surfaces, with an average composition of 24.8%, 4.2%, 11.8%, 59.2% for Sr, V,

Mo, O, respectively. The low vanadium concentration can be explained by the formation of the $\text{SrMoO}_{4-\delta}$ scheelite phase on the surface and vanadium migration to the bulk, which was exhibited in redox cycling. RBS confirmed that the bulk elemental compositions of samples were close to the starting ratios of Sr/Mo/V with the remainder being 58-64% O.

$\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets exhibited an average yield strength of 260.8 MPa, which is higher than published values of 61.5-88.5 MPa for traditional Ni/YSZ cermets [1]. The high strength of the $\text{Sr}_2\text{VMoO}_{6-\delta}$ sintered pellets observed during hardness testing indicates that the double perovskite should be sufficiently strong for the fabrication of a fuel electrode supported SOFC. Of the sintering temperatures explored (1100°C, 1200°C and 1300°C) $\text{Sr}_{2-x}\text{VMoO}_{6-\delta}$ pellets sintered at 1300°C showed the highest conductivity at both SOFC operating temperature (800°C) and room temperature after cooling from 800°C.

The Exciting Electrical Properties of this MEIC

$\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples exhibited high (1250-3000 S/cm @ 800 °C) metallic like conduction after thermal cycling in a wet reducing atmosphere (2.9% H_2O /4.9% H_2 /92.2% N_2). After thermal cycling the conductivity values measured agree best with those reported at room temperature by Karen et. al. [2] as opposed to other referenced conductivities. Upon room temperature exposure to air after thermal cycling conductivity values were observed to degrade.

XRD spectra obtained from powders ground from samples before and after being subjected to the same conditions as conductivity tests indicate minor contributions from the $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 secondary phases in the bulk of the $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ samples. However XPS spectra of the surface of these samples prior to any additional treatment after sintering revealed a high (85-90%) content of the V^{5+} and Mo^{6+} valence states. These valence states are consistent with the presence of the highly insulating $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 phases. These valence states were found to be reduced upon annealing in hydrogen at temperatures ranging between 400-700 °C. This temperature region is similar with the temperature region reported for the reduction of SrMoO_4 to SrMoO_3 [3] and $\text{Sr}_3\text{V}_2\text{O}_8$ to SrVO_3 [4] in reducing environments. Upon room temperature exposure to air after reduction, XPS confirmed surface oxidation of both V and Mo valence states. The DC electrical conductivities of $\text{Sr}_3\text{V}_2\text{O}_8$ and SrMoO_4 are semiconductor like, while SrVO_3 , SrMoO_3 and $\text{Sr}_{2.0}\text{VMoO}_{6.0}$ exhibit metallic conduction with values many orders of magnitude higher than their oxidized counterparts.

The presence of an unusual Mo $3d_{5/2}$ core line, similar to the $\text{Mo}^{\beta+}$ phase reported in this study, has been reported in other studies of double perovskite materials with B site Mo [5-7] Sarma et al. suggest this spectral feature is due to a complex Mo 3 d core state while Santiso et al. suggest this may be due to charging effects. The expected insulating valence states, V^{5+} and Mo^{6+} , are reduced by annealing in a hydrogen environment. The reported $\text{V}^{\beta+}$ and $\text{Mo}^{\delta+}$ states remain constant and are not reduced upon annealing.

XRD, XPS, TGA and referenced publications [2,8,9] are consistent with the conclusion that reduction of highly insulating secondary phases in $\text{Sr}_{2-x}\text{VMoO}_{6-y}$

materials synthesized by methods described here leads to a metallic like material with high conductivity. XRD patterns in this study did not always contain measureable amounts of secondary phase; however, given the phase detection limits of XRD in the 3-5% range this is not unexpected. In contrast, XPS confirmed a surface valence state distribution dominated by the V^{5+} and Mo^{6+} states in all samples studied. In other studies of Sr_2MMoO_6 ($M=Fe, Mn, Mg, Cr, Co, Ni$) double perovskite materials where the expected state of molybdenum is Mo^{6+} , it is difficult to distinguish between Mo in a double perovskite phase and Mo in $SrMoO_4$ through XPS and possibly is unnoticed in XRD patterns. The variability in reported conductivities for these materials may be due to the presence of these contaminant phases arising from differences in processing techniques and the environmental conditions of the conductivity tests.

The electrical conductivity of $Sr_{2-x}VMoO_{6-y}$ materials at 800 °C in a 2.9% H_2O /4.9% H_2 /92.2% N_2 environment exceeds that reported for state of the art Ni-YSZ anodes by a factor between 1.25 and 3 at the same temperature in similar environments. The metallic like conduction is the result of highly delocalized d-electrons, an undistorted metal-oxygen bond angle and a bond length that allows for overlapping of the metal t_{2g} and oxygen p_π electron orbitals [2,8,10]. Polycrystalline $Sr_{1.9}VMoO_{6-y}$ samples exhibited higher room temperature electrical conductivity than that reported for $SrMoO_3$ polycrystalline samples ($SR19 > 30,000$ S/cm). A fully dense, single crystal sample of $Sr_{1.9}VMoO_{6-y}$ would be a candidate for exhibiting the highest electrically conducting oxide known.

The pursuit of growing a single crystal of these $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ materials by pulse laser deposition is of interest for future research. At this point we can only allude to the fact that these materials may exhibit the highest electrical conduction values of any known oxide. The facilities and resources are available here at MSU to pursue this as a research goal and funding should be pursued.

The XRD study of the material was used to distinguish between a main perovskite phase and the secondary phases mentioned. No attempt was made to deconvolute the XRD signal associated with the perovskite structure into the various possible contributing phases, SrVO_3 , SrMoO_3 and Sr_2VMoO_6 . Karen et al. [2] state that their processing technique yields a phase pure double perovskite that does not oxidize over time in room temperature air resulting in no degradation in electrical conductivity values over time. The processing technique described here results in a material with contrasting properties. It is possible that our technique results in a material with some amount of SrVO_3 and SrMoO_3 which oxidizes in room temperature air. The ability to deconvolute XRD spectra into contributions from these three phases will assist in the further development of processing techniques.

In regards to $\text{Sr}_{2-x}\text{VMoO}_{6-y}$ materials as SOFC anodes only the property of electrical conduction has been discussed here. Other critical anode properties such as ionic conduction and catalytic activity will have to be evaluated before this material becomes an alternative to Ni-YSZ. Investigation of these anode properties is of interest as further research topics.

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CHAPTER FOUR

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