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, ZrO$_2$-25 molecular percent (m/o) MgO or ZrO$_2$-15 m/o Y$_2$O$_3$ 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 ZrO$_2$ with ~9 m/o Y$_2$O$_3$ 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$_2$O$_3$ [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$_2$O$_3$ 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
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].
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

Table 2.1: Ionic conductivities for various SOFC electrolyte membrane materials

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

YSZ – ZrO₂ stabilized with 10 m/o Y₂O₃  
LSGMO30 – La₀.₈Sr₀.₂Ga₀.₉Mg₀.₁₂O₂.₈₅  
CGO10 – Ce₀.₉Gd₀.₁O₂₋δ  
LSGMO35 – La₀.₈Sr₀.₂Ga₀.₈₅Mg₀.₁₅O₂.₈₂₅  
CGO20 – Ce₀.₈Gd₀.₂O₂₋δ  
LSGMNO – La₀.₈Sr₀.₂Ga₀.₈₅Mg₀.₁₃Ni₀.₀₇O₃

recently reported La₀.₈Sr₀.₂Ga₀.₈₅Mg₀.₁₃Ni₀.₀₇O₃ (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 µm 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 (< 5 µm) YSZ films on porous La$_{0.8}$Sr$_{0.2}$MnO$_3$ 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 µm/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,
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 µm/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 µsec of 6-40 V positive bias followed by 10.2 µsec 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°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°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.
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 (Al₂O₃) and silica (SiOₓ) 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 substrate biasing leads to measurable ion currents through the substrate, and, as a result, dense alumina coatings have been deposited at rates of 6 – 9 μm/min and dense silica coatings at 12 – 36 μm/min [56-59]. Although Morgner et al. [56] report that silica films deposited at 0.4 Pa and 12 μm/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 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.
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 (7.5x10^{-4} – 7.5x10^{-2} Torr). In the plasma assisted DVD environment, the process chamber pressure is expected to be in the range of 1 and 100 Pa (7.5x10^{-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 µm/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.