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Electrical conductivity and oxygen semipermeability of terbia and yttria stabilized zirconia

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This paper reports an electrochemical study on terbia and yttria stabilized zirconia. (Tb, Y)–ZrO_2 solid solutions with a fluorite type structure were prepared by using citrate synthesis and sintered at 1500 °C. They are mixed electronic and oxygen ionic conductive, as well as oxygen semipermeable materials at elevated temperatures. The total electrical conductivity reaches $3.8\,S\,m^{-1}$ at 900 °C and the oxygen permeation is about $6.5 \times 10^{-6}\,mol\,m^{-2}\,s^{-1}$ at 1100 °C. The electrical conductivity of zirconia doped with a total of 30 mol % of terbia and yttria increases with oxygen partial pressure when P_{O_2} is below 10^{-2} atm, and decreases as the oxygen partial pressure rises above 10^{-2} atm. This is ascribed to the defect association and the predomination of oxygen ionic conductivity. The oxygen semipermeation is proportional to the square root of the oxygen partial pressure, and is not influenced by the variation of oxygen ionic or electronic conduction. The results indicate that the surface exchange reaction is most probably the rate limiting step for the oxygen semipermeation.

1. Introduction

Ionic and mixed electronic–ionic conductive materials have drawn a lot of attention because of their potential applications such as dense membranes for gas separation, dense cathodes in solid oxide fuel cells (SOFC) and in electrocatalytic reactors. Among other oxygen ionic conductive materials, zirconia with a fluorite type structure stabilized by doping with metal and rare earth oxides such as CaO and Y_2O_3 has been widely investigated for its high oxygen ionic conductivity, and excellent chemical and thermal stability. However, such materials show, in general, only very limited electronic conductivity, which in turn limits their oxygen semipermeability, since, in most cases, a small electronic conductivity is the rate limiting factor for oxygen semipermeation through ionic conductive materials. To improve the electronic conductivity, and thus enhance the oxygen semipermeability, some metal and rare earth oxides, such as CeO_2, TiO_2 and $Tb_2O_{3.5}$ the cations of which have multivalence states, have been introduced as dopants into the zirconia system [1–3]. In such a system, the presence of trivalent cations, which occupy the zirconium ion sites and introduce an effective negative charge on each site, results in the formation of oxygen ionic vacancies in the lattice to maintain the overall charge neutrality. At elevated temperatures these positively charged oxygen ionic vacancies are mobile under an electrochemical gradient. The oriented motion of the charged oxygen vacancies results in ionic conduction, while the coexistence of both tri- and tetravalent cations introduces electronic conductivity due to the hopping of electrons (or electron holes) between tri- and tetravalent ions.

Iwahara *et al.* [4] have recently reported that terbia doped zirconia solid solutions with a fluorite type structure have shown both higher electrical conductivity and higher oxygen semipermeation compared with yttria stabilized zirconia (YSZ). The increase in the electrical conductivity and oxygen semipermeation is ascribed to the increase in the electronic conductivity due to the addition of terbia into the system. In a previous paper [5] we have reported a preliminary study of the zirconia solid solutions doped with both terbia and yttria, and demonstrated that they have higher oxygen semipermeation due to enhanced electronic conductivity caused by the addition of terbia into the zirconia and yttria systems, although the total electrical conductivity remains of the same order compared with the YSZ materials. This indicates that the electronic conductivity is very likely to be the rate limiting factor for oxygen semipermeation in the YSZ materials. In the present paper we report a more detailed study of the influences of temperature and oxygen partial pressure on both electrical conductivity and oxygen semipermeability.

2. Experimental details

2.1. *Preparation of the specimens*

The citrate synthesis method [6] was applied for the preparation of the powder mixtures. The raw materials used were $ZrOCl_2 \cdot H_2O$ (> 99 wt %,

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Table 1. Chemical composition and density of the materials studied

Specimen	*Composition*/mol %			*Density*	
	ZrO_2	$Tb_2O_{3.5}$	Y_2O_3	/g cm^{-3}	/%
TYX-1	70.0	22.8	7.2	6.19	91
TYZ-2	70.0	25.0	5.0	6.33	92
TYZ-3	70.0	27.5	2.5	6.54	93
TYZ-4	70.0	30.0	0	6.47	92
TYZ-5	50.0	40.0	10.0	6.39	89
TYZ-6	50.0	44.9	5.1	6.51	88
TYZ-7	50.0	47.6	2.4	7.00	94

Merck), Y_2O_3 (99.99%, Aldrich Chemical Company Inc.) and $Tb_2O_{3.5}$ (99.9%, Highways Int.). The composition of the starting mixtures is presented in Table 1. The synthesized powders were calcined at 1000 °C in air for 10 h, and then pressed isostatically (at 400 MPa) into pellets of 25 mm in diameter and 5 mm in thickness. The pellets were sintered at 1500 °C in air for 3 h.

2.2. *Measurement of electrical conductivity and ionic transport number*

Measurement of total electrical conductivity was made using a conventional four probe method with a digital impedance meter (Solartron 1255) having frequencies ranging from 10 mHz to 1 MHz. The specimens, 12 mm in diameter and 2 mm in thickness, were polished on both sides. Platinum or gold electrodes were made by sputtering on both sides of the specimens for 30 min followed by heat treatment at 950 °C in air for 60 min. Ionic transport numbers were determined by using an oxygen concentration cell [7]. Air was flushed along one side of the specimen and oxygen gas along the other side. The flow rate for both gases was the same, 30 ml(STP) min^{-1}. The total pressure on both sides was kept at 1 atm and the influence of the gas flow rate was negligible from the experience of earlier work.

2.3. *Oxygen semipermeability measurement*

The oxygen semipermeation was determined in an oxygen permeation reactor; the details of the apparatus and the measurements were described previously by Bouwmeester *et al.* [8]. The specimens were sealed with Pyrex glass rings to a quartz permeation cell, which was then heated to preassigned temperatures. A mixture of oxygen and nitrogen, with oxygen partial pressure, P_{O_2}, ranged from 1.7×10^{-2} to 1 atm, was flushed along one side of the specimen while helium gas ($P_{O_2} = 10^{-4}$ atm) along the other side. The total pressure was maintained at 1 atm on both sides and the flow rate for each side was 20 ml(STP) min^{-1}. The nitrogen in the feed gas also served as a detecting gas for the gas-tightness of the specimens throughout the measurements. Only data obtained from those gas-tight specimens are presented and discussed in this paper.

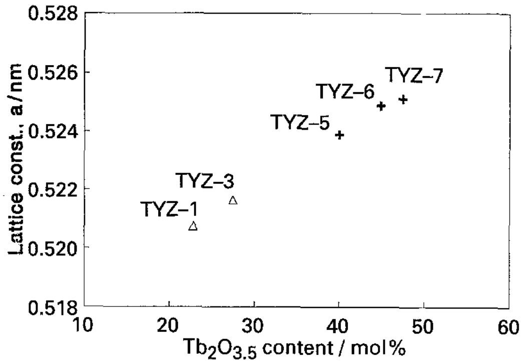

Fig. 1. The lattice parameter *a* of (Tb, Y)–ZrO_2 solid solutions as a function of terbia content.

3. Results and discussion

3.1. *Preparation of the specimens*

The sintered specimens were relatively dense with a density of about 90% of the theoretical density (Table 1) and the weight loss during sintering was always smaller than 2 wt% for all compositions. However, some small cracks were found in most specimens and it was difficult to achieve a higher density, especially in the presence of large amounts of terbia. This is partly due to the valence change of terbium ions, which is always accompanied by a size change of the terbium ions (Tb^{3+}, $r = 104$ pm, and Tb^{4+}, $r = 88$ pm) and, thus, of the unit cell, as the temperature changes [3, 9]. Specimens containing terbia higher than 30 mol % were always severely cracked and not gas-tight. X-ray diffraction (XRD) analysis indicated that all composition $(ZrO_2)_{1-x-y}(Tb_2O_{3.5})_{1-x}(Y_2O_3)_y$ with $x = 0.3$–0.5 and $y = 0.0$–0.1, after sintering at 1500 °C in air for 3 h formed yttria and terbia stabilized zirconia solid solutions with a fluorite type structure. The lattice constant of the (Tb, Y)–ZrO_2 solid solutions, determined by XRD, increased almost linearly with the amount of the doping terbia as shown in Fig. 1. However, the influence of the doping yttria on the lattice constant was negligible and this was probably due to the relatively small amount of yttria present in the system. No other phase was detectable in the sintered specimens. Scanning electron microscopic (SEM) analysis indicated that the sintered specimens had a homogeneous microstructure with round shaped particles and an average grain size of approximately 1 μm.

3.2. *Electrical conductivity*

The total electrical conductivity and ionic transport number at 900 °C of the materials studied are summarized in Table 2. The electrical conductivity and ionic transport number as a function of (reciprocal) temperature are plotted in Figs 2 and 3, respectively. It is seen that the zirconia solid solutions doped with a total of 30 mol % of yttria and terbia (samples TYZ-1, TYZ-2 and TYZ-4) have a lower

Table 2. Electrical conductivity, ionic transport number and oxygen semipermeability of (Tb, Y)–ZrO₂ solid solutions at 900 °C

Specimen	σ_t /S m^{-1}	t_i	J_{O_2} /mol m^{-2} s^{-1}
TYZ-1	0.86	1	3.7×10^{-7}
TYZ-2	1.2	0.72	2.3×10^{-7}
TYZ-4	1.2	0.37	2.6×10^{-7}
TYZ-6	1.8	0.046	–
TYZ-7	3.8	0.038	–

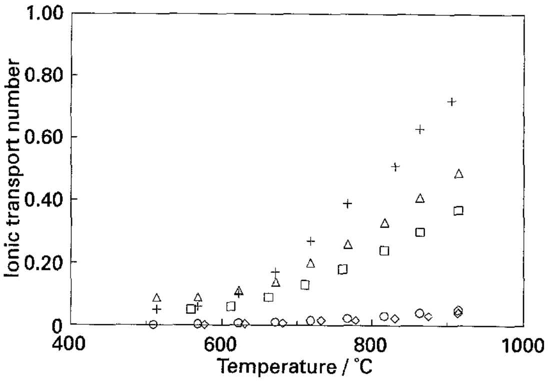

Fig. 3. Ionic transport number of (Tb, Y)–ZrO$_2$ solid solutions as a function of temperature, determined by using an oxygen concentration cell. Key: (+) TYZ-2; (△) TYZ-3; (□) TYZ-4; (○) TYZ-6; (◇) TYZ-7.

total electrical conductivity compared with those doped with a combination of 50 mol % of yttria and terbia (samples TYZ-6 and TYZ-7). Although the electrical conductivity increases with the amount of dopants, the ionic transport number decreases strongly when the amount of dopants increases from 30 to 50 mol %.

The total electrical conductivities of TYZ-1 as functions of reciprocal temperature and oxygen partial pressure are shown in Fig. 4. From this figure it can be seen that, at temperatures ranging from about 500 to 900 °C, as the oxygen partial pressure rises, the total electrical conductivity increases when $P_{O_2} < 10^{-2}$ atm but decreases when $P_{O_2} > 10^{-2}$ atm. This phenomenon is attributable to the change of the concentration ratio of tri- to tetravalent terbium ions caused by the increase in the oxygen partial pressure and also a possible defect association, as discussed below.

Under thermodynamic equilibrium, ZrO$_2$–Tb$_2$O$_{3.5}$–Y$_2$O$_3$ solid solutions can be formulated as

$$Zr_{1-x}[Tb^{4+}_{1-z}(Tb^{3+}, Y^{3+})_z]_xO_{2-\delta}V_\delta \qquad (1)$$

where δ is the oxygen deficiency and is equal to $zx/2$, and V represents the oxygen ionic vacancy. Under the experimental conditions used in the present study it is safe to assume that yttrium ions have a stable trivalent state, while terbium ions can have either tri- or tetravalent states. The ratio of the concentrations of Tb^{3+} to Tb^{4+} is dependent on the temperature and the oxygen partial pressure. Using Kröger–Vink notation, the system undergoes the following reaction:

$$O^x + 2h^o \rightleftharpoons V^{oo} + \tfrac{1}{2}O_2 \qquad (2)$$

The electron holes, h^o, are generated by the reaction:

$$Tb^{4+}_{Zr} \rightleftharpoons Tb^{3+}_{Zr} + h^o \qquad (3)$$

The overall electroneutrality condition in the ZrO$_2$–Tb$_2$O$_{3.5}$–Y$_2$O$_3$ system requires:

$$[Tb^{3+}_{Zr}] + [Y^{3+}_{Zr}] = 2[V^{oo}] \qquad (4)$$

Combining Reactions 2 and 3, gives:

$$2Tb^{4+}_{Zr} + O^x \rightleftharpoons 2Tb^{3+}_{Zr} + V^{oo} + \tfrac{1}{2}O_2 \qquad (5)$$

According to the law of mass action, we have a relationship between the oxygen partial pressure and the concentrations of both oxygen vacancies and terbium ions:

$$K_{(5)} = \{[Tb^{3+}_{Zr}]^2[V^{oo}] \times P^{0.5}_{O_2}\}/\{[Tb^{4+}_{Zr}]^2 \times [O^x]\} \qquad (6)$$

where $K_{(5)}$ is the equilibrium constant of Reaction 5 and is temperature-dependent.

The oxygen ionic vacancies are responsible for the ionic conduction, σ_i, while the hopping of the electron holes (or electrons) between the Tb^{3+} and Tb^{4+}

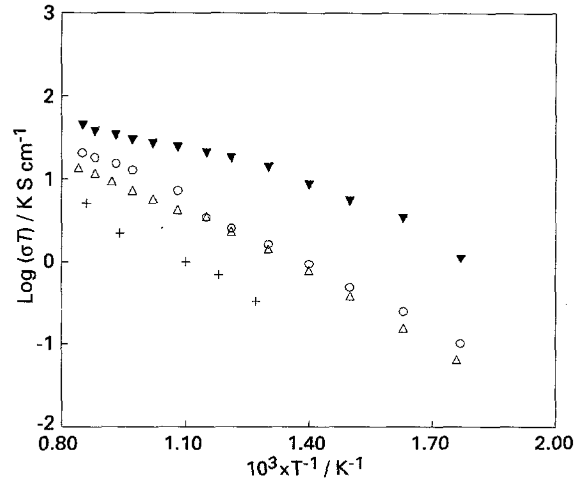

Fig. 2. Arrhenius plot of the total electrical conductivity of (Tb, Y)–ZrO$_2$ solid solutions as a function of reciprocal temperature; measurements were performed in air. Key: (▼) TYZ-7; (○) TYZ-6; (△) TYZ-4; (+) TYZ-1.

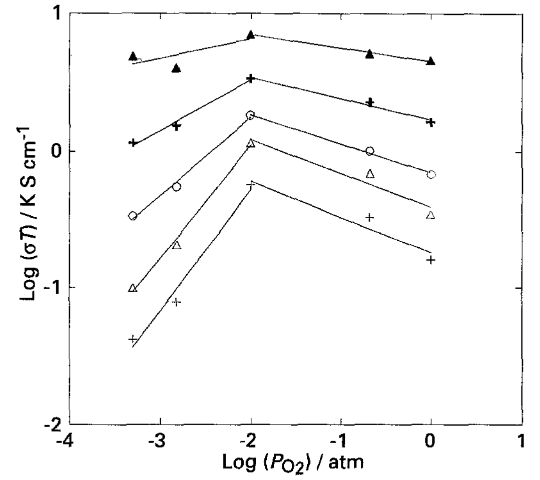

Fig. 4. Total electrical conductivity of (Tb, Y)–ZrO$_2$ solid solution, sample TYZ-1, as functions of oxygen partial pressure and temperature. Key: (▲) 887 °C; (+) 791 °C; (○) 636 °C; (△) 571 °C; (+) 517 °C.

ions contributes to the electronic conduction, σ_e. Therefore, the total electrical conductivity, σ_t, is given by

$$\sigma_t = \sigma_e + \sigma_i = [h^o] \times u_h \times q + 2[V^{oo}] \times u_o \times q \quad (7)$$

where u_h and u_o are the mobilities of electron holes and oxygen ionic vacancies, respectively, and q is the unit charge. From Equation 6, it can be seen that a decrease in the oxygen partial pressure results in an increase in the concentrations of both oxygen ionic vacancies and trivalent terbium ions, at the expense of the concentration of tetravalent terbium ions. Clearly, an increase in the oxygen ionic vacancy concentration enhances the oxygen ionic conductivity.

In a given total terbium concentration, a maximum electronic conductivity can be expected when the ratio of the concentrations of tri- to tetravalent terbium ions is unity. Variation of the concentration ratio away from unity results in a decrease in the electronic conductivity, which is then determined by the concentration of the minority terbium ions. Arashi *et al.* [9] and Van Dijk *et al.* [3] have studied the relationship between the temperature and concentration ratio of tri- to tetravalent terbium ions in ambient air. Their results indicated that the concentration of tetravalent terbium ions is always lower than that of trivalent terbium ions at temperatures ranging from room temperature to 900 °C in air. Thus, the electronic conductivity of terbia and yttria doped zirconia is determined by the concentration of tetravalent terbium ions which increases with P_{O_2}, as indicated in Equation 6. Consequently, the electronic conductivity decreases as P_{O_2} decreases. Since the oxygen ionic vacancy concentration increases with decreasing P_{O_2}, as shown in Equation 6, the oxygen ionic conductivity also increases as P_{O_2} decreases. The total electrical conductivity is a sum of the electronic and oxygen ionic conductivities, as indicated in Equation 7, and therefore can vary with the oxygen partial pressure in two opposite ways, depending on whether electronic or ionic conductivity is predominant. The decrease in the total electrical conductivity of sample TYZ-1, as the oxygen partial pressure rises when $P_{O_2} > 10^{-2}$ atm (Fig. 4), probably implies that the oxygen ionic conductivity is predominant. This is in agreement with the ionic transport number measurement.

From Equation 7 it can be seen that the electrical conductivity is also dependent on the mobilities of both oxygen ion vacancies and electron holes. Not all oxygen vacancies and electron holes are effective for electrical conduction, particularly at high doping concentrations the defect association may occur:

$$\begin{aligned} V^{oo} + 2[\mathrm{Tb,Y}]_{\mathrm{Zr}}^{3+} &\rightleftharpoons (V^{oo}[\mathrm{Tb,Y}]_{\mathrm{Zr}}^{3+})^{o} + [\mathrm{Tb,Y}]_{\mathrm{Zr}}^{3+} \\ &\rightleftharpoons ([\mathrm{Tb,Y}]_{\mathrm{Zr}}^{3+} V^{oo}[\mathrm{Tb,Y}]_{\mathrm{Zr}}^{3+})^{x} \quad (8) \end{aligned}$$

Obviously, a defect association would result in a decrease in the effective concentration of the oxygen ionic vacancies and, thus, a decrease in the ionic conductivity, and consequently a decrease in the total electrical conductivity if the ionic conduction in the system is predominant. So the decrease in the total electrical conductivity of sample TYZ-1, as oxygen partial pressure decreases when $P_{O_2} < 10^{-2}$ atm (Fig. 4), is ascribed to a possible defect association.

From Fig. 4 it is also seen that, as the temperature rises, the influence of the oxygen partial pressure on the total electrical conductivity declines. According to the literature [3, 9], the fraction of the tetravalent terbium ions is about 20% at 500 °C and decreases as temperature rises, and is almost zero at 900 °C when P_{O_2} equals 1 atm. Since the concentration of Tb^{4+} is already very low at high temperatures, the change of concentration ratio of Tb^{4+} to Tb^{3+} is not large as the oxygen partial pressure decreases. Consequently, the influence of oxygen partial pressure on electrical conductivity falls at high temperature.

3.3. *Oxygen semipermeation*

Figures 5 and 6 show the oxygen semipermeation of (Tb, Y)–ZrO_2 solid solutions (sample TYZ-1) as functions of oxygen partial pressure and reciprocal temperature, respectively. From Fig. 5 it can be seen that the oxygen semipermeation is proportional to ($P'^{0.49}_{O_2} - P''^{0.49}_{O_2}$) at 1100 °C, where P'_{O_2} is the oxygen partial pressure ranging from 1.7×10^{-2} to 1 atm at the oxygen feed side, while P''_{O_2} is the oxygen partial pressure (in helium gas) at the permeate side and is fixed at 10^{-4} atm in the present study. The activation energy for the oxygen semipermeation is found to be approximately 210 J mol^{-1} at temperatures ranging from 925 to 1100 °C according to Fig. 6.

Oxygen semipermeation, through a dense mixed ionic–electronic conductive material, consists of

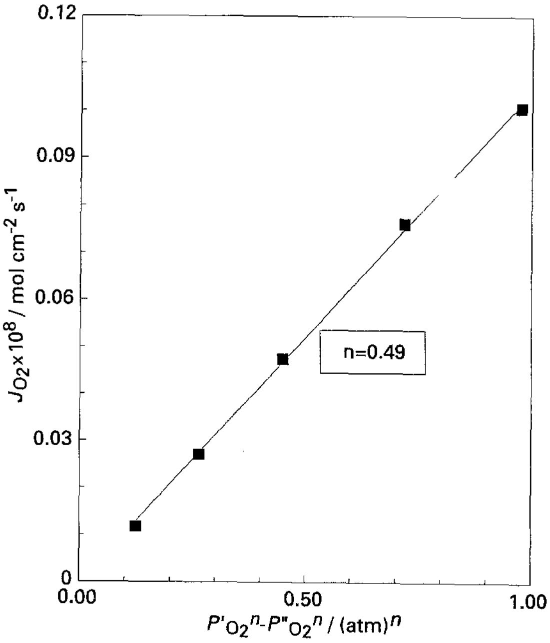

Fig. 5. Oxygen permeation of (Tb, Y)–ZrO_2 solid solutions, sample TYZ-1, as a function of oxygen partial pressure of the feeding side at 1100 °C. Feed side: 1×10^{-2}–1 atm; permeate side: helium gas; temperature: 1100 °C; thickness: 2.0 mm.

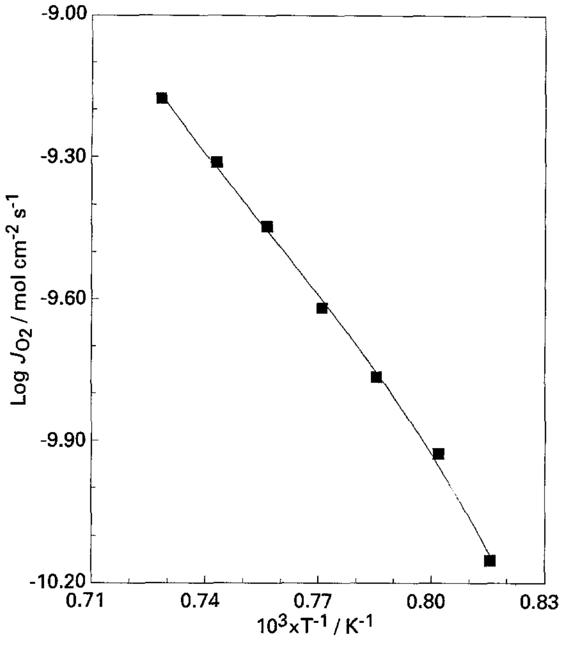

Fig. 6. Oxygen permeation of (Tb, Y)–ZrO_2 solid solutions, sample TYZ-1, as a function of temperature under an oxygen partial pressure of 1 atm at the feeding side and 10^{-4} atm at the permeate side. Feed side: air; permeate side: helium gas; temperature: 925–1100 °C; thickness: 2.0 mm.

three progressive processes: the surface exchange reaction at the oxygen feed side, the bulk electrochemical diffusion, and the surface exchange reaction at the permeate side. Details of the theoretical analysis and the description of these three processes can be found in [8, 10]. Each of these three processes can be a rate limiting step. When the specimen thickness is large and/or the surface exchange reactions proceed very rapidly, the bulk electrochemical diffusion is the rate limiting step. The bulk diffusion process can be controlled by either oxygen ionic or electronic conduction, or both of them. For a bulk electrochemical diffusion rate limited process, the oxygen semipermeation, J_{O_2}, is given by [8, 10]

$$J_{O_2} = A(P'^{1/4}_{O_2} - P''^{1/4}_{O_2}) \qquad (9)$$

where A is a temperature dependent constant and is inversely proportional to the thickness of the specimen in question. When the bulk electrochemical diffusion proceeds very rapidly and/or a very thin specimen is used, the surface exchange reaction in the feed or permeate sides may become rate limiting. In this case the oxygen semipermeation is given by

$$J_{O_2} = B(P'^{1/2}_{O_2} - P''^{1/2}_{O_2}) \qquad (10)$$

where B is a temperature dependent constant which is proportional to the concentration of the oxygen ionic vacancies in the specimen.

When bulk electrochemical diffusion and surface exchange reaction are partially rate limiting, the oxygen semipermeation can be given in a general form:

$$J_{O_2} = C(P'^{1/n}_{O_2} - P''^{1/n}_{O_2}) \qquad (11)$$

where C is also a temperature dependent constant and $1/n$, is between 1/2 and 1/4.

The results of the present study show that the oxygen semipermeation is approximately proportional to the square root of the oxygen partial pressure as demonstrated in Fig. 5. This fits well with Equation 10, and implies that oxygen semipermeation in (Tb, Y)–ZrO_2 solid solutions is probably a surface exchange reaction rate limited process.

The oxygen semipermeability of samples TYZ-1, TYZ-2 and TYZ-4 at 900 °C is presented in Table 2. It is seen that the oxygen semipermeabilities of these three samples are almost the same, although their chemical composition differs. In contrast to the oxygen semipermeation, the ionic and electronic conductivities of these three samples differ significantly. The ionic conductivity at 900 °C of samples TYZ-1, TYZ-2 and TYZ-4, calculated from the total electrical conductivity and the ionic transport number (Table 2), are 0.86, 0.86 and 0.44 S m^{-1}, respectively. The ionic conductivity of samples TYZ-1 and TYZ-2 is twice as large as that of sample TYZ-4. As for the electronic conductivity, it increases drastically from nearly zero in sample TYZ-1, to 0.34 in sample TYZ-2, to 0.76 S m^{-1} in sample TYZ-4. This is due to an increasing concentration of the oxygen ionic vacancies caused by the addition of trivalent yttrium ions into the Tb–ZrO_2 system. The above results indicate that oxygen semipermeation is determined neither by ionic or electronic conduction nor by the total electrical conduction, and, thus, imply that the oxygen semipermeation is not a bulk electrochemical diffusion rate limited process, but rather a surface exchange reaction rate limited process. Furthermore, the activation energy of the oxygen semipermeation calculated from Fig. 6 is high and this suggests also a surface exchange reaction rate limited process.

The different oxygen partial pressure dependence of oxygen semipermeation and electrical conductivity is also indicative that the oxygen semipermeation process is not bulk electrochemical diffusion (i.e., electronic and oxygen ionic conduction) controlled.

4. Conclusions

In the ZrO_2–$Tb_2O_{3.5}$–Y_2O_3 system, zirconia solid solutions with a fluorite type structure can be formed in a range between 30 to 50 mol % terbia and 0 to 10 mol % yttria. The (Tb, Y)–ZrO_2 solid solutions are mixed electronic and ionic conducting materials. Their total electrical conductivity is in the same order as that of YSZ (8 mol %). The oxygen semipermeation is about two to three orders higher than that of YSZ. This is ascribed to the enhanced electronic conductivity due to the hopping of the electron holes between tri- and tetravalent terbium ions. The electrical conductivity varies with oxygen partial pressure and is ascribed to change of the carrier concentration and defect association. The oxygen semipermeation of the terbia and yttria stabilized zirconia solid solutions is probably a surface exchange reaction rate limited process. It is clear that a further increase in oxygen semipermeation can be achieved by improvement of the surface exchange reaction process.

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