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Development of zirconia–magnesia/zirconia–yttria composite solid electrolytes

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Abstract

Composite solid electrolytes were prepared by thoroughly mixing ZrO_2:8 mol% MgO (Z8Mg) and ZrO_2:3 mol% Y_2O_3 (Z3Y) ceramic powders followed by pressing and sintering at 1500 °C/1 h. The properties of the sintered pellets were studied by X-ray diffraction for evaluation of the structural phases by the Rietveld method, by high-temperature dilatometry for analysis of the thermal shrinkage/expansion behavior, and by impedance spectroscopy for determination of the oxide ion conductivity. The x(Z8Mg)+(1−x)(Z3Y) specimens, x=0.2, 0.4, 0.5, 0.6, 0.8 and 1.0, are partially stabilized (monoclinic, cubic and tetragonal phases) with density >94% of the theoretical density and show thermal shock resistance and electrical conductivity values suitable for high-temperature oxygen gas detection. One-end closed tube samples of the composite solid electrolytes were assembled in Pt/Z8Mg+Z3Y/Cr+Cr_2O_3/Pt electrochemical cells for exposure to different levels of oxygen in the 1–850 ppm range. The total electrical conductivity increases for increasing the relative Z3Y content. Addition of Z3Y to Z8Mg (80 wt.%–20 wt.%) suppresses the electronic contribution to the electrical conductivity at 620 °C.
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Keywords: Oxygen sensor; Composite material; Impedance spectroscopy; Rietveld analysis

1. Introduction

The fabrication of steel, mainly those for high technology applications, requires the knowledge of the level of oxygen dissolved during steel production, a process control carried out at temperatures higher than 1600 °C [1–4]. It is important that the oxygen content be measured before and after deoxidant addition to the melt [1]. Oxygen sensors based on the oxygen ion conducting stabilized-zirconia ceramic solid electrolytes operating in the potentiometric mode have been used in the analysis and control of oxygen content in a wide variety of situations [2]. Ceramic solid electrolytes find their use here in harsh environments due to their electrical response, high melting point and chemical inertness. For industrial processes that require the measurement of low oxygen potentials (<200 ppm) at high-temperatures, the electronic conduction of magnesia-partially stabilized zirconia (Mg-PSZ) electrolyte introduces error in the emf values [2]. The main reason for using Mg-PSZ solid electrolytes in commercial oxygen sensors, besides their high emf signal, is their high thermal shock resistance. One attempt to decrease the electronic conductivity of a Mg-PSZ sensor was done by coating the Mg-PSZ tubular sensor with a thin yttria-fully stabilized zirconia layer. The double layer tube showed much lower electronic conductivity while maintaining satisfactory thermal chock resistance [2,5].

In this article we describe the development of composite solid electrolytes, made from Z8Mg (ZrO_2:8 mol% MgO, Mg-PSZ) and Z3Y (ZrO_2:3 mol% Y_2O_3, Y-TZP). We actually preferred to use Z3Y instead of fully stabilized cubic Z8Y, because the former has higher thermal shock resistance than the latter. Moreover, even though the ionic conductivity of the tetragonal Z3Y is lower than that of the cubic Z8Y, its ionic conductivity is larger than that of Z8Mg. The electrical characterization of the sintered pellets was performed by the impedance spectroscopy technique [6] at 430 °C. At this

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temperature, the blocking of oxygen vacancies at grain boundaries is pronounced and both bulk and grain boundary semicircles are detected. Moreover, the evaluation of the electrical resistivity of the composites exposed to different levels of oxygen was done at 620 °C. The blocking of charge carriers is negligible at that temperature, which is the minimum temperature for oxygen detection.

2. Experimental

Z8Mg+Z3Y ceramic pellets were prepared by mixing ZrO_2:8 mol% MgO (Zirconia Sales, USA) and ZrO_2:3 mol% Y_2O_3 (Tosoh, Japan) powders with different relative amounts, pressing at 50 MPa and sintering at 1500 °C for 1 h. The phase content was analyzed by X-ray diffraction (Bruker-AXS D8 Advance, Cu-k_α radiation, 40 kV–40 mA) using the Rietveld method with the software GSAS [7]. Cerium oxide (Alfa Aesar, USA) was used as the instrument standard [8]. Crystallographic data were collected in ICSD files 89426, 88022 and 89429 for the monoclinic, tetragonal and cubic phases of zirconia, respectively. The linear shrinkage/expansion measurements were carried out in a dilatometer (Netzsch DIL 402 ES/3/E).

One-end closed tubular samples composed of Z8Mg+Z3Y were also prepared. The powders were mixed with different relative amounts, cold-pressed (8 mm diameter, 20 mm length) and pre-sintered at 800 °C for 1 h for machine drilling a 3.5 mm diameter, 17 mm deep hole) before sintering at 1500 °C for 1 h. Cr_2O_3+Cr (10:90 wt.%) powder tightly packed inside the cylinder was used as reference electrode with Ni–Cr wire terminal leads, hereafter called Pt/Z8Mg+Z3Y/Cr_2O_3+Cr/Pt electrochemical cell.

The impedance spectroscopy data were collected on a HP 4192A impedance analyzer (100 mV signal, 5 Hz–13 MHz frequency range) in both ceramic pellets (in air) and tubular solid electrolytes (inserted in a furnace connected to a p_{O2} station [9]). Silver paste was used as electrode for the pellets and platinum paste (Demetron 308A, Degussa, France) for partially coating the internal and external cylindrical surfaces of the tubular specimens.

3. Results and discussion

Table 1 shows the monoclinic, tetragonal and cubic phase contents of the sintered x wt.% Z8Mg+(100−x) wt.% Z3Y pellets, x=0, 20, 40, 50, 60, 80 and 100. These values were determined by Rietveld analysis of the X-ray diffraction data. The hydrostatic densities are also shown. All pellets have densities higher than 94% of the theoretical density, determined according to the Rietveld data. The zirconia–yttria specimen is fully tetragonal while all other specimens have different contents of monoclinic, tetragonal and cubic structural phases.

Table 1
Percent values of the monoclinic (m), tetragonal (t) and cubic (c) phase contents, density and the percent of the theoretical density of the x wt.% ZrO_2:8 mol% MgO+(100−x) wt.% ZrO_2:3 mol% Y_2O_3 sintered pellets

X	%m/%t/%c	Density (g/cm^3) hydrostatic/Rietveld	%T.D.
0	0/100/0	6.04/6.06	99.7
20	31.7/43.3/25.0	5.89/5.99	98.3
40	52.0/18.2/29.8	5.79/5.95	97.3
50	53.1/15.1/31.8	5.76/5.96	96.6
60	47.0/12.1/41.0	5.75/6.00	95.8
80	43.0/10.0/46.8	5.74/6.03	95.2
100	44.4/11.8/43.8	5.69/6.05	94.0

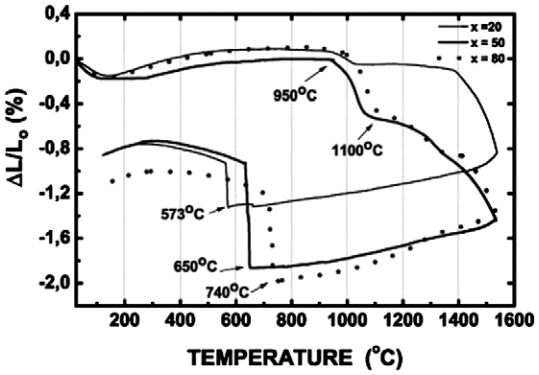

Fig. 1. Linear shrinkage of the x wt.% ZrO_2:8 mol% MgO+(100−x) wt.% ZrO_2:3 mol% Y_2O_3 sintered pellets, x=20, 50 and 80.

The partially stabilized zirconia presents lower thermal expansion coefficient (TEC) than the cubic or tetragonal stabilized zirconia, contributing to the better thermal shock resistance than that of fully tetragonal zirconia [10]. The low TEC is achieved by decreasing, upon heating, the volume change associated with the monoclinic-tetragonal phase change [10,11].

The linear shrinkage/expansion behavior measurements of the x wt.% Z8Mg+(100−x) wt.% Z3Y sintered pellets, x=20, 50 and 80, are shown in Fig. 1. The x=20 composition shows the lowest volume variation, approximately 0.1%, related to the monoclinic-tetragonal crystallographic transformation [10,12,13] in the 930–1030 °C range. During cooling, hysteresis occurs due to the cubic/tetragonal phase transformation. The dilatometric variations detected upon heating and cooling are similar to the variations found in commercial high-temperature oxygen sensors [11], allowing for emf signal detection before disruption of the electrochemical sensors. The composition with the minimum dilatometric variation is the one with the best thermal shock performance. This is advantageous for designing high-temperature oxygen sensors.

Fig. 2 shows impedance spectroscopy diagrams, measured at 430 °C, of the sintered x wt.% Z8Mg+(100−x) wt.% Z3Y pellets with x=0, 20, 50 and 100. The total resistivity, determined at the intersection of the impedance diagram with the real axis in the low frequency region, increases for increasing Z8Mg content. Hence, the addition of zirconia:3 mol% yttria improves the total conductivity of the composite. This is important because the better the electrical conductivity is, the larger is the signal response to oxygen. Consequently, lower values of oxygen levels could be detected.

The dependence of the dc resistivity on the oxygen level of the electrochemical cell with tubular electrolytes (x wt.% Z8Mg+(100−x) wt.% Z3Y, x=0, 20, 50 and 100) is shown in Fig. 3. The

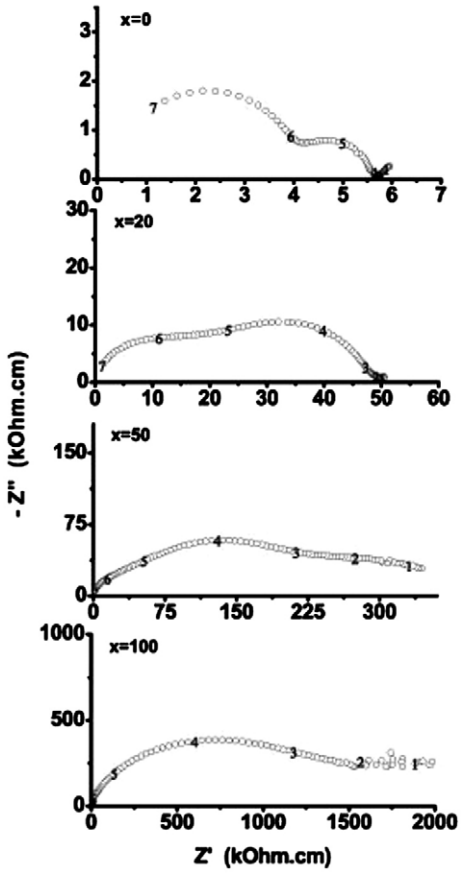

Fig. 2. Impedance spectroscopy diagrams of the x wt.% ZrO_2:8 mol% MgO+(100−x) wt.% ZrO_2:3 mol% Y_2O_3 solid electrolytes, measured in the frequency range 5 Hz–13 MHz at 430 °C for x=0, 20, 50 and 100. The numbers stand for the logarithm of frequency (Hz).

impedance spectroscopy measurements were performed at 620 °C. At that temperature there is no blocking of charge carriers at grain boundaries, being consequently the lowest operation temperature of commercial oxygen sensors. The specimens with x=0 and 20 have the widest ionic conduction domain, namely, they behave as pure ionic conductors, while the other compositions show an electronic component at low oxygen levels. For low partial pressure of oxygen (<100 ppm) the addition of ZrO_2: 3 mol% Y_2O_3 to ZrO_2:8 mol% MgO (80 wt.%–20 wt.%) promotes a 85% increase of the electrical response for exposure to 1 ppm oxygen and 78% to 97 ppm.

4. Conclusions

An improvement of the electrical response at 620 °C to low levels of oxygen by solid electrolytes has been achieved using composite solid electrolytes prepared with 80 wt.% ZrO_2:3 mol% Y_2O_3 and 20 wt.% ZrO_2:8 mol% MgO. The impedance spectroscopy measurements at 620 °C as a function of oxygen show that the electronic conductivity is absent in that composition. Besides the enhanced electrical response, the thermal shock behavior is similar to that measured in ZrO_2-8 mol% MgO solid electrolytes used in commercial sensors.

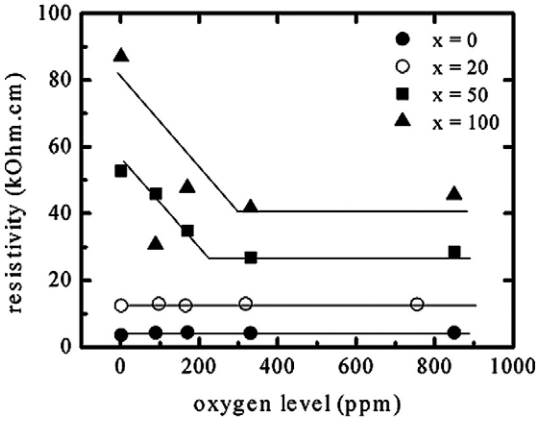

Fig. 3. Total electrical resistivity of the x wt.% ZrO_2:8 mol% MgO+(100−x) wt.% ZrO_2:3 mol% Y_2O_3 ceramic solid electrolytes, x=0, 20, 50 and 100, as a function of the partial pressure of oxygen at 620 °C.

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