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Alan F. Jankowski

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THIN-FILM SOLID-OXIDE FUEL CELLS

Alan Jankowski
University of California - Lawrence Livermore National Laboratory
Chemistry and Materials Science Department, P.O. Box 808, L-350
Livermore, California USA 94551-9900

Thin-film solid-oxide fuel cells (TFSOFCS) will provide an alternative for clean and efficient power generation. Potential applications will range from stationary power plants to portable power generation and transportation. Developments within this energy technology are described along with needs to be met for realizing the great potential of TFSOFCS.

INTRODUCTION

Fuel cells are energy conversion devices that would save billions of dollars in fuel costs alone each year in the United States if they could be implemented today for stationary and transportation applications (1-5). There are a wide variety of fuel cells available, e.g. molten carbonate, phosphoric acid, proton exchange membrane and solid-oxide. However, solid-oxide fuel cells (SOFCs) are potentially more efficient and less expensive per kilowatt of power in comparison to other fuel cells. For transportation applications, the energy efficiency of a conventional internal combustion engine would be increased two-fold as replaced with a zero-emission SOFC.

The basic unit of a SOFC consists of an anode and cathode separated by an oxygen-ion conducting, electrolyte layer. Manifolded stacks of fuel cells, with electrical interconnects, enable the transport and combination of a fuel and oxidant at elevated temperature to generate electrical current. Fuel cell development has proceeded along different paths based on the configuration of the anode-electrolyte-cathode. Various configurations include the tubular, monolithic and planar geometries. A planar geometry for the anode-electrolyte-cathode accompanied by a reduction in layer thickness offers the potential for high power density. Maximum power densities will require yet additional innovations in the assembly of fuel cell stacks with all of the manifolding stipulations for gas flow and electrical interconnects.

Wide spread application of SOFCs have been limited for several reasons including the slow warm-up to high operation temperatures (>1000 °C). Although SOFCs appear promising the hurdle to leap for use in transportation, for example, is the need to significantly reduce the cost for mass production while scaling the 10^1 kilowatt power plant requirement to an appropriately small volume as just a few liters.

A decrease in the electrolyte thickness from mils to microns, in particular, addresses further issues of reducing both the operating temperature by several hundred centigrade and the warm-up, cycle times from hours to minutes for fuel cell operation. These issues lead to the evolution of an all thin-film fuel cell solution. Physical vapor deposition processes access control of the electrode-electrolyte interface geometry and chemistry as well as the optional addition of very thin (10^2 nm thick) layers for further reduction of polarization losses.
EXPERIMENTAL METHOD

Motivation to step beyond the barriers in conventional bulk SOFC development is found through approaches which emphasize thin film and multilayer deposition technologies. Problems intrinsic to TFSOFCS include the need to synthesize defect-free, submicron thick layers and minimization of interfacial polarization losses. In addition, there are engineering obstacles that need to be overcome in order to form three-dimensional, integrated SOFC devices.

SOFCs based on zirconia electrolyte layers were developed over recent years for stationary electric power generation and are considered as future alternatives for vehicular power supplies (1-5). If the electrolyte layer can be made thinner, for example, as reduced from $10^1$ µm to $10^0$ µm, then the operating temperature for the SOFC can be reduced by several hundred degrees from $10^3$ °C to $10^2$ °C (6). If the composition of the electrolyte can be optimized, as for yttria-stabilized zirconia (YSZ), then the ion conductivity is maximized improving the kinetics of the SOFC (2,7). Therefore, thin films are well suited for use in SOFCs as the electrolyte layers. In addition to precise control of electrolyte layer composition, vacuum deposition processes access control of the electrode-electrolyte interface geometry and chemistry as through the addition of very thin interfacial layers. To improve the i-V output performance of the fuel cell by enhancing catalytic activity, $10^2$ nm thick interfacial layers are added at both the anode and cathode sides of the electrolyte to reduce interfacial reaction resistances (8). For example, yttria-stabilized Bi$_2$O$_3$ is added at the cathode-side and yttria-doped CeO$_2$ is added at the anode-side of the YSZ electrolyte layer.

EXPERIMENTAL RESULTS

The TFSOFC program at Lawrence Livermore National Laboratory was begun to show the feasibility of producing an entire fuel cell using thin film processing (9). Initial efforts were directed toward synthesizing thin film components of a single fuel cell, i.e. thin film electrodes (both anode and cathode) and electrolyte layers.

Cermet Electrodes

Progress in electrode development is illustrated using hybrid methods that bridge conventional, bulk ceramic synthesis with vacuum deposition technology. By supplementing bulk cermet processing of the electrodes, an anode wafer has been formed (Fig. 1) as a sintered compact of nickel-coated zirconia powders. The nickel coating minimizes the metallic content to ten percent yet provides the conductivity (Fig. 2) found for bulk cerments with >30% metal by volume (10). The use of the low metal percent provides the electrode with a coefficient of thermal expansion (CTE) that nearly matches the electrolyte (Fig. 3) thereby minimizing thermal-cycling induced failure of the SOFC, for example, by delamination. This CTE match is unlike the significant CTE difference with the electrolyte found for bulk cermet anodes with >30% metal by volume (11).

A drawback in the use of fuel cell electrode wafers composed of metal coated powders is that a bonding process must be developed to form a unit cell, i.e. an electrolyte coated electrode must be bonded to its counterpart electrode to form the anode-electrolyte-cathode trilayer. Currently, a sintering procedure is under development to create this bond. However, there is a clear advantage to explore an alternative method to form the anode-electrolyte-cathode as through a continuous synthesis procedure.
Thin Film Electrolyte

Synthesis of the electrolyte layer must be compatible with the geometry of the electrodes. Several synthesis techniques which have shown measurable success include tape calendaring and melt spinning. Physical vapor deposition techniques as magnetron sputtering offer the added flexibility of controlling the electrode-electrolyte interface composition and geometry. Thin-film fabrication of the electrolyte has met the requirement for interfacing a dense, oxygen-ion conductor to a porous electron conductor. We have an rf-sputter deposited a dense, thin film YSZ electrolyte layer on a porous Au electrode using a (Y2O3)5.6(ZrO2)94.4 target that yields a flexible composite (12). A high sputter-gas pressure (e.g. 30 mTorr Ar) initially facilitates filling surface voids of the porous substrate. The high gas pressure maximizes contact area of the deposition flux over the porous substrate surface by favoring low surface mobility in combination with greater incident scattering. The initial (planar magnetron) deposit is followed by continuing the coating at a decreased working gas pressure. The lower sputter gas pressures (e.g. 14-16 mTorr) favor more energetic sputtered neutrals and line-of-sight deposition. This deposition process sequence leads to the formation of a defect-free electrolyte layer of cubic YSZ as examined with transmission electron microscopy in plan-view bright field imaging and the selected-area electron diffraction mode. To minimize residual stress effects often encountered using high sputter-gas pressures at elevated substrate temperatures, the deposition process was simplified to follow a room temperature deposit with an air anneal at the cell operating temperature. The structural integrity and conductivity of the sputtered YSZ electrolyte films will be further assessed since grain boundary effects are reported for fine-grain structures used at low to intermediate temperatures, i.e. less than 700 °C (2).

Alternatively, reactive sputter deposition of the cubic YSZ phase for an electrolyte layer at elevated substrate temperatures is achievable using a Zr-Y composite target (13). The composite target consisted of individual pieces of Y and Zr metal. Thin film deposits from this target were limited in application as electrolyte layers by residual stresses causing delamination at low sputter gas pressures and crazing at high pressures. Successful control of film stress was found for intermediate (3-20 mTorr) gas pressures.

To maximize the ion conductivity of the electrolyte, a Y-Zr alloy is cast with a vacuum arc melt process and machined into a planar magnetron target. The 15 at.% yttrium metal alloy target is sputter deposited in the dc mode to yield an 8% yttria, i.e. (Y2O3)0.08(ZrO2)0.92 film (14). The sputtering parameters of gas flow, gas pressure and deposition rate are experimentally iterated in order to produce the cubic zirconia phase, as verified with x-ray diffraction. The substrate temperature is inductively heated to 700 °C, the nominal operating temperature of a YSZ-based fuel cell. A high deposition rate is desirable and achievable when the sputtering mode of the alloy target is metallic as opposed to oxide. A YSZ layer suitable for a SOFC electrolyte is formed at a 0.22-0.23 nm s⁻¹ deposition rate using a 5 mTorr pressure and 7 sccm flow of an Ar-20%O2 working gas mixture. A fuel cell produced with the reactive deposition of the Y-Zr alloy target to evaluate the YSZ electrolyte layer utilizes Pt electrodes (Fig. 4), a thin foil as the base and a sputtered overcoat layer.

The vertical resistance (ρ) of the YSZ electrolyte layers are measured using a technique developed for thin-film cermet dielectrics (15). The 8% yttria-stabilized film, produced by reactive sputter deposition of the 15 at.% yttrium alloy target, has a ρ of 2 x 10¹¹ Ω-cm which is greater than the 8 x 10¹⁰ Ω-cm value of the 5.6% yttria electrolyte deposited by rf sputtering a 5.6% yttria target. In this case the higher electrical resistivity
corresponds to a greater value, $2 \times 10^{-2} \Omega^{-1}\text{-cm}^{-1}$ in comparison to $9 \times 10^{-3} \Omega^{-1}\text{-cm}^{-1}$, for the ion conductivity as measured at 800 °C elsewhere (7).

**Electrode Deposition**

Thin film cathodes can be formed using simultaneous sputter deposition from silver and YSZ targets. Most recently, a single SOFC (Fig. 5) is formed using the component and processing steps as innovated for the coating of powders (16) and the hybrid deposition of a SOFC (9). To form the fuel cell, the electrolyte and cathode layers are deposited onto a thermal expansion-matched, anode substrate. The anode is formed as a sintered compact of Ni-coated zirconia powders. The YSZ electrolyte layer is then rf-sputter deposited from a stoichiometric YSZ target onto the anode wafer, followed by the co-deposition of a Ag-YSZ cathode layer. With this result as an example, progress towards a TFSOFC is demonstrated in cost-effective processes for synthesizing porous electrodes, dense electrolytes and their combinations. Ultimately, provision for gas passages and electrical interconnects will be accomplished in cell synthesis.

**Thin Film Stacks**

To broach the difficulties of joining electrolyte-coated (anode) electrodes to counterpart (cathodes) electrodes to form a unit cell, the use of thin film deposition enables the unit cell to be synthesized in a continuous process. The electrodes (as the Ag-YSZ cathode) can be a vapor deposited composite of metal and ceramic. The transport of the fuel and oxidant through the electrodes is controlled through layer thickness and the vapor deposition parameters. Appropriate metals are selected for use in the anode and cathode synthesis. The ceramic chosen for the electrode matrix, if necessary, is the same material as then used for the vapor deposition of the electrolyte. Therefore, a CTE match between the fuel cell components is ensured as is structural stability upon temperature cycling. A TFSOFC sequence of Ni-anode/YSZ-electrolyte/Ag-cathode (Fig. 6) is formed by continuous, rf sputter deposition using three source targets. As previously mentioned, electrolyte-electrode interfacial layers can be incorporated to improve the fuel cell performance by enhancing catalytic activity. The feasibility of using a thin film approach to SOFC development rests in process steps that lead to a manufactureable stack assembly. Process integration for the provision of interconnect lines, gas flow manifolds and temperature control is found in work underway implementing the various available microtechnologies.

**SUMMARY**

Thin-film technologies are relevant to the development of new or alternative solid-oxide fuel cell and stack design. The use of thin films is shown feasible for the electrolyte and both electrodes in SOFCs based on YSZ. Thin-film solid-oxide fuel cells (TFSOFCs) will provide increased power density and specific power as well as lower operating temperature and manufacturing cost. Progress is being made towards the ultimate deliverable of the fabrication and performance evaluation of a TFSOFC stack.

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REFERENCES


FIGURES

Figure 1. A scanning electron micrograph (SEM) of fracture cross-sectioned cermet anode wafer that has a metal content of only 8% Ni by volume and was formed by sintering a compact of Ni-coated zirconia powders. Bar = 1 μm.
Figure 2. Variation of conductivity with metal content for (□) conventional Ni-zirconia cermets at 1000 °C (see ref. 10) versus (■) Ni-coated powder anodes.

Figure 3. Variation of the coefficient of thermal expansion (CTE) with volume % metal for (▲) conventional Ni-zirconia cermets (see ref. 11) and (△) Ni-coated powder anodes.
Figure 4. A SEM of a fracture cross-sectioned TFSOFC formed by Pt overcoating the YSZ electrolyte that is rf sputter deposited onto a Pt foil substrate. Bar = 3 μm.

Figure 5. A SEM of a fracture cross-sectioned SOFC. The anode wafer substrate is a sintered-compact of Ni-coated ZrO2 powders on which the YSZ electrolyte is rf-sputter deposited on which a Ag-YSZ cathode is co-sputtered to complete the cell. Bar = 1 μm.

Figure 6. A SEM of a fracture cross-sectioned TFSOFC deposited by continuous rf and dc sputtering to form a Ni-anode/YSZ-electrolyte/Ag-cathode trilayer. Bar = 1 μm.