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Oxygen Permeability Measurement of ZrO_2-TiO_2-Yb_2O_3 Mixed Conductor

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Electrical properties of ZrO_2-TiO_2-Yb_2O_3 mixed conductor (Ti-YbSZ) were investigated. This mixed conductor can be applied as a membrane for gas separation at high temperatures. The total conductivity decreased with increasing the TiO_2 concentration. At high temperatures, the rate of the conductivity degradation became smaller than that at low temperatures. From the oxygen partial pressure dependence of the total conductivity of Ti-YbSZ, the electronic conductivity increased with increasing TiO_2 concentration at low oxygen partial pressures and at high temperatures. Both 15 and 20 mol% TiO_2 doped YbSZ showed high oxygen permeability. Mixed conductors, which has high TiO_2 concentration in YbSZ, are promising materials for using as a membrane for gas separation at high temperatures.

Key words: ZrO_2-TiO_2-Yb_2O_3, Mixed conductor, Oxygen permeability, Membrane for gas separation

I. Introduction

Mixed ionic and electronic conductors have many applications such as electrodes and membrane for gas separation.[1] A zirconia (ZrO_2)-based mixed conducting material is stable at high temperatures and exhibits high oxygen ionic conductivity. This material can be used as a membrane, which separates hydrogen and oxygen produced by the water dissociation at high temperatures, and other thermochemical processes.[2-4] TiO_2 doped yttria stabilized zirconia (Ti-YSZ) shows mixed conduction and its electrical properties have been studied by several researchers.[5-7] The electronic conductivity of Ti-YSZ increased with increasing TiO_2 concentration and decreasing oxygen partial pressure. On the basis of this result, we carried out the hydrogen production from direct water splitting at high temperatures using Ti-YSZ membrane and revealed that hydrogen was produced under strongly reducing condition and at high temperatures.[8]

Considering the energy revenue and expenditure, this hydrogen production system should be operated at relatively high oxygen partial pressure and low temperatures. Therefore, to produce hydrogen effectively, a membrane, which has high ionic and electronic conductivity, should be used. Ytterbia(Yb_2O_3) stabilized zirconia (YbSZ) exhibits high ionic conductivity in zirconia based electrolytes and it is stable at high temperatures. TiO_2 doped YbSZ (Ti-YbSZ) is also expected to show high ionic and electronic conductivity and be used for a membrane for direct water splitting at high temperatures.

In this paper, we report the electrical properties and oxygen permeability measurement of Ti-YbSZ. From the results, we also discuss the applicability of Ti-YbSZ to a membrane of the hydrogen production system.

II. Experimental Procedure

1. Sample Preparation

Samples were synthesized by means of a solid state reaction. ZrO_2, and Yb_2O_3 powders with a level of purity of 99.99%, and TiO_2 with 99.5% were used as starting materials. The Yb_2O_3 concentration was set to 10 mol% to keep the ionic conductivity higher and the oxygen vacancies at constant level. Powders weighed at the appropriate proportions were mixed and ball-milled in methanol for 24 h, using zirconia balls. After drying, the mixtures were ground and isostatically pressed into rods under a pressure of 200 MPa and sintered using a Mo furnace at 1973 K for 5 h in air. The crystal structures of the synthesized samples were identified using X-ray diffractometer (JEOL, JDX-3530). Sintered rods were cut into 1.5×3×15 mm^3 parallelepipeds as the samples for electrical conductivity measurements. A part of mixtures were pressed into tubes closed at one end and sintered as the same manner as described above for oxygen permeability measurements. The sample size of the sintered tubes had an outer diameter of 13 mm, wall thickness of 2 mm, and length of 35 mm. The tube was joined with a commercially available Y_2O_3 stabilized ZrO_2 tube (Nikkato, ZR-8Y) using a Pt-ring at 1973 K in air. The gas tightness of the tube before and after the experiments was checked and no leakage was found.

2. Electrical Properties Measurement

The temperature dependence of the total electrical conductivity was measured by standard dc four-probe technique in the temperature range from 873 to 1673 K. The

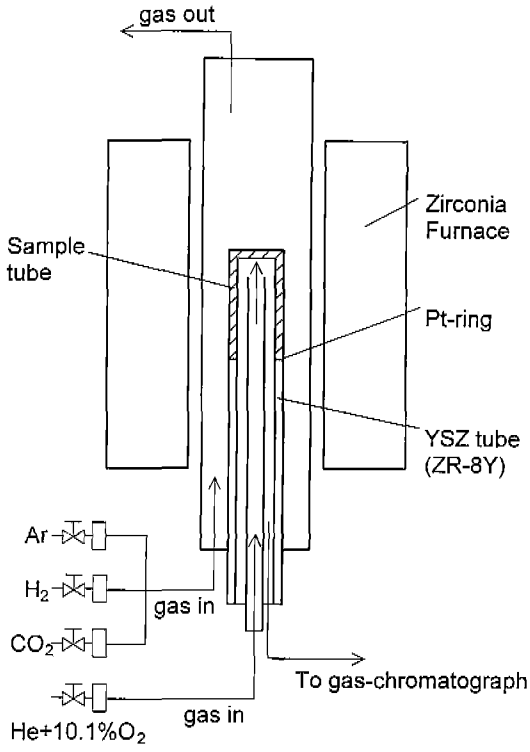

Fig. 1. Schematic drawing of oxygen permeability measurement.

oxygen partial pressure dependence of the total conductivity was also measured in the oxygen partial pressure (Po_2) range from 0.21×10^5 (air) to 1×10^{-20} Pa and temperature range of 1273-1673 K. The control of Po_2 was performed by flowing the mixtures of H_2 and CO_2 gases. The value of Po_2 was determined from the thermodynamic data from the reactions given in the JANAF Tables.[9]

3. Oxygen Permeability Measurement

The experimental apparatus for measuring oxygen permeability is shown in Fig. 1. Sample tube was heated by a zirconia furnace. He +10.1%O_2 gas was introduced into the inner side of the tube. Po_2 of the outer side was controlled to be lower than that of inner side by flowing H_2 and CO_2 mixed gases. Oxygen permeates from inside to outside of the tube. The amount of the oxygen permeation was calculated by measuring the oxygen remained in the inner side of the tube using gas chromatograph (Shimadzu, GC-9A). Oxygen permeability was measured at 1623, 1869 and 1933 K and Po_2 range of the outer side of the tube was from 10^2 to 10^{-8} Pa.

III. Results and Discussion

1. Phase Characterization

X-ray diffraction (XRD) patterns of TiO_2 doped Yb_2O_3 stabilized ZrO_2 (Ti-YbSZ) are shown in Fig. 2. This indicates that the samples which contain TiO_2 up to 20 mol% show single cubic fluorite structure. Samples which contains TiO_2 more than 20 mol% show two phases, that is, α-PbO_2 struc-

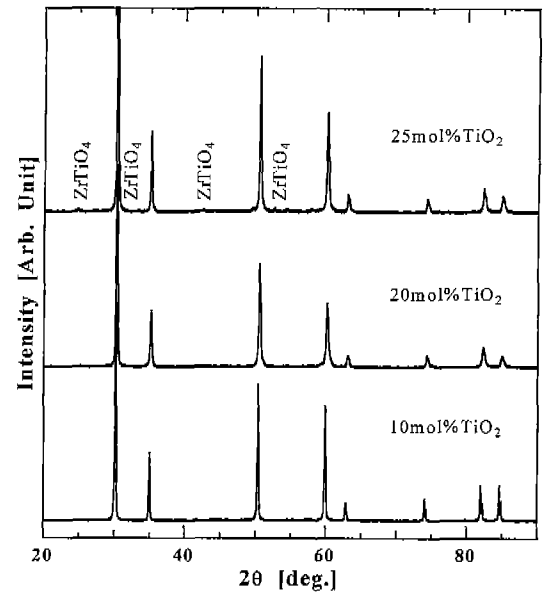

Fig. 2. XRD patterns of Ti-YbSZ.

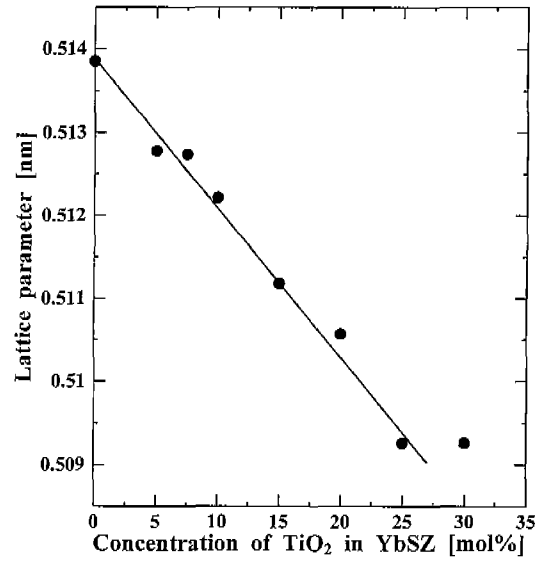

Fig. 3. Relationship between TiO_2 concentration in Ti-YbSZ and lattice parameter.

ture phase which indicates the existence of $ZrTiO_4$, and cubic fluorite structure phase. Fig. 3 shows the measured lattice parameters of Ti-YbSZ. The lattice parameter decreases linearly with increasing TiO_2 concentration up to 20 mol%. This indicates that Ti ion replaces Zr ion on normal lattice sites. The solubility range of TiO_2 into YbSZ is larger than that in the case of YSZ. A sample with higher TiO_2 concentration is expected to exhibit high electronic concentration. A relative density of 98% was obtained for each sample.

2. Electrical Properties

The temperature dependence of the total electrical conductivity of Ti-YbSZ measured in air is shown in Fig. 4.

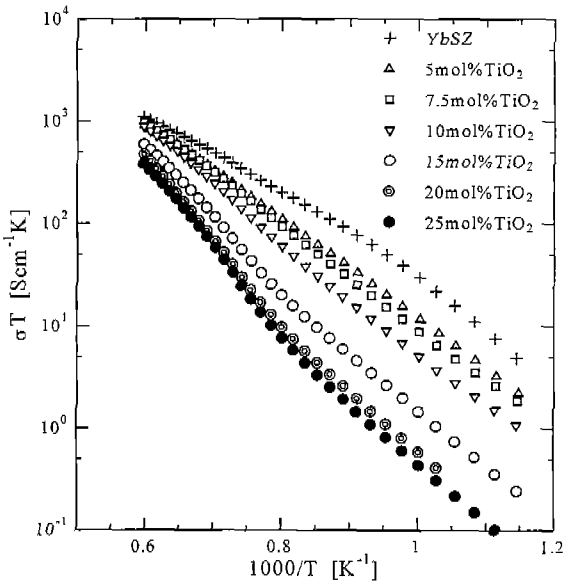

Fig. 4. Arrhenius plots in air for YbSZ containing various amount of TiO_2.

Doping TiO_2 into YbSZ, the activation energy, which was derived from the slope of the arrhenius plot, changed at temperature about 1250 K. This phenomenon also observed in n-type and total electronic conductivity in $Zr_{1.012}Ti_{0.988}O_4$[10]. They attributed the anomalous behavior is due to the anomalous increase in the lattice constant along the c-axis in $ZrTiO_4$. In the case of Ti-YbSZ, the ionic conductivity is dominant in air, and the crystal structure is considered to be stable. By doping TiO_2 into YbSZ, total conductivity decreases as shown in Fig. 4. Therefore, it is considered that this conductivity change is caused by trapping of oxygen ions by Ti ions, which made crystal structure a little distorted near them because of the difference of the ionic radius and coordination number for those of Zr. At higher temperatures, the oxygen trapped near Ti ions were released and the electrical conductivity increased.

The oxygen partial pressure dependence of total conductivity in Ti-YbSZ are shown in Fig. 5. In this Po_2 range, the conductivity of YbSZ was constant. This means that the ionic conductivity is dominant in YbSZ. Conductivity increased with decreasing Po_2 for samples which contains TiO_2. Furthermore, this phenomenon is remarkable as the TiO_2 concentration increases. At higher temperatures, the increase of the conductivity occurs at the higher Po_2. This conductivity change is caused by the increase of n-type electronic conduction by doping of TiO_2.

The appropriate defect model of this system is discussed and the oxygen partial pressure dependence of the electrical conductivity is predicted. In this Po_2 range, the charged carriers are considered to be electrons and oxygen ions. Oxygen vacancy $V_O^{\cdot\cdot}$ is generated in the sample as follows,

$$O_O^x \Leftrightarrow V_O^{\cdot\cdot} + 2e^- + \frac{1}{2}O_2 , \tag{1}$$

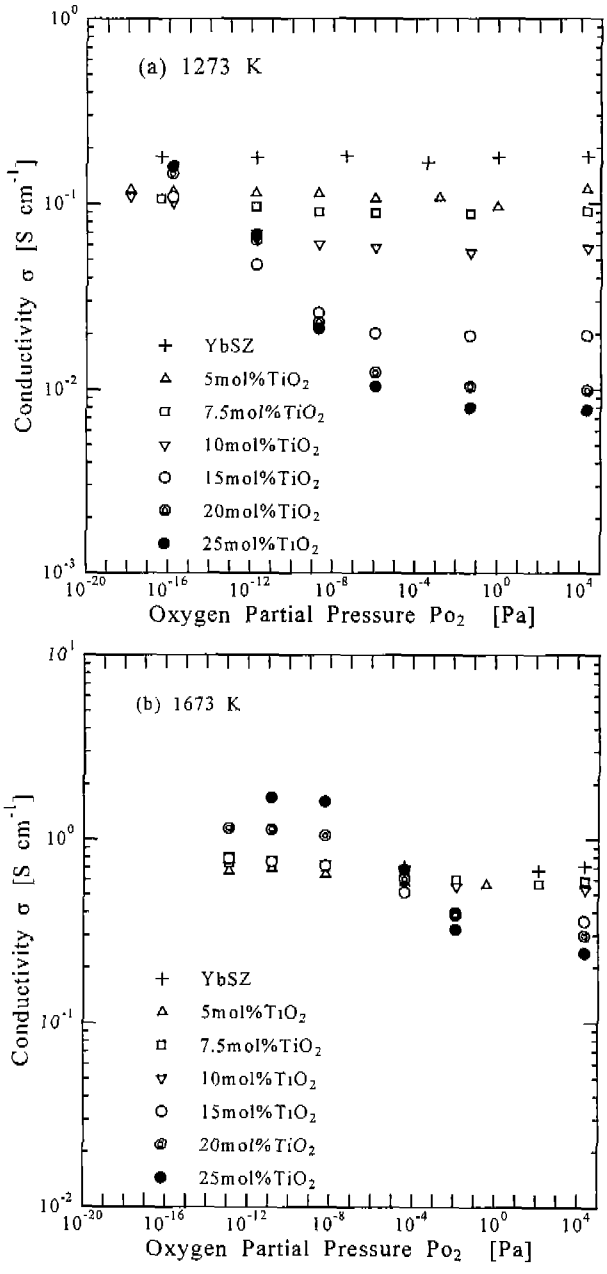

Fig. 5. Oxygen partial pressure dependence of total electrical conductivity in Ti-YbSZ. (a) 1273 K and (b) 1673 K.

$$K = \frac{[V_O^{\cdot\cdot}]n^2 P_{O_2}^{1/2}}{[O_O^x]} , \tag{2}$$

where K is the equilibrium constant, [M] is the concentration of the component M, and the Kröger-Vink notations are used[11]. The charge neutrality condition is given by

$$[Yb'_{Zr}] + n = 2[V_O^{\cdot\cdot}] \tag{3}$$

When the concentration of the electrons, which are produced by the reduced atmosphere, are small, $[V_O^{\cdot\cdot}]$ stays at a constant level, which is equal to $1/2[Yb'_{Zr}]$, and the following relation is derived;

$$n \propto P_{O_2}^{-1/4}. \quad (4)$$

In this case, the total conductivity is expressed as

$$\sigma = \sigma_i + \sigma_e = \sigma_i + \sigma_e^0 P_{O_2}^{-1/4} \quad (5)$$

where σ_i, σ_e, σ_e^0 are ionic conductivity, electronic conductivity, and electronic conductivity at Po_2=1 atm (1.013×10^5 Pa), respectively. When n is very large compared to $[Yb'_{Zr}]$ ($n >> Yb'_{Zr}$), the electronic conductivity is proportional to −1/6 power of Po_2. From the results of electrical conductivity measurements, the concentration of electrons produced by changing Po_2 is considered not to be negligible compared to $[Yb'_{Zr}]$, that is, the concentration of oxygen vacancies is increased. The further investigations such as measurement of the ionic conductivity and the electronic conductivity separately, are required for determine the Po_2 dependence of the ionic and electronic conductivity.

The produced electrons are considered to be trapped by Ti ions changing their valence state from tetravalent to trivalent according the reaction,

$$Ti^x_{Zr} + e^- \Leftrightarrow Ti'_{Zr} \quad (6)$$

In this case, the electronic conduction mechanism is described by small polaron hopping process. The existence of both tri- and tetravalent Ti ions in the sample quenched at the reduced condition are confirmed by the electronic Raman spectroscopy. Vohrer *et al.*, however, indicated that no remarkable electronic conduction nor trivalent titanium ions in zirconia-titania-yttria system were found in the temperature range 873-1173 K, and oxygen partial pressure below 10^{-12} Pa.[12] Whereas, they also reported that the band gap decreased by increasing titania concentration. As YbSZ containing titania exhibits higher conductivity compared with that of YSZ doped with titania[4], smaller band gap and the valence change of Ti ions from tri- to tetravalent in this system in reduced condition and at higher temperatures are expected.

3. Oxygen Permeability

Fig. 6 shows a result of the oxygen permeability of Ti-YbSZ as a function of lower side of oxygen partial pressure Po_2^{II}. The oxygen permeability increased with increasing TiO_2 concentration and decreasing Po_2^{II}. Oxygen permeability of this system is larger than that of a zirconia-titania-yttria system.[13] As the solubility of titania, which promotes electronic conduction, into YbSZ was larger than that into YSZ, it was considered that the electronic conductivity was the rate determining step of the oxygen permeability in this study. As mentioned in the sample preparation, a Pt-ring was used to joint the sample tube and ZR-8Y tube. Therefore, there is a possibility that Pt ring works as a short current circuit, that is, electrons conduct in Pt ring and oxygen permeation is promoted. It is considered that the oxygen permeation in this study includes a short current circuit effect. However, the oxygen permeation in Ti-YbSZ samples by this effect was less than 10% of the total oxygen permeation, which is estimated from the oxygen permeability of

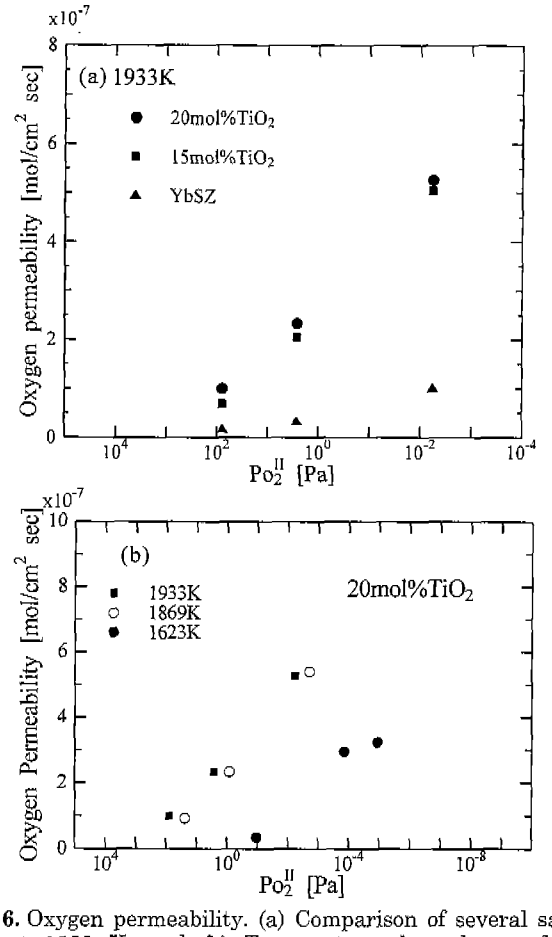

Fig. 6. Oxygen permeability. (a) Comparison of several samples at 1933 K. and (b) Temperature dependence of 20 mol%TiO_2 doped YbSZ.

YbSZ and our previous work.[8]

As the conducting species in Ti-YbSZ are oxygen ions and electrons, the oxygen permeability Jo_2 is given as follows[14];

$$J_{O_2} = \frac{1}{8e^2} t_e t_i \sigma \, \mathrm{grad}\mu_{O_2} \quad (7)$$

where, t_e and t_i are electronic and ionic transference number, respectively, and μ_{O_2} is chemical potential of oxygen. The relationship between the oxygen permeability and the oxygen partial pressure is calculated by substituting the following relation.

$$\mu_{O_2} = \mu^0_{O_2} + RT \ln P_{O_2}, \quad (8)$$

where, $\mu^0_{O_2}$ is the chemical potential of oxygen at standard condition. The oxygen permeability of this sample is calculated from the experimental results of electrical conductivity of Ti-YbSZ and the eq. (7). The electronic conductivity can be determined using these equations and experimental results.[15] Fig. 7 shows a temperature dependence of electronic conductivity at oxygen partial pressure of 1×10^5 Pa (= 1 atm). The electronic conductivity of Ti-YSZ calculated in our previous study are also plotted in the same figure.[13] The electronic conductivity calculated from the oxygen permeability shows good agreement with that derived from the

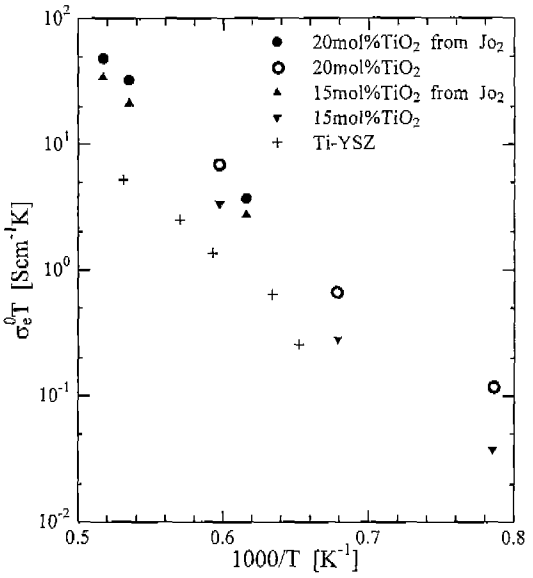

Fig. 7. Temperature dependence of electronic conductivity of Ti-YbSZ (at Po_2=1×10^5 Pa).

total electrical conductivity measurement, though this calculation was performed under the condition that the ionic conductivity was independent on the oxygen partial pressure in the subjected oxygen partial pressure range. The electronic conductivity increased with increasing titania concentration and Ti-YbSZ shows higher electronic conductivity than that of Ti-YSZ. Therefore, Ti-YbSZ can be a candidate for a membrane for gas separation.

IV. Conclusions

Titania was soluble into YbSZ up to 20 mol% by substituting Ti ions with Zr ions. This solubility limit of titania is larger than that of YSZ. Ti-YbSZ shows high electronic conductivity at high temperatures and low oxygen partial pressures. The electronic conductivity increases with increasing titania concentration, and enhanced by the existence of trivalent Ti ions. The oxygen permeability of Ti-YbSZ was higher than that of Ti-YSZ. This mixed conductor can be a candidate for a membrane for a gas separation.

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