FABRICATION AND CHARACTERIZATION OF YSZ-COATED CERIA ELECTROLYTES

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ABSTRACT

Doped ceria electrolytes were fabricated by pressureless sintering powder compacts. Thin (~2 μm) layer of yttria-stabilized zirconia (YSZ) was deposited by sputtering over the sintered discs. Heating to 900°C led to cracking of the YSZ films. However, thermal treatment at 1500°C improved the quality of the film by crack healing. On some of discs, a film of YSZ was deposited by electrochemical vapor deposition (EVD). It was shown that YSZ films do not delaminate. Open circuit voltage (OCV) was measured across the discs, with hydrogen fuel on one side and oxygen on the other, by exposing the YSZ-coated side to fuel as well as oxygen. It is shown that the OCV is higher if the coated side is exposed to oxygen. The underlying rationale is discussed.

I. INTRODUCTION

State-of-the-art solid oxide fuel cells (SOFCs) utilize yttria-stabilized zirconia (YSZ) electrolytes and are generally operated at ~1000°C. It is well known that lowering the operating temperature in the range of ~650 to 800°C is preferable for several reasons: (1) Generation of electricity by use of a gaseous fuel such as natural gas is a noncyclic process for which the lower the temperature, the greater is the thermodynamic efficiency [1]. (2) Operation at a lower temperature should permit the use of low cost metallic components such as the interconnect. The use of metallic interconnect is particularly advantageous from the standpoint of planar SOFCs. However, for low temperature SOFCs to be technically feasible, two important obstacles must be overcome: (1) Lowering of the electrolyte resistance: This can in principle be achieved by decreasing the thickness of the YSZ electrolyte or using a higher conductivity electrolyte. (2) Minimization of electrode/electrolyte interfacial losses: This would require improvements in the electrodes currently in use or the development of different, more efficient electrodes. The focus of the present work has been on the former aspect - lowering of the electrolyte resistance via the development of alternate electrolyte materials.

There are numerous solid electrolytes with ionic conductivity significantly greater than YSZ. These include, for example, stabilized Bi₂O₃ [2], doped CeO₂ [3], and certain perovskites [4]. All of them, however, do have certain shortcomings which must be overcome if these are to be viable candidates as solid electrolytes for SOFCs. Stabilized Bi₂O₃ has the highest conductivity of these materials. However, in a reducing atmosphere, Bi₂O₃-containing electrolytes are unstable and reduce to metallic bismuth. Recent thermodynamic study of alkaline earth - Bi₂O₃ systems has shown that the
decomposition partial pressure of oxygen ($pO_2$) of even the most stable of these materials is still too high compared to $pO_2$ in a typical fuel [5]. Ionic conductivity of doped CeO$_2$, although not as high as that of stabilized Bi$_2$O$_3$, is still much higher than that of YSZ. Additionally, unlike Bi$_2$O$_3$, CeO$_2$ is thermodynamically stable in fuel. The decomposition $pO_2$ (that for CeO$_2$/Ce$_2$O$_3$ equilibrium) at 1000 K is $\sim$5 x $10^{-27}$ atm [6], which is much lower than the partial pressure of oxygen in a typical fuel. However, ceria develops significant electronic conductivity in a reducing atmosphere [7] which is unacceptable for the intended application as an electrolyte. Thermodynamic data on most perovskites of interest are not available. However, since all of these contain either a transition element or cerium, it is expected that these too will either become electronic (mixed) conductors or in some cases may be unstable. For the reasons enumerated above, it appears that doped CeO$_2$ is probably the best alternate electrolyte material. For this reason, it was selected for the present study. Use of ceria, however, requires suppression of electronic conduction before it can be successfully implemented in SOFCs.

Yahiro et. al. [8] deposited a thin layer of YSZ by RF sputtering on ceria electrolytes with the objective of suppressing the electronic current. These electrolytes were tested in a fuel cell mode with hydrogen as the fuel. The YSZ-coated ceria electrolytes exhibited higher open circuit voltage (OCV) compared to uncoated ceria thus demonstrating that YSZ coating is useful in suppressing electronic conduction. In a subsequent paper, Virkar [9] has analyzed the conditions under which a YSZ coating may also improve thermodynamic stability of an otherwise unstable electrolyte material such as bismuth oxide. In the work of Yahiro et. al. [8], the YSZ coating was deposited by RF sputtering at room temperature. The YSZ-coated side was exposed to fuel in subsequent testing. The YSZ-coated side was exposed to fuel in subsequent testing. As will be discussed in what follows, it is not obvious that the YSZ-coated side should be exposed to fuel. To the contrary, it will be argued here that the YSZ-coated side should in fact be exposed to air. Experimental evidence in support of this will be presented. Further, it will be shown that a high temperature treatment is necessary to ensure a crack-free, adherent YSZ coating provided the film is deposited at low (room) temperatures. Finally, the deposition of YSZ by electrochemical vapor deposition (EVD), in addition to sputtering, will also be discussed.

II. EXPERIMENTAL PROCEDURE

II(a): Fabrication of Doped Ceria Electrolytes:

Ceria electrolyte discs containing either Y$_2$O$_3$ or several rare earth oxides such as Yb$_2$O$_3$, Er$_2$O$_3$, Gd$_2$O$_3$, Dy$_2$O$_3$, and Ho$_2$O$_3$ were fabricated. The typical dopant concentration was 11 mol.%. The procedure of fabrication is briefly described below. Respective oxides in the desired proportions were wet mixed in cyclohexane. The mixed powders were dried and pellets were die-pressed followed by isostatic pressing at 207 MPa. Finally, the pellets were sintered in air at 1600°C for 6 hours. Density of the as-sintered materials was measured by the standard fluid immersion method.

II(b) Deposition of a YSZ Coating and Thermal Treatment:

Deposition of a thin (~2 µm) coating of 8 mol. % yttria-stabilized zirconia (YSZ) by RF sputtering was done at a commercial facility. Several of the discs were heated to 900°C for 2 hours in air after the deposition of a YSZ film. The objective was to explore the effect of heating (to the anticipated maximum fuel cell operation temperature) on the integrity of the YSZ coating. Some of the discs were subsequently heated to 1500°C for 2 hours. On some of the discs, with and without a sputtered YSZ coating, a second YSZ
coating was deposited by electrochemical vapor deposition (EVD). This was achieved at 1100°C using ZrCl₄ and YCl₃ as Zr and Y precursors, respectively. YCl₃ was placed in the hot zone of the furnace very close to the ceria disc upon which a YSZ film was to be deposited. ZrCl₄ powder was also kept in the hot zone. Thus, at the deposition temperature, it existed in a gaseous state. Deposition time was typically about 2 hours.

II(c): Microstructural Characterization:

YSZ-coated discs were examined in a scanning electron microscope (SEM) in the as-received state (YSZ-coated), after heating to ~900°C and after heating to 1500°C. Both the coated surface as well as the film/disc interface in cross-section were examined. The objective was to examine the quality of the coating, its cracking and potential delamination.

II(d): Evaluation of YSZ-Coated Ceria Discs in a Fuel Cell Mode:

An apparatus for the testing of electrolyte discs was designed and built. The apparatus consists of two long alumina tubes with inconel end-fittings between which an electrolyte disc can be secured. Both sides of each electrolyte disc were coated with platinum paste as electrodes. Silver metal foils as gaskets were used to ensure leak-proof seals between the electrolyte disc & the inconel fittings and between the fittings & the alumina tubes. The alumina tubes were spring-loaded such that the springs were outside the hot zone maintaining a constant pressure on the gaskets. Electrical connections were made directly to the inconel fittings which also served as electrical contacts. This prevented delamination of the electrodes which often occurs if the external contacts are made directly to the electrodes. Hydrogen bubbled in water at room temperature was circulated through one of the alumina tubes on one side of the disc while oxygen gas at 1 atm pressure was circulated on the other side. Open circuit voltage (OCV) was measured over a range of temperatures. In several experiments, the voltage-current curves were obtained by varying the external load. The focus of this manuscript, however, is primarily on the OCV. Experiments were conducted on uncoated as well as YSZ-coated discs. Experiments were conducted in both configurations, YSZ-coated side exposed to air and to fuel. The significance of this will be discussed later.

III. RESULTS

III(a): Density and Microstructure:

Densities of samples were typically between ~6.5 and ~7.34 gm/ml which corresponds a density in excess of 95% of the theoretical density assuming oxygen vacancies as the predominant point defects. Microstructural examination of thermally etched samples showed the structure to be equiaxed with a grain size on the order of ~7 μm.

III(b): Characterization of YSZ Films:

Figure #1 shows an SEM micrograph of an as-deposited YSZ film. Thickness of the YSZ coating was measured (by examining the film in cross section on an SEM) to be about 2 μm. The film appeared to adhere well to the baseline ceria electrolyte. The disc was subsequently heated to ~900°C. The objective was to determine the effect of heating YSZ-coated discs to the anticipated upper limit of the fuel cell operation temperature. Figures #2(a) and #2(b) show SEM micrographs of the top and the side views, respectively, after heating a YSZ-coated disc to ~900°C. Two points are worth noting. (1) The film is cracked severely. (2) The film does not delaminate and the bonding continues to be excellent. A cracked film is no longer impervious and gaseous products
can permeate through the cracks to the baseline electrolyte during a fuel cell operation. Many of the discs were subsequently heated to \( \sim 1500^\circ{\text{C}} \) for 2 hours in an attempt to heal the cracks. It has been demonstrated in many other ceramics that crack healing can be accomplished by heating cracked samples to a temperature above which diffusion of the slowest moving species is significant. Figure #3 shows an SEM micrograph of a sample after the high temperature thermal treatment. Note that the cracks are nearly healed. Cross-sectional view indicated that the film was well bonded to the baseline electrolyte. Finally figure #4 shows an SEM micrograph (cross section) of a sample on which after sputter deposition, a layer of YSZ was deposited by EVD. The thickness of the layer deposited by EVD is \( \sim 1 \) to \( 1.5 \mu{\text{m}} \).

III(c): Evaluation of YSZ-Coated Ceria Electrolytes in Single Cells:

Several of the YSZ-coated discs were tested in a fuel cell mode with hydrogen as the fuel. In the case of ceria electrolytes, an important question is which side should be exposed to fuel, the uncoated side or the coated side. Experiments were done in both configurations. Figures #5(a) and #5(b) show OCV vs. temperature for YSZ-coated Gd\(_2\)O\(_3\)-doped and Er\(_2\)O\(_3\)-doped ceria electrolytes, respectively, with the coating exposed to fuel as well as oxygen. These discs had been annealed at \( \sim 1500^\circ{\text{C}} \) for 2 hours to effect crack healing. Note that in both cases, the OCV is higher when the YSZ-coated side was exposed to oxygen. Significance of this will be discussed later. The highest OCV measured was about 0.89 volts.

Figure #6 shows OCV vs. temperature plots for uncoated and YSZ-coated Y\(_2\)O\(_3\)-doped Ce\(_2\)O\(_3\) discs. The coated discs had their coated side exposed to oxygen. The various conditions examined were: (a) Uncoated, (b) YSZ-(sputter) coated as-received, (c) YSZ-(sputter) coated and annealed at \( 1500^\circ{\text{C}} \), (d) YSZ-(sputter) coated (as-received) with a YSZ coat by EVD at \( 1100^\circ{\text{C}} \), and (d) YSZ-(sputter) coated, annealed at \( 1500^\circ{\text{C}} \), and with a YSZ coat by EVD at \( 1100^\circ{\text{C}} \). The lowest OCV observed was that for uncoated discs while the highest one was for a YSZ-coated disc upon which after thermal treatment at \( 1500^\circ{\text{C}} \), a layer of YSZ was deposited by EVD. The highest OCV measured was about 0.94 volts. The present results thus demonstrate the advantage of a YSZ coating in suppressing electronic conduction and enhancing the OCV.

IV. DISCUSSION

IV(a): Cracking and Crack Healing of YSZ Films:

YSZ films were deposited by RF sputtering at room temperature. These films were fully dense and appear to have well-bonded to the substrates. Thermal expansion coefficients of YSZ (\( \alpha_Z \)) is much lower than that of most doped ceria electrolytes (\( \alpha_C \)). Typical values of thermal expansion coefficients of YSZ and ceria are \( \alpha_Z \approx 10 \times 10^{-6}/^\circ{\text{C}} \) and \( \alpha_C \approx 12.5 \times 10^{-6}/^\circ{\text{C}} \), respectively. At the deposition temperature, which is room temperature (\( T_0 \)), both the film and the substrate are under no stress. However, when heated to a high temperature (\( T_1 \)), thermal expansion of the film will be lower than that of the substrate. Thus, the film will be under tension. As the substrate is much thicker than the film, it is to be expected there will be a negligible (compressive) stress in the substrate while the film will be under a large (biaxial) tensile stress. The magnitude of this stress is given by

\[
\sigma \approx \frac{(\alpha_C - \alpha_Z)(T_1 - T_0)E}{(1 - \nu)} 
\]

(1)
where \( E \) and \( v \) are respectively Young's modulus of elasticity and Poisson's ratio of the YSZ coating. With \( E = 200 \text{ GPa} \), \( v = 0.25 \), and a temperature \((T_1)\) of 900°C, the calculated value of tensile stress in the film is \( s = 580 \text{ MPa} \), which is well in excess of the fracture stress of cubic YSZ at 900°C. Thus, films are expected to crack when heated to the cell operation temperature, as observed. As seen in Figure #2(a), the crack pattern is very uniform and the intercrack spacing is small. Uniformity of cracks and small intercrack spacing (\( \sim 4 \text{ to } 5 \mu\text{m} \)) suggests that the fracture stress of the YSZ film must be much lower than 580 MPa. If the film had been heated to a lower temperature, the crack density would also have been lower. In order to verify this aspect, YSZ-sputter coated discs were heated to a temperature between 300 and 900°C in intervals of 100°C. It was observed that the higher the temperature of this treatment, the greater was the crack density. The uniform cracking pattern seen in Figure #2(a) is in accord with what is expected on the basis of Weibull statistics.

Although upon heating to 900°C, the YSZ films develop cracks, the interface between the film and the substrate continues to be strong. Whether delamination will or will not occur depends on a number of parameters including the thermally induced strain differential, interfacial energy of debonding, \( \gamma_{\text{fm}} \) (mode II interfacial fracture energy) and thickness of the film, \( h \). It can be shown that delamination will occur provided \( [10] \)

\[
|\alpha Z - \alpha C| (T_1 - T_0) = |\Delta \alpha \Delta T| \geq \frac{2\gamma_{\text{fm}}(1 - v^2)}{hE}
\]

Note that the thinner the film, the lower is the likelihood of its delamination. If \( \gamma_{\text{fm}} \) is assumed to be 10 J/m², delamination may occur if the thickness is in excess of \(-6 \mu\text{m} \). If \( \gamma_{\text{fm}} = 1 \text{ J/m}^2 \), delamination may occur for film thickness \( \geq 2 \mu\text{m} \). The observation that delamination of a film 2 \( \mu\text{m} \) in thickness does not occur implies that \( \gamma_{\text{fm}} \geq 1 \text{ J/m}^2 \). Clearly, the higher the \( \gamma_{\text{fm}} \), the stronger the bonding and the lower is the likelihood of its delamination. It is to be emphasized that there may be situations when the strain differential may be quite large and the occurrence of delamination then is a real possibility. In the present case with ceria electrolytes, delamination of well-bonded, thin films seems unlikely.

Cracked films are unsatisfactory for the intended purpose as they are not impervious. The samples were subjected to a high temperature treatment in order to heal the cracks formed. It is well known that crack healing can be effected by heating cracked ceramic bodies to a temperature at which diffusion can occur. Since oxygen diffusion is rapid, it is the cation diffusion which dictates the kinetics of crack healing. Crack widths are \( = 1 \mu\text{m} \). Thus, for crack healing to occur in 2 hours, the cation diffusion must be \( \geq 1 \times 10^{-12} \text{ cm}^2/\text{sec} \). This value of cation diffusion is in accord with literature data on diffusion in zirconia at 1500°C. Indeed, Figure #3 shows that substantial crack healing does occur when annealed at 1500°C for 2 hours. The coating is well-bonded to the substrate and most of the cracks are healed. Although this thermal treatment is quite effective in crack healing and improving the film quality, the procedure is not entirely satisfactory because interdiffusion between ceria and YSZ is also expected to occur in addition to crack healing as the thickness of the YSZ film is only about 2 \( \mu\text{m} \). Such interdiffusion would imply that the film is no longer pure YSZ but will be contaminated with ceria. This is undesirable since it would increase the electronic conductivity of YSZ. From a practical point of view, the deposition of a YSZ film must be
accomplished at a temperature equal to or higher than the intended service temperature of an SOFC. Then, the YSZ coating will be under a state of biaxial compression at temperatures lower than the deposition temperature and the film will not crack. If the magnitude of compression is too high, there is the possibility that the film could delaminate. However, for this to occur, the stress (compressive) in the film must be very high, about 1.5 GPa and the bonding must be weak. The bonding between YSZ and ceria is very good and delamination is unlikely. Indeed, experimentally delamination of the YSZ coating on ceria has not been observed. From this standpoint, the film deposition should be done by RF sputtering at a high temperature, ~900°C, or by EVD which is a high temperature process. Alternatively, sol-gel may be suitable process as well.

IV(b): Effect of YSZ Coating on OCV:

As the electronic transference number of YSZ is much smaller compared to the ceria substrate, the net electronic (leakage) current through the (composite) electrolyte is also expected to be lower compared to the uncoated electrolytes. This should lead to a higher OCV with YSZ-coated discs, as seen in Figure #6. However, it is also clear that the film quality needs to be improved. As-received YSZ-coated electrolytes exhibit higher OCV compared to the uncoated discs indicating that even a cracked YSZ film is effective in suppressing the electronic current to some degree. Discs heat treated at 1500°C exhibit a marked improvement since crack healing improves the quality of the film even though the film may not be fully impervious. Deposition of a YSZ film by EVD over previously YSZ-(sputter)coated ceria discs leads to a significant improvement in the OCV. The highest OCV was measured for a cell with a YSZ-coated disc that had been heated to 1500°C for 2 hours to effect crack healing, followed by the deposition of an additional thin YSZ layer by EVD.

The purpose of a YSZ film is to block off the electronic current. In some cases, a YSZ film may also serve as a protective layer which could prevent decomposition of an otherwise unstable electrolyte such as bismuth oxide. It is then obvious that the YSZ-coated side should be exposed to fuel otherwise Bi2O3 will simply be reduced. Conditions under which a YSZ coating may prevent degradation have been previously discussed by Virkar [9]. However, when the baseline electrolyte such as ceria is thermodynamically stable in fuel, the only purpose of a YSZ coating is to block off the electronic current. The integrity of the electrolyte is not compromised even when exposed to fuel. In such a case, the important question is whether the YSZ-coated side or the uncoated side be exposed to fuel. As seen in Figures #5(a) & #5(b), the OCV is higher when the YSZ-coated side is exposed to oxygen. The significance of the results and rationale for exposing the coated side to air are discussed in what follows.

It is well known that in a reducing atmosphere, ceria develops significant electronic conduction [7]. At any temperature, the lower the pO2, the greater is the electronic conduction (assuming the electron concentration to be much greater than the hole concentration). For the purposes of the present discussion, we will assume that at any given temperature, there will be a partial pressure of oxygen, pO2(c), below which ceria develops substantial electronic conductivity. In order to achieve as high an OCV as possible, it is imperative that the electronic transference number should be negligible. From a practical point of view, the objective is to ensure that the electronic transference number be maintained below some critical value, e.g. 0.02. YSZ also develops electronic conduction except that the corresponding partial pressure of oxygen, pO2(z), is significantly lower than that for ceria. Figure #7 shows schematics with YSZ-coated
side exposed to fuel ((a)) and to oxygen ((b)). Also, the figure shows the variation of \( \log p_{O_2} \) through the composite electrolyte and \( \log p_{O_2} \) (dashed lines) below which ceria and YSZ develop electronic conduction, \( \log p_{O_2(c)} \) (for ceria) is higher than \( \log p_{O_2(z)} \) (for YSZ). It will be assumed that the partial pressure of oxygen in fuel, \( p_{O_2(f)} \), is even lower than \( p_{O_2(z)} \). Thus, when the YSZ-coated side is exposed to fuel, assuming the interface partial pressure of oxygen is lower than \( p_{O_2(z)} \), the entire YSZ coating will have developed significant electronic conduction. As the \( p_{O_2(c)} \) is higher than \( p_{O_2(z)} \), the \( p_{O_2} \) in some regions of ceria will be lower than \( p_{O_2(c)} \). That part of ceria exposed to oxygen, however, is expected to equilibrate with oxygen and thus should not develop electronic conduction. However, if the electrodes are not perfectly reversible, the \( p_{O_2} \) just inside the oxygen electrode (into ceria) may be significantly lower (see Figure #7(a)). The higher the electrode losses, the greater will this difference be. In such a case, there will be a continuous flux of oxygen (that is oxygen ion flux and a balancing electronic flux for electroneutrality) from the oxygen electrode through the electrolyte to the fuel side. That is, the cell behaves like an internally leaky battery. In such a case, the \( p_{O_2} \) just inside the ceria (oxygen electrode) will be lower than \( p_{O_2(c)} \). The net effect is that electronic conduction in the entire composite electrolyte will be significant. The result will be a lowering of the OCV below the theoretical Nernst value. The abrupt changes in \( \log p_{O_2} \) at electrode/electrolyte interfaces signify electrode losses and are expected in the open circuit condition only if electronic conduction is significant. Clearly, the electrode behavior is of great importance.

If the YSZ-coated side is exposed to oxygen, the \( p_{O_2} \) throughout the YSZ film is expected to be greater than \( p_{O_2(z)} \). Thus, the electronic conduction in YSZ will be negligible. In a quasi-steady state, the ionic and the electronic current densities must be uniform through both regions (YSZ and ceria). Thus, the electronic current in ceria will also be negligible. In an open circuit, this means the electronic transference number of the composite electrolyte will be negligible and the OCV should be near theoretical. In such a case, there will be negligible effect of the electrodes on \( p_{O_2} \). That is, there would be a very little abrupt change in \( \log p_{O_2} \) at electrode/electrolyte interfaces. However, when the cell is in operation such that there is a net flux, there will be losses at the electrode which would translate into abrupt changes in \( \log p_{O_2} \) at electrode/electrolyte interfaces. Figure 7#(b) shows a schematic variation of \( \log p_{O_2} \) through the YSZ film and the baseline electrolytes when the coated side is exposed to oxygen. The preceding shows that in order to achieve the highest possible OCV, the YSZ-coated side should be exposed to oxygen and not to fuel, even though intuition may suggest otherwise. This scenario, however, assumes that the baseline electrolyte is thermodynamically stable in fuel, which is the case with ceria. Since bismuth oxide is unstable in fuel, if it is used in an SOFC, the YSZ-coated side will have to be exposed to fuel. In addition, it is also necessary that criteria which ensure that the interface \( p_{O_2} \) is above the decomposition partial pressure of bismuth oxide are satisfied [9].

VI. CONCLUSIONS

The present work has shown that a thin coat of YSZ over ceria can be deposited by sputtering and by EVD. The films are strongly bonded to the substrates and do not exhibit delamination. Deposition of a YSZ coating at low temperatures is not satisfactory since upon heating to the cell operating temperature, the film cracks due to differences in thermal expansion coefficients. Thermal treatment at ~1500°C is effective in improving
the quality of the film by crack healing. Even though crack healing can be achieved by a thermal treatment, the preferred approach involves deposition of the film at a temperature equal to or greater than the service temperature. In this sense, EVD is an ideal method for film deposition. Other alternatives include sputtering on heated substrates or sol-gel.

The OCV of cells with YSZ-coated discs is consistently higher than those with uncoated discs showing the effectiveness of the film in suppressing the electronic current. Contrary to the intuition, it is preferable to expose the YSZ-coated side to oxygen and not to fuel in order to achieve the highest possible OCV. The rationale is that if the YSZ-coated side is exposed to fuel, conditions can exist under which both the YSZ film as well as the baseline ceria develop electronic conduction thereby decreasing the effectiveness of the YSZ film in suppressing the electronic current. When the YSZ-coated side is exposed to oxygen, however, electronic transference number of the film can be kept to a minimum ensuring higher OCV. Although the effectiveness of a YSZ film in enhancing the OCV has been demonstrated, further improvements in the quality of the film are necessary.

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REFERENCES

1) A. McDougall, "Fuel Cells", The MacMillan Press, London, (1976).
2) T. Takahashi, H. Iwahara, and T. Arao, J. Appl. Electrochem., 5 187 (1975).
3) R. N. Blumenthal, F. S. Brugner, and J. E. Garnier, J. Electrochem. Soc., 120 [9] 1230-1237 (1973).
4) R. L. Cook and A. F. Sammells, Solid State Ionics, 45 311 (1991).
5) H. D. Baek and A. V. Virkar, J. Electrochem. Soc., 139 [11] 3174-3182 (1992).
6) L. B. Pankratz, 'Thermodynamic Properties of Elements and Oxides', Bureau of Mines Bulletin 672.
7) H. L. Tuller and A. S. Nowick, J. Electrochem. Soc., 122 [2] 255-259 (1975).
8) H. Yahiro, Y. Baba, K. Eguchi, and H. Arai, J. Electrochem. Soc., 135 2077-2080 (1988).  
9) A. V. Virkar, J. Electrochem. Soc., 138 [5] 1481-1487 (1991).  
10) G. P. Cherepanov, "Fracture of Brittle Materials", McGraw-Hill, New York (1973).
Figure #1: An SEM micrograph of a YSZ-coated (by sputtering) ceria sample.

Figure #2(a): An SEM micrograph of a YSZ-coated sample heated to 900°C showing the presence of cracks formed due to thermal expansion mismatch.
Figure #2(b): The same sample as in Figure #2(a) showing a cross-section. Although the film is cracked, it is still well-bonded to the substrate.

Figure #3: An SEM micrograph of YSZ-coated (by sputtering) sample that was heated to 1500°C/2 hours to cause crack healing. Note that most of the cracks are healed.
Figure #4: An SEM micrograph (cross-section) of a sample upon which an additional layer of YSZ was deposited by EVD.

Figure #5: OCV vs. temperature: (a) YSZ-coated Gd$_2$O$_3$-doped CeO$_2$; a - YSZ film exposed to oxygen, b - YSZ film exposed to fuel, (b) YSZ-coated Er$_2$O$_3$-doped CeO$_2$; a - YSZ film exposed to oxygen, b - YSZ film exposed to fuel.
Figure #6: OCV vs. temperature for uncoated and YSZ-coated Y$_2$O$_3$-doped CeO$_2$ discs: a - uncoated, b - YSZ-(sputter) coated as-received, c - YSZ-(sputter) coated and annealed at 1500°C/2 hours, d - YSZ-(sputter) coated as-received with a YSZ coat deposited by EVD, and e - YSZ-(sputter) coated and annealed at 1500°C/2 hours followed by a YSZ coat by EVD.

Figure #7: Schematics showing the variation of log$\text{pO}_2$ through the composite electrolyte for two conditions: (a) YSZ-coated side exposed to fuel, and (b) YSZ-coated side exposed to oxygen.