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Electrical conductivity of praseodymia doped ceria

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The electrical conductivity (σ) and oxide ion transference number (t_0) of praseodymia doped ceria systems were measured. The former increased rapidly with the praseodymia content, while the latter decreased. At 600° C, for instance, σ of CeO_2 and $Ce_{0.6}Pr_{0.4}O_2$ under 0.21 atm of oxygen were 2.0×10^{-5} and 3.6×10^{-2} S cm^{-1}; and t_0 in them were 0.59 and 0.11, respectively. This mixed conductor having high electrical conductivity might be useful as a fuel cell electrode if it could be combined with a suitable solid electrolyte.

1. Introduction

Some catalytically active oxides showing mixed conduction could find application as fuel cell electrodes, because they tend to lower the polarization effect arising at the electrode–electrolyte interface [1, 2]. The effective electrode–electrolyte area of contact is much higher in comparison to a purely electronic conductor [2]. But to be useful, the oxide should not only be catalytically active for electrode reactions but also have high electronic and ionic conductivities. According to studies of catalytic oxidation and reduction with a series of rare earth oxides, praseodymium oxide was often found to be the most active catalyst [3, 4]. Moreover, praseodymium oxide seems to show high electronic conduction at elevated temperatures. On the other hand, there has been much interest in the use of cerium oxide doped with divalent (Ca^{2+}) or trivalent (Ln^{3+}: Y, La, Sm, Nd, Eu, Gd, Dy, Ho, Er, Yb) cations as a solid electrolyte for fuel cells [5–8]. Doping of such cations into the ceria increases both the electrical conductivity and the oxide ion transference number. For instance, Kudo and Obayashi [6] have found that the electrical conductivity and the ionic transference number of $Ce_{0.77}Gd_{0.23}O_{1.885}$ at 750° C were 6.7×10^{-2} S cm^{-1} and unity, respectively. These values rival the values of calcia stabilized zirconia at 1000° C.

In this study, several compositions of praseodymia doped ceria were prepared to develop an oxide electrode having high electronic and ionic conductivities, and the electrical conductivity and the ionic transference number were measured.

2. Experimental details

2.1. *Sample preparation*

In order to have good reproducibility, the starting materials, Pr_6O_{11} and CeO_2, were recrystallized as follows. The oxide Pr_6O_{11} (Shiga Kikinzoku Kagaku, 99.9%) was firstly dissolved in concentrated HCl, followed by boiling to evaporate the excess HCl on a sand bath. A saturated solution of oxalic acid was added to the above solution at room temperature to form the oxalate. The oxalate was ignited in air at 800° C to reform Pr_6O_{11}. CeO_2 was also prepared by the above procedure but $CeCl_3$ (Wako Pure Chemical, 99.9%) was used as the starting material. The mixture of these oxides was pressed (200 kg cm^{-2}) to form a disc (13 mm in diameter, 0.6–2 mm in thickness) and heat treated at 1400° C in air for 50 h. The lattice constants of these mixed oxides were determined by X-ray diffractometry.

2.2. *Measurement of ionic conduction*

The oxide ion transference number t_0 was calculated by the following equation,

$$t_0 = \frac{E_{\text{obs}}}{(RT/4F)\ln(P''_{O_2}/P'_{O_2})} \qquad (1)$$

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where, E_{obs} means the observed e.m.f. of the oxygen concentration cell.

$$O_2(P'), \mathrm{Pt}/Ce_xPr_{1-x}O_2/\mathrm{Pt}, O_2(P'')$$
$$P' = 1\,\mathrm{atm} \qquad P'' = 0.21\,\mathrm{atm} \qquad (2)$$

A vertical type gas flow apparatus similar to the apparatus reported by Verkerk *et al.* [9] was used for the measurement of e.m.f. The electrical contacts were made using platinum paste electrodes to both sides of a disc sample. The e.m.f. of the cell was measured by an electrometer (Takeda Riken, TR-8651). The electrical conductivity was measured by an a.c. bridge method. A frequency generator (Kikusui Electric, Model 417-RC) and a direct reading impedance bridge (Ando Electric, DR-2-2) were used. The frequency used was 10 kHz.

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows the lattice constants of the praseodymia doped ceria system which had the fluorite structure. With increased praseodymia contents, the Ce^{4+} sites were ideally replaced by Pr^{4+} ions up to 70 mol % of praseodymia. At low ceria contents, the β-phase analogous to Pr_6O_{11} coexisted with the mixed oxide phase. This is consistent with the well known observations of other investigators [10, 11]. The reasons why the lattice parameters of this oxide system almost follow the linear function of Vegards rule over a wide composition range are that, (1) both CeO_2 and Pr_6O_{11} have fluorite-type cubic crystal structure, and (2) the difference between the radii of Pr^{4+} and Ce^{4+} is only 0.4%. The single phase mixed oxides formed dense discs, while praseodymia and two praseodymia-rich oxides did not form any dense disc which could be used for the electrical conductivity measurements.

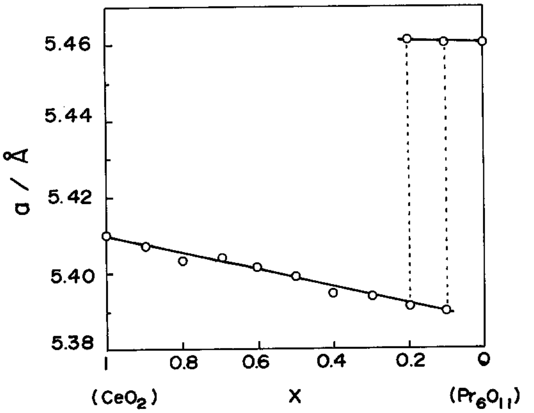

Fig. 1. Lattice constants of praseodymia-doped ceria system having fluorite structure.

3.2. *Electrical conductivity measurements*

Figure 2 shows the relation between σT and the reciprocal temperature for various compositions of the $Ce_xPr_{1-x}O_2$ system. The electrical conductivity increases with increase in the content of praseodymia throughout the temperature range measured, with only one exception. At 600° C, for instance, σ of $Ce_{0.6}Pr_{0.4}O_2$ was $3.6 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ which is about two thousand times higher than that of pure CeO_2, and the oxide ion transference number t_0 was 0.11, as shown in Fig. 3. With increased praseodymia contents, the ionic transference number t_0 decreases from 0.59 to 0.11 at 600° C. Similar to other mixed conductors, both the ionic transference number and the conductivity increase with temperature. There are no clear criteria for the selection of ionic and electronic conductivities for the mixed conduction-type electrodes, but $Ce_{0.6}Pr_{0.4}O_2$ seems to have high ionic and electronic conductivities above 600° C. Kudo and Obayashi [6] reported the

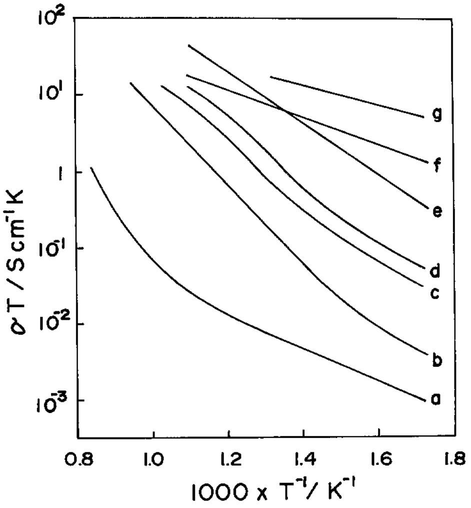

Fig. 2. Variation of conductivity in 0.21 atm of oxygen with reciprocal temperature for the $Ce_xPr_{1-x}O_2$ system. The value of x; a:1, b: 0.9, c: 0.8, d: 0.7, e: 0.6, f: 0.5, g: 0.3.

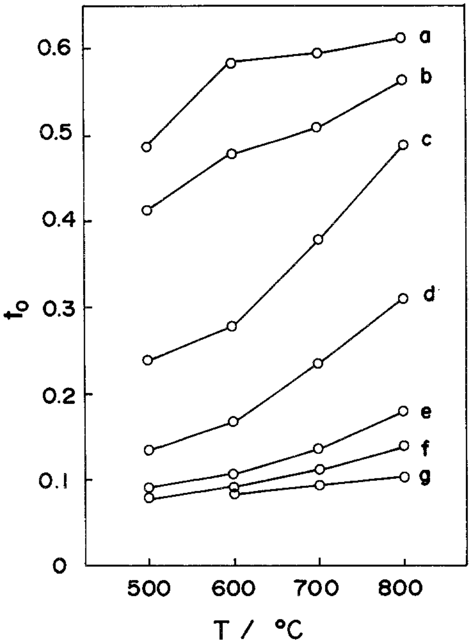

Fig. 3. Ionic transference number of the $Ce_xPr_{1-x}O_2$ system as a function of temperature. The value of x; a: 1, b: 0.9, c: 0.8, d: 0.7, e: 0.6, f: 0.5, g: 0.3.

oxide ion transference number of $Ce_{0.7}Ln_{0.3}O_{1.9}$ (Ln: Gd, Er) to be unity above 600° C. The lattice constants were 0.5428 nm (Ln: Gd) and 0.5391 nm (Ln: Re), respectively, and the electrical conductivities were about 7×10^{-3} S cm^{-1} at 600° C. If these electrolytes can be well contacted with the $Ce_xPr_{1-x}O_2$ electrode, one might develop a new type of fuel cell.

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