



Two-Layer Fuel Cell Electrolyte Structure by Sol-Gel Processing

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Abstract. Thin layers of yttria-stabilized zirconia (YSZ) at 11 mol % Y_2O_3 doping level was deposited on a sintered disk of Y_2O_3 doped ceria electrolyte by spin-coating from an alkoxide solution. Dense sintered films were obtained by heat-treatment at $600^\circ C$. Open circuit voltage (OCV) was measured across the disk in a fuel cell mode with hydrogen fuel on the ceria side and pure oxygen on the YSZ side. Marked improvement of OCV was obtained on the two-layer electrolyte structure with the sol-gel YSZ film.

Keywords: fuel cell, YSZ, thin film processing, solid electrolyte

Introduction

High temperature solid oxide fuel cells (SOFCs) utilize yttrium stabilized zirconia (YSZ) as the electrolyte that operate at temperatures above $850^\circ C$. At high operating temperatures, problems arise when thermal expansion mismatch between the various oxide ceramic components are significant. In addition, limited choice of electrical interconnecting materials are available in the high temperature range. A number of alternative electrolyte materials such as doped ceria or bismuth oxide were suggested for the use in SOFCs at lower operation temperatures. These oxides, however, exhibit high electronic conduction and are thermodynamically unstable at low oxygen partial pressures. A two-layer structure with YSZ coated on the surface of doped ceria or bismuth oxide disks was suggested [1] for their improved thermal stability and lower electronic conduction. A number of publications [2, 3] has reported the improvement of the open-circuit voltage (OCV) by this approach.

The operation of SOFC relies on the separation of ionic conduction and electronic conduction in the cell structure. The electrolyte's primary function is to conduct oxygen ions while blocking electronic conduction. Unfortunately, most solid-state electrolyte materials present mixed ionic and electronic conduction at

elevated temperatures. Among commonly used oxide electrolytes, YSZ has the highest ionic to electronic conductivity ratio σ_i/σ_e , while other oxides, such as ceria or bismuth oxide have much lower ratios. However, the ionic conductivity σ_i for ceria or bismuth oxide can reach reasonable level even at moderate temperature range, which makes these oxides attractive candidates for low operating temperature electrolytes in SOFC. The high electronic conductivity inherent to ceria and bismuth oxide, tend to cause reduction of oxides at the surface exposed to the fuel. To combat this problem while maintaining a reasonable level of total ionic conductivity at intermediate to low temperature range, a thin layer of YSZ coated on a doped ceria or bismuth oxide seems to be the ideal electrolyte structure for a fuel cell. The objective is then to fabricate such a bi-layer electrolyte structure and seek to obtain reasonably high OCV at low temperatures.

Presently, the thin film deposition techniques widely used for the deposition of YSZ layers include physical vapor deposition (PVD) [2, 4], chemical vapor deposition (CVD) [5], electrochemical vapor deposition (EVD) [2, 6, 7], metalorganic vapor deposition (MOCVD) [8, 9], and sol-gel processing [10]. Recently, there is a renewed interest in sol-gel processed YSZ films for epitaxy and phase transformation [11, 12], porous xerogels and membrane for catalytic and

ultrafiltration applications [13, 14], and nanophase materials [15, 16]. Sol-gel processing possess the advantages of precise composition control, simple processing procedures, and low processing temperatures. In the geometry of thin layers on a substrate surface, the sol-gel processing is ideal for the fabrication of two-layer electrolyte structures. There has not been an investigation of the electrochemical characteristics of sol-gel derived thin layers for SOFC applications. In particular, the sol-gel processing is ideally suited to the fabrication of large area planar SOFC stacks compared with the vapor deposition techniques. In this communication, we report the sol-gel processing of thin (1000–3000 Å) YSZ layers on yttrium-doped ceria disks for fuel cell applications. We further present the characteristics of the layers by X-ray diffraction, electron microscopy. Finally, we discuss the use of the two-layer structure in a fuel cell and the prospect of the sol-gel method in SOFC applications.

Experimental Procedures

Doped ceria disk containing 11 mol % Y_2O_3 was prepared by a pressureless sintering method. CeO_2 and Y_2O_3 powders were wet mixed by a ball mill in ethanol for 24 h. The mixed powders were then dried and pellets were formed by die-pressing. Isostatic pressing of the pellets were performed at 207 MPa. The resulting disks were then sintered in the air at 1600°C for 6 h. The disks were ground to regular shapes and polished on one side to 0.5 μm .

An ethyl alcohol solution containing 11 mol % $Y(i-OC_3H_7)_3$ and 89 mol % $Zr(i-OC_3H_7)_4$ were made by dissolving yttrium isopropoxide (Aldrich Chemical,

99.9%) and Zirconium isopropoxide (Aldrich Chemical, 95% with 5% methoxide) in anhydrous isopropanol. The solvent was slightly heated and a small amount of HNO_3 was added to promote dissolution. The small amount of water was incorporated in the solution in the form of 1–2 ml concentrated HNO_3 . The combined precursor concentration in the solution was approximately 0.25 M. The solutions remain stable for a period over 4 months. A collection of xerogel powder was obtained from the solution by air drying. Differential thermal analysis of the xerogel powder was performed on a Seiko Instrument TG/DTA-220 model analyzer.

Spin coating of the solution on the polished surface of the doped ceria disk was performed at 1500–2000 rpm in the ambient. Optical quality coatings were obtained after aging in the ambient for a few hours. The sample was then heated at 1–4°C/min rate in air up to 600°C and kept at this temperature for 1 h. The YSZ layer were then examined under a Cambridge Stereoscan 240 scanning electron microscope to observe the film morphology and interface bonding. X-ray diffraction on the surface was performed to study the layer crystallinity.

A H_2 - O_2 fuel cell was designed and constructed for the testing of the two-layer electrolyte disks, as shown in Fig. 1. The apparatus consists of two alumina tubes with inconel end fittings between which an electrolyte disk can be tightly mounted. Platinum paste was applied on both sides of the disk as electrodes. Silver metal foils were employed as gaskets to ensure leak proof seals between the disk and the inconel fittings. A constant pressure was maintained on the gaskets with the help of a spring. Electrical connections were made directly to the inconel fittings by silver wires.

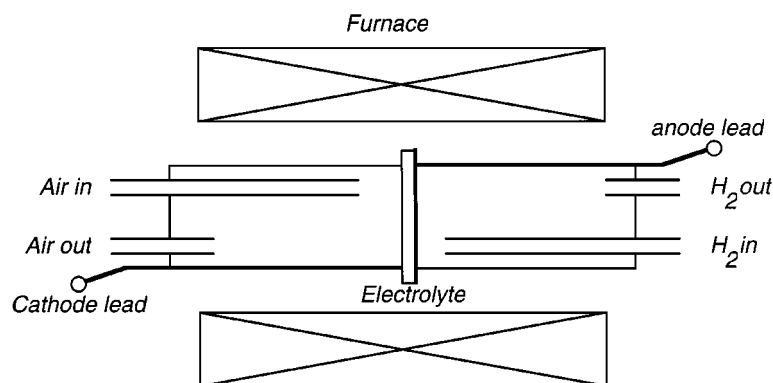


Figure 1. Electrolyte test apparatus used to measure OCV in a fuel cell mode.

Hydrogen gas was bubbled in water at the room temperature and circulated through one of the alumina tubes on the YSZ coating side. Oxygen gas was circulated in the tube on the other side of the disk. The open circuit voltage (OCV) was measured over a range of temperatures from 600 to 800°C. The voltage current curves were obtained by varying an external load consisting a decade resistor box. The two-layer electrolyte disk and a doped ceria disk were tested separately in the fuel cell mode for comparison.

Results and Discussion

Xerogel powder was subjected to thermal analysis in the temperature range from 50 to 600°C. 6.4 milligrams of xerogel powder was placed in the analyzer under 400 ml/min nitrogen flow, and analyzed simultaneously for salient thermal event and accompanying weight loss. Figure 2 shows the results. Starting from the left side, the first curve on top of figure is the weight loss (TG), with the percent loss represented by the scale on the right side. The second curve from the top represents the derivative of the weight loss curve (DTG), corresponding to the scale on the far left side. The third curve is the result of the differential thermal analysis (DTA),

with scale immediately on the left. The initial weight loss below 100°C corresponds to the evaporation of absorbed alcohol or water. On the DTA curve, this event is highly endothermic, consistent to evaporation. A second endothermic event occurred at 305°C. This corresponds to the pyrolysis of the remaining isopropoxyl groups in the xerogel. An exothermic event occurred at about 494°C with no accompanying weight loss or gain, indicating that this could correspond to a phase transition. The likely event is the crystallization of YSZ cubic phase from the amorphous xerogel. Based on the information obtained from the thermal analysis, the heat treatment of the YSZ films should be conducted at temperatures above 494°C. In this work, we have heated the films up to 600°C in air for 1 h to induce crystallization of the cubic YSZ phase. We have not conducted further verification of the above discussion on the thermal history because the primary objective was to identify a crystallization temperature for the cubic YSZ phase for fuel cell application, and this objective is met with satisfaction.

The 0.25 M solution used in spin coating on the doped ceria disks results in about 1000 Å thick YSZ layer after heat treatment. The spinning rate was about 1500–2000 rpm. Disks with up to three layers of coating were prepared. From the SEM micrograph, as

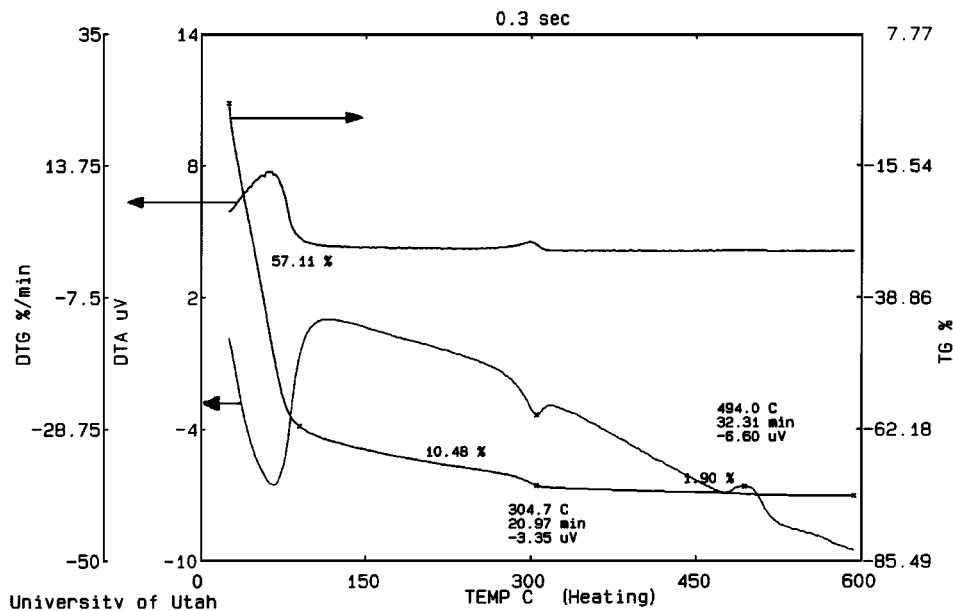


Figure 2. Thermal analysis result of the xerogel powder. From the left side, top curve (scale on far right): percent weight loss (TG); Second curve from top (scale on far left): differential weight loss (DTG); Bottom curve (scale second from left): differential thermal analysis (DTA).

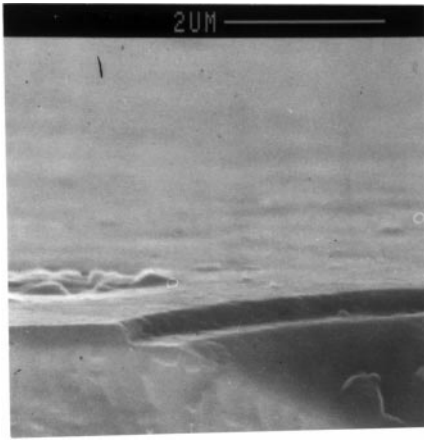


Figure 3. SEM picture of cubic YSZ film on yttria-doped ceria disk. Film deposited by three-layer spin coating, with total thickness approximately 3000 Å.

shown in Fig. 3, it is clear that the film appeared dense and crack-free. The 3000 Å film was well bonded to the coarse grain substrate. The surface of the YSZ film is smooth and shows no apparent signs of grain and porosity. The YSZ layer on the surface of ceria discs were well crystallized at 600°C in 1 h. X-ray diffraction pattern taken on the YSZ layer surface showed clear peaks corresponding to the cubic YSZ

structure. Figure 4 is the X-ray diffraction pattern for a three-layer YSZ coating on a yttrium-doped ceria disk. Due to the X-ray penetration the substrate peaks corresponding to the cubic ceria are shown as strong peaks.

The two-layer electrolyte was tested in a fuel cell mode in which the open circuit voltage (OCV) was measured. The results are shown in Fig. 5. Through the temperature range of 600–800°C, the OCV values are significantly improved for the two-layer disk in comparison to those from an uncoated disk. We note that the OCV improvement is achieved with a very thin YSZ coating, about 3000 Å thick. An interesting observation is that the variation in the thickness of the YSZ layer in the range 1000–3000 Å seems to have little effect on the OCV. The exact cause for this is not clear at this point. One possibility is the coarse structure of the doped ceria disk has closed pores at 1 μm diameter. The thicknesses of the YSZ layer in this study, in the range of 1000–3000 Å is unable to cover those isolated 1 μm pores on the surface of the ceria disk. Consequently, a very small fraction of the ceria disk is left uncovered. This problem can be solved by using a disk with finer microstructures, lower porosity. Alternatively, thicker YSZ coating is expected to further improve the OCV of the fuel cell.

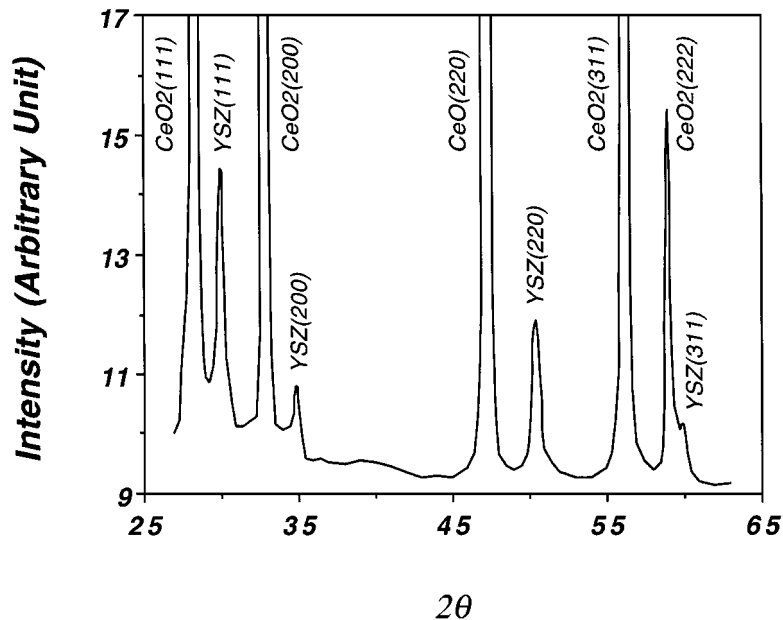


Figure 4. X-ray diffraction pattern of cubic YSZ film on yttria doped ceria disk. Peaks indexed correspond to cubic ceria and cubic YSZ.

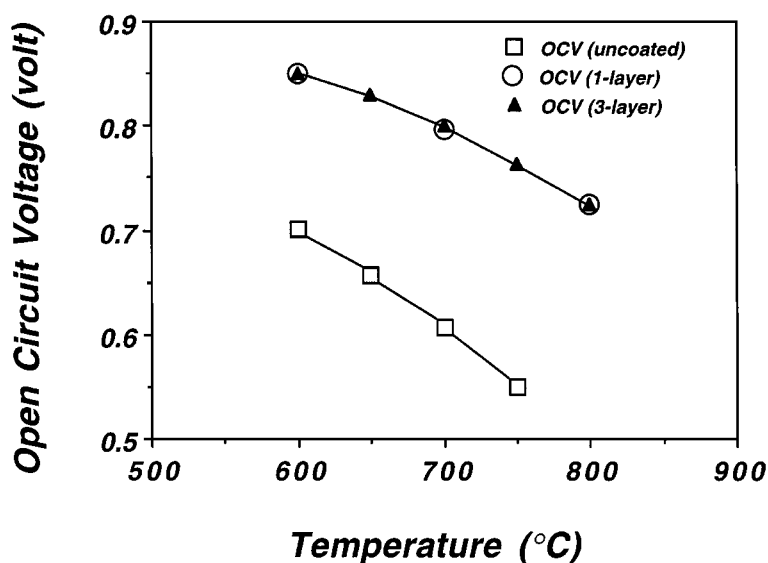


Figure 5. Open circuit voltage result from a fuel cell test. Top curve: OCV from the two-layer electrolyte structure with one-layer coating (open circle) and three-layer coating (solid triangle). Bottom curve: OCV from an uncoated disk.

Conclusions

We have demonstrated the application of a sol-gel process for the fabrication of a two-layer electrolyte structure for solid oxide fuel cell applications. Homogeneous solution was prepared by dissolving yttrium isopropoxide and zirconium isopropoxide in anhydrous isopropanol. Pyrolysis and crystallization of the cubic YSZ phase was achieved at 600°C in air. X-ray diffraction indicated the formation of the cubic YSZ phase in the film. SEM picture of the film reviewed dense, crack-free YSZ films coated on a yttria-doped ceria disk. The two-layer electrolyte structure showed marked improvement of the open circuit voltage in a fuel cell test.

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