MIXED-CONDUCTING OXIDE ELECTRODES FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

Novel mixed-conducting yttria-stabilized zirconia-titania solutions have been synthesized and electrically characterized. The dissolution of titania into yttria-stabilized zirconia increases significantly the percentage of electronic conductivity in this oxygen-ion conductor. The total electrical, lattice and grain-boundary conductivities have been determined using impedance spectroscopy at temperatures between 350 and 900°C and at oxygen pressures between 10⁻²³ and 0.21 atm. The electronic conductivity has been measured at temperatures between 800 and 1000°C using a platinum electrode to block oxygen-ion transport. The percentage of electronic conductivity is calculated from the electronic/total electrical conductivity ratios and from separate Emf cell measurements. The percentage of electronic conductivity increases with increasing titania concentration and with decreasing temperature. Our results establish not only the magnitudes of the electronic and oxygen-ion conductivities but also the optimum compositions of the yttria-stabilized zirconia-titania solutions for mixed conduction. The results are used to estimate the electrode current densities of these new mixed-conducting oxides in solid oxide fuel cells.

1. INTRODUCTION

Mixed-conducting oxides, which exhibit oxygen-ion and electronic conductivity, are novel materials. Particularly attractive applications of these materials are as electrodes in solid oxide fuel cells (SOFC). Current electrode materials (nickel-zirconia cermets and strontium-doped manganite) are electronic conductors, and the charge-transfer reactions such as expressed in Eq. (1) are

\[ \frac{1}{2} O_2 \text{(gas)} + 2e^- \text{(electrode)} = O^- \text{(electrolyte)} \]  

restricted geometrically to the intersection lines of the gas, electrode and electrolyte phases. With a mixed-conducting oxide electrode, the charge transfer-reaction, Eq. (1), occurs over the entire electrode surface because both electrons and oxygen ions are mobile in the electrode material. Thus polarization losses at the
electrode-electrolyte interface will be reduced significantly due to the large increase in the charge-transfer reaction area.

There are other major advantages of using mixed-conducting oxide electrodes in SOFC. These materials would eliminate the necessity to fabricate and to maintain the intricate, porous electrode structures in the present cells. Although such electrode structures are necessary to maximize the intersection lines of the gas, electrode and electrolyte phases, it is very difficult to avoid sintering and the associated reduction of the optimum porous electrode structure during cell operation. Secondly, mixed-conducting oxide electrodes which are based on stabilized zirconia should have excellent chemical compatibility and interfacial adhesion with the yttria-stabilized zirconia electrolyte currently used in SOFC. For example, the chemical composition and thermal-expansion coefficients of the mixed-conducting stabilized zirconias described in this paper should be very similar to yttria-stabilized zirconia. Thirdly, mixed-conducting oxide electrodes should exhibit superior sulfur tolerances over the metal cermets currently used as fuel electrodes.

The paper is a summary of the synthesis and electrical characterization of new, mixed-conducting yttria-stabilized zirconia-titania solutions. The concept is to introduce electron-hopping or small polaron conduction into an oxygen-ion conductor such as yttria-stabilized zirconia by dissolution of an oxide such as titania which has a multivalent cation. Our results establish not only the magnitudes of the electronic and oxygen-ion conductivities, but also the optimum compositions in the yttria-stabilized zirconia-titania solutions for mixed-conduction. The results are used to estimate the electrode current densities of these new mixed-conducting oxides in SOFC.

2. PREVIOUS WORK

Some previous researchers also have recognized the advantages of mixed-conducting stabilized zirconias. Transition-metal oxides such as iron oxide, manganese oxide and cobalt oxide were dissolved into stabilized zirconia [1]. However, only small solubilities of these oxides in stabilized zirconia were observed, and the percentage of electronic conductivity was low. More recently, mixed-conducting zirconia-ceria-yttria solutions have been prepared [2]. Significant percentages of electronic conductivity were observed only at very high temperatures (above 1200°C). Furthermore, the mixed conduction was a strong function of temperature and oxygen pressure.

3. SYNTHESIS AND PHASE CHARACTERIZATION

New ternary-oxide solutions containing 10 or 12 mole percent (m/o) yttria-stabilized zirconia containing between 0 and 30 m/o titania have been prepared [3,4]. The starting powders are isostatically cold-pressed and then sintered in air at 1400°C for 12 hours to obtain the cubic-fluorite phase and then sintered at 1600°C for 12
hours to densify and chemically homogenize the oxide solutions. After sintering, the polycrystalline specimens are opaque and pale yellow with a density of 5.18 g/cm³ (88% of the theoretical value). No leakage of helium through the specimens is detected using a Veeco leak detector. The average grain size, determined from scanning electron micrographs (SEM's), is 20 to 40 microns for the 10 m/o yttria-stabilized zirconia-titania solutions and 10 to 20 microns for the 12 m/o yttria solutions.

Figure 1 shows that the lattice parameters for yttria-stabilized zirconia containing no titania are in excellent agreement with previous studies [5,6]. The results also indicate that the single-phase fluorite structure is retained in the 10 and 12 m/o yttria-stabilized zirconia solutions with titania concentrations as high as 12.5 and 15 m/o, respectively. The observed decrease in the lattice parameter with increasing titania concentration is presumably due to the substitutional replacement of zirconia ions with the smaller titanium ions. The 12 m/o yttria-stabilized zirconia has a higher lattice parameter, and the titania solid solubility is less in 10 m/o yttria-stabilized zirconia than in the 12 m/o yttria solution. Although a second phase has been observed in the SEM's of the 20 and 25 m/o titanium solutions, we have been unable to determine its composition using EDAX.

4. ELECTRICAL CHARACTERIZATION

Impedance spectroscopy has been used to determine the electrical conductivity of our polycrystalline oxide solutions. Its major advantage over d.c. conductivity measurements is that one can determine the lattice and grain-boundary contributions to the total electrical conductivity. The impedance spectra have been interpreted in terms of the brick-layer model [7,8] which assumes a well-developed microstructure and uniform grain size. Results have been obtained at temperatures between 350 and 900°C and at oxygen pressure between 0.21 and 10132 atm. The lattice, grain-boundary and total electrical conductivities are independent of oxygen pressure. Our results for the lattice and total electrical conductivities for 12 m/o yttria-stabilized zirconia containing no titania are in excellent agreement with previous results using single-crystals [9,10] and a four probe d.c. technique [10,11]. This agreement indicates the quality of our polycrystalline materials and the reliability of our impedance-spectroscopy data.

The temperature variation of the total electrical conductivity for 10 and 12 m/o yttria-stabilized zirconia containing 0 to 10 m/o titania is shown in Figs. 2 and 3, respectively. The electrical conductivity of 10 and 12 m/o yttria-stabilized zirconia increases with the addition of 5 m/o titania and then decreases for the 7.5 and 10 m/o titania solutions. The initial increase is due to an increase in the grain-boundary conductivity, while the observed decreases at higher titania concentrations reflect the decreases in grain-boundary and lattice conductivities.
The electronic conductivity of 10 and 12 m/o yttria-stabilized zirconia containing 5, 7.5 or 10 m/o titania has been determined at temperatures between 800 and 1000°C using a platinum electrode to block oxygen-ion conductivity. The results shown in Fig. 4 indicate that the electronic conductivity increases significantly with increasing titania concentration. This reflects the increase in the number of electronic charge carriers, i.e. $\mathrm{Ti}^{3+}$, with increasing titania concentration. Figure 4 also indicates that the activation energy of 0.73 (± 0.3) eV is constant for all the yttria-stabilized zirconia-titania solutions.

5. PERCENTAGE OF ELECTRONIC CONDUCTIVITY

The percentage of electronic conductivity has been determined using two approaches. The values have been calculated from the blocking-electrode results by dividing the electronic conductivity shown in Fig. 4 by the total electrical conductivity (Figs. 2 and 3). Electromotive force (Emf) cells with the mixed-conducting oxides as electrolytes have also been used to determine the percentage of electronic conductivity. The measured open-circuit cell voltage is divided by the value which would be observed if the electrolyte exhibited negligible electronic conductivity. Results from the blocking-electrode and Emf-cell measurements are compared in Figs. 5 and 6. There is excellent agreement between the results obtained from the two difficult experimental techniques. The large scatter in the results for the 10 m/o titania composition shown in Fig. 6 is believed due to the high percentage (55 to 89%) of electronic conductivity and the associated difficulty in obtaining steady, consistent Emf values.

The results shown in Figs. 5 and 6 confirm our initial concept that the dissolution of titania into yttria-stabilized zirconia should introduce significant amounts of electronic conductivity. The percentage of electronic conductivity clearly increases with increasing titania concentration, presumably due to electron hopping or small polaron conduction via multivalent titanium cations. The results also show that the percentage of electronic conductivity decreases with increasing temperature. This reflects the fact that the activation energy (0.90 eV) for oxygen-ion conductivity at temperatures above 700°C is higher than that for electronic conductivity (0.73 eV). Thus increasing temperature has a larger effect on the oxygen-ion conductivity.

6. EVALUATION OF ELECTRODE CURRENT DENSITIES

For a given total electrical conductivity, the optimum composition for a mixed-conducting electrode is that at which the transference numbers or percentages of electronic and oxygen-ion conductivity are equal. If they are not equal, the species with the lowest percentage will control the transport of electrons and oxygen ions through the mixed conductor. The titania compositions at which the electronic conductivity equals the oxygen-ion conductivity are shown in Table I for the 10 m/o yttria-stabilized zirconia-titania solutions.
solutions. The resistivity of these optimum compositions is also tabulated.

The resistivities ($\rho$) shown in Table I are used to estimate electrode current densities for mixed-conducting 10 m/o yttria-stabilized zirconia-titania solutions. The oxygen-pressure gradients across the electrodes currently used in SOFC vary from $10^0$ to $10^7$. We have assumed an oxygen-pressure gradient of 100 to calculate values for the potential ($E$) across the mixed-conducting electrode and the current density ($i$). The calculated current densities tabulated in Table II vary from 223 to $9,621 \text{ mA/cm}^2$ depending upon temperature and electrode thickness. These values indicate that mixed-conducting yttria-stabilized zirconia-titania solutions should have attractive electrode applications in SOFC.

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TABLE I

Titania composition and resistivity when the percentage of electronic conductivity equals the oxygen-ion conductivity for 10 m/o yttria-stabilized zirconia-titania solutions.

| Temperature (°C) | Titania (Mole%) | Resistivity (ohm-cm) |
|------------------|----------------|----------------------|
| 800              | 7.4            | 120                  |
| 900              | 8.3            | 63                   |
| 1000             | 9.3            | 33                   |

TABLE II

Variation of the calculated electrode thickness (t) for zirconia-titania electrodes with temperature and mixed-conducting 10 m/o yttria-stabilized zirconia-titania electrodes.

| T (°C) | t (microns) | p·t (ohm-cm²) | E (mV) | i (mA/cm²) |
|--------|-------------|----------------|--------|------------|
| 1000   | 10          | \(3.3 \times 10^{-2}\) | 127    | 962        |
|        | 5           | \(1.7 \times 10^{-2}\) | "     | 1,868      |
|        | 1           | \(3.3 \times 10^{-3}\) | "     | 9,621      |
| 900    | 10          | \(6.3 \times 10^{-2}\) | 117    | 464        |
|        | 5           | \(3.2 \times 10^{-2}\) | "     | 914        |
|        | 1           | \(6.3 \times 10^{-3}\) | "     | 4,643      |
| 800    | 10          | \(12 \times 10^{-2}\) | 107    | 223        |
|        | 5           | \(6 \times 10^{-2}\)   | "     | 446        |
|        | 1           | \(1.2 \times 10^{-2}\) | "     | 2,229      |
Fig. 1 Variation of the lattice parameter with titania concentration in 10 and 12 mole % yttria-stabilized zirconia.

Fig. 2 Variation of the total electrical conductivity with temperature for polycrystalline 10 mole % yttria-stabilized zirconia containing 0 to 10 mole % titania.
Fig. 3 Variation of the total electrical conductivity with temperature for polycrystalline 12 mole % yttria-stabilized zirconia containing 0 to 10 mole % titania.

Fig. 4 Temperature variation of the electronic conductivity for 10 and 12 mole % yttria-stabilized zirconia containing 5, 7.5 or 10 mole % titania.
Fig. 5 Temperature variation of the percentage of electronic conductivity in 10 mole % yttria-stabilized zirconia containing 5, 7.5 or 10 mole % titania.

Fig. 6 Temperature variation of the percentage of electronic conductivity in 12 mole % yttria-stabilized zirconia containing 5, 7.5 or 10 mole % titania.