LOW TEMPERATURE SOLID OXIDE FUEL CELLS WITH DIP-COATED YSZ ELECTROLYTES

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ABSTRACT

YSZ/Ni + zirconia electrolyte/electrode discs of ~2.5 cm in diameter were fabricated by a single step dip-coating process followed by sintering. NiO was used as the source of Ni. Discs were sintered in air at 1450°C. The typical electrolyte thickness was between ~10 and ~20 μm, the anode thickness was between 1 to 2 mm and the anode porosity was ~25 vol.%. Various cathodes were deposited on the YSZ electrolyte. Single cell testing was performed with humidified hydrogen as the fuel and both oxygen and air as the oxidants. All cell testing was conducted at 800°C. Power densities in excess of ~0.55 watt/cm² at 0.7 volts in air were measured without correction for lead wire resistance. Estimated maximum power density, corrected for lead wire resistance, is ~1 watt/cm².

INTRODUCTION

Solid oxide fuel cell technology has received much attention during the past decade or so [1]. An excellent review of the current technology has been recently given by Minh [2]. State-of-the-art solid oxide fuel cells usually operate at ~1000°C. The need for the development of solid oxide fuel cells that can operate at temperatures ≤ 800°C has been long-recognized. The three principal benefits to be gained by lowering the cell operating temperature are as follows: (1) The lower the temperature, the higher is the efficiency of this noncyclic process. (2) Lower temperature should facilitate the use of low cost metallic components such as the interconnect instead of the more expensive ceramic interconnects. This is particularly important for the planar design of solid oxide fuel cells. (3) Lower temperature also means less potential for materials degradation. For example, interdiffusion between the electrolyte and electrodes has been cited as a potential source of concern at the higher operating temperatures. The state-of-the-art electrolyte used in solid oxide fuel cells is the yttria-stabilized zirconia (YSZ) which is known to exhibit excellent stability and an ionic transference which is unity over a wide range of partial pressures of oxygen. However, the resistance of YSZ electrolytes of thickness ≥100 μm at ≤ 800°C is too high to be practical. There are two possible approaches: (1) To develop other electrolytes with higher conductivity compared to YSZ. The potential candidates are doped ceria and some perovskites. Much work on these materials has been reported. However, transference number less than unity in reducing atmospheres, especially in the case of ceria, is the principal shortcoming of these materials. (2) The second approach is to reduce the thickness of YSZ from ~150 μm, typical of tape cast and sintered materials, down to ~20 μm or lower. With resistivity of YSZ of 50 Ωcm at 800°C, this translates into lowering the electrolyte contribution to the overall cell specific resistance from ~0.75 Ωcm² to ~0.1 Ωcm². Indeed, this approach has been used recently. However, with electrolyte thickness so small, it can not be used as the supporting member. The obvious approach is to use one of the electrodes as the support structure [2]. In the present work,
porous anode is used as the support structure. The approach consisted of pressing discs of a mixture of NiO and zirconia upon which a thin layer of YSZ is deposited by dip-coating. The discs were subsequently sintered in air and reduced in hydrogen to convert NiO to Ni. Cathodes were subsequently applied to the YSZ layer. Microstructures of the discs were examined in a scanning electron microscope. Single cell testing was conducted at 800°C with humidified hydrogen as the fuel and both oxygen and air as the oxidants.

EXPERIMENTAL PROCEDURE

Fabrication of YSZ/Ni Zirconia Discs by Dip-Coating: NiO and 8 mol.% Y2O3-doped ZrO2 (YSZ) powder obtained from commercial vendors were mixed such that NiO was typically ~60 vol.% and YSZ was ~40 vol.%. The powders were wet-mixed with ethanol as the fluid, the powder mixtures were dried, and discs of diameter ~32 mm and thickness ~4 mm were die-pressed. A slurry of YSZ in ethanol was made. The discs were dip-coated with the slurry, dried and then isostatically pressed at ~200 MPa. The discs were sintered in air at 1450°C for 1½ hours. The resulting discs were in excess of 98% of theoretical density. Subsequently, requisite cathodes were applied on the YSZ surface. After application of the cathodes, the discs were heated in hydrogen to reduce NiO to Ni metal. This reduction of NiO to Ni created a porosity of ~25 vol.% in the anode. Samples were examined under a scanning electron microscope to examine the microstructure.

Bar-shaped samples of Ni + YSZ and Ni + TZP (3 mol.% Y2O3-doped zirconia) were made by die-pressing a mixture of NiO and the requisite zirconia, followed by isostatic pressing, sintering in air, and reducing in hydrogen. The amount of NiO was varied between 50 and 70 vol.%. The corresponding volume percent Ni metal was between ~37% and ~58%. The bar-shaped samples were subsequently broken in four point bending to determine their strength. The objective of this work was to determine the mechanical properties, namely strength, of the prospective anodes.

Single Cell Testing: Single cells were tested with humidified hydrogen as the fuel and both oxygen and air as the oxidants. Figure #1 shows a schematic of the fuel cell testing set up. It consists of two alumina tubes in between which the electrolyte/electrode disc is placed. It is secured in place via two inconel bushings and mica gaskets. One silver mesh each is placed on the cathode and the anode. The entire assembly is spring-loaded from the outside so that a constant pressure is always exerted on the electrolyte disc. No glass is used to seal the electrolyte disc. Thus, the same cell can be removed from the testing set up, remounted, and tested again. Hydrogen gas bubbled through water is circulated on the anode side while the oxidant (oxygen or air) is passed on the cathode side. Some testing was also conducted using a mixture of 80% O2 and 20% N2. The objective was to assess the effect of the presence of nitrogen on the area specific resistance. All testing was done at 800°C. In order to determine the resistance of the lead wires, a silver disc with the same silver lead wires used for cell testing attached, was also heated in the set up and its resistance was measured. Data are reported here with and without correction made for the lead wire resistance.

RESULTS AND DISCUSSION

Microstructure of the Sintered Anode/Electrolyte Discs: Figure #2 shows a typical micrograph of a sintered electrolyte/electrode disc that was heated in hydrogen at 800°C to reduce NiO to Ni. The electrolyte is essentially fully dense with thickness on the order
of 13 μm. The typical electrolyte thickness is ≤ 20 μm. The anode morphology is clearly seen in the micrograph which is quite porous. No cracking of either the electrode or the electrolyte was observed. The electrolyte resistivity at 800°C was measured to be ~54 Ωcm. Thus, for an electrolyte thickness of ~20 μm, the corresponding electrolyte area specific resistance is ~0.11 Ωcm².

Mechanical Properties of Ni + Zirconia Anodes: Figure #3 shows the strength of the anodes plotted vs. volume percent Ni metal for both Ni-YSZ and Ni-3Y-TZP samples. The corresponding volume percent porosity is shown in parentheses. Note that the strength of Ni-3Y-TZP cermet is higher than that of Ni-YSZ cermet. However, the strength of Ni-YSZ increases with Ni content while that of Ni-3Y-TZP decreases with Ni content. Higher strength of Ni-3Y-TZP at lower Ni content is understood to be due to the inherently higher strength of YTZP ceramics (which contain tetragonal zirconia) compared to YSZ ceramics (which contain cubic zirconia). Increase in strength of Ni-YSZ with increasing Ni content may be due to the higher strength of Ni compared to YSZ. It thus appears that the strength of Ni is in between that of YTZP and YSZ. The present results suggest that if higher Ni content (and thus higher porosity) is desired, then there is little advantage of YTZP over YSZ for application in the anode. However, if it is desired that the anode contain about 30 to 40 vol.% Ni, use of Ni-YTZP with strength over 300 MPa may be of significant advantage over Ni-YSZ which has a strength of ~120 MPa. YTZP ceramics are known to undergo degradation in moisture over a range of temperatures between ~100 and 300°C. However, as the present application is at much higher temperatures, degradation in strength due to moisture is not expected to pose a problem. Further, as these cerments are porous, it is anticipated that any moisture-assisted tetragonal → monoclinic transition at low temperatures would not degrade the strength. In the present work, all anodes were of Ni-YSZ.

Single Cell Testing: The Effect of Oxidant Composition: Single testing was done on one cell with Sr-doped LaMnO₃ (LSM) as the cathode (with a platinum paste current collector backed by a silver wire mesh) with pure oxygen gas, a mixture consisting of 80% O₂ - 20% N₂, and air (~21% O₂) as the oxidants. The objective was to determine the possible effect of nitrogen on the voltage-current density plots. If the partial pressure of oxygen in the oxidant is \( p_{\text{O}_2(c)} \) and that in the fuel is \( p_{\text{O}_2(0)} \), then the open circuit voltage is given by

\[
E_o = \frac{RT}{4F} \ln \left( \frac{p_{\text{O}_2(c)}}{p_{\text{O}_2(0)}} \right)
\]  

or,

\[
E_o = \frac{RT}{4F} \ln \left( \frac{1}{p_{\text{O}_2(0)}} \right) + \frac{RT}{4F} \ln(p_{\text{O}_2(c)}) = E(0) + \frac{RT}{4F} \ln(p_{\text{O}_2(c)})
\]

where \( E(0) \) is the Nernst potential with oxygen at 1 atm as the oxidant. If air is the oxidant with oxygen partial pressure of 0.21 atm, at 800°C, the correction to the open circuit potential is only ~0.036 volts or ~36 mv. That is, the open circuit potential will be 36 mv smaller than with oxygen as the oxidant. This should lead to a modest change in voltage-current density plots and a modest decrease in the power density, provided electrolyte/electrode interfacial effects are negligible. Figure #4 shows voltage-current
density plots obtained with oxygen, 80% O₂ - 20% N₂, and air as the oxidants. All data in Figure #4 have been corrected for the lead wire resistance which contributed 0.15 Ωcm² to the total area specific resistance. The lead wire resistance was independently measured. Note that all of the voltage vs. current density plots in Figure #4 are linear (ohmic) over the range of current densities (up to a maximum of 0.8 amp/cm²) studied. Thus, the interfacial (both cathodic and anodic) overpotentials must be nearly ohmic and can be described in terms of charge transfer resistances. In some studies, however, a nonlinear, Tafel type of relation has been observed. For example, Kawada et al. [3], have observed a Tafel type of relation between current density and overpotential with Ni + YSZ electrodes. Figure #5 shows the corresponding power density vs. current density plots. Note power density is in excess of 0.5 watts/cm² with oxygen as the oxidant and ~0.22 watts/cm² with air as the oxidant. As is evident from these figures, the effect of the oxidant is profound. The overall area specific resistances with O₂, 80% O₂ - 20% N₂, and air (~21% O₂) are respectively 0.498, 0.58, and 1.165 Ωcm². That is, in the present case the area specific resistance does depend upon the amount of nitrogen gas present in the oxidant. The electrolyte thickness is on the order of 20 μm and the ionic resistivity of YSZ at 800°C is ~54 Ωcm. Thus, the electrolyte contribution to the overall cell specific resistance is ~0.11 Ωcm². Theoretical calculations of the effect of gas diffusion through porous electrodes shows that the effect of concentration polarization should be small. Thus, the greatest contribution appears to be related to the electrolyte/electrode interfacial effects. In particular, the fact that by changing the oxidant from pure O₂ to air (~0.21% O₂) the cell specific resistance increased by ~0.67 Ωcm² shows that charge transfer resistance (activation polarization) must be the principal contributor. Since the only change made was the type of oxidant used, the principal contribution to the charge transfer resistance is on the cathode side. A plot of the cell specific resistance vs. nitrogen concentration, albeit with three data points only, is linear. This seems to suggest that the presence of nitrogen renders fewer three phase boundary locations accessible to oxygen. These experiments suggested that for further improvement in power density, cathodes with lower charge transfer resistance will have to be developed. Subsequent work was directed towards this objective.

Single Cell Testing with Improved Cathodes: Electrolyte/electrode discs were fabricated by the same procedure as discussed earlier. Certain electrodes were developed for potential use as cathodes. In this manuscript, results on cells with two of the electrodes, labeled A and B, are described. Active area of the electrode/electrolyte interface for a typical cell was 2 cm². Figure #6 shows voltage vs. current density traces for a single cell with cathode A tested with both air and oxygen as the oxidants. Figure #7 shows the corresponding power density vs. current density plots. Note that the cell specific resistance with oxygen as the oxidant is 0.32 Ωcm² and with air as the oxidant is 0.38 Ωcm². Also, the power density with oxygen is ~0.9 watts/cm² and with air it is excess of 0.65 watts/cm². The actual measured power density at 0.7 volts in air is in excess of 0.55 watts/cm². Similar plots with cathode B are shown in Figures #8 and #9, respectively. In this case also, a significant reduction in overall cell specific resistance was achieved. In both of these tests, the data have not been corrected for the lead wire resistance. If this correction is made, power density in excess of 1 watt/cm² in air is estimated. This correction was not made as the lead wire resistance itself is now a significant part of the total cell resistance. What this suggests is that in future work, efforts will have to be made to reduce lead wire and other extraneous sources of resistance. As the data in Figures #6 through #9 have not been corrected for lead wire resistance, the actual power densities are even higher than the ones measured. The
preceeding shows that power densities well in excess of 0.5 watts/cm² at 800°C are possible with air as the oxidant.

SUMMARY

YSZ electrolyte/Ni + zirconia discs with electrolyte thickness typically less than ~20 μm were fabricated by single step dip-coating followed by sintering. Single cell tests were conducted with LSM as the cathode with pure O₂, 80% O₂ - 20% N₂, and air (~21% O₂) as the oxidants. The results showed that the cell area specific resistance increased with increasing nitrogen concentration in the oxidant. This suggested that activation polarization at cathode/electrolyte interface is probably a major source of the cell resistance. Improved cathodes were developed using which power density in excess of 0.55 watts/cm² at 0.7 volts in air 800°C was measured. Since correction for the lead wire resistance was not made, the actual power density was even higher.

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REFERENCES

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2) N. Q. Minh, J. Am. Ceram. Soc., 76 [3] 563-588 (1993).

3) T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, M. Mori, and T. Iwata, J. Electrochem. Soc., 137 [10] 3042-3047 (1990).
1. Alumina Tube Support;
2. Steel Spring;
3. Steel Ring;
4. Alumina Tube;
5. Furnace;
6. Silver Gasket;
7. Super Alloy Fitting;
8. Fuel Cell;
9. Mica Gasket;
10. Thermocouple;
11. Oxygen or Air;
12. Load.

Figure #1: A schematic of the single cell testing used in the present work.
Figure #2: A scanning electron micrograph of a YSZ/Ni-zirconia electrolyte/anode disc fabricated by a single step dip-coating process followed by sintering. Note that the electrolyte thickness is on the order of ~13 μm and it is fully dense. The anode porosity is about 25%.

Figure #3: Flexure strength of Ni-YSZ and Ni-3Y-TZP sintered anodes as a function of Ni content.
Figure #4: Voltage - current density traces with oxygen, 80% O₂ - 20% N₂, and air as the oxidants for a cell with LSM as the cathode, tested at 800°C.

Figure #5: Power density - current density plots for cell whose voltage - current density plots are shown in Figure #4.
Figure #6: Voltage - current density traces for a single cell with cathode A obtained at 800°C with air and oxygen as the oxidants. The overall specific resistances are ~0.32 Ωcm² in oxygen and ~0.385 Ωcm² in air. The above values have not been corrected for the lead wire resistance. Thus, the actual cell specific resistances should be even lower.

Figure #7: Power density - current density for the single cell with cathode A (Figure #6) obtained at 800°C with air and oxygen as the oxidants.
Figure #8: Voltage - current density traces for a single cell with cathode B obtained at 800°C with air and oxygen as the oxidants. The overall specific resistances are ~0.48 \( \Omega \text{cm}^2 \) in oxygen and ~0.56 \( \Omega \text{cm}^2 \) in air. The above values have not been corrected for the lead wire resistance. Thus, the actual cell specific resistances should be even lower.

Figure #9: Power density - current density for the single cell with cathode B (Figure #8) obtained at 800°C with air and oxygen as the oxidants.