

Conductivity measurements at low oxygen partial pressure of the stabilized ZrO₂ ceramics prepared by SHS

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Abstract

The ionic conductivity of cubic solid solutions in the system Y₂O₃-ZrO₂ prepared by SHS was examined. Conductivity-temperature data obtained at 1000 °C in atmosphere of low oxygen partial pressure (10⁻⁴⁰ atm) for Y₂O₃-ZrO₂ cubic solid solutions indicated that these materials could be reduced, the degree of reduction being related to the measuring electric field. At low impressed fields no reduction was observed. Thus, these conductivity data give a transference number for the oxygen ion in Y₂O₃-ZrO₂ cubic solid solutions greater than 0.99.

Key Words: Self-propagating High-temperature Synthesis, low oxygen pressure, Y₂O₃-ZrO₂

1. Introduction

Oxide ionic conductors are very important functional materials for the application in oxygen sensors, solid oxide fuel cells, and so forth. In practice, materials with high oxide ion conduction can be obtained by introducing extrinsic oxide ion vacancies into some fluorite- or perovskite-type oxides. It is well known that the fluorite structured oxide consisting of tetra valent cations exhibits good oxide ion conductivity and Zr-based oxides are generally used as the oxide ionic conductor. However, zirconium dioxide has a melting point of 2700 °C and transforms from the monoclinic to the tetragonal form at about 1100 °C with a large, disruptive volume change. This unstable phase transformation can be eliminated by stabilization of the cubic phase with an addition of a selected alkaline earth or rare-earth oxide. For example, fast oxide ion conductors are obtained by substituting fluorite-type ZrO₂ with an optimal amount of di- or tri valent cations such as Ca²⁺ or Y³⁺ [1]. These stabilized ZrO₂-base solid solutions possess rather unique electrical properties, and as a result

have considerable potential as solid electrolytes in galvanic and fuel cells and, possibly, as heating elements in high-temperature furnaces.

Self-propagating high-temperature synthesis (SHS) has been the subject of many analytical and experimental investigations because of its potential for the synthesis of solid materials [2]. Demonstrated advantages of SHS include higher purity of the products, low energy requirements, and the relative simplicity of the process. Because of large temperature gradients and extremely high heating and cooling rates experienced by the materials during combustion, high defect concentrations and nonequilibrium phases are likely to be present in the products. The existence of high concentrations of defects gives rise to expectations of more "reactive" products, although the investigations [3] have shown that the differences in sinterability between combustion-synthesized and conventionally prepared titanium carbide and titanium diboride are either insignificant or are more complex in nature than the suggested general expectation. In the present work effects of the addition of di- or tri valent cations for Zr dioxide upon oxide ionic conductivity were investigated for compounds prepared by SHS. Based on the observed conductivity, the factors that influence its magnitude in these oxides have been clarified.

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2. Experimental Part

Y_2O_3 - ZrO_2 (YZ) composition was prepared by SHS method from a mixture of solid powders (Zr (Aldrich, 99.9+ %), Y_2O_3 (Johnson Matthey, 99.99%), ZrO_2 (Aldrich, 99.9%) and $NaClO_4$ (Johnson Matthey, ACS)) pressed to 50-60 % of the theoretical density. Ignition was initiated by electrical heating of a chemical match of $Al_2O_3 + Ti + BaO_2$. The combustion was conducted in air and with an internal oxygen supply from $NaClO_4$. A detailed synthesis procedure is described in [4]. The combustion temperatures were measured using an optical pyrometer (Promin-M1) and B-type (Pt30%Rh-Pt6%Rh) thermocouple, which was more suitable than tungsten one due to the highly oxidizing environment. The phase composition and morphology of the samples were analyzed by X-ray diffraction (XRD) (DRON 3M spectrometer using Ni filtered CuK radiation), scanning electron microscope (SEM, type JSM-35 C). Element distribution information inside the specimens was examined by an electron probe microanalysis (EPMA) (JEOL, JXA/8600) on the specimens polished and coated with carbon. Then SHS product powder was pressed into cylindrical specimens which were sintered at 1750 °C for 3 hours in an oxygen-propane furnace. Specimen densities were calculated from weight and geometric measurements and the apparent densities of all specimens were in the range 90 to 95 % of theoretical density. Electrodes were applied to the circular faces of the specimens by spraying on a platinum-organic mixture and heating the coated specimens at 1100 °C for 1 hour. The specimen was cut and polished to form a rectangular bar (3 x 3 x 11 mm), placed in a ceramic sample holder, and mounted in a programmable furnace. Specimens were heated in a platinum-wound tube furnace to various temperature levels up to (1000-1300) °C. The electrical conductivity was measured as a function of temperature and oxygen partial pressure ($1 \cdot 10^{-40}$ atm) using the conventional DC four-probe method. The potential drop between two potential probes was measured using a digital multimeter. The electrical conductivity were measured isothermally, $P(O_2)$ was controlled by flow of O_2 , air, or Ar.

3. Results

a) SHS synthesis of stabilized Zr dioxide

The highly exothermic reaction of powders raised the temperature to 1400 °C. White smoke was generated during the combustion and pellet turned into a porous cake due to a partial melting in the pellet center (Fig. 1. a).

The combustion wave propagated at a velocity of about 1 mm/s. This produced a solid which was ground in a pestle and mortar, washed with distilled water (3 x 200 ml) filtered through a Buchner funnel and dried in air at 80 °C for 4 h. Yields were essentially quantitative. No traces of NaCl were detected by XRD and electron probe microanalysis in the combusted samples, indicating that it evaporated during the combustion due to the high reaction temperature. In present work we used pre-heating the green pellet (Fig. 1. b), which enhanced the homogenization of the product. It was found two effects. (1) it increases the combustion temperature T_c ; (2) it prolongs the exposure time of the combusted sample to high temperatures. Both effects increase the homogeneity of the product.

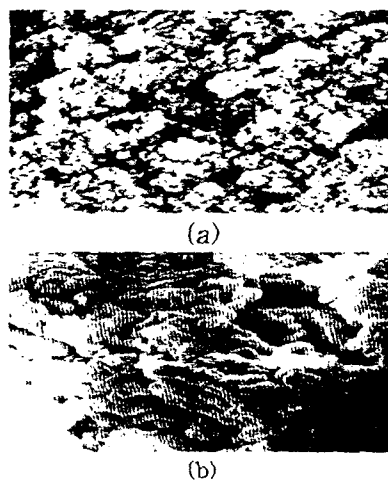


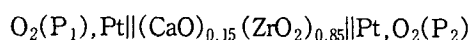
Fig.1. Scanning electron microscopy (SEM) photomicrograph of fracture surface of SHS-sintered YZ specimen without pre-heating (a); with pre-heating (b)

The pre-heating temperature to 500 °C increased T_c almost 200 °C higher than that of the sample ignited at room temperature. The wave propagation velocity through the pre-heated pellet was about 2-3 times faster than in the sample that was not pre-heated. The higher combustion temperature increased the fraction of the pellet that melted. The microstructure of the product was similar to that of the unheated sample, but with larger and more uniform spherical particles. The product density was higher than that of the sample without pre-heating.

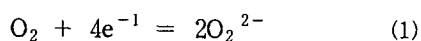
b) Electrical conductivity

The electrolyte characteristic of oxide solutions of this compound type was first observed by Nernst,

who detected the electrolytic evolution of oxygen from a specimen of composition $(Y_2O_3)_{0.15}(ZrO_2)_{0.85}$. Well-known Wagner's postulates reported that oxide solid solutions of the type $(CaO)_x(ZrO_2)_{1-x}$ or $(Y_2O_3)_x(ZrO_2)_{1-x}$ are defect solid solutions. The defects being oxygen vacancies created to preserve lattice neutrality when either Ca^{2+} or Y^{3+} ions are substituted for Zr^{4+} ions in the fluorite type structure. He suggested that these oxygen vacancies should give rise to high oxygen ion mobilities. In [5] have shown that the transference number for the oxygen ion in $(CaO)_{0.15}(ZrO_2)_{0.85}$ is near unity. Using a vacuum-tight single cell they confirmed that the type



have shown that the electrode reactions at temperatures above 600 °C correspond closely to the reversible reaction



and the voltage obtained was in good agreement with the theoretical emf calculated from thermodynamic relations.

Since the prime conducting species in these oxides is the oxygen ion, a reasonable estimate of the oxygen ion transfer number might be obtained by measuring the decrease in DC conductivity of a specimen as the surrounding atmosphere is depleted of oxygen. The removal of oxygen from the surrounding atmosphere reduces the anionic conduction by elimination of the conducting species. The residual conductivity can then be attributed almost wholly to electronic and/or cationic conduction. Thus, the approximate transference number for the oxygen ion would be

$$t_0^{2-} \cong (\sigma_0 - \sigma_t) / \sigma_0 \quad (2)$$

where σ_0 is the specimen conductivity in air and σ_t is the conductivity in an oxygen-depleted atmosphere. The oxygen depletion can be achieved by use of a vacuum or by flowing an inert gas over the specimen. Argon gas (99.9% purity) was passed through a dry ice-acetone cold trap, over titanium metal heated to 700 °C, and into a tube furnace at 1000 °C which contained the specimen to be measured. Since the free energies of TiO, TiO₃, and TiO₂¹⁸ at 700 °C are of the same order of magnitude, this system would give an oxygen partial pressure of about 10⁻⁴⁰ atm regardless of the extent of oxidation of the titanium.

c) Conductivity measurements at low oxygen partial pressure

Passing a constant current through the specimen and measuring the resistance with a bridge-type circuit made conductivity measurements. A specimen of composition $(Y_2O_3)_{0.09}(ZrO_2)_{0.91}$ (stable cubic solid-solution) was tested at constant current levels of 0.50, 0.75, 1.0 and 10 mA dc. To eliminate thermoelectric effects, two measurements were made at each current level with the polarity being reversed in the second measurement. The specimen was reoxidized in air for 5 to 10 minutes at 1000 °C after each test run. In each case, the original resistance value (12 Ohms) was obtained.

The resistance-versus-time data at the various current levels are plotted in Fig. 2. Note that at currents of 0.75 mA or larger, the specimen resistance reaches a relatively constant value after a period of 1 hour, whereas at 0.5 mA the resistance is still increasing. Extending the measurement period to 3 hours showed a continuously increasing resistance for a test current of 0.5 mA but a definite leveling of resistance for test currents of 0.75 mA or larger. The higher conductivities obtained with the larger currents are believed to be caused by reduction of Zr^{4+} to Zr^{3+} , which would give rise to a mixed valence conduction mode. The oxidation potentials of Y^{3+} and Zr^{4+} indicate that Zr^{4+} would be more easily reduced than Y^{3+} .

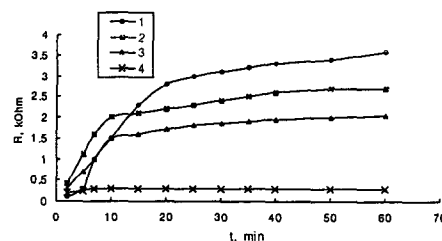


Fig.2. Resistance vs time at 1000 °C for a pellet specimen (size 1.2 cm high, 1.2 cm diameter) of composition $(Y_2O_3)_{0.09}(ZrO_2)_{0.91}$ at a low partial pressure of oxygen. Numbers above curve indicate direct current in milliamperes; curve 1 - 0.5mA, curve 2 - 0.75mA, curve 3 - 1.0mA, curve 4 - 10mA.

The data presented in Fig.2 were interpreted as follows. Partial reduction of the specimen occurred in those tests which exhibited a resistance leveling and the degree of reduction in some manner associated with the impressed voltage which increases with increasing resistance to maintain a constant current level. The threshold voltage for reduction appears to be about 2.0 V. Thus, the resistance-time data for a constant current of 0.5

mA represents the case of negligible reduction. These data also suggest that the specimen had not attained equilibrium with surrounding atmosphere, since a static resistance level was not observed after a 4-hour test. However, a conservative estimate of the transference number for the oxygen ion can be obtained from the original specimen resistance (12 Ohms) and the specimen resistance after a 1-hour test period (3600 Ohms). Using these values and equation (2) gives an oxygen ion transference number ($t_{O^{2-}}$) greater than 0.99.

If reduction occurs in the high-current tests, it will manifest itself as both a weight loss and a change in specimen color. To have specimens show these changes, several specimens were subjected to extreme reducing conditions of 50 mA in a depleted-oxygen atmosphere for a period of 2 hours. After this test, specimens were gray and on reoxidation exhibited a weight gain of approximately 0.2%. This is too great a weight loss to be attributed to reduction of impurities in the specimens and consequently must represent reduction of Zr^{4+} to Zr^{3+} .

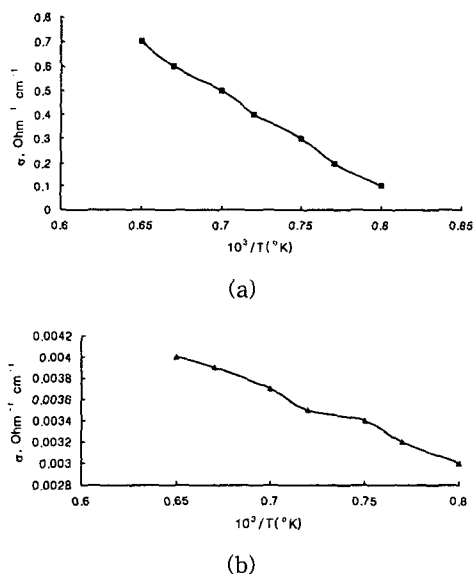


Fig.3. Conductivity vs. reciprocal temperature for 10 mA dc measurements in a low partial pressure of oxygen for a specimen of composition $(Y_2O_3)_{0.09}(ZrO_2)_{0.91}$ (a, $E=0.32$ eV), and ac measurements in air (b, $E=0.79$ eV)

Conductivity-temperature measurements were made in an inert atmosphere on a specimen, which had attained a constant conductivity level after subjected to a direct current of 10 mA for a period of 2 hours. These data are shown in Fig.

3.a along with the conductivity-temperature data obtained for the same specimen in air (Fig. 3.b).

The change in activation energy from 0.79 to 0.32 eV gives additional evidence for the presence of a different conduction mode.

4. Conclusion

The ionic conductivity of cubic solid solutions in the system Y_2O_3 - ZrO_2 prepared by SHS was examined. For this system, the composition of highest conductivity was found to lie in the Y_2O_3 - ZrO_2 binary at 9 mole % Y_2O_3 near the low yttria cubic solid solution limit. Conductivity-temperature data obtained at 1000 °C in atmosphere of low oxygen partial pressure (10^{-40} atm) for Y_2O_3 - ZrO_2 cubic solid solutions indicated that these materials could be reduced, the degree of reduction being related to the measuring electric field. At low impressed fields no reduction was observed. Thus, these conductivity data give a transference number for the oxygen ion in Y_2O_3 - ZrO_2 cubic solid solutions greater than 0.99.

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