Solid Oxide Fuel Cell Electrolyte Membrane Fabrication

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Abstract

This thesis explores the use of the University of Virginia's plasma-assisted directed vapor deposition (DVD) technology for creation of a dense, pinhole-free solid oxide fuel cell (SOFC) electrolyte membrane layer. Within a fuel cell, the electrolyte membrane is a central component that permits passage of ions (but not electrons) as part of an electricity generation process. To maximize energy production efficiency, the electrolyte membrane must prevent direct contact between electrochemical reactants on either side of the membrane. In a solid oxide fuel cell, guaranteed separation dictates that the electrolyte membrane be a dense, pinhole-free layer, usually composed of a metal oxide. For this thesis, a simple deionized water droplet test, scanning electron microscopy, and x-ray diffraction were used to evaluate the atomic structure of yttria-stabilized zirconia (YSZ) electrolyte membrane layers deposited onto porous nickel oxide/YSZ substrates under different DVD process conditions. The study suggested that increasingly dense layers were created as the YSZ vapor stream was ionized and the deposition substrate was subjected to an electrical bias. For conditions studied, the best plasma-assisted DVD process conditions appeared to be those that heated the deposition surface to 800°C, injected a 120 A plasma current into the YSZ vapor stream, and applied of a 200 V / 21 kHz bias potential to the substrate. The material deposition rate was approximately 45 μ m/hr, comparable to commercial processes available today for SOFC electrolyte membrane fabrication. While the deionized water test suggested that coatings deposited under these conditions were denser than other DVD synthesized coatings, the SEM images showed that they were not fully dense. The primary cause of continued film porosity appears to be the background gas pressure in the DVD chamber (8 Pa / 60 mTorr) which produces low energy neutral atoms for deposition onto the coating surface.

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List of Symbols

A	Cross-sectional area
AC	Alternating current
ст	Centimeter
d	Distance
DC	Direct current
e_{ideal}	Maximum energy conversion efficiency (ideal)
eV	Electron volt
g	Gas
Ι	Current
kg	Kilogram
kW	Kilowatt
l	Liquid
L	Length
λ	Wavelength
mA	Milliamp
min	Minute
mm	Millimeter
m/o	Molecular percent
μm	Micrometer
mTorr	MilliTorr
Р	Power
P_b	Carrier gas mixing chamber pressure
P_o	Process chamber pressure
Pa	Pascal
R	Resistance
ρ	Resistance coefficient

List of Symbols

S	Siemens – unit of conductivity
slm	Standard liter per minute
T_L	Absolute temperature of cold reservoir
T_H	Absolute temperature of hot reservoir
θ	Angle
V	Volt
w/o	Weight percent

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Chapter 1 Introduction

The research of this thesis will investigate a new process pathway for the creation of electrolyte membrane layers within solid oxide fuel cells. Solid oxide fuel cells have been under development for decades, and numerous aspects of the technology are being actively studied and improved. This thesis explores the use of the University of Virginia's plasma-assisted directed vapor deposition (DVD) technology for the creation of dense, pinhole-free solid oxide fuel cell (SOFC) electrolyte membrane layers from metal oxide. The material processing capabilities of DVD are different than those of other techniques used so far to produce SOFC electrolyte membrane layers more quickly and efficiently than existing methods, with compositions not easily attainable via the other methods. If DVD proves capable of creating such layers, it could become a valuable new technology for the continued development of fuel cells as alternate, clean energy production systems that may one day supplant many of the internal combustion engines and gas turbines employed around the world today.

1

1.1 The Development of the Fuel Cell

Fuel cells were originally envisioned in the nineteenth century when Sir William Robert Grove described their principle of operation in 1839 [1]. Grove was familiar with the process of electrolysis whereby electrical energy can be used to split a molecule such as water apart into its constituents:

$$2H_2O(1) \rightarrow 2H_2(g) + O_2(g).$$
 (1.1)

He reasoned that it should be possible to reverse the process, reacting hydrogen with oxygen to generate electricity and water. To create such an electricity production unit, Grove enveloped two platinum electrodes in oxygen and hydrogen at room temperature and submerged those electrodes into a dilute sulfuric acid electrolyte solution. His early design worked. Near the end of the nineteenth century, Ludwig Mond and Charles Langer coined the term "fuel cell" and attempted to use air and coal gas to generate electricity, following Grove's basic design. At that time no conventional batteries (e.g. today's lead acid, nickel cadmium, or lithium ion batteries) were yet available, and so their fuel cell stack¹ applied to the electrolysis of water represented a first electric high power supply [2].

The basic components of a fuel cell are illustrated in Fig. 1.1. In any fuel cell, both the anode and cathode are composed, at least in part, of materials that stimulate chemical reactions or transformations, i.e. they include catalysts. The catalyst within the anode promotes release of free electrons from the cell's fuel source. The catalyst within the cathode promotes the generation of oxygen ions from the cell's oxygen source. When separated by an electrolyte membrane layer that allows passage of ions while limiting electron flow, fuel cell anodes and cathodes work together to release free electrons that are available to do work as part of an external circuit.

¹ Fuel cell stack – a set of individual fuel cell units linked together in series to increase voltage output.



Figure 1.1 Basic configuration of a fuel cell.

Fuel cells have been recognized since the early days as efficient, environmentallycompatible energy conversion devices when compared to internal combustion engines and later gas turbines [3]. Internal combustion engines and gas turbines are types of heat engines, and their maximum energy conversion efficiency (e_{ideal}) is defined by:

$$\mathbf{e}_{\text{ideal}} = 1 - T_{\text{L}}/T_{\text{H}} \tag{1.2}$$

where T_L and T_H are the absolute temperatures of the cold and hot reservoirs respectively. Despite more than a century of refinement, most internal combustion engines struggle even today to achieve energy conversion efficiencies above 15-20%. In contrast, fuel cells regularly achieve efficiencies of 40-60%, or as high as 85-90% when the heat from their internal chemical reactions is captured [4]. Similarly, when fuel cells and internal combustion engines are used to generate the same power output, fuel cells generate lower carbon dioxide emissions, and they produce negligible amounts of SO_x and NO_x, the main constituents of acid rain and photochemical smog [4]. When utilizing natural gas as a fuel, fuel cells produce 60% less carbon dioxide than a coal burning power plant and 25% less carbon dioxide than a natural gas fired power plant [5]. Still, fossil fuel-burning internal combustion engines and gas turbines have dominated the energy and power production

markets for over a century because of their ability to satisfactorily meet the diverse demands of the market - mechanical robustness (service life), cost of production (complexity), cost of use (efficiency), environmental impact (emissions and source of fuel), power to weight ratio, availability of fuel (infrastructure and source of fuel), and customer satisfaction [6].

In contrast, the introduction of fuel cells into widespread use has been hampered in large part by their cost of production and long-term reliability. For instance, the high cost of fuel cells limited early market penetration in the 1960s to space-based applications where the use of internal combustion engines or gas turbines was impractical [3]. More recently, environmental impact restrictions placed upon energy producers and transportation system manufacturers have begun to generate additional interest in fuel cells, despite their continued high cost, e.g. \$4500 per kW compared to \$800-\$1500 per kW for a diesel generator [5, 7]. Efforts are underway to decrease the cost of fuel cell units, and much of this effort is focused upon development of lower cost, more reliable fuel cell materials. Degradation of fuel cell performance is reported and generally attributed to evolution of their materials over time, even though fuel cells have no moving parts [8, 9].

Four types of fuel cells are being developed around the world. These are the polymer electrolyte fuel cell (PEFC), the phosphoric acid fuel cell (PAFC), the molten carbonate fuel cell (MCFC), and the solid oxide fuel cell (SOFC). The chief difference between each is the material used for the electrolyte membrane, anode, and cathode. The characteristics of the different types of fuel cell are summarized in Table 1.1 [3, 10, 11], and desirable physical characteristics of the various cell components are presented in Table 1.2 [3].

	Solid oxide (SOFC)	Molten carbonate (MCFC)	Phosphoric acid (PAFC)	Polymer membrane (PEFC)
Electrolyte	Ceramic (e.g., yittria stabilized zirconia (YSZ), ceria doped gadolinia (CGO))	Immobilized liquid molten carbonate (molten Li ₂ CO ₃ -K ₂ CO ₃)	Immobilized liquid phosphoric acid (H ₃ PO ₄)	Ion exchange membrane (e.g. Nafion)
Electrolyte support	None	LiAlO ₂	SiC	None
Cathode	Sr doped La MnO_3 , Sr doped La $Co_{0.2}Fe_{0.8}O_{3-x}$	Li doped NiO	polytetrafluoro ethylene (PTFE) bonded Pt on C	PTFE bonded Pt on C
Anode	Ni/YSZ, Ni or Cu/CGO	Ni	PTFE bonded Pt on C	PTFE bonded Pt on C
Interconnect/ Bipolar	Doped LaCrO ₃ , Inconel X-750, FeCrAlY	Stainless steel clad with Ni	Glassy carbon	Graphite
Catalyst	Nickel, copper	Nickel	Nickel	Platinum
Operating T	600-1000°C	650°C	205°C	80°C
Fuel	H ₂ , CO, CH ₄ , higher order hydrocarbons	H ₂ , CO, CH ₄	2, CO, CH ₄ H ₂	
Efficiency	45-65%	50-60%	40-50%	40-50%

Table 1.1: Characteristics of fuel cell types being actively developed

Table 1.2: Fuel cell components properties

	Anode	Cathode	Electrolyte	Interconnect	
Conductivity	High electronic conductivity		High ionic conductivity, negligible electronic conductivity		
Stability	Chemical, phase, morphological and dimensional stability in fuel and / or oxidant environment				
Compatibility	No damaging chemical interactions or interdiffusion with adjoining components				
Porosity	Porous Fully dense				
Thermal expansion	Match adjoining components				

1.2 The Solid Oxide Fuel Cell

In the realm of fuel cell technology, solid oxide fuel cells have been identified by certain energy producers as particularly attractive. These producers note the elevated energy production efficiency of SOFCs (Table 1.1) and have recognized that the high operating temperature of the cells, usually around 1000°C today, allows useful heat to be generated as a byproduct. The core efficiency and heat production of SOFCs help to reduce the cost/kW in these systems. As a result, many energy producers have singled out SOFCs as stationary energy production systems, and some industrial developers such as ITN Energy Systems (Littleton, Colorado) have recently proposed SOFCs for mobile applications. While SOFCs are efficient, their high operating temperatures (driven by materials identified as suitable for the anode, cathode, and electrolyte membrane) put severe restrictions upon the materials that can be used reliably within all portions of the fuel cell system, and this drives up SOFC unit costs. The development of new, lower temperature materials is critical to broader acceptance of SOFCs. Availability of such materials likely depends upon the continued development of material synthesis pathways capable of generating atomic structures and compositions that deliver high SOFC power densities at reduced operating temperatures [12].

Fig. 1.2 shows the configuration and operating principle of a SOFC. A single SOFC unit consists of the two standard electrodes separated by an electrolyte membrane. Fuel, e.g. H₂, CH₄ or more complex hydrocarbons, arrives at the anode, where it is oxidized by oxygen ions supplied through the electrolyte membrane from the cathode. On the other side of the fuel cell, oxidant, e.g. O₂ or air, is fed to the cathode, where it supplies the oxygen ions (O^{2-}) to the electrolyte membrane. The electrolyte membrane conducts these ions between the electrodes, maintaining overall electrical charge balance, and the flow of electrons from the anode into the external circuit provides useful power. The electrochemical

reactions occurring within a SOFC utilizing a hydrocarbon as fuel are as follows:

Anode:
$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$
 (1.3)
 $CO + O^{2-} \rightarrow CO_2 + 2e^-$ (1.4)
Cathode: $O_2 + 4e \rightarrow 2O^{2-}$ (1.5)

Overall:
$$H_2 + 1/2 O_2 \rightarrow H_2O$$
 (1.6)



Figure 1.2 **Physical configuration and operating principle of a state-of-the-art SOFC.**

1.3 Applications of Solid Oxide Fuel Cells

While the major applications of fuel cells are currently seen as stationary electric power plants, auxiliary power units in transportation vehicles, and on-board power for aircraft or space vehicles [3, 13], the work of this thesis has been motivated by a Defense Advanced

Research Projects Agency (DARPA) project to develop a power pack small enough to be carried by soldiers in the field. Within this initiative the University of Virginia (UVA) has been part of a DARPA-funded team led by ITN Energy Systems Inc. that is developing a solid oxide fuel cell (SOFC) system that will operate directly on JP-8 fuel and deliver 20 watts of 12 volt DC power continuously for 3 days, or longer with refueling. JP-8 jet fuel (similar to commercial/international jet A-1 fuel) is the standard military fuel for all types of vehicles and is composed of a mixture of complex hydrocarbons. ITN Energy Systems has envisioned an 8 x 10 x 15 cm Palm Power system consisting of a 12-cell stack and a fully-loaded weight of just 0.7 kg (Fig. 1.3) [14]. Though under development for DARPA, future applications could include remote commercial and recreational uses.



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Figure 1.3 ITN Energy Systems' proposed DARPA Palm Power generator [14].

1.4 Directed Vapor Deposition for Electrolyte Membrane Synthesis

Many present SOFC designs use thin film deposition technologies to create cathode, anode, electrolyte membrane, and interconnect [3]. The exact techniques utilized differ

depending upon system developer and cell configuration, e.g. tubular or planar [15]. The task addressed by this thesis is fabrication of a thin electrolyte membrane for the planar ITN Energy Systems cell. Thin electrolytes are favored in SOFCs because they should make possible useful power production and effective oxygen ion transport through the electrolyte membrane at reduced temperatures, below 1000°C. Such operation will allow less expensive materials to be utilized throughout the system. The literature suggests that by reducing electrolyte membrane layer thickness, it is possible to increase the oxygen ion gradient across the membrane and thus reduce oxygen ion trapping and dwell time within the membrane [10]. By minimizing ion trapping and dwell time within the membrane, a high density of useful power can be efficiently delivered to the external circuit.

Specifically, this thesis examines the use of UVA's plasma assisted directed vapor deposition (DVD) technology for the fabrication of dense, pinhole-free electrolyte membrane layers on anode supporting layers supplied by ITN Energy Systems. If DVD can create these layers from metal oxides such as yttria-stabilized zirconia (YSZ), the technique could become a key element that accelerates SOFC introduction into a host of energy production devices. Additionally, DVD has great flexibility in the alloy compositions that it can deposit, making it attractive for the synthesis of new, lower-temperature SOFC materials. Before exploring new SOFC electrolyte membrane layer compositions, this thesis will focus upon dense, pinhole-free layer fabrication. Finally, the DVD system has the prospect of increasing deposition rates to 1-15 µm/min [16-18]. Other technologies of electrolyte fabrication in planar units include chemical vapor deposition, electrochemical vapor deposition, pulsed laser deposition, sputtering, slurry/sol-gel coating, tape casting, and plasma spray. Disadvantages of these technologies include either a low deposition rate (0.15-4 µm/h) [10] uneconomical for large-scale production or an inability to create thin electrolyte membrane layers (< 20 µm).

The directed vapor deposition (DVD) technology employed in this thesis has been under study and development at UVA since the early 1990s, and it was first patented in 1996 [17]. The spark for DVD was generated by an industrial desire to enhance material utilization efficiency and deposition rate in vapor technologies. Coinventors Wadley and Groves believed that, by introducing electron beam (e-beam) evaporant into a flowing gas stream, it would be possible to focus the vapor and enhance material deposition rates and utilization efficiencies. Subsequent study of DVD [16] also suggested that, by coupling low vacuum e-beam evaporation and flowing gas transport of vapor with additional technology components, plasma activation of the vapor stream and electrical biasing of the coating surface, it should be possible to impart useful control over the composition and structure of growing films. These subsequent studies led to the assembly of a plasma-assisted directed vapor deposition system that was delivered to UVA during the summer of 2000 by the Fraunhofer Institute for Electron Beam and Plasma Technology (Dresden, Germany) [18-20]. This system was developed with the goal of providing a highly flexible film creation tool for the vapor deposition community (Figs. 1.4 and 1.5).

This thesis will report upon investigations targeted at the synthesis of dense, pinhole-free solid oxide fuel cell electrolyte membrane layers by plasma assisted directed vapor deposition. A set of DVD process conditions will be sought that produce thin, compositionally correct electrolyte membrane layers. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) will be used to analyze the layers produced by DVD.



Figure 1.4 Schematic illustration of a plasma-assisted directed vapor deposition system. This is the tool utilized for this thesis work.



Figure 1.5 **Plasma-assisted directed vapor deposition facility.**

Chapter 2 Literature Review

As noted in the Introduction, fuel cell research began over 150 years ago. Since that time, scientists and engineers have employed numerous materials and fabrication techniques to develop fuel cell systems that deliver useful energy. This chapter will briefly review the material compositions, atomic structures, and fabrication methods that have been employed for solid oxide fuel cell fabrication. It will also review relevant details of directed vapor deposition material synthesis performed prior to the work of this thesis as well as important aspects of the underlying technology incorporated into the plasma-assisted DVD system. Since the research of this thesis concentrates upon fabrication of the electrolyte membrane layer, only those material composition, structure, and fabrication issues that impact the development of the solid oxide fuel cell electrolyte membrane layer will be addressed within this literature review.

2.1 SOFC Materials

Although fuel cell development began in the mid nineteenth century, the first *solid oxide* fuel cell was built by Baur and Preis in 1937. It operated at a temperature of 1000°C [6, 21, 22], and, during selection of material for the cell, Baur and Preis recognized that the electrolyte membrane layer needed to conduct oxygen ions, O^{2-} , while preventing the conduction of free electrons (See Fig. 1.2.). By establishing such a charge flow configuration they could create a supply of free electrons to an external circuit for energy production. In their cell, ZrO₂-25 molecular percent (m/o) MgO or ZrO₂-15 m/o Y₂O₃ was used as the electrolyte membrane layer. Baur and Preis based their metal oxide materials selection in part upon the earlier work of Nernst who, as early as 1899, suggested that ZrO₂ with ~9 m/o Y₂O₃ was a solid oxide ion conductor [23].

Interestingly, the most prevalent material in use today as a SOFC electrolyte membrane is yttria-stabilized zirconia (YSZ) with 8-10 m/o Y_2O_3 [5]. This material system has long been favored for this application because of its high temperature ionic conductivity (0.02 S/cm at 800°C, 0.1 S/cm at 1000°C), low electron conductivity, and stable crystal structure [5, 6, 24]. The crystal structure of YSZ with 8-10 m/o Y_2O_3 derives from cubic zirconia (Figure 2.1). Within YSZ, yttrium (3+) substitutes for zirconium (4+), and, to maintain charge neutrality, some number of oxygen lattice site vacancies are formed. At high temperature, thermally activated oxygen ion transport becomes possible using these vacancy sites.

While YSZ will be utilized for the work in this thesis, other electrolyte membrane materials are being actively investigated [25-39]. Such materials are generally being considered because they offer the prospect of SOFC operation at temperatures well below 1000°C, and lower temperatures translate into lower cost and possibly more reliable fuel cell units. The



Figure 2.1 **The lattice of cubic zirconia.** The oxygen atoms are located at the 'tetragonal' interstitial sites.

two major material systems currently under wide study are doped ceria [26, 27, 30-34] and doped lanthanum gallate [26, 29, 30, 35-39]. Ceria has the same crystal structure as zirconia for doping. Lanthanum gallate's structure is described by the more complex perovskite lattice shown in Fig. 2.2 [25, 30].



Figure 2.2 **The lattice of lanthanum gallate.** a) one-fourth of the unit cell b) the entire perovskite unit cell [40]

Research into these electrolyte material systems and structures has been driven in large part

by a search for robust oxygen ion conductivity at temperatures below 1000°C. Using YSZ's 0.10 S/cm ionic conductivity as the baseline for comparison, Table 2.1 records how recent research has uncovered a set of proposed electrolyte membrane layer materials with high oxygen ion conductivity at reduced temperatures. For the selected materials, the

	YSZ [26]	CGO10 [32, 33]	CGO20 [28, 32-33]	LSGMO30 [37]	LSGMO35 [37]	LSGMNO [38]
500°C	0.0010 S/cm	0.0095	0.0053	0.010	0.0080	0.018
600°C	0.0028	0.025	0.018	0.029	0.028	0.056
700°C	0.014	0.054	0.048	0.071	0.10	0.12
800°C	0.025	0.060	0.089	0.18	0.14	0.28
900°C	0.050	0.10	0.16	-	-	0.35
1000°C	0.10	0.16	0.23	-	-	0.56

Table 2.1: Ionic conductivities for various SOFC electrolyte membrane materials

 $YSZ - ZrO_2$ stabilized with 10 m/o Y_2O_3

 $LSGMO30 - La_{0.8}Sr_{0.2}Ga_{0.9}Mg_{0.1}O_{2.85}$

 $CGO10 - Ce_{0.9}Gd_{0.1}O_{2-\delta}$

 $CGO20-Ce_{0.8}Gd_{0.2}O_{2\text{-}\delta}$

 $LSGMO35 - La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$

 $LSGMNO - La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.13}Ni_{0.07}O_3$

recently reported La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.13}Ni_{0.07}O₃ (LSGMNO) system shows ionic conductivity of 0.10 S/cm at a temperature below 700°C [38]. Importantly, some of the doped lanthanum gallate structures have shown almost pure ionic conduction over a wide

range of oxygen partial pressures [36, 38]. While there are unresolved material performance issues associated with doped lanthanum gallates, they do appear to be promising materials for intermediate temperature SOFCs [40]. Their potential to reduce SOFC operating temperature by more than 300°C opens up the possibility of utilizing other lower cost materials throughout the rest of the fuel cell unit [12, 30, 38]. The doped ceria materials have shown a propensity towards significant electronic transport under low oxygen partial pressures (as experienced in the vicinity of the anode) [33]. Electronic conductivity acts as a short circuit in the cell and reduces overall device efficiency. It should be noted that the degree of electronic conductivity in CGO is a strong function of temperature and below 600°C, minimal electronic conductivity develops [32].

Although doped ceria and doped lanthanum gallate material systems have been identified as promising electrolyte membrane layers, the specific anode and cathode material systems that should be coupled to these electrolyte membranes have not been so clearly established [30-38]. For the work of this thesis, the use of nickel-YSZ or copper-YSZ cermets for the anode and lanthanum strontium manganite for the cathode is well established within the literature [41]. Since the research of this thesis is focused upon the delivery of materials for working SOFCs for the U.S. military, the decision has been made to demonstrate metal oxide densification in the well-characterized YSZ system first before considering explorations of ceria- or lanthanum gallate-based systems for the future.

2.2 SOFC Fabrication Methods

As noted in the Introduction, many manufacturers are searching for cost-effective production technologies that facilitate the creation of thin, dense electrolyte membranes (1 $-10 \mu m$ thick) to be used within anode-supported planar SOFCs [12]. To achieve this

goal, manufacturers have examined a host of fabrication processes, including plasma spraying [42, 43], tape casting [42], slurry/sol-gel [42, 44, 45], chemical vapor deposition (CVD) [42, 46], electrochemical vapor deposition (EVD) [42, 47], electrostatic assisted spray deposition (EAVD) [42, 48], sputtering [42, 49-51], pulsed laser deposition [42], and others [42]. For each fabrication process, deposition rate, composition, density, and cost represent key considerations for use of these techniques in the manufacture of SOFC electrolyte membrane layers. Will *et al.* [42] have provided an excellent overview and summary of the various deposition technologies that have recently been applied to SOFC electrolyte membrane layer synthesis.

Study of the literature does not reveal any one deposition technique that stands out as the best method for planar SOFC electrolyte membrane layer synthesis. Survey of the literature reveals that films have been deposited on a host of substrates with different porosity characteristics and surface roughnesses. Because of these differences and because the porosities and roughnesses have not been well-characterized, a definitive comparison of techniques for the creation of dense, pinhole-free electrolyte membranes is difficult. For the plasma-assisted DVD metal oxide synthesis study undertaken within this thesis, the work of Tsai and Barnett, Yashar et al., and Hobein et al. [49-51] appears to be the most relevant. These three articles focus upon the sputter deposition of dense electrolyte membrane layer materials. Tsai and Barnett [49] report the creation of thin ($\leq 5 \mu m$) YSZ films on porous La_{0.8}Sr_{0.2}MnO₃ substrate/electrodes by DC reactive magnetron sputtering. The deposition occurred in an argon/oxygen chamber pressure of 6 mTorr / 0.8 Pa, at a rate of ~ 4 μ m/hr, and onto a substrate heated to 450°C. No specific information is provided about substrate porosity or roughness. During deposition, the substrate was biased with various negative DC potentials ranging from 0 to 300 V. Results showed that the films created with O V of electrical potential were porous while coatings with 75 V, 150V, and

300 V were dense. As the substrate bias was increased, the deposited film became thinner, suggesting that a more intense ion bombardment was leading to resputtering of the film during the deposition process [49].

In a follow-on study to the work of Tsai and Barnett, Yashar *et al.* [50] deposited YSZ via a reactive magnetron sputtering process, achieving a deposition rate of 12-13 μ m/hr onto steel, stainless steel, and glass substrates. The deposition occurred in an argon/oxygen chamber pressure of 2-8 mTorr / 0.2-1 Pa, and the article does not report any substrate heating. For deposition onto the steel and stainless steel substrates, the effect of a pulsed substrate bias was assessed by employing 4 μ sec of 6-40 V positive bias followed by 10.2 μ sec of 45-300 V negative bias. The specific form of the pulse cycle is reported in [50]. The results of these experiments indicated that the pulse bias was effective in densifying the depositing metal oxide films on the steel/stainless steel substrates. It also led to a modification of the film's crystal texture, as determined by x-ray diffraction (XRD), from a (200) to a (111) preferred growth direction.

In a more recent study of DC reactive sputtering, Hobein *et al.* [51] report on the deposition of YSZ films on NiO/YSZ anode substrates at $500 - 700^{\circ}$ C in a 1.5 mTorr / 0.2 Pa argon/oxygen chamber pressure. Deposited films were 1-10 µm thick, and the deposition rate was 1.56 µm/hr. The NiO/YSZ substrates were reported to have 32% porosity, and, prior to sputter coating with electrolyte membrane material, they were covered by a sintered slurry coating of NiO/YSZ to enhance substrate density. The deposited YSZ coatings laid down on top of this slurry coating were reported to have connected porosity that allowed helium to pass through the film. Post-deposition annealing of the substrates at temperatures of $1100 - 1300^{\circ}$ C for an unreported length of time did reduce but not eliminate the helium leak rate through the sputter deposited film.

2.3 Plasma-assisted Directed Vapor Deposition

For this project electrolyte membrane layers will be synthesized on anode supporting substrates using the University of Virginia's plasma-assisted directed vapor deposition tool. DVD is a physical vapor deposition-based technology that uses an electron beam (e-beam) to heat and vaporize a source material before capturing that vapor in a flowing carrier gas stream for transport to a coating surface (Fig. 2.3a) [17]. Use of the carrier gas stream in DVD has been shown to enhance material utilization efficiency and deposition rate [16, 52]. DVD has also been designed to allow different elements to be evaporated from closely neighboring sources prior to vapor capture in the gas stream (See Fig. 1.4.) [18]. When evaporated simultaneously, the elements from these separate sources can form precise alloys [53], and when evaporated sequentially, they can form multilayers.

Within *plasma-assisted* DVD, the gas and vapor stream can be ionized by a hollow cathode plasma activation unit (Fig. 2.3b) that affects the chemistry of the vapor species and attracts atoms and molecules to the coating surface with an applied electrical bias [18-20]. The activation and bias subsystems have been added to the DVD technology package to enhance the technology's ability to control deposited atomic structure [16]. DVD's plasma activation subsystem is designed to modify a significant number of the carrier gas and vapor atoms, transforming them from neutral particles into charged ions. While images such as Fig. 2.3b suggest that the DVD plasma activation unit does ionize gas and vapor atoms in the system, the gas and vapor ionization percentages for different plasma assisted DVD process conditions have not been characterized.



Figure 2.3 a) Directed vapor deposition [18]. b) Plasma assisted directed vapor deposition [18].

Additionally, use of DVD plasma activation and substrate biasing to modify the atomic structure of deposited films, e.g. to create dense metal oxides, has not been reported. DVD has been used to create porous columnar metal oxide structures from YSZ [54, 55]. Thus, this investigation of plasma assisted DVD's ability to form dense, pinhole-free electrolyte membrane layers from metal oxides represents one of the first reported studies of plasma activation and substrate biasing in the DVD material processing environment.

While plasma-activated DVD has not been used to create dense layers of metal oxide, the hollow cathode plasma and substrate bias technologies incorporated into DVD have been used by others to create dense metal oxide layers. Morgner, Schiller, Zywitzki and others report the use of hollow cathode plasma activation to densify films of alumina (Al_2O_3) and silica (SiO_x) deposited onto polished steel sheets or plastic films [56-59]. In these systems, the hollow cathode plasma technology modifies the deposition process by intersecting the vapor stream with a low voltage electron beam (LVEB) [56-59]. The energies of these electrons are at a level that generates frequent ionization of the vapor species, with as much

as 30% of the vapor stream ionized prior to deposition [56]. As a result of these ionization events, the kinetic energy of the ionized species during deposition increases from a few tenths of an electron volt to 4-6 eV, the angle of deposition becomes increasingly perpendicular to the coating surface, and the reactivity of the depositing species increases [56]. Using plasma activation or plasma activation with subtrate biasing leads to measurable ion currents through the substrate, and, as a result, dense alumina coatings have been deposited at rates of $6 - 9 \mu m/min$ and dense silica coatings at $12 - 36 \mu m/min$ [56-59]. Although Morgner *et al.* [56] report that silica films deposited at 0.4 Pa and 12 $\mu m/min$ with plasma activation (200 A) are dense, films deposited at the same rate and higher pressures (0.7 - 1.7 Pa) are increasingly columnar and porous. The substrate temperature during these silica deposition experiments is not reported.

Schiller *et al.* [57] report densification of alumina films on steel when the potential of the LVEB is 15 V and the current is 300 A. These conditions generated an ion current density at the substrate of 50 mA/cm². In a follow-on study of alumina deposition on plastic films, Schiller *et al.* [58] show that increasing the plasma current from 0 A to 100 A and then 200 A has a significant impact upon film density (Fig 2.4). Finally, in a study of alumina deposition on stainless steel, Zywitzki *et al.* [59] report the effect of combining a 30 V / 250 A hollow cathode plasma LVEB with a 50 kHz alternating current substrate bias voltage of 75 or 150 V (positive and negative). The 150 V bias led to a maximum substrate ion current density of 75 mA/cm². X-ray diffraction analysis of the films revealed that the plasma activation motivated a film transition from amorphous to crystalline, with a high intensity (400) peak. Addition of the densified the films while the pulse bias increased the surface roughness of the films, substrate bias removed the (400) peak from the XRD results and replaced that with a (440) peak. Scanning electron microscopy of the films revealed that the plasma activation perhaps as the result of intense ion bombardment of the surface.



Figure 2.4 Effect of plasma activation upon thin alumina film structure a) I_{plasma} _{current} = 0 A, hardness = 3.2 GPa, b) I_{plasma current} = 100 A, hardness = 5.2 GPa, c) I_{plasma current} = 200 A, hardness = 6.3 GPa [56].

While Morgner, Schiller, Zywitzki and others have reported metal oxide film densification results for hollow cathode plasma and substrate bias environments on relatively smooth, dense coating surfaces, the specific plasma environment for the work of this thesis is different. In the work reported in the literature [56-59], the pressure in the process chamber during film synthesis has been between 0.01 and 10 Pa ($7.5 \times 10^{-4} - 7.5 \times 10^{-2}$ Torr). In the plasma assisted DVD environment, the process chamber pressure is expected to be in the range of 1 and 100 Pa ($7.5 \times 10^{-3} - 0.75$ Torr). The impact of this slightly higher background chamber pressure upon densification results is not known. Additionally DVD deposition rates could be higher (up to 15 μ m/min), and substrate surfaces will be porous.

2.4 Summary

Solid oxide fuel cell electrolyte membrane materials and processing methods have been reviewed, providing perspective for the work of this thesis. The state-of-the-art in plasma-assisted DVD has been clarified, and while plasma-assisted DVD includes process technologies that could facilitate the deposition of dense electrolyte membrane layers, such capability has not been demonstrated. The subsequent chapters of this thesis will report upon plasma-assisted DVD of YSZ SOFC electrolyte membrane layers.

Chapter 3

Experimental Procedure

3.1 Overview

Prior to this study, DVD has not been used to create the type of dense metal oxide layers needed for the SOFC electrolyte membrane application. Few directed vapor deposition experiments have employed the plasma activation or substrate bias subsystems expected to be key elements facilitating dense oxide layer synthesis. Since little DVD specific process information exists to guide these experiments, a systematic set of experiments has been designed to provide insight into the importance of a group of DVD process parameters expected to influence dense layer formation. Figure 3.1 shows the general geometrical configuration of the DVD system for all experiments described in this thesis.


Figure 3.1 System configuration for material synthesis experiments.

3.2 Constant Experimental Conditions

As with other vapor deposition technologies, DVD has a large number of process parameters that can affect the material properties of deposited thick or thin films. Performing an exhaustive study is beyond the scope of this thesis. However, by holding many experimental conditions constant and varying a select few, it should be possible to shed light upon the relative importance of parameters thought to be keys to the creation of dense, pinhole-free metal oxide films. Table 3.1 summarizes experimental parameters that were held constant during these studies. Details associated with each of these constant parameters will be addressed in subsequent sections.

Substrate surface	Porous NiO-yttria-stabilized zirconia (YSZ)
Evaporation source	12.7 mm diameter YSZ (8.0 m/o Y ₂ O ₃)
Total material deposition time	20 minutes
Electron beam scanning pattern	"SpiraleYSZS"
Source material feed rate sequence	 0.2 mm/min for 5 minutes 0.5 mm/min for 5 minutes 0.7 mm/min for 10 minutes
Electron beam power setting sequence	 5 minutes at 25 mA (1.75 kW) 5 minutes at 30 mA (2.10 kW) 10 minutes at 35 mA (2.45 kW)
Temperature on the front of the sample at start of deposition	800°C
Heater configuration	Backside heating only (See Fig. 3.1.)
Carrier gas flow	Helium, 5.0 standard liters per minute (slm) ¹
Reactive gas flow	Oxygen, 0.35 slm

Table 3.1: Experimental constants for electrolyte membrane synthesis

3.3 Substrate Surface

As researchers have worked to enhance solid oxide fuel cell performance, they have reduced the thickness of the electrolyte membrane layer to minimize resistance to ionic transport and facilitate cell operation at lower temperature. Thus, while earlier SOFC

¹ Standard liter – one liter of any gas at atmospheric pressure and room temperature.

designs with 250 µm thick electrolyte membranes were capable of building the cell starting with the electrolyte membrane layer, new designs with electrolyte membranes of just 5-25 µm must use one of the other cell layers as the base building block for structural In many cases, including the work of this thesis, the anode serves as that base. support. The anode substrates used in this study were provided by ITN Energy Systems and consisted of a cermet of YSZ and NiO fabricated via a standard tape casting process. The anode material, shown in Figure 3.2, was generally cut into a 1 mm x 25 mm x 25 mm piece for deposition. The anode substrate is designed to have a porous structure to maximize the contact area between the fuel and anode material. In the fabrication process envisioned by ITN Energy Systems, the NiO in the anode would be reduced to Ni following the addition of the electrolyte membrane and cathode layers. The NiO-YSZ anode pieces were used in this study because of their higher density compared to the Ni-YSZ parts. It was thought that the denser substrate would facilitate creation of a dense, pinhole-free electrolyte membrane layer. The porous microstructure of the NiO-YSZ anode can be seen in Figure 3.3.

3.4 Evaporation Source

For this DVD synthesis study, a 12.7 mm diameter, "fully stabilized" yttria-stabilized zirconia rod was used as the evaporation source material. The source material, acquired from Trak Ceramics Inc. (Hagerstown, Maryland), contained 8.0 m/o yttria. Also, the source rods were fabricated so that the material was not in a fully-dense state. Fully dense YSZ of this composition should have a density of 5.94 g/cm³. However, studies have shown that a more consistent melt pool can be created using a source rod with



Figure 3.2 Anode substrate. NiO-YSZ cermet supplied by ITN Energy Systems.



10 µm

Figure 3.3 SEM cross section view of anode substrate.

 \sim 30% porosity, and indeed physical vapor deposition fabricators of thermal barrier coatings utilize partially-dense, partially-stabilized YSZ as the standard source material for coating of aircraft engine turbine components [60]. Thus, the rods used in this study and shown in Figure 3.4 all had a density of approximately 3.91 g/cm³.



Figure 3.4 YSZ source rod.

At the start of each experiment the YSZ source material was placed in a water-cooled crucible so that the top of the rod was at the same vertical position as the top lip of the crucible (Figure 3.5). During deposition, a computer-controlled motor was used to raise the source to the top of the crucible at the same rate that YSZ was melted and vaporized.

While a single, 12.7 mm diameter YSZ source rod was utilized for this study, DVD can be reconfigured to simultaneously evaporate material from four 3.2 mm diameter sources as shown in Figure 3.6. Use of this alternate system configuration would allow yttrium and zirconium to be evaporated separately and independently, followed by reaction with oxygen during the vapor transport stage of the material synthesis process. This utilization of separate material sources could allow the composition of the deposit to be carefully controlled, and it has been suggested that utilization of metal source rods (rather



Figure 3.5 Crucible with source rod installed.



Figure 3.6 Four-rod crucible configuration for DVD.

than metal oxide) and reactive deposition could lead to denser deposits [61]. At the outset of this project, this multi-source evaporation pathway was considered, and initial yttrium and zirconium evaporation rate data was generated (See Appendix). The pathway was not pursued due to project time constraints.

3.5 Electron beam heating of the source rod

For the SOFC electrolyte membrane work of this thesis, it was desirable to create dense, pinhole-free layers of about 5-25 µm thickness. Within the DVD system, material is evaporated by scanning an electron beam across the surface of the source material, creating a molten pool of material, and generating a stream of vapor atoms that can be captured in the carrier gas flow for transport to the coating surface (See Fig. 2.3a, 3.6.). Evaporation of different elements from a single source was possible for the YSZ source material employed in this project because of the similar vapor pressures of yttria and zirconia at the expected melt pool temperature [62, 63]. The rate of vapor generation during an experiment is highly dependent upon process parameters such as source material composition, electron beam current, electron beam scanning pattern, and background gas pressure in the process chamber.

At the outset of this experimental study, it was not certain what electron beam current and scan pattern should be utilized for evaporation. Through trial-and-error experimentation, it was decided that all experiments should last for 20 minutes, that a specific scan pattern called "SpiraleYSZS" should be used, and that beam current should follow a defined sequence: 5 minutes at 25 mA, 5 minutes at 30 mA, and finally 10 minutes at 35 mA. This evaporation sequence led to a reasonably stable melt pool with a well-formed liquid zone and minimal spitting. In the DVD system, the electron beam is scanned across the surface of the source material in a spiral pattern (Figure 3.7). "SpiraleYSZS" was an experimentally-developed scan pattern that appeared to generate a consistent evaporation of metal oxide from the YSZ source rods. The energy distribution for this pattern deposits more e-beam power along the outer ring of the YSZ rod, as suggested by the brighter spiral at the edge of the pattern. The pattern also overscans the source rod (12.7 mm diameter) with a pattern diameter of 18 mm. This overscan is large enough to cover the entire molten pool and appeared to help limit the build up of evaporant along the top lip of the funnel shaped, water-cooled crucible (See Fig. 3.1.).



Figure 3.7 **"SpiraleYSZS" electron beam scan pattern.** This e-beam scan pattern was employed for all experiments of this study, depositing more energy at the edge of the rod than in the center. The pattern was centered on the surface of the evaporation source.

3.6 Substrate Heating

Substrate temperature is a processing parameter known to affect the atomic structure of deposited thick and thin films, with higher temperatures leading to increasingly dense deposits [64]. For the experimental work of this thesis, a custom-built heater assembly was constructed. Figure 3.8 shows a schematic drawing of the heater assembly that was mounted on the backside of each sample fabricated during this study.



Figure 3.8 Schematic drawing of substrate heater. The heater assembly consists of a backplate, insulating base, heater filament, and cover.

The backplate, made of 316 stainless steel sheet (thickness 1.5 mm), provided mechanical support for the whole heater. The base of the heater was made of alumina and provided electrical and thermal insulation of the substrate region from the rest of the process chamber. The filament was made of tungsten sheet (thickness 0.25 mm). Tungsten was selected, instead of molybdenum or tantalum, because of its high melting point and good operational stability in a high temperature oxygen environment. The filament was prepared by cutting the sheet into a zig-zag pattern using a Norton diamond wheel installed in an Isomet 1000 high speed saw (Figure 3.9). The zig-zag pattern was designed to increase the electrical pathway through the filament and generate the desired level of substrate heating. When a current is flowing through the filament, it generates heat with a power defined by $P=I^2*R$, where I is current and R is the resistance. R is



Figure 3.9 **Isomet 1000 high speed saw.** This saw assembly was used to machine the cuts into the heater filament.

defined by $R = \rho^* L/A$ where ρ is the filament material's resistance coefficient, L is the length of the filament, and A is the cross-sectional area of the filament. The cover, made of stainless steel (thickness = 0.4 mm), was designed to hold the edges of the anode substrate while exposing the majority of the substrate to the gas and vapor flow. In addition to these primary heater assembly components, several other items were necessary to create a complete unit. The heater filament was connected to an electrical power supply (model LV750 from R.D. Mathis Inc.) by two stainless steel screw These two screws were used to introduce large AC currents into the electrodes. filament (20-40 A). To make certain that the screw electrodes did not melt under such high current, screws of at least 3 mm diameter were used. The filament and electrode screws were consumable and had to be replaced occasionally. To heat the substrate evenly and prevent sticking problems caused by hot contact points, a piece of boron nitride (thickness 2 mm) was always mounted between the filament and the substrate. Additionally, a boron nitride spray was applied to the backside of the substrate to further reduce the chance of sticking. The completed heater assembly is shown in Figure 3.10. During initial testing of the heater assembly in an oxygen process environment it was observed that different current / voltage readings on the power supply were necessary to generate the same, desired 800°C temperature on the front of the anode substrate, as measured by a thermocouple. With each subsequent heating in the oxygen environment, the current / voltage continued to shift slightly, away from initial readings of 31 A and 3.9 A constant heating power was maintained by keeping the product of current and V. voltage constant. The cause of the current / voltage shift appeared to be oxidation of the tungsten filament which changed the electrical resistivity of the filament. Understanding this shift was important because it was not possible to attach a thermocouple to many of



Figure 3.10 Heater assembly.

the samples during the experimental runs. Certain experiments required application of an electrical bias to the substrate, and the presence of the thermocouple created an electrical short circuit. Thus it was necessary to rely upon an understanding of the current/voltage relationship to maintain a constant substrate temperature during all experiments.

3.7 Configuration of substrate in process chamber

Once the heater assembly was completely put together, the unit had to be inserted into the process chamber and properly positioned for the deposition experiment. As shown in Figure 3.11 the heater assembly was attached to two mounting rods with insulating posts to provide electrical isolation so that substrates could be electrically biased. Following attachment to the mounting rods, the entire unit was inverted, installed in the top of the deposition chamber, and aligned directly above the source rod, with a source to substrate separation of 130 mm. Then, the substrate heater wires and, when needed, the substrate bias wires were attached to the back side of the assembly as shown in Figure 3.12. The bias wire was attached to a screw that contacted the substrate cover on the front side of the substrate assembly. During substrate bias experiments the cover transfers electrical potential to the heated substrate.



Figure 3.11 Isolated substrate assembly.



Figure 3.12 Attachment of heater and substrate bias wires.

3.8 Carrier gas and reactive gas flows

One of the unique features of directed vapor deposition, when compared to other physical vapor deposition technologies, is the possibility of using a carrier gas flow to focus and transport evaporant from the source rod to the coating surface. For all experiments described in this thesis, 5 slm of helium was used as the carrier gas. In addition, 0.35 slm of oxygen was introduced into the flow to help ensure that stoichiometrically-correct YSZ was deposited onto the anode substrate. Numerous researchers have reported that evaporation of oxides will lead to deposits deficient in oxygen unless additional oxygen gas is introduced into the process chamber. Earlier work with ceramic evaporation in the DVD system confirmed these literature reports and suggested that ~0.35 slm of oxygen flow would be sufficient to replace oxygen lost from the solid source during the evaporation process [61].

3.9 Experimental variables

In addition to the experimental constants listed above, this thesis study manipulated a set of experimental variables in an effort to assess the ability of DVD to synthesize dense, pinhole-free electrolyte membrane layers. Specifically, these experiments explored specific plasma-activation unit settings, selected substrate bias conditions, and different substrate preparation techniques. These three sets of experimental variables will be described in more detail in the following sections.

3.10 Plasma activation

As noted in Chapter 2, certain researchers have suggested that plasma activation of vapor prior to deposition on the coating surface can generate a denser film. The apparent explanation for this effect is increase of the kinetic energy of the individual ions. Then, when the ions reach the coating surface, they have an increased ability to move across the coating surface to form a well-organized, dense coating. To explore the effect of plasma activation upon DVD's ability to synthesize dense, pinhole-free electrolyte membrane layers, the hollow cathode plasma activation subsystem in the tool was activated for many of the experiments reported in this thesis. Figure 3.13 shows the basic electrical circuit of the plasma unit while Figure 3.14 illustrates the hollow cathode electron flow during plasma unit operation. During initial heat-up, the connection to the resistor is closed while the hollow cathode warms to operation temperature (Fig. 3.13). At ignition, the resistor circuit is broken, and the electrons generated within the hollow cathode begin to flow through the process chamber to the anode, completing a new circuit and ionizing vapor found in the free (open) space between the cathode and anode.



Figure 3.13 Electrical circuit of the hollow cathode plasma source [65].



Figure 3.14 Hollow cathode electron flow.

Within the plasma subsystem, there are a set of geometrical and subsystem variables that can be adjusted to modify the performance of the plasma unit. These variables include:

- The separation distance between the end of the hollow cathode and anode,
- The vertical position of the cathode and anode relative to the vapor source and deposition substrate,
- The rate of gas flow out of the end of the cathode,
- The rate of gas flow out of the face of the anode (back towards the cathode), and
- The plasma current.

For these experiments, a single geometrical configuration was selected. The separation of cathode and anode and the vertical position of the plasma unit are recorded in Figure While the plasma cathode can pass 0.050 - 1 slm of argon through its core out into 3.1. the process chamber, a single setting of 0.050 slm was selected for all experiments. This low number was selected to minimize the disruption of the carrier gas and vapor stream caused by the intersection of the plasma flow with that stream. Study of Figure 3.14 shows how the plasma cathode is positioned so that the gas flow emanating from the end of the hollow cathode is perpendicular to the main vapor and carrier gas stream. It was decided that no gas would be passed through the plasma anode back towards the In the original design of the system, this anode flow was designed to keep main flow. the surface of the anode clean so that a circuit would be maintained throughout the Experience showed that this flow was not necessary for the 20 minute experiment. experiments performed here. Finally, the current generated by the hollow cathode can be varied between 30 A and 200 A. Based on hollow cathode results published in the literature (Chapter 2), it was expected that higher plasma currents would contribute to

denser coatings. For these experiments several different plasma currents were examined: 60 A, 120 A, and 180 A.

3.11 Substrate bias

In addition to the plasma activation unit, the DVD system has a substrate bias subsystem that allows the coating surface to be energized with an electrical potential, either DC or AC. Application of a bias to the coating surface can pull ions into that surface with higher energy, potentially generating a denser coating structure. The literature reports that substrate biasing can enhance metal oxide density (Chapter 2). Furthermore the literature suggests that the NiO-YSZ anode material used in this study has sufficient high temperature electrical conductivity to allow a substrate bias to be utilized [66]. The DVD substrate bias system is capable of applying up to 200 V of positive or negative DC potential. It is also capable of applying a similar level of AC potential. When applying an AC potential, the positive and negative pulse widths can be varied independently. Each half of the pulse can last from 4 µsec up to 815 µsec. For this study, both DC negative potentials and AC potentials were applied to certain samples during the deposition process. DC potentials were either 50 V or 200 V. The AC potential was always 200 V with pulse widths of 24 μ sec⁺/24 μ sec⁻. This pulse width duration was arbitrarily chosen.

3.12 Substrate preparation

While most experiments were performed using as-received SOFC anode pieces, it was suggested that polishing the surface of the anode material could motivate formation of a

denser ceramic coating [67]. Thus two experiments were attempted in which the anode surface was polished flat prior to deposition of metal oxide. The polished substrates were prepared using a four step process involving Buehler and Phoenix 4000 polishing clothes of varying surface roughness. Diamond clothes with roughnesses of 30, 10, 6, and 3 microns were used to create a mirror-like, glossy surface. After polishing the SOFC anode substrate with the 6 micron lapping film, a carbon powder spray was applied to fill surface pores in the anode. Then, the anode was polished with the 3 micron lapping film to achieve a final polishing result.

3.13 Experimental sequence

Table 3.2 shows a summary of the experimental conditions utilized for the individual experiments of this investigation. All experiments employed the constant experimental parameters outlined in the first half of this chapter (Table 3.1). Then, in addition to those experimental constants, the variables of Table 3.2 were applied. Finally, Figure 3.15 shows the display for the DVD system, ready to control the multitude of experimental parameters.

3.14 Post-deposition sample characterization

After the electrolyte membrane layer samples were created, a set of characterization activities were undertaken to assess the suitability of the deposited films for use in solid oxide fuel cells.

Experiment	Experimental setpoints
1	a) As-received substrate
2	a) As-received substrate b) 60 A plasma current
3	a) As-received substrateb) 60 A plasma currentc) 50 V, DC- substrate bias
4	a) As-received substrateb) 120 A plasma currentc) 50 V, DC- substrate bias
5	a) As-received substrateb) 120 A plasma currentc) 200 V, DC- substrate bias
6	 a) As-received substrate b) 120 A plasma current c) 200 V, AC substrate bias (24 μsec⁺/24 μsec⁻)
7	 a) Polished substrate b) 120 A plasma current c) 200 V, AC substrate bias (24 μsec⁺/24 μsec⁻)
8	 a) Polished substrate b) 180 A plasma current c) 200 V, AC substrate bias (24 μsec⁺/24 μsec⁻)

Table 3.2: Setpoints for electrolyte membrane layer experiments

3.14.1 Deionized water test

After deposition, each film was first subjected to a very simple test in which a drop of deionized water was placed on the surface of the metal oxide deposit. Researchers at ITN Energy Systems suggested that this "deionized water test" was a good first check of deposited film density [68]. While a porous film will act like a sponge, quickly absorbing the deionized water droplet, a dense, pinhole-free layer will not allow the water to penetrate, leaving a bead of water on the surface of the metal oxide deposit. All samples were subjected to this first, simple test of film porosity.



Figure 3.15 **DVD computer control screen at start of deposition process.**

3.14.2 Scanning electron microscope (SEM) analysis

Following the deionized water test, each coated anode piece was sectioned to allow for more in-depth study. Several of the coated pieces were prepared for examination using a scanning electron microscope (Figure 3.16). Because of the insulating nature of the deposited films at room temperature, each film was coated with a thin layer of gold to enhance microscope imaging. Then, pictures of both the top surface and cross-section of each film were taken at various magnifications to assess deposit microstructure.



Figure 3.16 Jeol JXA-840A scanning electron microscope

3.14.3 X-ray diffraction (XRD) analysis

Finally, in addition to the other post-deposition analysis, x-ray diffraction was performed on each sample. Using a XDS 2000 XRD system from Scintag Inc. (Figure 3.17), a collimated beam of x-rays was directed to the coating surface. The Cu K α x-rays (1.5418 Angstrom) were then diffracted by the crystalline phases in the specimen



Figure 3.17 Scintag XDS 2000 x-ray diffraction system.

according to Bragg's law ($\lambda = 2dSin\theta$, where λ is the wavelength of the x-rays, d is the spacing between atomic planes in the crystalline phase, and 2 θ is the angle between the incident and diffracted x-rays), and the intensity of the diffracted x-rays was measured as a function of the diffraction angle and the specimen's orientation. The resulting diffraction pattern was collected into the Diffraction Management System Software for Windows NT (version 1.1) from Scintag, Inc., which was then used to identify the specimen's crystalline phases. Additional peak identification on the XRD scans was performed using data from the powder diffraction files produced by the International Centre for Diffraction Data [69].

3.15 Summary

Having developed a detailed procedure for evaluation of plasma-assisted DVD synthesis of solid oxide fuel cell electrolyte membrane layers on anode support substrates, a set of experiments could now be performed. The subsequent chapter will present the findings of the studied outlined here.

Chapter 4

Results

4.1 Strategy

To explore the ability of the DVD technology to create dense, pinhole-free metal oxide layers and to develop an initial understanding of the relationship between various DVD processing conditions and deposited film properties, especially film density, the experiments outlined in Table 3.2 have been conducted. For the numerous results presented in this chapter, the figure captions will refer to the experiment numbers listed in Table 3.2.

During each experiment, the process chamber pressure and the pressure in the carrier gas mixing chamber prior to the nozzle (See Fig. 1.4.) were recorded. For all experiments, these pressures were 8.0 Pa / 60 mTorr in the process chamber and 56 Pa / 420 mTorr in the carrier gas mixing chamber. The introduction of a small amount of argon through the plasma hollow cathode during select experiments generated only a nominal rise in these readings.

4.2 Deionized water test pictures

After each DVD film was deposited, the sample was removed from the sample holder in the deposition chamber, and a deionized water test was immediately performed. The results of these water tests could be grouped into three categories. For samples 1, 2 and 3, the deionized water droplet soaked into the deposited film as soon as it was placed on the surface, suggesting a porous deposit (Fig 4.1). For samples 4 and 5, the deionized water droplet did not soak into the deposited film immediately. Rather the droplet spread out broadly across the film surface and absorbed into the film over a span of several minutes (Fig 4.2). This suggested that the DVD process conditions of these experiments had created a slightly denser film. For samples 6, 7 and 8, the deionized water droplet remained on the film surface for at least ten minutes, suggesting that these DVD deposits were the densest of all (Fig 4.3).

Chapter 4. Results





Figure 4.1 **Deionized water test of sample 3.** Porous film, water penetrates through film quickly.





Figure 4.2 **Deionized water test of sample 4.** Denser film, water penetrates through the film after several minutes.



 $10\,\mathrm{mm}$

Figure 4.3 **Deionized water test of sample 6.** Dense film, water stays on top of the deposited film for 10 minutes.

4.3 SEM and XRD analysis of deposited films

SEM and XRD analysis was designed to provide additional insight into the atomic structure of deposited films.

4.3.1 Analysis of Sample 1

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto an as-received anode substrate. No plasma activation or substrate biasing was employed. The SEM images and XRD results from this sample are shown in Figs. 4.4 - 4.9.

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Figure 4.4 **Top (deposition) surface of sample 1, 400x.**



Figure 4.5 **Top (deposition) surface of sample 1, 3000x.** This image reveals a highly faceted deposition surface.



Figure 4.6 **Top (deposition) surface of sample 1, 8000x.** Large gaps (pores) are clearly visible between the faceted YSZ deposits.



Figure 4.7 **Cross-section of sample 1, 400x.** The deposited coating is approximately 120 μm thick, with clearly defined growth columns.



Figure 4.8 Cross-section of sample 1, 4000x.



Figure 4.9 **XRD scan of sample 1.** The x-ray diffraction scan reveals peaks for yttria-stabilized zirconia. The peak locations are consistent with cubic YSZ.

4.3.2 Analysis of Sample 2

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto an as-received anode substrate while also running the DVD plasma unit with a 60 A current. No substrate bias was applied to the sample during deposition. The SEM images and XRD results for this sample are shown in Figs. 4.10 - 4.15.



Figure 4.10 Top (deposition) surface of sample 2, 400x.



Figure 4.11 **Top (deposition) surface of sample 2, 3000x.** The faceted columns of sample 1 have been replaced by a cauliflower-like rough surface with apparent gaps (pores) betweeen YSZ deposits.



Figure 4.12 Top (deposition) surface of sample 2, 8000x.



Figure 4.13 Cross-section of sample 2, 400x. The deposited coating is approximately 84 µm thick.



Figure 4.14 Cross-section of sample 2, 4000x.



Figure 4.15 **XRD scan of sample 2.** This scan reveals the peaks for yttria-stabilized zirconia and nickel oxide (presumably from the anode substrate). The peaks for the nickel oxide are labeled "s" for substrate.

4.3.3 Analysis of Sample 3

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto an as-received anode substrate while also running the DVD plasma unit with a 60 A current and 50 V DC⁻ substrate bias. The SEM images and XRD results from this sample are shown in Figs. 4.16 - 4.21.

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Figure 4.16 Top (deposition) surface of sample 3, 400x.



Figure 4.17 **Top (deposition) surface of sample 3, 3000x.** Gaps (pores) are clearly visible between finely textured YSZ deposits.


Figure 4.18 Top (deposition) surface of sample 3, 8000x.



Figure 4.19 Cross-section of sample 3, 400x. The deposited coating is approximately 30 µm thick.



Figure 4.20 Cross-section of sample 3, 4000x.



Figure 4.21 **XRD scan of sample 3.** This scan reveals peaks for yttria-stabilized zirconia, nickel oxide, and zirconia. The peaks for the nickel oxide are labeled "s" while the zirconia peaks are labeled "z".

4.3.3 Analysis of Sample 4

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto an as-received anode substrate while also running the DVD plasma unit with a 120 A current and 50 V DC⁻ substrate bias. The SEM images and XRD results from this sample are shown in Figs. 4.22 - 4.27.



Figure 4.22 Top (deposition) surface of sample 4, 400x.



Figure 4.23 **Top (deposition) surface of sample 4, 3000x.** YSZ deposits between open porosity is again visible.



Figure 4.24 Top (deposition) surface of sample 4, 8000x.



Figure 4.25 **Cross-section 400x - sample 4.** The deposited coating is approximately 20 µm thick. Introduction of plasma activation and substrate biasing is leading to reduced coating thicknesses.



Figure 4.26 Cross-section of sample 4, 4000x.



Figure 4.27 **XRD scan of sample 4.** Peaks are visible for YSZ and nickel oxide ("s").

4.3.5 Analysis of Sample 5

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto an as-received anode substrate while also running the DVD plasma unit with a 120 A current and 200 V DC⁻ substrate bias. The SEM images and XRD analyses of this sample are shown in Figs. 4.28 - 4.33.

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Figure 4.28 Top (deposition) surface of sample 5, 400x.



Figure 4.29 **Top (deposition) surface of sample 5, 3000X.** Porosity is visible between deposits of YSZ but not as distinctly as in Fig. 4.17.



Figure 4.30 Top (deposition) surface of sample 5, 8000x.



Figure 4.31 Cross-section of sample 5, 400x. The deposited coating is just 15 μ m thick.

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Figure 4.32 Cross-section of sample 5, 4000x.



Figure 4.33 **XRD scan of sample 5.** Peaks are visible for YSZ, nickel oxide ("s"), and zirconia ("z").

4.3.6 Analysis of Sample 6

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto an as-received anode substrate while also running the DVD plasma unit with a 120 A current and 200 V AC substrate bias. The SEM images and XRD results for this sample are shown in Figs. 4.34 - 4.39.



Figure 4.34 Top (deposition) surface of sample 6, 400x.

μm

Figure 4.35 **Top (deposition) surface of sample 6, 3000x.** The appearance of this deposition is similar to that of sample 3, but at a different length scale. (See Fig. 4.18.)



Figure 4.36 Top (deposition) surface of sample 6, 8000X.



Figure 4.37 Cross-section 400x - sample 6. The deposited coating is just 13 µm thick.



Figure 4.38 **Cross-section of sample 6, 4000x.** The deionized water test suggests that this columnar film is dense enough to resist water penetration.



Figure 4.39 **XRD scan of sample 6.** Peaks are visible for YSZ, nickel oxide ("s"), and zirconia ("z").

4.3.7 Analysis of Sample 7

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto a polished anode substrate while also running the DVD plasma unit with a 120 A current and 200 V AC substrate bias. The SEM images and XRD analyses of this sample are shown in Figs. 4.40 - 4.45.

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Figure 4.40 Top (deposition) surface of sample 7, 400x.



Figure 4.41 **Top (deposition) surface of sample 7, 3000x.** Porosity appears evident between growth columns.



Figure 4.42 Top (deposition) surface of sample 7, 8000x.



Figure 4.43 Cross-section of sample 7, 400x. The deposited coating is just 13-15 μm thick.



Figure 4.44 Cross-section of sample 7, 4000x.



Figure 4.45 **XRD scan of sample 7.** Peaks are visible for YSZ, nickel oxide ("s"), and zirconia ("z").

4.3.8 Analysis of Sample 8

Creation of this sample employed the experimental constants listed in Table 3.1 to deposit material onto a polished anode substrate while also running the DVD plasma unit with a 180 A current and 200 V AC substrate bias. The SEM images and XRD analyses of this sample are shown in Figs. 4.46 - 4.51.



Figure 4.46 Top (deposition) surface of sample 8, 400x.



Figure 4.47 Top (deposition) surface of sample 8, 3000x.



Figure 4.48 **Top (deposition) surface of sample 8, 8000x.** Porosity is clearly evident in this thin YSZ deposit.

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Figure 4.49 Cross-section of sample 8, 400x. The deposited coating is just 5 µm thick.



Figure 4.50 Cross-section of sample 8, 4000x.



Figure 4.51 **XRD scan of sample 8.** Peaks are visible for YSZ, nickel oxide ("s"), and zirconia ("z").

4.3.9 SEM image comparison

To faciliate comparison of atomic structures between samples, the SEM images presented on the previous pages are reproduced in the following Figures 4.52 through 4.56.



Figure 4.52 Top (deposition) surface of all samples, 400x.



Figure 4.53 Top (deposition) surface of all samples, 3000x.



Figure 4.54 Top (deposition) surface of all samples, 8000x.





Figure 4.55 Cross-section of all samples, 400x.

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Figure 4.56 Cross-section of all samples, 4000x.

4.3.10 XRD results summary

For the yttria-stabilized zirconia detected in each sample, Table 4.1 records the peak positions for the cubic YSZ observed in each of the eight samples. The table also shows the comparable reference data from the literature for $Y_{0.15}Zr_{0.85}O_{1.93}$ [69]. Table 4.2 records the normalized XRD peak intensities (I) with respect to the height of the {111} peak in each sample. Peak heights for a randomly oriented YSZ sample are also presented for comparison. While no discernible texture preference is evident, the deposited samples also have not grown in a purely random manner. It is interesting to note the change in preferred growth between samples 6 and 7 in which the only difference between experiments was the condition of the substrate, as-received versus polished.

Sample	{111}	{200}	{220}	{311}	{400}
1	2.946	2.546	1.811	-	1.275
2	2.932	2.544	1.805	1.542	1.280
3	2.949	2.549	1.813	1.555	1.293
4	2.950	2.582	1.814	1.556	1.294
5	2.936	-	1.816	-	-
6	2.944	2.584	1.814	1.558	1.298
7	2.955	-	1.814	-	-
8	2.941	2.577	1.810	-	-
Reference	2.968	2.571	1.818	1.550	1.285

 Table 4.1: Peak positions (d spacings) from XRD patterns of the YSZ films

 deposited with different process conditions (in Angstroms)

		-	-		
Sample	I _{111}	I _{200}	I _{220}	I _{311}	I _{400}
1	1	0.58	1.18	0.02	0.14
2	1	0.35	1.09	0.85	0.14
3	1	0.18	0.35	0.44	0.10
4	1	0.78	1.14	0.74	0.14
5	1	0.70	0.96	0.36	0.00
6	1	0.93	0.66	0.76	0.33
7	1	0.22	1.28	0.68	0.33
8	1	0.69	0.69	0.50	0.00
Random	1	0.25	0.55	0.40	0.05

 Table 4.2: Relative peak intensities from XRD patterns of the yttria-stabilized zirconia films deposited with different process conditions

4.4 Summary

The results of this chapter suggest that DVD plasma activation and substrate biasing can increase film density. The XRD results show that the deposited film has the same crystal structure as the vapor source. A more detailed examination of the results of this study will be presented in Chapter 5 Discussion.

Chapter 5

Discussion

The research of this thesis has been designed to explore the relationship between process conditions in a plasma-assisted directed vapor deposition system and the atomic structure of synthesized metal oxide thin films. Indeed it has generated information about the effect of plasma activation, substrate biasing and substrate temperature on the DVD thin film deposition of ceramic materials. This discussion chapter will consider the observed film structure trends, discuss the various physical phenomenon motivating observed trends, and give suggestions for future, related work with the DVD system. This chapter will also address the particular question of DVD suitability for synthesis of solid oxide fuel cell electrolyte membranes.

5.1 Density of metal oxide deposits

As noted in Chapters 1 and 2, the ability of plasma-assisted DVD to create dense layers of metal oxide has not been systematically examined and reported prior to the work of this thesis. The material synthesis conditions selected and the material characterization techniques employed for sample analysis in this research were thought to offer opportunities for discovery and confirmation of dense metal oxide fabrication. Indeed, the deionized water test results of Chapter 4 reveal a trend in which denser films are created by the systematic application of additional plasma-assisted DVD process technologies. Specifically, deionized water testing shows that the water does not absorb into the deposited film and anode substrate of samples 6, 7, and 8. These results suggest dense film creation.

Closer inspection of these results suggests that the underlying cause of the positive water tests on samples 7 and 8 is unclear, with the result being generated by either dense film deposition or anode polishing. Separate deionized water droplet testing on a polished anode substrate surface prior to YSZ deposition revealed that a water droplet would remain intact on the polished surface, in contrast to the rapid absorption of a droplet on an as-received substrate surface. Thus, it appears that the positive results for these two samples could be caused by substrate polishing and / or dense film deposition. The SEM images of sample 8 (Figs. 4.46 - 4.50) show a very thin film with distinct porosity between deposited oxide regions. For this sample, it appears that the positive water droplet result has most likely been generated by polishing of the anode surface rather than deposition of dense YSZ. The positive deionized water test for sample 8, *and* dense deposition, as suggested by the result for sample 6.

The positive deionized water test result of sample 6 appears to provide the strongest evidence that DVD has the ability to create dense metal oxide layers. Specifically the application of DVD plasma activation (120 A) and substrate biasing (200 V AC bias with 24 μ sec positive and negative pulses), the experimental conditions of Table 3.1, and the system geometry configuration of Fig. 3.1 appear to create a film that resists the

absorption of deionized water. While samples 6 and 7 are dense enough to prevent rapid penetration of water through the film, the micrographs of Figs. 4.34 - 4.38 and Figs. 4.40 - 4.44 do not reveal the fully densified film envisioned at the outset of the project (e.g. Fig. 2.4c for alumina films). Instead, the micrographs reveal dense, columnar structures that are more like those found in Fig. 2.4b. The structures of samples 6 and 7 appear to be those described by Thornton as Zone T or Zone II microstructures [64], typified by dense columns of material with little open porosity from top to bottom in the structure, Fig. 5.1. (The film shown in Fig. 2.4c is more likely a Zone III structure.) While Thornton correlates changes in film density to changes in substrate temperature or background chamber pressure, recent research analysis suggests that atomic structure changes from Zone II to Zone III occur more generally because of an increase in the



Figure 5.1 **Thornton's zone diagram.** Experimental study of sputtering (e.g. Ti, Cr, Fe, Cu, Mo, and Al) has revealed repeatable microstructural trends [64].

energy available to atoms arriving at the film growth surface, either as the result of substrate heating or the actual deposition process [16, 70]. Since the process conditions used with samples 6 and 7 have generated deposits denser than the other six experiments it is useful to examine these process conditions in more detail and suggest reasons why they have proven best for dense metal oxide film creation in the plasma-assisted DVD environment.

In the experiments that produced samples 6 and 7, the 120 A current of the hollow cathode plasma unit and the 200 V potential of the substrate bias were unchanged from the conditions used to fabricate sample 5, a sample that partially resisted deionized water penetration. In contrast to the experiment for sample 5 which employed a DC substrate bias, the experiments for samples 6 and 7 utilized an AC 200 V potential with 24 μ sec dwell time of both the positive and negative potential. Apparently the shift from DC to AC bias enhanced the ability of the neutral adatoms and depositing ions to organize into a dense structure. While a detailed understanding of the link between AC bias conditions and film densification is beyond the scope of this thesis, it does seem possible to propose some initial qualitative explanations for the observed trend.

As noted in Chapter 4, samples 4 and 5 partially resisted deionized water penetration through their coatings. These results suggest that plasma activation (120 A) and DC substrate bias (50 or 200 V DC⁻) stimulated some film densification. This trend matches the results reported by Tsai and Barnett [49] and Morgner [56], although in both literature reports the densification appears to have been more complete than the DVD results of this thesis. Interestingly, the results for samples 6 and 7 suggest that application of an AC substrate bias is more effective than a DC bias for film densification.

It is reasonable to assume that the use of an AC bias rather than DC leads to attraction of different atomic and molecular species to the surface of the growing film during the negative and positive portions of the bias cycle. Under all bias conditions, neutral metal and gas species will contact the growth surface. In the DVD process, these neutral species are expected to constitute the majority of all atoms and molecules being deposited, on the order of 70% or more of the depositing species [56]. Within an argon plasma such as that generated by the DVD hollow cathode system, positively charged argon atoms and metal atoms (e.g. Y and Zr) are expected to be present to bombard or deposit onto the coating surface during the negative portion of the bias cycle [71]. Survey of the literature also suggests that some of the oxygen atoms and molecules from the YSZ source rod and the carrier gas flow will be positively charged and thus attracted to the coating surface during negative pulses [72]. During the positive portion of the AC pulse, negatively charged oxygen ions and free electrons are expected to be available for deposition on and interaction with the growing film surface [72]. Introduction of negative oxygen ions and free electrons into the surface coating process, combined with positive species deposition during just half of the process has led to a somewhat denser coating. The density increase could result from one or more of the following factors.

First, in separate DVD experiments, application of a positive bias to a coating surface has been noted to generate a significant rise in the temperature of the coating surface, in some cases melting high temperature molybdenum substrates [73]. Attraction of electrons to the coating surface in the experiments here could have had a similar effect, raising the deposit temperature closer to its melting point. As shown in the Thornton diagram of Fig. 5.1, higher substrate temperatures lead to denser coatings.

Second, introduction of additional oxygen into the deposition process, during the positive portion of the bias cycle, could lead to creation of a film that is more stoichiometrically-correct, more regular, and thus denser. During the various deposition experiments performed for this thesis and other related experiments [74], subtle color changes have been observed in deposited YSZ films. Films deposited without a substrate bias were often slightly gray unless higher oxygen flow rates were employed. Those films deposited with a bias were whiter or, in the case of AC bias, more transparent, suggesting a preferred stoichiometry and increasingly dense coating. In other work, this color change has been attributed to changes in the oxygen content of the film [61]. Subtle changes in the stoichiometry of the films from sample to sample should be evident in the XRD scan results of Chapter 4. Indeed careful inspection of the peak positions in the different scans does reveal slight variations in location that could be the result of small changes in film composition.

Third, inspection of Figs. 4.31, 4.37, and 4.43 suggests that the films of samples 6 and 7 are slightly thinner than the film of sample 5, 13 μ m thick versus 15 μ m. A thinner coating would correspond to a reduced deposition rate that allows adatoms more time to organize on the coating surface prior to being buried in place by newly depositing material. Though unlikely to be the sole cause of film densification, slower deposition rates are known to enhance deposit density [16].

Before leaving the discussion of metal oxide film density as generated by plasma-assisted DVD, it seems important to consider why the dense films of this study are not as dense as those reported in the literature ([49], [56], and Fig. 2.4). Although a definitive statement is not possible, it seems reasonable to suggest that some fraction of the density difference is due to a difference in the energy of the neutral species in the DVD system when

compared with the sputtering and electron beam evaporation experiments of [49] and [56]. Sputtering systems are known to generate neutral particles with an average kinetic energy of 5 eV and a high energy distribution ranging up to several tens of eV [75]. Standard electron beam evaporation systems are known to generate neutral particles with an average kinetic energy of 0.2 - 0.6 eV [16, 76]. Previous model-based study of neutral species in the DVD environment has revealed that such neutrals have on average just 0.05 eV of kinetic energy [16]. In the DVD system the lower kinetic energy is the result of vapor atom collisions with background gas atoms that are moving at slower velocities. These collisions lead to thermalization of the vapor atoms. It appears that the silica deposition results reported by Morgner *et al.* [56] and noted in the Literature Review are the result of a similar thermalization effect. As summarized Chapter 2, while their plasma-assisted deposition experiments at 0.4 Pa chamber pressure generated dense coatings, similar activated electron beam deposition at higher chamber pressures (e.g. 0.7 -1.7 Pa) generated columnar structures [56]. The pressure in the DVD chamber during deposition was 8 Pa, perhaps explaining the dense but columnar structures observed here.

5.2 Deposition rate

One of the interesting and somewhat unexpected trends revealed by the experiments of this thesis was the dramatic decrease in deposition rate or deposition efficiency caused by application of the different DVD process controls (i.e. plasma activation and substrate biasing). The dramatic decrease in deposited film thickness is apparent in Fig. 4.55, and the trend is summarized below in Fig. 5.2.

The link between plasma activation and reduced YSZ deposition rate as observed from experiments 1 to 2, 3 to 4, and 7 to 8 appears to be fairly understandable. As shown in



Fig. 2.3b, Fig. 3.14, and in more detail in Fig. 5.3, the flow of plasma electrons and ions

Figure 5.2 Effect of DVD process controls upon deposition rate. Application of plasma activation and substrate biasing led to significant reductions in YSZ deposition during each 20 minute experiment.



Figure 5.3 Intersection of plasma and carrier gas flows. The perpendicular intersection of carrier flow and high energy plasma flow disrupts the directed momentum of the vapor towards the coating surface.

out of the DVD hollow cathode unit is perpendicular to the carrier gas and YSZ flow emanating from the vapor source and directed towards the coating surface. The intersection of perpendicular gas and vapor flows has been shown to redirect such flows significantly, modifying the directed momentum of vapor streams and affecting deposition efficiencies onto surfaces [16, 52]. It should be noted that in references [16] and [52], the intersecting flows are both composed of neutral gas and vapor atoms. In the current experiments, the hollow cathode flow also includes ionized argon atoms and free electrons.

Interestingly, as the electron current of the low voltage electron beam (LVEB) in the plasma flow increases, there appears to be a resulting drop in YSZ deposition efficiency on the anode surface. While a full explanation of the link between LVEB current and deposition efficiency is beyond the scope of this thesis, it can be noted that Morgner *et al.* state that ionization of gas and vapor atoms in a hollow cathode plasma leads to an increase in the kinetic energy of ions in the system, even without application of an electrical bias on the coating surface [56]. Once these ions reach higher kinetic energy levels, it is not at all certain that their enhanced momentum will be directed towards the coating surface. Thus, as the plasma current increases from 60 to 120 and then 180 A, more ions are created in the system with elevated kinetic energies. If this energy is not directed towards the coating surface (and there is no reason to believe it will be), the result could be decreased deposition rates as ionized and neutral gas and vapor atoms are scattered from the initially directed carrier gas / vapor atom flow emanating from the DVD nozzle (Fig. 3.14).

The other interesting relationship shown in Fig. 5.2 is that between deposition rate and substrate bias. In Fig. 5.2, the largest drop in deposition efficiency and rate occurred
when a 50 V DC+ bias was applied to the coating surface. A smaller but equally distinct drop in deposition efficiency was observed when the DC+ substrate bias was increased from 50 to 200 V. The exact cause of this relationship is unclear. It could be the result of ion bombardment and resputtering as observed by Tsai and Barnett [49]. Without additional investigations, the exact cause of the link between deposition rate and substrate bias will remain uncertain.

Observation of the dramatic drop in deposition rate (Fig. 5.2) might suggest that DVD cannot produce dense electrolyte membrane layers at "high" rate. For experiment 6, the deposition rate is approximately $0.75 \,\mu$ m/min (40-45 μ m/hr). While this rate is obviously lower than the 1-15 μ m/min envisioned at the outset of this thesis and lower than what DVD can achieve for porous metal oxide coatings (experiment 1), it is actually quite high when compared with the rates of other techniques being examined for the creation of solid oxide fuel cell electrolyte membranes. A chart of deposition methods compiled by Will et al. [42] shows that, of the other deposition methods available for dense coating fabrication, only spray pyrolysis and electrochemical vapor deposition (EVD) can match the DVD dense-film deposition rates recorded here. It should also be noted that EVD requires the use of corrosive gases, and spray pyrolysis coatings often must undergo a post-deposition heat treatment to ensure pinhole-free coatings. So, even though the DVD coatings are not as dense as desired and even though the deposition rates are not as high as desired, the plasma-assisted DVD coating method does show promise as a method of creating dense, pinhole-free electrolyte membrane layers for solid oxide fuel cells.

5.3 Future Work

The experimental study of this thesis has revealed distinct trends in metal oxide deposition density and deposition rate in the plasma assisted DVD environment. The work has shown that plasma activation and substrate biasing can be used in a DVD environment to increase the density of depositing metal oxide films. Still, the underlying cause of film densification has not been definitively identified in this thesis, and there is clearly room for further film densification as the deposited coatings of this thesis are Zone T or Zone II structures, not fully dense, recrystallized Zone III structures.

To determine whether the denser coatings of samples 6 and 7 are the result of the combination of the three factors suggested here (and others) or the result of just one factor will involve additional detailed experimental work as a follow-on to this thesis. As noted in Chapter 3, measurement of substrate temperature during application of the AC pulse bias is complicated since the metal wires of a standard thermocouple act as a short-circuit that prevents charging of the substrate surface. To investigate the electron heating question, measurement of substrate temperature during AC biasing of the substrate will need to involve some type of non-contact (e.g. pyrometer-based) sensor. Information about the specific stoichiometry of the deposited films could be obtained via a host of quantitative chemical analysis techniques that are more sensitive than the XRD technique employed here. Such techniques could include SEM-based energy-dispersive x-ray spectroscopy, transmission electron microscopy, particle-induced x-ray emission, and x-ray fluorescence techniques [77]. Finally, a more accurate determination of material deposition rates might simply involve doubling of the deposition time from 20 to 40 minutes, creating a more definitive difference in deposit thickness.

Efforts to increase the density of films deposited in a plasma-assisted DVD environment

could involve additional explorations. Hass *et al.* have suggested that modification of the DVD gas flow nozzle could allow the process chamber pressure to be lowered while still allowing vapor to be focused and directed to the coating surface [78]. Further experimental and model-based investigation of such modifications appears warranted given the pressure dependence of coating density observed in this study [16, 56, 79]. Direct simulation Monte Carlo models appear to hold promise as a means for better understanding of the plasma, vapor, and carrier gas interactions experienced in plasma-assisted DVD [80, 81].

Additionally, Morgner *et al.* [56] suggest that film densification should be possible using only plasma activation without substrate biasing. To explore their assertion more fully, a new set of DVD experiments could be performed in which hollow cathode plasma current is raised from 60 to 120 to 180 A without application of any substrate bias. Such experiments should eliminate the loss of deposition rate caused by application of a substrate bias while also creating dense Zone II or Zone III coatings.

Further examination of AC pulse bias parameters also appears prudent. In this thesis, the selection of pulse length (24 μ sec +/-) was somewhat arbitrary. The results of experiments 6 and 7 suggest that this AC bias setpoint generated a denser coating. However, there is no reason to believe that the 24 μ sec pulses are optimized. The DVD system allows the positive and negative pulse lengths to be set independently over a broad range (4 – 815 μ sec). Thus, there could be a setting which maximizes film densification while also maximizing deposition rate [50]. The subtle effects of the AC pulse bias upon DVD film synthesis remain largely unexplored.

Finally, since the original motivation of this thesis work was creation of electrolyte membrane layers for solid oxide fuel cells, it seems appropriate to suggest that dense

DVD-synthesized electrolyte membrane layers should be incorporated into fuel cell assemblies to judge the power production capabilities of these materials.

Chapter 6

Conclusions

The motivating task of this thesis was to determine whether or not plasma-assisted directed vapor deposition could be used to synthesize dense, compositionally-correct solid oxide fuel cell electrolyte membrane layers at rates greater than or equal to those of other processes being considered for such fabrication. During the work of this thesis, the following observations were made:

- 1. The DVD process conditions explored in this thesis were not fully effective at densifying films.
- When examined next to specific results reported in the literature, the experimental results of this thesis suggest that process chamber pressure significantly influences the ability of hollow cathode plasma process technologies to densify metal oxide deposits.
- The present physical configuration of the hollow cathode plasma unit in the plasma-assisted DVD system is suboptimal. The orthogonal intersection of its ion

and electron flow with the carrier gas and vapor stream disrupts the directed flow of material towards the coating surface, decreases material deposition rates, and reduces material utilization efficiency.

- 4. For the plasma-assisted DVD experimental conditions examined during this study, the following conditions appeared most promising for fabrication of dense electrolyte membrane metal oxide layers: elevated substrate temperatures (800°C), low process chamber pressures (8 Pa / 60 mTorr), moderate source material deposition rates (0.75 μ m/min), plasma activation of the vapor stream (120 A plasma current), and alternating current biasing of the coating surface (200 V, 24 μ sec +/-).
- 5. Yttria-stabilized zirconia films deposited via plasma-activated DVD possess the expected cubic crystal structure as determined by x-ray diffraction.

The work of this thesis suggests that plasma-assisted directed vapor deposition holds promise for the creation of solid oxide fuel cell electrolyte membrane layers. Still, the current configuration of the technology is less than optimal, and it is not clear that the best DVD process conditions for dense, pinhole-free metal oxide layer synthesis have yet been identified. To move DVD processing of such layers to the point where it is well-understood, characterized, and controllable, additional efforts will need to be made to study the subtle interplay of substrate temperature, plasma activation, and substrate biasing with vapor deposition from a flowing gas stream.

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Appendix - Multirod E-beam Evaporation Results

During development of the experimental procedure for this thesis, several different pathways were considered for the creation of yttria-stabilized zirconia deposits. For instance, separate evaporation of pure metal yttrium and zirconium into a helium / oxygen carrier gas flow was considered. During this stage of thesis development, a set of experiments was performed using the plasma-assisted DVD system to evaporate separate, 3.175 mm diameter rods of zirconium and yttrium from a special, multirod copper crucible system (Fig. A.1).



Figure A.1 DVD's multisource evaporation capability. a) The DVD system can establish different beam current intensities on neighboring melt pools. b) The single electron beam gun can simultaneously generate two or more electron beams for evaporation. c) The specially-designed multi-rod crucible can be used to evaporate up to four source rods simultaneously.

To create a stoichiometrically-correct YSZ deposit on the deposition surface, the evaporation rates of zirconium and yttrium must be carefully controlled in this system configuration. To ensure continuous evaporation of the materials, new zirconium and yttrium must be fed into the bottom of the melt zone at the same rate it is evaporated from the molten rod surface in the top of the crucible. For the experiments, an initial material feed rate was selected for a given electron beam current settings. For a given beam current, the source rod feed rate was then adjusted up or down until a consistent melt pool was established. The data point was recorded, and the experiment progressed to establish the next feed rate – beam current point on the graph. Figures A.2 and A.3 show the results of this exploration.



Yttrium evaporation in the DVD II system

Figure A.2 Yttrium evaporation in the DVD II system.



Figure A.3 Zirconium evaporation in the DVD II system.