A NEW SINGLE-COMPONENT SOLID OXIDE FUEL CELL

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ABSTRACT

A novel approach is being used to solve inherent chemical and mechanical compatibility problems in solid oxide fuel cells. An example of our single-component cell concept based on the chemical modification of the two sides of a yttria-stabilized zirconia electrolyte (YSZ) to produce mixed-conducting anodic and cathodic surfaces is described. The experimental investigations used to demonstrate and prove our concept include electrical characterization and overpotential measurements of mixed-conducting YSZ-based electrodes (containing titania and terbia), and single-cell studies. Our initial single-cell results show that a single-component SOFC is a viable concept. Continuing investigations of the effects of the preparation technique, starting particle size, electrode composition, porosity and thickness on single-cell performance will enable us to optimize the mixed-conducting YSZ anodic and cathodic surfaces.

INTRODUCTION

All current solid-oxide fuel cells (SOFCs) are fabricated using three separate components (materials): an anode and a cathode which are separated by a yttria-stabilized zirconia electrolyte (YSZ) (1). Some of the major challenges in the development of high-performance SOFCs are due to the mechanical and chemical incompatibilities among these three cell components. Minimization of the problems caused by such incompatibilities has required the use of expensive fabrication techniques as well as complex multi-component designs.

In our program, a novel approach is being used to develop a single-component oxide fuel cell to eliminate the chemical and mechanical compatibility problems between the YSZ electrolyte and the two electrodes in the current multi-component SOFCs. The lower materials-processing and fabrication costs of a single-component oxide fuel cell would result in lower-cost multi-cell systems with increased efficiencies and reliability's. Furthermore if these single-component fuel cells were operated in an intermediate temperature range (700 to 900°C), additional technological advantages would include increased lifetime and reliability of cell components, fewer problems with multiple-cell stacking and seals, and less costly materials options such as the use of metals or alloys as interconnectors. An operating temperature at or above 700 °C is also high enough to achieve internal reforming without carbon deposition and to be a thermally self-sustaining system through the recovery and use of the P2R heat generation.
Our single-component oxide fuel cell (2) is contrasted with a current multi-component planar cell in Fig. 1. The oxide electrolyte in a single-component fuel cell must satisfy the following criteria: (a) high oxygen-ion conductivity with minimal electronic conductivity in the electrolyte region; (b) good mixed (oxygen-ion and electronic) conductivity in the very low oxygen-pressure anode environment; (c) good mixed-conductivity in the cathode (air) environment; and (d) high chemical, mechanical and thermal stability at the cell-operating temperature.

In this paper we summarize our progress in 1) the synthesis and electrical characterization of mixed-conducting YSZ containing titania and terbia, 2) overpotential measurements of mixed-conducting YSZ-based cathodes and anodes in typical fuel-cell environments at 800 to 900 °C and 3) our single-cell investigations using mixed-conducting YSZ-based cathodes and anodes.

SYNTHESIS AND ELECTRICAL CHARACTERIZATION OF MIXED-CONDUCTING YSZ CONTAINING TITANIA AND TERBIA

Because of its high chemical stability and high oxygen-ion conductivity, YSZ is the electrolyte of choice in solid oxide fuel cells. A major challenge in our development of the single-component oxide cell shown in Fig. 1 is the chemical modification of the surfaces of the YSZ electrolyte to produce a n-type mixed-conducting anodic surface and a p-type mixed-conducting cathodic surface. The optimum YSZ electrolyte surfaces must have p-type conductivity in an oxidizing environment (air) and n-type mixed conductivity in a reducing environment (fuel gas). Thus we have dissolved titania and terbia into the cubic-fluorite phase of YSZ to produce n-type mixed-conducting YZTi anodes and p-type mixed-conducting YZTb cathodes.

Mixed-Conducting Yttria-Stabilized Zirconia-Titania (YZTi)

We have used a wet-chemical co-precipitation method to obtain a homogeneous distribution of titanium cations in YSZ. The appropriate mixtures of the three solutions (ZrOCl₂·8H₂O, YCl₃·6H₂O and TiCl₄ dissolved in distilled water) were added to distilled NH₄OH to obtain YZTi hydroxide precipitates. The precipitated hydroxides were then heated at various temperatures and in different atmospheres to maximize the titania solubility in YSZ. The X-ray diffraction results show that the decrease in the YZTi lattice parameter with increasing titania concentration is in excellent agreement with our previous results (3, 4). However, the maximum titania solubility in the cubic-fluorite YSZ phase has been increased by using the co-precipitation method. For example, our recent results (5) show that the maximum solubility of titania (TiO₂) in the cubic-fluorite phase of 12 mole % yttria-stabilized zirconia (Y12SZ) heated in air at 1500°C is between 20 and 25 mole %.

The n-type electronic conductivity of YZTi becomes significant when the oxygen pressure is below ~ 10⁻¹⁵ atm due to the presence of both Ti⁺³ and Ti⁺⁴ cations and the associated electron hoping which occurs in these very low oxygen-pressure environments (4, 6, 7). Because typical oxygen pressures at the fuel-gas anode in a SOFC vary from 10⁻¹⁵ to 10⁻²² atm, a YSZ surface region containing titanium cations would have excellent mixed (oxygen-ion and n-type electronic) conductivity.

Our determinations of the effect of titania concentration, oxygen pressure and temperature upon the n-type electronic conductivity in YZTi provide the fundamental
understanding and data necessary to optimize the titanium cation composition in the anodic surface of a YSZ electrolyte. The electronic conductivity of titanium-doped YSZ increases not only with decreasing oxygen pressure but also with increasing titania concentration and temperature (4-7). For example, the electronic conductivity of YZTi20 (YSZ containing 20 mole % titania) is higher than that of YZTi10 in the same oxygen-pressure and temperature environment.

Mixed-Conducting Yttria-Stabilized Zirconia-Terbia (YZTb)

Because YZTi is not a mixed-conductor in high oxygen-pressure (e.g. air) environments due to the absence of Ti+3 cations and the associated electronic conductivity, another multivalent-cation must be present in YSZ to produce a useful cathode surface. In the air environment of the cathode, the best multivalent-cation would be the one which provides the highest p-type electronic conductivity with no significant degradation of the oxygen-ion conductivity in YSZ.

Mixed (oxygen-ion and p-type electronic) conductivity has been reported in Tb2Zr2O7+δ and Gd2Zr2O7 zirconates (8), pyrochlores (Tb2Gd1-x)2Zr2O7+δ (9), terbia-zirconia cubic-fluorite (ZrO2)1-x(Tb2O3.5)x (10) and (ZrO2)1-x-y(Tb2O3.5)x(Y2O3)y (11). Furthermore, the coexistence of both trivalent and tetravalent terbium cations in cubic fluorite ZrO2-Tb2O3.5 solid solutions has been confirmed using the X-ray-absorption near-edge structure technique (12).

In our program, mixed-conducting YZTb has been prepared by dissolving terbia (TbO1.75) into YSZ using the citrate synthesis method (13-15). The cubic-fluorite phase is retained in YZTb at terbia concentrations as high as 50 mole %. Measurements of the total electrical and partial electronic conductivities of these solid solutions show that YZTb20 (YSZ containing 20 mole % TbO1.75) and YZTb30 have significant oxygen-ion and p-type electronic conductivities (13-15). The observed increases in the p-type electronic conductivity with increasing oxygen pressure (10⁻⁵ to 1 atm) indicate that the hole conductivity is related to the increasing Tb⁺⁴ content. The oxygen-ion conductivity decreases with increasing terbia content, presumably due to the oxygen vacancy-cation interactions. Our results not only show that YSZ containing terbium has excellent mixed (oxygen-ion and p-type electronic) conductivity but also provide the fundamental information necessary to optimize the terbium-cation composition in the cathodic surface of a YSZ electrolyte.

OVERPOTENTIALS OF MIXED-CONDUCTING YSZ-BASED CATHODES AND ANODES IN TYPICAL FUEL-CELL ENVIRONMENTS

At a given current density, the maximum performance and efficiency of a SOFC occur with those electrodes having the minimum overpotential losses. An ideal SOFC is one in which the anode and the cathode overpotentials are negligible and the ohmic resistance losses are minimal during cell operation. Thus a major factor in the optimization of mixed-conducting YSZ surfaces for SOFC electrode applications is the minimization of their overpotentials.

Mixed-Conducting YZTi Anodes

Mixed-conducting YZTi anodes have been prepared by mixing, for example, Y8ZTi20 (8 mole% Y₂O₃ and 20 mole% TiO₂) powders with polyethylene glycol, painting
the slurry on a YSZ electrolyte, and then heating at 1400 °C for 2 hrs in air (5). A Ni/YSZ cermet anode has also been made by mixing YSZ and NiO powders with polyethylene glycol, painting the mixture on the YSZ electrolyte and heating at 1400 °C for 2 hrs in air. The overpotentials of the YSZTi10, the YSZTi20 and a Ni(30 vol %)/YSZ cermet anode have been measured using the current-interruption method in a three-electrode configuration. In these measurements, the anode discs are typically 8-10 microns thick with a radius of about 0.48 cm and a surface area of 0.725 cm². The measured overpotentials of the YSZTi10 and the YSZTi20 anodes at 915°C are compared with those of a Ni(30 vol %)/YSZ cermet anode in Fig. 2. Although the overpotentials of the mixed-conducting YSZTi10 anode are higher than those of the Ni(30 vol %)/YSZ cermet anode, the overpotentials of the YSZTi20 anode are much lower than both the YSZTi10 and the Ni(30 vol %)/YSZ cermet anodes. The lower overpotentials of the YSZTi20 anode are believed due to its higher electronic conductivity and the associated increase in the charge-transfer reaction area.

Our impedance spectroscopy measurements (5) also indicate that the YSZTi20 anode has a low interfacial resistance, which is in agreement with the low overpotentials shown in Fig. 2. The preparation technique, the starting particle size, the composition, porosity and thickness of the YSZTi20 anodes can be being optimized to provide even lower anode overpotentials than those shown in Fig. 2.

Mixed-Conducting YZTb Cathodes

Mixed-conducting YSZTb20 and YSZTb30 cathodes have been prepared (14) using the procedures described above for the YSZTi20 anodes. The preparation of the Tb30A and Tb20A cathodes shown in Fig. 3 consisted of first annealing the powders for 12 hrs in oxygen at 1600°C, mixing with polyethylene glycol, and then painting the slurry on the YSZ. The geometric cross-section area of the two Tb30A cathode discs were 0.445 and 0.458 cm². The preparation technique for Tb30B cathode was essentially the same except that the powders were not annealed at 1600°C. This cathode disc had a geometric cross-section area of 0.437 cm². The preparation of the Tb30C and Tb20C cathodes was the same as that for Tb30B except that the painted slurry’s annealing time was 10 hrs instead of 2 hrs. The cross-section areas were 0.737 cm² for Tb30C and 0.463 and 0.288 cm² for the two Tb20C cathodes. The preparation of the Tb30D cathode was the same as that for the Tb30C cathode except that smaller starting powders (supplied by a vendor) were used. The resulting geometric cross-section area was 0.29 cm².

The porosity and thicknesses of the six YSZTb cathodes were examined using SEM. As shown in the parenthesis of the cathode-identification column of Fig. 3, the cathode thicknesses varied from ≤10 to 17 microns except for the Tb20A cathode (40 μm thickness), which was prepared using Pt gauze as a template on the YSZ surface before brush painting. No sintering of the larger (~ 10 μm in size) and non-uniform starting YSZTb30 particles used in cathodes Tb30B and Tb30C (17 μm thickness) was observed. The closed-packed particles observed in cathodes Tb30A (< 10 μm thickness) and Tb20A (40 μm thickness) were more uniform in size and shape due to their pre-heating and grinding procedures. The smaller (~ 1 μm) Tb30D particles sintered into a 13-15 μm thick layer. The Tb20C cathode had a more uniform 12-16 μm thick layer with no observable cracks. Despite these variations in electrode particle-packing density (porosity) and thickness, the results summarized in Fig. 3 clearly show that the overpotentials of the six mixed-conducting YSZTb cathodes are smaller than those of the similarly prepared...
platinum and La0.85Sr0.15MnO3 cathodes. This is presumably due to the increased charge-transfer reaction area for the mixed-conducting Y8ZTb cathodes.

In Fig. 3 the Tb30A and Tb20C cathodes (two samples of each) have the lowest overpotentials (e.g., 40 mV at = 225 mA/cm²). The overpotentials of the Tb20A cathode (40 µm thick) are higher than that of the Tb30A cathode (≤ 10 µm thick), presumably due to its larger thickness. If the Tb20A cathode had the same thickness as that of the Tb30A cathodes, its overpotentials would have been even lower than those shown for Tb20A in Fig. 3. Furthermore, the overpotentials of an optimized Y8ZTb20 cathode should be lower than those of an optimized Y8ZTb30 cathode, because the oxygen-ion conductivity in Y8ZTb20 is higher than that in Y8ZTb30 (16). Thus we expect the overpotentials of optimized Y8ZTb20 cathodes to be even less than the lowest values shown in Fig. 3.

SINGLE-CELL INVESTIGATIONS USING MIXED-CONDUCTING YSZ-BASED ANODES AND CATHODES

The variation of voltage with current density for Y8ZTb/Y8SZ/Y8ZTi cells has been measured at temperatures between 800 to 920°C (5, 16). Although these single cells are not single-component ones, they provide the basic information necessary for the optimization of the Y8SZ anodic and cathodic surfaces. The voltage variation with current density for the (air) Y8ZTb20/Y8SZ/Y8ZTi20 (P02 = 2 x 10^-18 atm) cell at 915 °C is shown in Fig. 4. The large IR loss shown in Fig. 4 is due to the thicknesses of the electrolyte and the two electrodes, and our future cells will have thinner YSZ electrolytes and electrodes to minimize these IR losses. Although the cathode overpotential (ηc) is lower than that (ηa) of the anode, both electrode overpotential losses could be improved.

The geometric cross-section area of this cell is 0.725 cm², and the thickness of the YSZ electrolyte is ~ 1.5 mm. The electrodes are made by mixing the Y8ZTb20 and Y8ZTi20 particles with polyethylene glycol and then painting the slurry on a Y8SZ electrolyte. The size of the Y8ZTb20 and Y8ZTi20 particles are nonuniform and vary from 1 to 10 µm. The cell is first heated to 1400°C and held for 1 hr to sinter the electrode particles to each other and to the Y8SZ electrolyte. The resulting Y8ZTb20 and Y8ZTi20 electrodes have some porosity and good adherence to the electrolyte. Scanning electron micrographs of the cross-section of the cell show that the thickness of both electrodes is about 40-50 µm.

Our initial cell with the mixed-conducting Y8ZTb cathodes and Y8ZTi anodes have shown that a single-component YSZ electrolyte-based cell is a viable concept. Furthermore, continuing investigations of the effects of the preparation technique, the starting particle size, the electrode composition, porosity and thickness on single-cell performance will enable us to optimize the mixed-conducting YSZ anodic and cathodic surfaces.

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REFERENCES

1. N. Q. Minh, J. Am. Ceram. Soc., 76, 563 (1993).
2. W. L. Worrell and P. K. Davies, U. S. Patent 5,298,235, March 29, 1994.
3. S. S. Liou and W. L. Worrell, Appl. Phys., A49, 25 (1989).
4. S. S. Liou and W. L. Worrell, in Solid Oxide Fuel Cells, S. Singhal, Editor, PV 89-11, p. 81, The Electrochemical Society Proceeding Series, Pennington, NJ (1989).
5. Y. Uchimoto and W. L. Worrell, to be published.
6. K. E. Swider, S. Loughin and W. L Worrell, in Ionic and Mixed Conducting Ceramics, T. A. Ramanarayanan and H. L. Tuller, Editors, PV 91-12, p. 73, The Electrochemical Society Proceeding Series, Pennington, NJ (1991).
7. K. E. Swider and W. L. Worrell, submitted to J. Electrochem. Soc.
8. M. P. Van Dijk, K. J. De Vries and A. J. Burggraaf, Solid State Ionics, 9/10, 913 (1983).
9. M. P. van Dijk, K. J. de Vries and A. J. Burggraaf, Solid State Ionics, 16, 211 (1985)
10. H. Iwahara, T. Esaka and K. Takeda, in Advances in Ceramics: Science and Technology of Zirconia III, S. Somiya, et al, Editors, Vol. 24, p. 907, The American Ceramic Society, Inc., Columbus, OH (1988).
11. G. Z. Cao, X.Q. Liu, H. W. Brinkman, K. J. de Vries and A. J. Burggraaf, The 5th Int. Conf. on the Science and Technology of Zirconia, Melbourne, Australia (1992).
12. H. Arashi, S. Shin, H. Miura, A. Nakashima and M. Ishigame, Solid State Ionics, 35, 323 (1989).
13. P. Han, J. Q. Huang and W. L. Worrell, in High Temperature Electrochemical Behavior of Fast Ion and Mixed Conductors, p. 461, F. W. Poulsen, J. J. Bentzen, T. Jacobsen, E. Skou and Østergrad, Editors, 14th Risø International Symposium on Materials Science, Risø National Laboratory, Roskilde, Denmark (1993).
14. P. Han and W. L. Worrell, in Ionic and Mixed Conducting Ceramics, PV 94-12, p. 317, T. A. Ramanarayanan, W. L. Worrell and H. L. Tuller, Editors, The Electrochemical Society Proceeding Series, Pennington, NJ (1994).
15. P. Han and W. L. Worrell, in press, J. Electrochem. Soc.
16. P. Han and W. L. Worrell, to be submitted to J. Electrochem. Soc.
Fig. 1. Our single-component oxide fuel cell (a) contrasted with a planar oxide fuel cell (b) made with three components.

Fig. 2. Comparison of the overpotentials of the Y8ZTi10 and Y8ZTi20 anodes with that of the Ni(30 vol%)/Y8SZ cermet anode at 915°C and 2 x 10^-18 atm P_{O2}.

T = 915 °C
Fig. 3. Comparison of the overpotentials of the Y8ZTb20 and Y8ZTb30 cathodes with platinum and La$_{0.85}$Sr$_{0.15}$MnO$_3$ cathodes at 820°C in air.

Fig. 4. Single oxide cell performance at 915°C for the cell: Air, Y8ZTb20 / Y8SZ / Y8ZTi20, P$_{O_2}$ = 2 x 10$^{-18}$ atm.