INFLUENCE OF POWDERS ON IONIC CONDUCTIVITY OF POLYCRYSTALLINE ZIRCONIAS

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ABSTRACT

Grain boundary resistivity in zirconia systems can significantly affect total conductivity below 800°C. The influence of starting powders on the total conductivity is investigated for the 8 mol% yttria-stabilized zirconia polycrystals prepared from powders synthesized by three different methods and from two commercial powders. Conductivity measurements by AC impedance spectroscopy show a factor of two differences between the lowest and highest values because of the grain boundary resistivity. The contribution of grain boundary resistivity can be more than 10% at the temperatures less than 800°C. The total grain boundary resistivity is reduced drastically and the total conductivity can be improved by as much as 50% when the sintering temperature is increased or the powder particle size is reduced. Similar results are obtained for the higher conductivity electrolyte prepared from 9 mol% scandia-stabilized zirconia.

INTRODUCTION

Reduction of the operating temperature of solid oxide fuel cells (SOFCs) has been pursued by several developers in order to lower stack fabrication costs by allowing for the use of inexpensive metal components for interconnect, heat exchangers, and structural components (1). The preferred temperature range is between 600 and 800°C, as opposed to the conventional operating temperature of 900-1000°C. Yttria stabilized zirconia (YSZ) is the most common material used as the oxygen ion conductor for SOFCs because of its thermal and chemical compatibility and its purely ionic conductivity over a wide range of conditions. As the temperature is lowered, problems with ionic conductors arise because the conductivity decreases exponentially with decreasing temperature. Accordingly, higher conductivity materials, such as scandia-stabilized zirconia (SSZ), and supported thin film electrolytes, are needed as the cell temperature is lowered (2). Still, the grain boundary resistivity of the polycrystalline electrolytes can contribute significantly to the total conductivity at the intermediate temperatures. From an economic point of view, ceramic powder processes for SOFC fabrication can be expected to be preferable to other methods, such as chemical vapor deposition (CVD). In this work, the influence of various starting powders on the conductivity of sintered 8 mol% yttria stabilized zirconia (8YSZ) and 9 mol% Scandia-stabilized zirconia (9SSZ) polycrystalline electrolytes is investigated. The powders were either synthesized by the...
Pechini (3-6), co-precipitation (7, 8) or glycine-nitrate (GN) (9) methods, or purchased from commercial suppliers.

EXPERIMENTAL

Powder and Pellet Preparation

8YSZ powders were synthesized using Pechini, co-precipitation, and GN methods. Zirconium oxynitrate (ZrO(NO$_3$)$_2$·xH$_2$O) and yttrium nitrate (Y(NO$_3$)$_3$·6H$_2$O) were dissolved in distilled water. This solution was used for the following syntheses. In the Pechini method, citric acid (CA) and ethylene glycol (EG) were added to the solution in a CA:EG:cation ratio of 4:20:1. The co-precipitation was carried out by adding dropwise the solution to 30% ammonium hydroxide solution. In the GN method, glycine was added to the solution in glycine/nitrate (G/N) ratios of 0.5 and 1.0. The powders were calcined at 1000°C or 1100°C for 4 h and then attritor-milled using YSZ balls (0.3 mm) in isopropyl alcohol, at 550 rpm, for 1 h (one powder was milled for 5 h 20 min). The calcined powders were used for XRD analyses. The milled powders and two commercial 8YSZ powders (PSZ-13.5Y-HW from Stanford Materials Co. and TZ-8Y from Tosoh Corp.) were uniaxially pressed and sintered at 1500°C or at 1600°C, for 4h, to make pellets (9 mm in diameter and 4 mm in thickness). Gold blocking electrodes applied on both sides of the sintered pellets were for AC conductivity measurements. 9 SSZ powders and pellets were also synthesized by the Pechini method with Scandium nitrate (Sc(NO$_3$)$_3$·xH$_2$O) following the same procedures as for the 8YSZ.

Characterization

XRD measurements were performed using a diffractometer (Siemens D-500) with CuK$_\alpha$ radiation in the range 20 = 10-80°. The AC conductivity was measured with a four-probe method using a frequency response analyzer (Solartron FRA-1260) over a frequency range 1 to 10$^7$ Hz with an applied potential of 50 mV. The measurements were done between 350 to 850°C, in air.

RESULTS

The crystalline phases were determined from the XRD spectra. The Pechini and co-precipitation powders did not show the monoclinic phase; the GN powder included a small amount of the monoclinic phase, depending on the G/N ratio as shown in Figure 1. Temperature variations due to the inhomogeneous combustion in the GN synthesis may have caused inhomogeneity of composition leading to the phase impurity of products. The particle sizes of milled powders were determined by light scattering spectroscopy. Pechini, co-precipitation, and GN powders milled for 1 h were 0.7, 0.8 and 0.2 μm in diameter, respectively, while the Pechini powder milled for 5 h 20 m was 0.5 μm in diameter.

The conductivity of 8YSZ was evaluated for specimens prepared from the various powders by AC impedance spectroscopy. The results are listed in Table 1, together with the sintered densities, and plotted in Figure 2. The conductivity of 8YSZ can
Figure 1. XRD patterns for 8YSZ powders synthesized by different methods. The powders were calcined at the indicated temperatures for 4 hours.

differ by as much as a factor of two depending on the preparation method. These differences arise not only from the difference in density, but also from the contribution of the grain boundary resistivity, as shown in Figure 3. The Cole-Cole plots for the synthesized powders show two clear semi-circles, and these can be assigned to grain interior impedance (at higher frequency) and grain boundary impedance (at lower frequency) (10-12). The synthesized powders show comparable grain boundary resistivity to grain interior resistivity at 350°C, whereas the commercial powders tested do not show such large contribution. The grain boundary resistivity decreases sharply with temperature compared to the grain interior resistivity, as shown in Figure 4. The ratio of the grain boundary resistivity to the total resistivity is examined as a function of temperature in Figure 5. It is clear that for the synthesized powders the grain boundary resistivity constitutes more than 10% of total resistivity in the intermediate temperature range of 600 to 800°C. The specimens were sintered at 1500°C for 4 h, and the starting powders synthesized were milled for 1 h unless noted otherwise. The commercial powders were not milled.
Table 1. Ionic conductivity of 8YSZ and 9SSZ polycrystals measured by AC impedance in air (S cm\(^{-1}\)).

| Temperature (°C) | 600   | 650   | 700   | 750   | 800   | 850   | d (g/cm³) |
|-----------------|-------|-------|-------|-------|-------|-------|-----------|
| 8 YSZ Pechini   | 0.0020| 0.0042| 0.0081| 0.0145| 0.0242| 0.0383| 5.44      |
| 8 YSZ co-precipitate | 0.0024| 0.0048| 0.0089| 0.0152| 0.0242| 0.0384| 5.02      |
| 8 YSZ glycine-nitrate | 0.0035| 0.0068| 0.0134| 0.0224| 0.0385| 0.0584| 5.50      |
| 8 YSZ Pechini sintered at 1600°C | 0.0030| 0.0057| 0.0124| 0.0224| 0.0385| 0.0550| 5.49      |
| 8 YSZ Pechini doping 2 mol% Al₂O₃ | 0.0226| 0.0093| 0.0098| 0.0171| 0.0271| 0.0407|           |
| 8 YSZ Pechini milled for 320 m and sintered at 1600°C | 0.0031| 0.0065| 0.0126| 0.0219| 0.0349| 0.0521| 5.83      |
| PSZ-13.5Y-HW     | 0.0061| 0.0114| 0.0205| 0.0338| 0.0506| 0.0734| 5.83      |
| TZ-8Y            | 0.0038| 0.0075| 0.0141| 0.0242| 0.0380| 0.0585| 5.50      |
| 9 ScSZ Pechini   | 0.0064| 0.0136| 0.0258| 0.0449| 0.0723| 0.1084| 5.28      |
| 9 ScSZ Pechini sintered at 1600°C | 0.0099| 0.0204| 0.0372| 0.0820| 0.0937| 0.1393| 5.10      |

Figure 2. Arrhenius plots of ionic conductivity of 8YSZ polycrystals measured by AC impedance in air.
Figure 3. Cole-Cole plots for 8YSZ polycrystalline electrolytes at 350°C in air.
Figure 4. Arrhenius plots of total, grain interior (gi), and grain boundary (gb) resistivity for 8YSZ polycrystalline electrolyte prepared from Pechini powder.

Figure 5. Temperature dependence of the ratios of grain boundary/total resistivity for 8YSZ polycrystalline electrolytes.
The Pechini powder, which led to the largest grain boundary contribution, was further investigated for reducing the grain boundary resistivity. Increasing the sintering temperature, reducing the particle size, and alumina doping were examined. Figure 6 shows that the second semi-circles contracted as a result of the treatments, especially increasing the sintering temperature to 1600°C and reducing the particle size to bring about considerable reduction in grain boundary resistivity. As a result, the conductivity is improved by as much as 50% (see the series of 8YSZ Pechini specimens in Table 1).

The conductivity of 9 SSZ was also examined using the specimens prepared from the Pechini powder. The conductivity is higher than any of the 8YSZ specimens shown in Table 1, though this 9 SSZ specimen has a relatively large grain boundary resistivity as suggested by Figure 7. Sintering at 1600°C improves the conductivity by 23-54% between 600 and 850°C. Consequently, zirconia ionic conductors can have significant grain boundary resistivity below 800°C, depending on the sintering conditions and the powder particle size.

Figure 6. Cole-Cole plots for 8YSZ polycrystalline electrolytes prepared from Pechini powders, measured at 350°C in air. The specimens were sintered at 1500°C for 4 h, and the starting powders synthesized were milled for 1 h unless noted otherwise.
SUMMARY

Oxygen ion conductivity was determined for 8YSZ polycrystalline electrolytes prepared from the powders synthesized by different methods; Pechini, co-precipitation, and glicine-nitrate (GN), and for commercial powders. The calcined GN powders were found to contain a small amount of the monoclinic phase, depending on the G/N ratio. The conductivity of the 8YSZ measured by AC impedance spectroscopy showed a factor of two differences between the lowest and highest values due to grain boundary contribution to the total resistivity. The contribution is more than 10% of the total for some powders at the temperatures 600-800°C. The grain boundary resistivity was drastically reduced by increasing the sintering temperature or reducing the powder particle size. As a result, the total conductivity was improved by as much as 50%. The 9SSZ polycrystals prepared from the powders synthesized by the Pechini method also showed a similar response. For the intermediate temperature SOFCs, it is suggested that the grain boundary contribution to the conductivity can becomes significant if the sintering condition or the powder particle size are not appropriate.

ACKNOWLEDGEMENTS

This work was supported by the U. S. Department of Energy, through the National Energy Technology Laboratory, under contract No. DE-AC03-76SF00098. Keiji Yamahara is also grateful for support from Mitsubishi Chemical Corporation.
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