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Review

Application of vacuum deposition methods to solid oxide fuel cells

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Abstract

The application of vacuum deposition techniques to the fabrication of solid oxide fuel cell (SOFC) materials and structures are reviewed, focusing on magnetron sputtering, vacuum plasma methods, laser ablation, and electrochemical vapor deposition. A description of each method and examples of use to produce electrolytes, electrodes, and/or electrical interconnects are given. Generally high equipment costs and relatively low deposition rates have limited the use of vacuum deposition methods in SOFC manufacture, with a few notable exceptions. Vacuum methods are particularly promising in the fabrication of micro-fuel cells, where thin films of high quality and unusual configuration are desired.

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Keywords: Solid oxide fuel cell; Magnetron sputtering; Vacuum plasma deposition; Laser ablation; Electrochemical vapor deposition

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1. Introduction

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Solid oxide fuel cells (SOFCs) offer an efficient means to convert chemical energy to electricity, with potential

applications in transportation, distributed generation, remote power, defense, and many others [1-5]. An individual SOFC cell is composed of a fully dense solid electrolyte, a porous cathode or air electrode, and a porous anode or fuel electrode. Fuel cell stacks consist of individual cells that are joined by electrical interconnect plates, and operate in the temperature range

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Fig. 1. (a) Schematic of an SOFC cell, with associated reactions. (b) Example of a design for the repeat unit of a planar SOFC.

 \sim 700–1000 °C. Fig. 1 provides a schematic of an SOFC cell and associated reactions, as well as one design for the repeat unit of a planar SOFC stack. Yttria-stabilized zirconia (YSZ) is the most commonly utilized solid electrolyte, while lanthanum strontium manganite (LSM) and nickel–YSZ most often serve as the cathode and anode, respectively. Metallic electrical interconnects are practical at the lower end of this temperature range, while conductive, refractory ceramics such as substituted lanthanum chromite are used in high-temperature fuel cells. Extending lifetimes, improving power density, and lowering cost are among the primary goals of current SOFC development efforts [4].

The purpose of this paper is to review the applicability of vacuum deposition techniques to SOFC technology, focusing on magnetron sputtering, vacuum plasma deposition, laser ablation, and electrochemical vapor deposition (EVD). A description of each of these methods is provided along with examples of how each has been used in fuel cellrelevant research and development. Many of the studies that are summarized here have used vacuum methods to prepare thin, fully dense YSZ electrolyte layers on porous and dense substrates, as a means to lower the internal resistance of the fuel cell. Researchers have also used vacuum deposition methods to produce alternate electrolyte compositions, a variety of air and fuel electrode compositions and forms, electrical interconnects, and corrosion-resistant barriers. Equipment cost and relatively low deposition rates present challenges to implementation in large-scale SOFC manufacture, though applications such as micro-fuel cells exist where high film quality and the ability to produce unusual configurations outweigh other considerations. Vacuum deposition methods have also been invaluable in preparing compositions and forms useful in studies of fundamental reaction mechanisms.

2. Magnetron sputtering

Magnetron sputtering is a form of physical vapor deposition that has been widely applied to deposit a variety of coatings aimed at improving optical properties, wear resistance, corrosion resistance, friction resistance, electrical properties and appearance [6], many of which are of industrial importance. Kelly and co-workers have reviewed recent developments magnetron sputtering technology, including relatively recent innovations such as unbalanced magnetron sputtering, closed field unbalanced magnetron sputtering, and pulsed magnetron sputtering [7–9], which provide significantly enhanced deposition rates.

There exist many examples of the use of magnetron sputtering to prepare components and protective coatings for SOFCs, owing to the versatility of this technique as well as the ability to control composition and morphology. Further, deposition at relatively low temperatures should lead to lower levels of unwanted interfacial reactions between the electrolyte and electrodes that may otherwise occur during sintering at high temperatures. Most often, the goal has been to prepare thin, dense electrolyte layers on porous supports. As discussed in recent reviews [10,11], this approach reduces the internal resistance of the fuel cell stack and enables lower operating temperatures and therefore greater flexibility in the choice of materials for stack construction. Though flexible, the cost of necessary equipment and relatively low deposition rates ($< \sim 5 \mu m/h$) limit the applicability of magnetron sputtering to largescale fuel cell manufacture [12]. The fabrication of thin electrolytes of various compositions, fuel and air electrodes. and corrosion-resistant thin films on metal interconnects are discussed below.

2.1. Thin zirconia electrolyte fabrication by sputtering

The formation of thin films of YSZ using sputtering technology that are generally free of cracks and interconnected porosity has been reported frequently [13–51]. A primary goal of these studies has been to lower the ohmic resistance associated with the electrolyte. Radio frequency (RF) magnetron sputtering using an oxide target and DC reactive magnetron sputtering using metallic targets have both been utilized to produce zirconia thin films of high quality.

RF sputtering has frequently been the method of choice to deposit YSZ thin films in part because of the ability to use either metallic or electrically insulating targets, the generally high quality of the deposit, and scalability to large substrates [14-18,21,23,24,27,29,30,32,34,35,44, 48-51]. With RF sputtering, positive ions from a plasma impinge on a target surface, ejecting a mixture of oxygen, metal and metal oxides that then condense on the substrate. Deposition rates are modest, usually less than $1 \,\mu$ m/h, and depend on RF power, oxygen partial pressure, bias potential, and other factors. Oxygen is often included in the sputter gas mixture even when an oxide target is used, as a means of controlling the metal to oxygen ratio in the target. However, RF sputtering yields decrease significantly with increased oxygen partial pressure, as is shown in Fig. 2 [50]. A correlation between deposition rate



Fig. 2. Relation of RF sputter deposition rates of YSZ to oxygen content with and without an applied bias potential at an overall sputter gas pressure of 1.33 Pa [50].

and RF power has been demonstrated in several studies [48–51] for YSZ deposition on a variety of substrates. Even without the presence of oxygen in the sputter gas mixture, YSZ thin films were nearly fully oxidized and thus do not require a post-deposition oxidation treatment as necessary with DC magnetron sputtering with a metal target [49].

Substrate temperatures most frequently are less than 70 °C during RF sputter deposition unless the substrate is deliberately heated. Columnar grain structures, such as those shown in Fig. 3 [31], are typically found where the electrolyte thickness is greater than several microns in thickness. These particular films required post-deposition annealing to 1600 °C to achieve full density and free of interconnected porosity. Equiaxed grain structures and full densities have been reported for extremely thin YSZ films prepared by RF sputtering and annealed at temperatures as low as 600 °C, where layer thickness and grain sizes were 70 and 12-20 nm, respectively. Columnar grains were produced in the porous Ni/YSZ support, however [27]. Low annealing temperatures are important in minimizing unwanted interfacial reactions between fuel cell components.

Recently, helicon wave-excited plasma (HWP) technology has been applied to the growth of thin YSZ films [18,29]. In HWP, magnetic mirrors are used to confine the plasma, leading to higher plasma densities at the target surface and higher sputtering rates. Greater crystallinity in the deposited YSZ film was also reported, as monitored by the intensity of the (111) reflection in X-ray diffraction (XRD) spectra [18].

Reactive DC current magnetron sputtering has also been widely applied to deposit thin YSZ electrolyte layers onto dense and porous supports [13,16,17,19,20,22,25,26,28, 36,37,39–41,43,45–47,52]. One approach is to employ a



Fig. 3. Cross-sectional SEM micrographs of 8-YSZ films grown on a NiO substrate by RF sputtering of an oxide target at two different power levels. The deposit consists of columnar grains [31].

single target consisting of an alloy of zirconium and yttrium; another is to use multiple targets of the pure metals, where the composition of the deposit is controlled by the relative exposed surface area of the targets. After initiation of the plasma, oxygen is admitted into the deposition chamber to produce an oxidized deposit on the negatively biased substrate. The substrate temperature reaches about 70 °C unless otherwise heated. Homogeneous, large-area coatings can be obtained with this method. Most commonly, a columnar grain structure results though deposits consisting of equiaxed, cubic grains have also been reported when the substrate is maintained at approximately 700 °C during deposition [26].

Barnett and co-workers described the formation of fully dense YSZ thin films on a variety of porous and dense substrates as well as porous electrode structures by reactive DC current magnetron sputtering, with post-deposition annealing temperatures as low as $350 \,^{\circ}$ C [38–41,43,52]. Deposition rates of somewhat less than 3 µm/h were reported, free of cracks if the deposition pressure was less than 20 mTorr. Electrical properties of the YSZ deposit were similar to those of films formed by other methods. The metal to oxygen ratio in the deposit was shown to depend critically on the oxygen partial pressure in the sputter gas, as shown in Fig. 4 [52]. Similar variations in the oxygen–metal ratio as a function of the oxygen content of the sputter gas and therefore the deposition rate have been found by Jankowski and Hayes using Auger electron spectrometry [22].

Elimination of interconnected porosity in sputter-deposited thin electrolyte films is of course a significant challenge. Interconnected porosity will lower the open cell potential of a SOFC because of a diminished chemical potential difference across the electrolyte. Achievable power densities are similarly lowered. Helium leakage rate measurements are one useful way to assess the concentration of such defects in the films as a function of film thickness and annealing conditions. For example, Wanzenberg et al. [45,47] have shown for thin YSZ films deposited onto a porous Ni-YSZ substrate that the helium leakage rate can be lowered by two or more orders of magnitude relative to the as-deposited condition by judicious choice of annealing conditions for the porous substrate and thin film. Hobein et al. [19] showed a nearly linear decrease in helium leakage with increased film thickness for films ranging from 1 to 10 µm in thickness. Post-annealing of the films from 1100 to 1300 °C resulted in a decrease in helium leakage rates of a factor of 2-10. Film quality appears to be of sufficient quality for use in SOFCs, as evidenced by respectable power densities that have been achieved. For example, Srivastava et al. [36,37] have reported power densities of approximately 400 mW/cm² at 800 °C at a cell potential of 0.7 V for button cells, and slightly lower power densities for large cells.

As with RF sputtering, deposition rates are adversely affected by the oxygen partial pressure in the sputtering gas for DC reactive magnetron sputtering of YSZ thin films. This behavior was shown to be especially apparent for oxygen partial pressures less than 10 mbar, as shown in Fig. 5 [16]. The crystal structure of the deposit was found to be affected by oxygen partial pressure in the sputter gas: both tetragonal and cubic zirconia phases were formed in the deposit at relatively low oxygen partial pressures, while only the cubic phase was apparent for high oxygen partial pressures [19]. In that study, the deposits were converted completely to the cubic phase upon annealing in air at 100-1300 °C. Variation in the Zr/Y ratio of the deposit with oxygen content of the sputtering gas has also been reported, as shown in Fig. 6 [16]. Given that the target composition is near the tetragonal-cubic boundary in the Y_2O_3 -ZrO₂ phase diagram, such compositional variations could lead to similar variations in the crystal structure of the deposit. Information on the composition of the sputtered deposit is only rarely reported.



Fig. 4. Measured oxygen to metal ratios normalized to fully oxidized YSZ as a function of oxygen flow rate [52].



Fig. 5. Relation of YSZ deposition rate by DC reactive sputtering to oxygen flow rate and oxygen partial pressure [16].

2.2. Deposition of other electrolyte compositions by sputtering

Sputtering has been applied to deposit thin electrolyte films and barrier layers other than YSZ, most notably ceria [20,39–41,44,53–58], lanthanum gallate [59], and bismuth oxide [39,40,60]. In addition, thin films of proton-conducting electrolyte CsHSO₄ have been grown on mesoporous silica by RF sputtering [61]. Because many of these electrolytes generally show higher ionic conductivity than YSZ, their use could enable the operating temperature of an SOFC to be lowered considerably. With lower operating temperatures, greater flexibility in the choice of fuel cell materials is gained, such as the ability use of inexpensive ferritic steel electrical interconnects. Substituted cerium oxides are potentially useful as the electrolyte in an SOFC, as the anode, and as an interlayer to prevent reactions between a zirconia-based electrolyte and the air electrode. Highest ionic conductivities have been reported for gadolinia and samaria-substituted compositions. Partial reduction of ceria at the anode side, especially for temperatures greater than 700 °C, results in lattice expansion, a substantial increase in the electronic component of overall conductivity and therefore a lower open cell potential. As such, cells based on ceria electrolytes are most promising for intermediate and low operating temperatures [62–64].

There are few examples of the use of sputtering to prepare ceria-based electrolytes for SOFCs, though sputtering has been more widely applied to depositing ceria



Fig. 6. Stoichiometry of YSZ thin film as a function of oxygen flow rate [16].

barrier layers. Gourba and co-workers used DC reactive magnetron sputtering to deposit dense gadolinia-substituted ceria ranging in thickness from about 0.5 to $5.5 \,\mu\text{m}$ onto glass slides [53,54]. The thin films exhibited a defect fluorite structure, similar to bulk material. Electrical properties were dominated by the grain boundaries, leading to higher activation energies for conduction than usually found for bulk material. Enhanced conductivity in nanocrystalline gadolinia-doped ceria deposited onto porous platinum and silicon wafers has also been reported [57]. The films were found to be compositionally homogeneous throughout the film thickness.

Ceria interlayers that were deposited by sputtering between a zirconia electrolyte and the cathode have been found to reduce interfacial reactions and to lower polarization losses. Wang and Barnett reported an almost three-fold decrease in polarization losses attributed to the air electrode due the deposition of a 1-2.5-µm-thick yttria substituted ceria film [40,41,60]. Honegger and co-workers similarly reported the deposition of a 5-µm-thick YSZ layer onto porous NiO/YSZ followed by a 1-µm-thick yttriasubstituted ceria barrier layer by reactive DC magnetron sputtering [20]. The ceria barrier layer was shown to be effective in reducing the formation of interfacial resistive pyrochlore phases. Wang and co-workers used RFsputtered samaria-substituted ceria thin films inserted between a zirconia electrolyte and a nickel-based anode to substantially lower anodic polarization losses [44]. Improved anode performance was attributed to mixed electronic and ionic conductivity exhibited by the ceria interlayer, which was 2–3 µm in thickness.

Sputtered thin films of YSZ have been applied as a means of improving the stability of ceria-based electrolytes against partial reduction. Yahiro et al. used RF sputtering to deposit thin YSZ films onto the anode side of yttria-substituted ceria electrolytes [56]. Unlike cells constructed

with unprotected ceria electrolytes, these cells exhibited nearly theoretical open cell potentials in the temperature range 600–800 °C. Mehta and co-workers reported that thin (2- μ m-thick) YSZ layers that were deposited onto ceria tended to form cracks when heated to 900 °C, though some healing occurred by further heating to 1500 °C [58]. Exposure of the coated side to oxygen at elevated temperatures led to lower concentrations of imperfections in the thin film, and open cell potentials closer to theoretical values.

Substituted lanthanum gallate also shows substantially higher ionic conductivity than does YSZ, and is considered to be a promising electrolyte for SOFCs operating at intermediate and low temperatures [62,65]. With a perovskite crystal structure, lanthanum gallate exhibits a thermal expansion behavior similar to YSZ and is less susceptible to reduction than ceria. Under conditions typically required to densify these materials by traditional methods, volatilization of gallium oxide and phase separation may occur. As such, sputtering may provide a superior method to form thin films of lanthanum gallate electrolytes due to milder thermal conditions that are required. Only one example of the use of sputtering to prepare lanthanum gallate electrolytes for possible fuel cell applications was found: that of Singh et al. [59]. This study revealed a much higher oxygen non-stoichiometry for sputter-deposited thin films than found for typical bulk materials. Some thin films exhibited linearly ordered, self-organized islands believed to be formed by the Stranski-Krastanov mechanism.

Electrolyte systems based on bismuth oxide also exhibit high oxide ion conductivity and have been proposed as good electrolyte materials for applications such as SOFCs and oxygen sensors [62,64,66–68]. Like ceria, instability under typical oxygen partial pressures present at the anode has limited the applicability of these materials to SOFCs. Structures and properties of bismuth oxide systems vary widely, depending upon the dopant concentration, temperature and atmosphere. There are a few examples in the literature of the use of sputtering to create multilayer electrolytes. Wang and Barnett lowered the cathodic polarization resistance of an SOFC by depositing a yttria-stabilized bismuth (YSB) oxide interlayer between a YSZ electrolyte and a lanthanum strontium cobaltite and other cathodes by DC reactive magnetron sputtering [39–41]. Coatings greater than 50 nm on YSZ were found to be continuous. A fuel cell constructed using a three-layer YSB/YSZ/YDC electrolyte resulted in a factor-of-three increase in power density over a cell constructed with a traditional YSZ electrolyte [40,41].

2.3. Formation of SOFC electrodes by sputtering

While sputtering technology has most often been applied to the deposition of thin film solid electrolytes, there are also many examples in the literature of the successful deposition of porous film electrodes and composites. Sputter-deposited electrodes include lanthanum manganite [60,69–75], lanthanum cobaltite [60,76,77], lanthanum cuprate [78], lanthanum nickelate [79], silver [41,43,60], platinum [33,57,80,81], and nickel [15,27,31,82-84], as well as composites of many of the above with zirconia or ceria. Sputtering generally allows lower processing temperatures to be employed, which diminishes the extent of unwanted interfacial reactions such as the formation of nonconductive pyrochlores [85]. Sputtering also allows flexibility in tailoring electrode microstructure, which has been used to advantage in studies of fundamental reaction mechanisms [73,75,81,84,86].

Strontium doped lanthanum manganites are perhaps the best-known cathode material for SOFCs, showing good stability at high temperatures, high electronic conductivity, a thermal expansion coefficient compatible with stabilized zirconia and good electrocatalytic activity [87–89]. Unlike compositions such as the ferrites, cobaltites, and nickelates, the manganites exhibit only very modest mixed conductivity. As such, electrode performance depends critically on the microstructure. Sputtering methods show significant promise as a means of controlling the length of the triple phase boundary (gas–electrode–electrolyte), and therefore activity.

Substituted lanthanum manganite cathodes and manganite/zirconia composite cathodes have been successfully prepared by sputtering methods. Good bonding of porous manganite films to the zirconia substrate, good mechanical stability, and acceptable electrode activity have been reported for both RF and DC magnetron-deposited films [69,74]. As for electrolyte thin films, deposition rates are quite modest—typically less than $0.5 \,\mu$ m/h. Composites of lanthanum manganite and zirconia have also been produced by RF sputtering [70,71], deposited under an atmosphere of oxygen and argon. Though the electronic conductivity of the composite was reduced compared to pure LSM, the measured electrode overpotential was lowered considerably and was superior to those obtained for similar electrodes made by spray pyrolysis or screen printing. Further, composite electrodes showed less grain growth during post-deposition thermal processing.

Klenov and co-workers conducted a very careful study of RF magnetron sputter deposition of lanthanum strontium cobaltite thin films onto SrTiO₃ and MgO single crystal substrates using a $La_{0.50}Sr_{0.50}CoO_3$ target [77]. Both the La/Sr and (La+Sr)/Co ratio was evaluated as a function of oxygen content in the sputter gas, total pressure, and RF power. The total sputter gas pressure was found to be the most important in controlling the composition of the deposit, believed principally to be due to the effect on re-sputtering that disproportionately affects light elements. High oxygen partial pressures were found to enhance sputtering rates, while increased overall pressures gave decreased rates due to re-sputtering. Through precise control of sputtering parameters, it was possible to achieve lanthanum cobaltite thin films that matched the stoichiometry of the target.

Photolithography has been combined with sputtering to produce unique, patterned electrodes of lanthanum manganite, lanthanum cobaltite, platinum, and gold [73,75,81,84]. These unique electrodes allowed aspects of cathode reaction mechanisms to be explored, not possible with traditional, heterogeneous electrode structures. Kato and co-workers found a linear relation between the length of the triple phase boundary of patterned LSM cathodes and the rate of oxygen reduction, and estimated an activation energy of 1.86 eV [73]. Radhakrishnan and coworkers prepared a series of patterned electrodes composed of either platinum or LSM, shown in Fig. 7, where the triple phase boundary length was varied while maintaining the cross-sectional area covered by the electrode constant [75,81,90]. Charge transfer resistances were established as a



Fig. 7. Scanning electron micrograph of a patterned LSM patterned electrode on YSZ [90]. This electrode is part of a series produced by sputtering and photolithography where the triple phase boundary was varied while the area covered by the electrode remained constant.

function of oxygen partial pressure and temperature in those studies. Platinum electrodes behaved as expected for a purely electron-conducting material, whereas LSM electrodes showed evidence of a small contribution due to mixed electron and ionic activity. The activation energy for LSM electrodes was approximately 1.5 eV, whereas values from 0.75 to 1.63 eV were obtained for Pt electrodes, depending on the oxygen partial pressure. Inter-digitated electrode structures produced by photolithography and sputtering are being considered for micro-SOFC applications [84,91]. Platinum and Au microelectrodes showed an electrode polarization conductance directly proportional to the triple phase boundary length, with activation energies in air of 0.77 and 0.91 eV, respectively. These unique structures offer promise for use in small energy conversion devices operating at reduced temperatures [91].

The formation of porous nickel and nickel-containing composites by either RF or DC reactive magnetron sputtering has been reported in several studies [15,27, 31,82-84]. Tsai and Barnett described the formation of Ni-YSZ composite electrodes by DC reactive magnetron sputtering of a Ni-Y-Zr target, and obtained an equiaxed structure with grain sizes of approximately 35 nm [83]. The conductivity was similar to that of bulk Ni-YSZ made by traditional ceramic processing methods. Hayashi and coworkers deposited Ni-YSZ composites by DC reactive magnetron sputtering of Ni and YSZ targets, and found that grain growth in co-sputtered films was suppressed [82]. Columnar Ni grains were produced by RF sputtering in Ni/YSZ/Ni three-layer films grown onto alumina substrates [15]. An inverse relation between electrode contact resistance and RF power was found in similar Ni/YSZ/Ni structures [31]. Porous NiO-YSZ electrodes produced by RF sputtering from an oxide target were found to consist of equiaxed grains less than 5 nm in diameter [27]. After reduction of the NiO to Ni metal, columnar grains were formed that were 13-75 nm in length and 9-22 nm in width, and well-adhered to the electrolyte.

2.4. Protective coatings on steel interconnects by sputtering

Certain ferritic stainless steels are being considered for use as the interconnect in SOFCs because of their relatively low cost, good thermal expansion match to YSZ and other fuel cell components, durability, formation of an electrically conductive scale, and other considerations [92]. However, with continuous operation at elevated temperatures, growth of the oxide scale can lead to increased electrical resistance. In addition, chromium volatilization can occur, resulting in poisoning of the fuel cell cathode.

To mitigate the effects of high-temperature corrosion of stainless steels, RF magnetron sputtering has been applied to deposit protective coatings of lanthanum chromite [86,93]. Though refractory, highly conductive, and compatible with other fuel cell components, bulk lanthanum chromite is not favored for planar fuel cells because its limited mechanical properties and cost of fabrication.

Fig. 8. Lanthanum chromite perovskite film deposited onto 446 stainless steel by RF sputtering, following a 1 h anneal at 700 $^{\circ}$ C [86].

Using a LaCrO₃ target in argon, an amorphous coating was formed on SS 446 substrates held at room temperature. The films were annealed in air to develop desired crystalline phases. The desired orthorhombic perovskite phase was obtained upon heating to 700 °C, and exhibited a dendritic microstructure, as is shown in Fig. 8 [86]. Structural characterization of the films was done by XRD, phase shift microscopy, scanning electron microscopy with energy dispersive X-ray analysis, and micro-Raman spectroscopy. Uncoated SS 446 specimens showed the formation of hematite and magnetite when heated in air to 700 °C, whereas coated samples showed only the presence of lanthanum chromite.

3. Vacuum plasma deposition methods

The plasma spray process is a high-temperature process (up to 15,000 K for a typical DC torch operating at 40 kW) [94]. Shown in Fig. 9 are the schematic diagrams of DC and RF plasma spray processes. Argon is ionized by a high current discharge in the plasma torch. The powders are injected into the plasma through a nozzle, then accelerated and melted in the fast plasma jet (100–300 m/s). Deposited layers are formed by a rapid solidification of the melts. Asdeposited layers often present characteristics such as: anisotropic microstructures, microcrack due to thermal stress and tensile quenching stress, and inter-lamellar porosity. This is particularly true in atmospheric plasma spray (APS).

Thin films produced by vacuum plasma spray (VPS) typically possess higher density than those prepared using APS, as well as exhibit better adhesion due to the higher plasma jet velocity. Velocities of melted particles up to 900 m/s have been reported [95], which favors densification. Hence, VPS becomes particularly important in fabricating the SOFC electrolyte, where the high density is a primary requirement. Advantages of the VPS process include: high deposition rate (tens of grams powders per min with 7 mm



nozzle), thus short fabrication time; and the ability to be an automated production line, thus potentially being a costeffective fabrication process. Typical VPS parameters are listed in Table 1.

Certain alternative SOFC cell designs are being developed, for which VPS methods may be well suited [96]. The most attractive design thus-far is the metallic substrate supported cells. Considerable progress has been made in VPS in depositing serial layers onto metallic substrates, particularly in Europe at the German Aerospace Center (DLR) [95,97–108] and Research Center Juelich (FZJ) [109,110]. The DLR has co-operated with various sectors in the automotive industry, such as BMW, Elring-Klinger, Rhodius and KruppThyssen [98]. The following sections address the use of VPS to fabricate metallic supported SOFCs as well as SOFC components.

3.1. Cathode formation by VPS

VPS methods offer an attractive means of depositing SOFC cathodes, because of the ability to prepare thin films with controlled porosity and a compositionally graded structure. Unwanted reactions between fuel cell components such as the formation of insulating pyrochlores $(La_2Zr_2O_7)$ may also be suppressed, a result of very short times that deposited materials remain at high temperatures. Earliest reports of the development of VPS processes for the deposition of SOFC components focused on fabrication of single components [111], while later studies

addressed the formation of composites such as those of (La,Sr)MnO₃ (LSM) and YSZ [98,100,112].

Porous composite electrodes consisting of varying fractions of LSM and YSZ and varying thicknesses were prepared on YSZ substrates using VPS by Rambert et al. [112]. Polarization losses compared favorably to that obtained for pure LSM cathodes deposited by screen printing. No insulating pyrochlore phase formation was observed, attributed to the fact that the deposit remained at high temperatures for times on the order of milliseconds. Pyrochlore formation from the interfacial reaction of LSM and YSZ at temperatures and times necessary for traditional ceramic processing is particularly well-known.

Vapor plasma spraying methods provide control of the porosity of cathode films, essential in achieving high fuel cell performance. For example, in a study by Lang et al. [100], the overall porosity in a LSM/YSZ composite cathode was $\sim 10 \text{ vol}\%$, which accounted for a majority of the total cell losses (\sim 70%). Very recently, the same team reported a 30 vol% fine porosity in the cathode and significantly improved cell performance [98]. The VPS process may also result in the formation of microstructural defects, which may appear as isolated pores and are likely the result of the inclusion of some unmelted large-size particles. Parameters such as the melting temperature of the raw materials [113] and particle size distribution [114] have been shown to play an important role in the ultimate microstructural quality of the films. One potentially important issue that has not been addressed is how cathode



Fig. 9. Schematic diagram of DC and RF plasma spraying apparatus [94].

Table 1			
Typical vacuu	m plasma	spray	parameters

	Chamber pressure	Spray distance	Plasma gas argon	Plasma gas hydrogen	Plasma current	Carrier gas argon	Powder feed rate
Range	40–100	275–400	25–30	9–12	680–840	1.7–2.3	20–40
Unit	mbar	mm	l/min	1/min	A	l/min	g/min

film quality may be affected by the low oxygen partial pressure during VPS deposition. Low oxygen activity can lead to oxygen non-stoichiometry during melting process, thus creating a local strain between the deposited layer and the substrate. Microcracks can be induced during a postannealing process due to strain relaxation. Such behavior might be expected for any vacuum deposition technique where metal oxides susceptible to reduction are heated to elevated temperatures.

3.2. Electrolyte formation by VPS

In the electrolyte deposition from VPS process, there exist two major concerns: namely anisotropic properties and significant thickness variations in the as-deposited YSZ. Strong anisotropy in the ionic conductivity of YSZ fabricated by VPS process was observed by Van Herle et al. [111]. The out-of-plane conductivities were several times lower than in-plane values. This anisotropy was eliminated after sintering the deposited YSZ layer at 1500 °C for 2h.

Gas tightness is a primary requirement for the electrolyte used in SOFC, whereas vacuum plasma sprayed electrolyte thin films are often incompletely dense. In early research (before 1994), rather thick YSZ layers were used to achieve leak-free films [111]. Subsequent research was carried out with an attempt to reduce the electrolyte thickness without introducing open porosity. Novel plasma torches with Laval-like nozzle contours providing a controlled expansion of the hot plasma jet core have been developed at DLR [95]. The new torches can generate a greater plasma velocity with a long and laminar plasma jet under vacuum conditions, which reduces the interaction of melt particles with the surrounding cold gas, thus improving spray conditions. Porosity in the range of 1.5-2.5 vol% was achieved in YSZ and ScSZ layers with a low thickness in the range of 30 µm. Fig. 10 illustrates a typical crosssectional view of a single cell fabricated from serial VPS depositions, and a schematic stack design for mobile applications [98]. Such thin electrolytes, particularly true for ScSZ, were found to contribute negligibly to the total area-specific resistance of the cell. Hence, anisotropy may not be a significant consideration in DLR's design, though the effect on long-term aging behavior is yet to be determined.

The technical advantages of metallic supports are intriguing, such as the possibility to weld the substrate to the cassette, the ability to tailor thermal–mechanical properties to match with cassette and cell components, and the capability of a rapid start-up and thermal cycling due to potentially small cell and stack volume. Also, the overall cost may be reduced because of replacing the anode support with less expensive metallic foam. Total cell thicknesses are approximately 100 μ m, in which the thickness of the electrodes are in the range of 30–50 μ m. Power densities of 300–400 mW/cm² at low operating temperatures of 750–800 °C have been achieved [101]. Recent thermal cycling and redox cycling tests conducted



Fig. 10. (a) SEM Image of SOFC layers deposite don to porous metallic substrates from VPS process; (b) plasma spray SOFC stack design for mobile applications [98].

at DLR revealed that the dynamic electrochemical behavior of the plasma sprayed cells depends strongly on the nature of the porous metallic substrate support, particularly thermal expansion coefficient. Redox cycling (10 times) did not result in severe cell failure, whereas the cells showed degradation in performance during thermal cycling [98,100,101,104].

Light weight, small volume and low cost are the key factors for commercializing SOFC, particularly for transportation applications. A potentially critical problem in metallic foam-supported SOFCs relates to the thermal mechanical stresses created during thermal cycling process, which can promote microcracks in the electrolyte and thus reduce the cell performance. In addition, electrode degradation may be caused by the diffusion of metallic elements from the support into the electrodes. Nevertheless, VPS is of substantial interest in the manufacture of low weight, small volume and low cost SOFC for such applications as auxiliary power units, through the improvement of the materials development and process optimization. The merits offered by VPS clearly outweigh its drawbacks. Further improvements can be implemented, for instance, by tailoring the thermal expansion properties of the metallic substrates, by employing barrier coatings to enhance chemical stability, and by improving the out-ofplane conductivity of the electrolyte. It is also worthwhile to note that substantial progress has been made at Ceres Power [115] in the development of low-cost ceramic routes to fabricate SOFC layers onto metallic substrates.

3.3. Coatings for steel interconnects by VPS

Interconnect plates in a planar SOFC stack serve as the electrical bridge between individual cells while providing a hermetic seal between the fuel electrode of one cell and the air electrode of an adjacent cell. Metallic interconnects are preferred because of relatively low cost, ease of fabrication and other issues. However, under the dual environment (oxidizing and reducing) to which interconnects are exposed at elevated temperatures, corrosion could lead to increased contact resistances and loss of a seal.

Multilayer and/or superlattice coatings in the Cr–Al–N system have been deposited onto several stainless steels using large area filtered arc deposition (LAFAD), aimed at improving corrosion properties on the air side [116,117]. The LAFAD system used in those studies consisted of a rectangular plasma-guide chamber with two rectangular deflecting coils installed on opposite sides of the chamber. Separate targets consisting of Al and Cr on the sidewalls were employed, surrounded by deflection coils and separated by an anodic baffle. A nitrogen atmosphere of 0.04 Pa led to the formation of nitrides. The plasma source uses a superimposed deflecting magnetic field to turn the metal/metal oxide ions through a 90° angle towards the



Fig. 11. (a) Schematic drawing of the multilayer structure of LAFAD coatings consisting of repeated sections of CrN and a CrAlN superlattice. (b) TEM image of the multilayer coating showing CrN (dark bands) and CrN/AlN superlattice (light bands) [116].

substrate. This serves to eliminate more massive droplets from the source from reaching the substrate. A rotating carousel arrangement in the deposition chamber allows multilayer structures to be deposited. Fig. 11 shows the structure of repeated sections of CrN and a CrAIN superlattice, where individual layer thicknesses of a few nanometers each were created in a deposit of ~1.5 µm thickness in total [116]. Coated stainless-steel specimens exhibited lower contact resistances than uncoated samples in high-temperature corrosion tests of a few hundred hours duration. This technology appears to be applicable to a broad range of material compositions.

4. Laser ablation

Laser ablation, also known as pulsed laser deposition, is applicable to the deposition of a wide variety of materials, including many with relevance to SOFCs. Laser ablation has been used to deposit air electrodes such as lanthanum strontium cobaltite [118–123], lanthanum cobalt iron oxide [123], and LSM [120,121,124,125]; electrolytes including YSZ [126-128], lanthanum gallate [129-131]; and lanthanum chromite-based electrical interconnects [132-135]. In laser ablation, material is removed from a target surface by irradiation with an excimer, Nd:YAG, or other laser, and collected on a substrate surface following the schematic shown in Fig. 12 [135]. Typically ~ 30 ns pulses with energies in the 0.01–0.3 J/pulse range and a repetition rate of $\sim 10 \,\text{Hz}$ are employed. An oxygen partial pressure of $\sim 10^{-4}$ Torr or less is maintained, depending on the tendency for reduction of the deposit. In the deposition of fuel cell-relevant materials, the substrate is most commonly heated to 700 °C or higher. Although very high deposition rates up to $\sim 600 \,\mu\text{m/h}$ have been reported [135], rates of $\sim 1 \,\mu\text{m/h}$ are more typically employed when high quality, epitaxial thin films are desired.

YSZ was the first fuel cell-relevant material to be deposited as thin films by laser ablation. Murray and coworkers used a frequency-doubled Nd:YAG laser



Fig. 12. Schematic of laser ablation method [135].

(0.53 μ m wavelength, 15 ns pulses, 5 Hz repetition rate) to deposit YSZ from an oxide target. Deposition rates were low, less than 0.15 μ m/h. Later work by Kokai and coworkers employed an XeCl excimer laser (0.308 μ m wavelength, 20 ns pulses, 10 Hz repetition rate) and a YSZ target to prepare well-adhered, fully dense thin films up to 2 μ m in thickness [126,127]. No recent studies were found that utilized laser ablation in preparing thin YSZ films for fuel cell applications, in contrast to many such examples that have employed other vacuum techniques such as magnetron sputtering, EVD, or vacuum plasma deposition.

Several papers were published in the mid-1990s by researchers from Osaka Gas that detailed the deposition of lanthanum strontium chromite interconnect layers by laser ablation on tubular SOFCs [132-135]. Siemens Westinghouse Power Corporation is developing a similar tubular SOFC technology, and has employed EVD to produce chromite interconnects [136], among other methods. Lanthanum strontium chromite is an electrically conductive ceramic that is stable to high temperatures under conditions typical of both the air and fuel electrode of an SOFC. In the tubular fuel cell configuration being developed by Osaka Gas, the chromite interconnect was deposited directly on a porous lanthanum manganite cathode tube, to a thickness of 20 µm. Chromite films were fully dense and free of voids, essentially identical in composition to that of the target, and exhibited electrical properties very similar to that of bulk material. Films of good quality were achieved even when very high deposition rates of $600 \,\mu\text{m/h}$ were employed. No recent studies were found that detail continued development of this approach for chromite interconnects on tubular fuel cells.

Although not being considered as a manufacturing method for air electrodes, laser ablation has proven to be a valuable tool in preparing novel electrode compositions and structures for use in fundamental reaction mechanism studies [118–125]. Laser ablation allowed thin, fully dense, and oriented air electrode films to be deposited onto various electrolytes, which enabled the role of mixed electron and oxygen ion conductivity to be assessed. Endo and co-workers studied the performance of dense lanthanum manganite air electrodes over a range of thicknesses, temperature, and oxygen partial pressure, and concluded that reaction rates were controlled by oxygen transport through the dense electrode layers [120,124,125]. Oxygen ion conductivities were established for an A-site deficient LSM (La_{0.81}Sr_{0.09}MnO₃) by Hebb-Wagner polarization $(\sim 6 \times 10^{-8} \text{ S/cm} \text{ at } 800 \,^{\circ}\text{C})$, and found to be consistent with fuel cell performance results. It would not have been possible to assess this contribution to the cathodic reaction without the formation of high quality thin films by laser ablation. Similar studies with strontium-substituted lanthanum cobaltite and lanthanum iron cobaltite allowed an assessment of the role of mixed conduction on electrocatalytic activity to be made [118–123,125]. Chen et al. found that the orientation of lanthanum cobaltite films was affected by the oxygen partial pressure in the deposition chamber [118,119], which also affected electrochemical properties. Lanthanum cobaltite/YSZ structures produced by laser ablation are shown in Fig. 13 [119]. Kawada et al. studied oxygen isotope surface exchange and bulk migration in laser ablation-deposited lanthanum cobaltite thin films, and showed that surface processes dominated electrochemical performance [122].

The most recent studies where laser ablation has been applied to fuel cell materials involved the deposition of alternative electrolytes. Matthews et al. first reported the deposition of a number of lanthanum strontium gallium magnesium oxide (LSGM) thin films onto quartz and silicon substrates [130]. The lanthanum gallates are of interest because of considerably higher ionic conductivity than YSZ and good stability in oxidizing and reducing atmospheres. The as-deposited films were amorphous, and



Fig. 13. TEM photos of thin $(LaSr)CoO_3$ (LSCo) and YSZ thin films deposited by laser ablation. The top image is an electron diffraction image of lanthanum cobaltite deposited on (111) YSZ, while the bottom image shows a cross-sectional view [119].

converted to single phase orthorhombic or cubic perovskite structures after annealing at 1500 °C [130]. Multiple ion and neutral species were found in the evaporated plume; major species that were detected included O⁺, Ga⁺, O, and Ga. Kanazawa et al. used laser ablation to deposit dense LSGM films onto porous nickel oxide, and studied plume dynamics as well as film composition and structure [131]. As-deposited films were amorphous in that study as well, but were fully crystallized by annealing in air at 1000 °C. No interconnected porosity remained for films greater than 45 µm in thickness. Small differences in composition were noted between the target and deposit. Deposited films tended to be enhanced with respect to Sr and depleted with respect to Ga compared to the target. Manoravi et al. were able to fully crystallize laser-ablated LSGM at 730 °C in air. These authors reported a factor of 10 higher ionic conductivity for LSGM films on sapphire than on strontium titanate [129].

Ceria-based electrolytes have also been deposited using laser ablation techniques [123,137]. Coccia et al. have found that the gadolinia/ceria ratio in cerium gallium oxide (CGO) varied significantly with changes in oxygen partial pressure, observing that ablation in CGO does not proceed stoichiometrically. High concentrations of molecular species such as Ce-O⁺ and Gd-O⁺ were detected in the plume, which were believed responsible for rare earth ceria films to grow well even in high vacuum. Yamaguchi et al. have used laser ablation to prepare barium cerium yttrium oxide thin films [137], which are proton conductors. The films, approximately 2 µm or less in thickness, were deposited onto a hydrogen-permeable Pd and Pd-Ag alloy foils. With a substrate temperature maintained at \sim 500 °C during deposition, as-deposited films were crystalline. Open cell potentials were lower than the theoretical value due to the presence of physical defects.

5. Electrochemical vapor deposition

Unlike the chemical vapor deposition (CVD) process where thin dense oxide films are grown by appropriate gas phase reactant interactions, the EVD process utilizes the transport of oxygen ions through an oxygen ion permeable membrane to participate in chemical reactions for the deposition and growth of ionically or electronically conducting oxides [138-141]. In comparison to conventional thin film deposition techniques for growing gas-tight films over the porous substrates, EVD technique offers the advantage of more than an order of magnitude faster deposition rate. For example, while the deposition rate for YSZ thin films by RF sputtering is typically 1 µm/h, EVD has been reported to deposit similar films at close to 60 µm/h [142,143]. It is also noteworthy to mention that EVD deposited electrolyte and anode electrodes have shown long-term stability during cell tests and 100 kw generator field tests [144].

Pioneering work of Isenberg [145] at Westinghouse Electric Corporation demonstrated the feasibility of the fabrication of thin, dense YSZ electrolytes on both porous lanthanum manganite cathode and porous nickel anode electrodes of tubular SOFCs. Isenberg also developed a unique nickel–YSZ cermet anode structure utilizing the EVD process known as the "EVD anode fix," where the deposited zirconia film covered the metallic anode and provided adherence during thermal cycling. Subsequent work performed at Westinghouse by his co-workers resulted in successful scale up of the EVD process for large scale manufacturing of 1.8-m-long cells and implementation of fabricated cells in 100 and 250 kW SOFC power generation systems [146].

The EVD zirconia electrolyte deposition process, film microstructure and underlying deposition and growth mechanisms have been widely investigated and reported in literature [145,147-151]. A schematic of the EVD process for the growth of dense electrolyte film on a porous substrate, as proposed by Isenberg, is shown in Fig. 14 [145]. The initial oxide deposit formation takes place by CVD at and within the porous substrate surface due to gas phase interactions between respective chloride vapors (ZrCl₄ and YCl₃), water vapor, and oxygen. As the oxide builds up and pores are closed, no further reaction occurs between the metal chlorides and gaseous water or oxygen. The morphology of the initial oxide and its penetration and encapsulation of the air electrode was studied by Singh [152], who modified the air electrodeelectrolyte interface to minimize the electrolyte penetration within the air electrode and enhance the triple phase boundary for the oxygen reduction. Subsequently, the film growth process changes from gas phase interactions to electrochemical reaction between chloride reactants and transporting oxygen ions through the electrolyte film. The water/steam oxidant mixture is flown through the air electrode support and a relatively higher oxygen partial pressure is maintained, whereas the chloride vapor and hydrogen mixture is flown over the growing oxide film.



Fig. 14. Schematic presentation of zirconia electrolyte deposition and growth on a porous substrate [145].

Oxygen anions are incorporated in the electrolyte film at the metal chloride–oxide interface. Film growth remains parabolic with time.

Electrolyte deposition is usually carried out at 1200 °C to achieve a faster growth rate [153]. During the film growth, an overall reactor pressure is maintained at around 10 Pa. The electrolyte film grows with oriented columnar grains and remains approximately 30-40 µm thick after 40 min deposition time. A cross-section of the deposited film is shown in Fig. 15. Development of columnar structure, as proposed by Van der Drift [154] is explained by relatively faster growth in the direction oriented perpendicular to the substrate at the expense of crystals growing in the direction parallel to the substrate. For thicker polycrystalline films, columnar growth is exhibited with the orientation of crystals becoming parallel to each other. Carolan et al. [150] studied the film composition and texture as a function of YCl₃ concentration in the feed stream and temperature and found that the film grew at the same yttrium to zirconium ratio as present in the gas phase. Film textures however showed large differences at different temperatures. Films grown below 1075 °C were found to be highly faceted, whereas films grown above higher temperatures remained smooth and featureless. As the EVD films are grown by counter diffusion of oxygen anions and electrons [150], the films became self-leveling.



Fig. 15. Microstructure of EVD-grown YSZ electrolyte on the porous air electrode. The electrolyte shows columnar structure [153].

A recent review by Tang [155] presents an overview of vapor deposition methods for forming nickel-zirconia cermet electrodes, which compares the performance of conventional and ideal vapor-phase produced anode structures. It was observed that the developed continuous zirconia skeleton created by vapor-phase reactions over porous nickel provides the best combination of ionic and electronic transport, large triple phase area for the electron exchange and structural stability. Ogumi et al. [156] also describe a method for preparing nickel-zirconia cermet using NiO as an oxygen source for forming zirconia surface film from chloride precursors. These processes resemble the EVD process described earlier by Isenberg [145]. A schematic of the oxide film growth over the metal and related reactions responsible for forming surface oxide is shown in Fig. 16. Nickel-zirconia cermet electrodes are formed by a combined slurry deposition followed by the EVD process. Nickel is oxidized to form a thin surface oxide initially by short-term exposure to an oxidizing atmosphere. A mixture of zirconium and yttrium chlorides is subsequently passed over the anode. Nickel oxide reacts with the chlorides and initially deposit a porous YSZ film, building up with time as the NiO is consumed. For tubular SOFCs, since an oxidizing gas flows through the air electrode, oxygen ions transporting through the electrolyte layer also contribute to the growth and thickening of the oxide layer over the electrolyte. The growing layer provides attachment to the electrolyte and also increases the triplephase boundary for the oxidation of hydrogen during the operation of fuel cells. A typical cell microstructure containing an EVD-produced electrolyte and an anode formed over the air electrode support is shown in Fig. 17.

Itoh et al. [157] examined the overall cost of fabrication of SOFCs using EVD and plasma spray processes, and concluded that the tubular SOFCs fabricated by the EVD process will remain very expensive and cannot be considered for practical applications. The handling of reactants and corrosive reaction products along with stringent requirements for the materials of construction for the reactor remain important issues for the scale up of the process. Process parameters such as pore closure time, exposure of the air electrode substrate to the reactive chloride, formation of insulating pyrochlores at the air



Fig. 16. Schematic presentation of the surface zirconia layer formation over the porous nickel anode electrode by EVD.

electrode-electrolyte interface remain of concern for the long-term stability and electrical performance of the cell.

6. Summary

This review surveys vacuum deposition techniques as methods to prepare materials and structures for use in SOFCs, considering magnetron sputtering, VPS deposition, laser ablation, and EVD. These techniques differ with respect to precursor materials, achievable deposition rates, control of composition, types of microstructures that are formed, cost and complexity of necessary equipment, quality of the deposited films, and scalability to a manufacturing scale, among other considerations. A



Fig. 17. Metallographic cross section of an air electrode supported tubular solid oxide fuel cell comprised of a porous $(La,Ca)MnO_3$ cathode, dense YSZ electrolyte and nickel-zirconia cermet anode. Both the electrolyte and anode were fabricated by the EVD technique [158].

comparison of characteristics of each of these methods is provided in Table 2.

Each of the vacuum deposition techniques suffer from relatively high equipment cost and complexity, especially when compared to traditional methods of manufacture that include tape casting, tape calendering, electrophoretic deposition, screen printing, and transfer printing, among others. In general, vacuum deposition methods also are characterized by relatively low deposition rates compared to traditional processing methods. Despite these challenges, vacuum methods offer a number of unique advantages. Very thin, fully dense layers can be produced on either porous or dense substrates, which may enable higher power densities to be achieved. Films can be formed at temperatures much lower than required in traditional ceramic processing. This allows unwanted interfacial reactions, such as that of zirconia and lanthanum manganite to form a resistive pyrochlore phase, to be reduced considerably. Vacuum methods are also wellsuited to the formation of interlayers, where small grain sizes and thin layer thickness are required. Among the most unique aspects of vacuum deposition is the ability to produce unique structures that are not otherwise achievable. Examples include micro fuel cells created at the Massachusetts Institute of Technology photolithography/ RF magnetron sputtering, and multilayer/super-lattice corrosion-resistant films developed at Montana State University using large area filtered arc plasma deposition. Fundamental studies of electrode reactions have especially benefited from capabilities offered by vacuum deposition techniques, including the formation of patterned electrode structures and oriented, fully dense electronic ceramic

Table 2

Comparison of vacuum deposition methods for producing thin films relevant to SOFC applications

-	-			
Technique	Precursor materials	Deposition rate	Typical microstructures	Features
RF and reactive DC magnetron sputtering	Oxide or metal target	$< \sim 5\mu m/h$	Dense or porous films, often obtain columnar structures	Produces dense, crack-free films on dense and porous substrates; applicable to wide range of compositions; low substrate temperature; can be combined with photolithography to produce unusual configurations
Vacuum plasma spray	Oxide or metal powder feed; variation (LAFAD) uses metal target	$< \sim 10 \mu m/h$	Dense or porous films, anisotropic grain structure; LAFAD method can produce multilayer, superlattice structures	Large-scale deposition possible; substrates may be dense or porous; relatively high substrate temperatures
Laser ablation	Oxide or metal target	Up to 600 $\mu m/h,$ most studies used 1 $\mu m/h$ rate	Dense films, used to produce epitaxial films	Intermediate substrate temperatures; not easily up-scaled; particularly useful in producing high-quality oriented films for fundamental research; can be combined with photolithography to produce unusual configurations
Electrochemical vapor deposition	Metal halides (ZrCl ₄ , YCl ₃)	$<$ 50 μ m/h	Dense films on porous substrate, columnar structures	Currently used in commercial SOFC production of thin electrolytes; high reaction temperatures; limited range of compositions possible; produces dense film on porous substrate

films. EVD is already being used in tubular SOFC manufacture by Siemens Westinghouse Power Corporation, a technique particularly well-suited to producing fully dense electrolyte films on a porous cathode support. Vacuum deposition methods are expected to continue to grow in importance in the manufacture of specialty fuel cells where unique architectures are desired, and in fundamental high-temperature electrochemistry studies.

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