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A Simple and Cost-Effective Approach to Fabrication of Dense Ceramic Membranes on Porous Substrates

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A simple and elegant approach to fabrication of dense ceramic membranes on porous substrates, a traditional dry pressing of foam powders, has been developed to reduce the cost of fabrication. Gd-doped ceria (GDC, $Gd_{0.1}Ce_{0.9}O_{1.95}$) electrolyte membranes as thin as 8 μm are obtained by dry-pressing highly porous GDC powders. The membrane thickness can be readily controlled by the amount of powder. The electrolyte membranes are studied in a solid-oxide fuel cell (SOFC) with air as oxidant and humidified hydrogen (3% H_2O) as fuel. Open-circuit voltages of about 1.0 V are observed, implying that the permeability of the membranes to molecular gases is insignificant. Power densities of 140 and 380 mW/cm² are demonstrated at 500° and 600°C, respectively, representing a significant progress in developing low-temperature SOFCs.

I. Introduction

PREPARATION of dense ceramic membranes on porous electrodes or substrates is the most critical step in fabrication of high-performance solid-state ionic devices or electrochemical systems such as solid oxide fuel cells (SOFCs), gas sensors, membrane reactors for gas separation or electrosysnthesis, and reformers for the processing of hydrocarbon fuels. In all of these applications, thin ceramic membranes must be supported by porous substrates (or porous electrodes) since the electroactive species and the reaction products must be able to transport to or away from the surfaces of the dense ceramic membranes. Various film deposition techniques have been explored for preparation of dense ceramic membranes on porous substrates, including a variety of atomic-scale physical and chemical vapor deposition, sol–gel process, electrochemical vapor deposition, combustion chemical vapor deposition, and more traditional particle deposition techniques.[1,2] The atomic-scale deposition techniques involving a vapor phase or a solution often face difficulties either in stoichiometry control or in preventing the gas or the solution from filtration into the porous substrates. On the other hand, the particle deposition techniques such as electrophoretic deposition, colloid coating, screen-printing, tape casting, and tape calendering often have difficulties in achieving the required density or desired thickness.[1,2] Further and in particular, many of these film deposition techniques are complex, difficult to control, and expensive. In fact, it is the cost of fabrication that makes the commercial realization of many advanced technologies unaffordable. For example, while the existing SOFC technology has demonstrated much higher energy efficiency with virtually no pollutant emission over conventional energy technologies, the cost of the current SOFC systems is prohibitive for wide commercial applications. The major cost of SOFC stacks is the cost of fabrication.

This communication reports an elegant and cost-effective approach to fabrication of dense ceramic membranes on porous substrates. In particular, the fabrication of an SOFC is taken as an example, which is the cleanest and most efficient device for converting chemical energy (hydrogen and fossil fuels) directly to electricity. The implementation of this cost-effective fabrication technique has great potential to dramatically reduce the cost of SOFC fabrication, making SOFCs economically competitive with the conventional technologies. Further, this technique is equally applicable to fabrication of other electrochemical devices or systems based on ceramic membranes such as mixed-conducting ceramic membranes for oxygen or hydrogen separation, reformer for the processing of hydrocarbon fuels to hydrogen, and membrane reactors for synthesis of high-value hydrocarbons.

Recent studies indicate that CeO_2-based SOFCs offer the highest power output at low temperatures.[3] To prepare a thin electrolyte membrane of $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC) on a porous anode of GDC–NiO, highly porous or "foam" GDC powder, synthesized by a glycine nitrate process, is uniaxially pressed onto a green substrate of GDC–NiO, which is formed by uniaxial pressing of GDC and NiO powders. Cofiring of the bilayer structure at 1350°C for 5 h yields a dense GDC membrane on a porous GDC–NiO electrode. The thickness of the GDC membrane is controlled by the amount of GDC powder. GDC electrolyte membranes as thin as 8 μm have been prepared and tested in SOFCs.

II. Experimental Procedure

The key to successful preparation of a thin, dense GDC membrane on a porous substrate is the preparation of highly porous or "foam" GDC powders with extremely low fill density. The powder was prepared using a glycine nitrate combustion process. In this process, stoichiometric amounts of $Gd(NO_3)_3$ and $Ce(NO_3)_3$ were dissolved in water. The solution was then mixed with glycine and heated on a hot plate to vaporize water, convert to gel, and finally ignite to flame, resulting in fine ash of pale yellow color. The resultant ash was then fired at 600°C for 2 h to form the "foam" GDC powder. X-ray diffraction (Scintag X1) analysis showed that the product had a fluorite structure. The specific surface area was 9.98 m²/g as measured by an isothermal nitrogen adsorption/desorption measurement (Coulter SA3100). A scanning electron microscope (SEM, Hitachi S800) was used to reveal the microscopic features. To make a membrane of GDC, a mixed powder of GDC and NiO (65 wt%) was prepressed at 200 MPa as a substrate; GDC powder was then added, distributed uniformly, and pressed on to the substrate at 250 MPa. The bilayer was subsequently sintered at 1350°C for 5 h, resulting in a GDC membrane on GDC/NiO substrate.

To characterize the electrical and electrochemical properties of the GDC membranes, a porous cathode of $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) was applied to the GDC membrane to form a single cell, consisting of a Ni–GDC anode, a GDC electrolyte membrane, and an SSC

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cathode. The cell was tested at 400°–600°C with humidified hydrogen (3 vol% H_2O) as fuel and stationary air as oxidant. The fuel cell performances were measured using an EG&G potentiostat/Galvanostat (Model 273A) interfaced with a personal computer. The impedances were measured with an EG&G lock-in amplifier (Model 5210) and an EG&G Potentiostat/Galvanostat (Model 273A) interfaced with a PC through electrochemical impedance software (Model 398).

III. Results and Discussion

Shown in Figs. 1(a) and (b) are SEM micrographs of an as-synthesized GDC particle, which is highly porous, and the pore size ranges from tens of nanometers to several micrometers. The powder is thus called a "foam" powder. Since the theoretical density of $Gd_{0.1}Ce_{0.9}O_{1.95}$ is about 7.12 g/cm³, the relative density (or fill density) of the foam powder is 0.84% of the theoretical value, implying that the apparent volume of this foam powder is about 120 times that of the same amount of material when it is dense. The commercially available CeO_2 powder (Aldrich) has a fill density of 45%; thus, the apparent volume of this foam powder is about 50 times larger than that of the commercially available CeO_2 powder. It is this extremely low fill density that makes it possible to prepare thin films of GDC by dry pressing; the films are processed by means of punches in a hardened metal die. The dry-pressing process is commonly used for pressing parts thicker than 0.5 mm using ordinary powders. To make a 0.5-mm-thick CeO_2 pellet with the commercially available powder, the average thickness of the loose powder in a die is about 1.1 mm. To make a 100-μm-thick CeO_2 film using the same powder, however, the loose powder must be uniformly distributed to form a 220-μm-thick layer during dry pressing, which is very difficult to accomplish. With the foam GDC powder prepared in this work (fill density of 0.84%), the thickness of the loose powder for making a 10-μm-thick film is 1.2 mm, which is thicker than that for making a 0.5-mm-thick ceria with the commercial powder. Thus, it is possible to make thin membranes by dry pressing with foam-structured GDC powder. Figure 1(c) shows a cross-sectional review of an 8-μm-thick GDC film fabricated by dry pressing.

The film thickness can be readily controlled by the amount of powder used. The thickness of the loose powder is about 120 times that of the dense film. Table I lists the film thickness measured under an SEM (L_{SEM}), the thickness as calculated from the amount of GDC powder and sample volume assuming it is fully dense (L_{film}), and the relative density of the sintered film (d_r) estimated as

$$d_r = (L_{film}/L_{SEM}) \times 100\%$$

It can be seen from Table I that the sintered density is influenced by film thickness. It appears that the thicker the film, the higher the sintered density. It is well known that, in a dry-pressing process, good powder flow is essential to uniform volumetric filling and rapid pressing. Dense, nearly spherical particles or granules coarser than 25 μm with smooth surfaces usually have good flow behavior.[4] However, the GDC powder has very poor flow behavior because it is highly porous (Figs. 1(a) and (b)) and is much finer than 25 μm. Poor flow behavior results inevitably in nonuniform distribution of powder and low packing density. This nonuniform distribution of powder is more severe as the thickness of film is reduced, leading to lower density for thinner films. The porosity of the membranes can be reduced by improving the flow behavior of the foam-structured GDC powder or by improving the filling techniques to achieve a uniform and reproducible filling.

Shown in Fig. 2 are the cell voltages and power densities of the cell with a 15-μm-thick GDC membrane as a function of current density at different temperatures. A cross-sectional view of the three-layer structure of the cell is shown in Fig. 1(d), from which it can be seen that both the cathode and the anode are porous while the electrolyte is relatively dense (87% theoretical density). The observed OCV for this cell was about 1.0 V at 400°C and OCVs
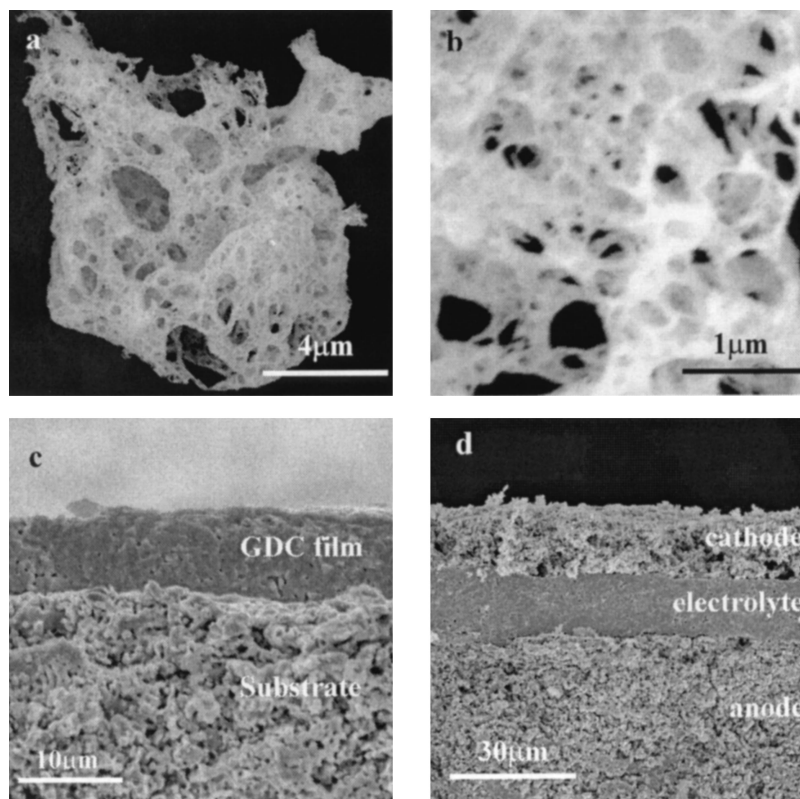
Fig. 1. SEM micrographs of (a) a highly porous "foam" GDC particle, (b) a portion of the particle shown in (a), (c) a cross section of an 8-μm-thick GDC film supported on a NiO–GDC substrate, and (d) a cross section of a fuel cell consisting of a 15-μm-thick GDC electrolyte, a Ni–GDC anode, and an SSC cathode.

Table I. Characteristics of GDC Electrolyte Membranes Fabricated by Dry Pressing

	Film in Fig. 1(c)	Film in Fig. 1(d)	Film	Bulk sample
Thickness, L_{SEM} (μm)	8	15	26	548
Estimated thickness when fully dense, L_{film} (μm)	6.4	13	24	522
Relative density, d_r (%)	80	87	92	95
Open-circuit voltages at 400°C (V)	0.75	0.97	1.01	
Conductivity at 500°C ($\times 10^{-3}$ S·cm^{-1})	2.12	3.93	4.50	6.20
Activation energy at 400–600°C (kJ/mol)	24.5	36.6	41.0	65.5

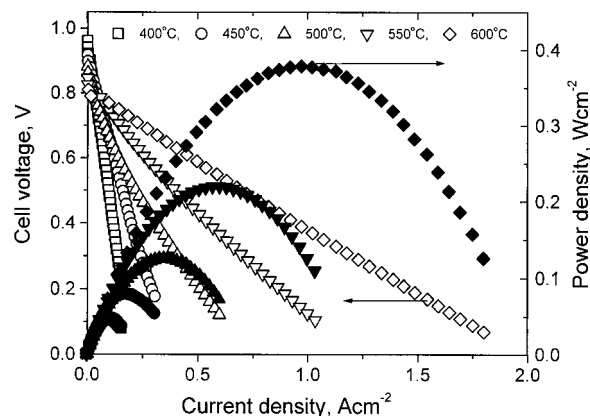**Fig. 2.** Cell voltages (open symbols) and power densities (solid symbols) as a function of current densities for a fuel cell with a 15-μm-thick GDC electrolyte, a Ni–GDC anode, and an SSC cathode. A cross-sectional view of the cell is shown in Fig. 1(d).

Fig. 3. (a) Typical impedance spectra of fuel cells with GDC electrolytes of different thickness, 15 and 26 μm, as measured at 550°C under open-circuit conditions and (b) Arrhenius plots of conductivities for GDC membranes of different thickness.

higher than 1.0 V were observed for cells with thicker electrolytes. The demonstrated usable power densities at 400°–600°C represent a significant progress in developing low-temperature SOFCs. A lower operating temperature would imply that much less expensive metallic materials might be used to replace very expensive materials for interconnect, heat exchanger, and other structural components of an SOFC system, significantly reducing the cost of SOFC technology. A lower operating temperature would also ensure greater system reliability and a longer operational life.

Figure 3(a) shows two typical impedance spectra under open-circuit conditions at 550°C for cells with GDC electrolyte films of different thickness, 15 and 26 μm. As shown in Fig. 3(a) the total resistance of the cell with a 15-μm-thick GDC at 550°C is 1.08 Ω·cm^2, of which 0.29 Ω·cm^2 comes from the 15-μm-thick electrolyte and 0.79 Ω·cm^2 from the interfacial polarization. Figure 3(b) shows Arrhenius plots of ionic conductivities for GDC membranes tested under open-circuit conditions. The conductivities were determined from the impedance measurements. Table I summarizes OCVs observed at 400°C, the conductivities at 500°C, values of activation energy for electrical conduction, relative densities, and GDC film thicknesses. It should be noted that the 548-μm-thick sample (measured by SEM) was prepared using the same procedures, but standing alone, and was tested in air with silver as electrodes. The activation energy for electrical conduction is calculated from the slopes of the Arrhenius plots of conductivities.

The activation energy of the bulk GDC (95% theoretical density) is 65.5 kJ/mol, which is typical for gadolinia-doped ceria.[5,6] It is noted that the conductivity of the 26-μm-thick film prepared in this study (4.50×10^{-3} S·cm^{-1} at 500°C) is similar to that for a 30-μm-thick $Gd_{0.2}Ce_{0.8}O_{1.9}$ film prepared by multilayer tape-casting technique (4.29×10^{-3} S·cm^{-1}).[7] Also, the activation energies and electrical conductivities of the electrolyte membranes depend on density, as expected because pores disrupt the transport of charged defects.
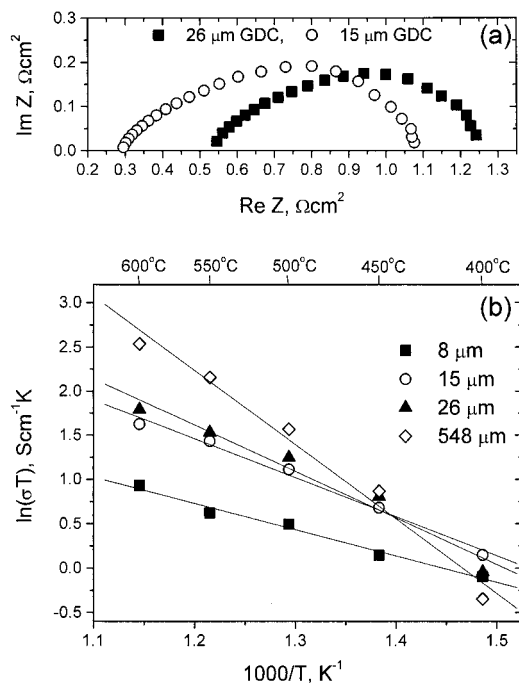
IV. Conclusions

In conclusion, a dry-pressing process is a simple, reproducible, and cost-effective approach to fabrication of dense ceramic films or membranes on porous or dense substrates. The use of this simple method may significantly reduce the fabrication cost of solid-state ionic devices or electrochemical systems, including SOFCs, membrane reactors for gas separation, electrosynthesis, and for fuel processing.

References

[1]J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, and L. J. Gauckler, "Fabrication of Thin Electrolyte for Second-Generation Solid Oxide Fuel Cells," *Solid State Ionics*, **131**, 79–96 (2000).

[2]S. C. Singhal, "Advances in Solid Oxide Fuel Cell Technology," *Solid State Ionics*, **135**, 305–13 (2000).

[3]C. R. Xia, F. L. Chen, and M. L. Liu, "Reduced-Temperature Solid Oxide Fuel Cells (SOFCs) Fabricated by Screen-Printing," *Electrochem. Solid State Lett.*, **4** [5] A52–A54 (2001).

[4]J. S. Reed, *Principles of Ceramics Processing*, 2nd ed.; Ch. 8. Wiley-Interscience, New York, 1995.

[5]B. C. H. Steele, "Appraisal of $Ce_{1-y}Gd_yO_{2-y/2}$ Electrolytes for IT-SOFC Operation at 500°C," *Solid State Ionics*, **129**, 95–110 (2000).

[6]R. S. Torrens, N. M. Sammes, and G. A. Tompsett, "Characterisation of $(CeO_2)_{0.8}(GdO_{1.5})_{0.2}$ Synthesised Using Various Techniques," *Solid State Ionics*, **111**, 9–15 (1998).

[7]R. Doshi, Von L. Richards, J. D. Carter, X. Wang, and M. Krumpelt, "Development of Solid-Oxide Fuel Cells That Operate at 500°C," *J. Electrochem. Soc.*, **146**, 1273–78 (1999).

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