JOURNAL OF MATERIALS SCIENCE 17 (1982) 2577–2584

Electrical conduction of partially stabilized zirconia $Zr_{0.94}Ca_{0.06}O_{1.94}$ as a function of temperature and oxygen partial pressure

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Partially stabilized zirconia (PSZ), $Zr_{0.94}Ca_{0.06}O_{1.94}$, was prepared by a hot kerosene drying method and a conventional oxide wet-mixing method. The total d.c. conductivities of these zirconia specimens were measured by the three-terminal technique as a function of temperature in the range 1088 to 1285 K and oxygen partial pressure in the range 1 to 10^{-24} bar. The specimen prepared by the hot kerosene drying method showed near oxygen ion conduction with four times higher conductivity than the specimen prepared by the conventional mixing method at $T = 1088$–1285 K and $P_{O_2} = 10^{-6}$–10^{-24} bar. The higher oxygen pressure conductivity tended approximately towards a $P_{O_2}^{+1/4}$ to $P_{O_2}^{+1/5}$ dependence, indicative of p-type conduction, whereas the lower oxygen pressure conductivity tended to be virtually independent of oxygen pressure, indicative of oxygen-ion conduction. The activation energy was found to be 130 kJ mol^{-1} at $T = 1088$–1285 K, $P_{O_2} = 0.2127$ bar (air) for pure electron-hole conduction and 153 kJ mol^{-1} at $T = 1088$–1285 K for ionic conduction.

1. Introduction

Fully CaO-stabilized zirconia (FSZ), $Zr_{0.85}Ca_{0.15}O_{1.85}$, has been shown to be a suitable solid electrolyte for the determination of oxygen potential in oxide systems. Steele [1] and Schmalzried [2] showed that FSZ could be used at a temperature of 1300 K and oxygen partial pressures above $\sim 3.24 \times 10^{-19}$ bar because of its pure oxygen-ion conduction in this range. However, at lower oxygen partial pressures the cubic FSZ exhibited a marked excess electron conduction [1, 3, 4], and thus could not be used as an oxygen sensor. A suitable oxygen sensor for the measurement of lower oxygen potentials is still needed.

The defect structures of pure monoclinic zirconia [5–7] and of cubic FSZ [8–12] are well known from measurements of the oxygen pressure dependence of electrical conductivity. However, the electrical conductivity of PSZ, $Zr_{0.94}Ca_{0.06}O_{1.94}$, as a function of temperature and oxygen partial pressure has not previously been reported.

The stabilization of zirconia is usually carried out by the conventional oxide wet-mixing method. However, it requires a high sintering temperature (~ 2273 K) and it is difficult to mix the zirconia powder homogeneously with a dopant oxide powder. For this reason, we used both a hot kerosene drying method [13, 14] and a conventional oxide wet-mixing method for the starting powders and compared the conductivity data for CaO-partially stabilized zirconia (PSZ) from each method.

The aim of the present work was firstly to determine if PSZ would still exhibit ionic conduction at lower oxygen partial pressures and secondly to compare the electrical behaviour of PSZ prepared by the hot kerosene drying

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0022–2461/82/092577–08$03.46/0

TABLE I Properties of hot-kerosene dried and conventionally wet-mixed partially stabilized zirconia (PSZ) $Zr_{0.94}Ca_{0.06}O_{1.94}$ specimens

Specimen	Bulk density ($g\,cm^{-3}$)	Open porosity (%)	Cubic-phase zirconia content (wt %)
Hot-kerosene dried PSZ	5.54 (95 % of theoretical density)	0.44	68
Conventionally wet-mixed PSZ	5.24 (90 % of theoretical density)	1.1	55

method and the conventional oxide-wet mixing method.

2. Experimental procedure

2.1. Specimen preparation

The method of specimen preparation mentioned in previous publications [13, 14] was used: 0.94 mol $ZrO(CH_3COO)_2$ (Ventron Co., USA, extra pure) and 0.06 mol $Ca(CH_3COO)_2 \cdot H_2O$ (Hayashi Pure Chemical Co., Japan, extra pure) were dissolved in water to give a composition of $Zr_{0.94}Ca_{0.06}O_{1.94}$ after firing. A commercial emulsifier (Span #80, Atlas Chemie, West Germany) was added to the aqueous homogeneous solution to lower its surface energy; this allowed very small droplets to be added to a hot kerosene bath (443 K) which yielded small atomically mixed acetate particles. The homogeneous powder was isolated from the kerosene bath by filtration.

The dried powders were calcined at 1373 K for 2 h in air and discs of 20 mm diameter and 3 mm thickness were compacted at a pressure of 170 MPa and then sintered at 1873 K for 4 h in air.

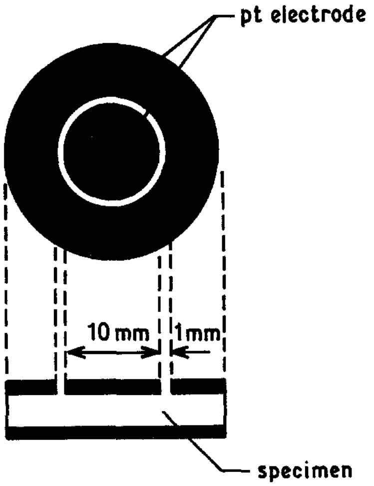

Figure 1 Shape of platinum electrode and specimen for the d.c. conductivity using the three-terminal method.

ZrO_2 (Semi-Elements Inc., USA) and $CaCO_3$ (Hayashi Pure Chemical Co., Japan) powders as starting materials were wet ball-milled for 15 h to give a composition of $Zr_{0.94}Ca_{0.06}O_{1.94}$ after sintering. The calcining, pressing and sintering of conventionally wet-mixed powder were carried out in the same way as described in the hot kerosene drying method.

The results of the sintering trials for hot-kerosene dried and conventionally wet-mixed specimens are presented in Table I. The sintered disc shown in Fig. 1 was circularly painted with platinum paste and then fired at 1373 K for 1 h in air.

2.2. Apparatus and method

2.2.1. Design of high-temperature furnace and specimen holder

Electrical conductivity and e.m.f. measurements were carried out in the furnace shown in Fig. 2. In order to shield the electromagnetic field induced by the electric current in the heating element, a nickel cylinder-tube with short skin depth, 48 mm in diameter, 5 mm thick and 600 mm long, was inserted into the furnace and then earthed. The platinum electrode and specimen were maintained under compression by a spring-loaded kanthal wire to ensure good electrical contact. The specimen temperature was held constant to ± 1° C measured with a Pt/Pt–10 % Rh thermocouple.

2.2.2. Specimen atmosphere control

Oxygen partial pressures employed in the measurements were in the range 1 to 10^{-3} bar and 10^{-15} to 10^{-24} bar. The high pressures were obtained by flowing various Ar/O_2 gas mixtures by means of a flow meter, while the low pressures were produced conveniently by using H_2/H_2O gas mixtures at various constant bath temperatures between 303 and 358 K, described in Table II. The experimental

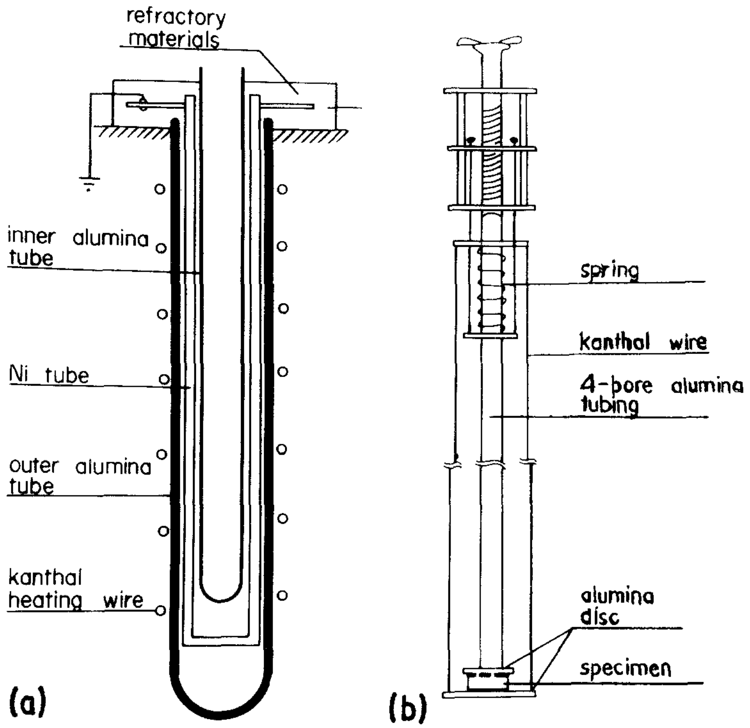

Figure 2 Schematic diagram of high-temperature electrical conductivity furnace (a) and specimen holder (b).

apparatus used for the H_2/H_2O gas mixture is illustrated in Fig. 3. Hydrogen gas should be passed only through gas inlet 1 with an appreciably slow flow rate of 2.5 to $5.0\,\mathrm{cm^3\,min^{-1}}$ to saturate the water vapour in the bath. A heating wire was wrapped around the glass tubing in order to prevent condensation of water vapour.

The partial pressure ratio is given as follows:

$$\frac{P_{H_2O}}{P_{H_2}} = \frac{P^{\circ}_{H_2O}}{P_M - P^{\circ}_{H_2O}}$$

where P_{H_2O}, P_{H_2}, P_M, and $P^{\circ}_{H_2O}$* denote partial pressure of water vapour and hydrogen, total pressure on manometer and saturated water vapour in the constant temperature bath, respectively. The P_{O_2} values were calculated from the equilibrium constants for $H_2 + \frac{1}{2}\,O_2 = H_2O$ and the measured P_{H_2O}/P_{H_2} values. If lower oxygen pressure were necessary, gas inlets 1 and 2 were used so that the ratio P_{H_2O}/P_{H_2} could be correspondingly reduced by the hydrogen gas.

2.2.3. Electrical conductivity measurements

Electrical conductivity was determined using the three-terminal d.c. technique with an electrometer (Keithley Model 610C) as an ammeter, a digital multimeter (Hewlett Packard Model 3465B) as a voltmeter and a Hochkonstant-Stromquelle (Kisch Messergeraete GmbH, 4401 Albachten, West Germany, Model KSQ 10) as a d.c. power source. The measuring arrangement is shown in Fig. 4. The current varied from 10^{-5} to 10^{-4} A and the voltage from 5×10^{-3} to 10^{-1} V.

2.2.4. Measurement of e.m.f.

The gas mixture (Ar/O_2, H_2/H_2O) was hermetically separated from the reference electrode (Ni/NiO) compartment with cement, and the difference in oxygen potential between the gas mixture and the Ni/NiO electrode was measured as the e.m.f.,

$$E = 4.9615 \times 10^{-3}\, T \log \frac{P_{O_2}^{\mathrm{I}}\ (Ar/O_2 \text{ or } H_2/H_2O)}{P_{O_2}^{\mathrm{II}}\ (\mathrm{Ni/NiO})^{*}}$$

where E represents the measured e.m.f. due to the difference in oxygen potential between both compartments. Schmalzried [17] assumed, in the above equation, that the condition $P_{\ominus} \ll P_{O_2}^{\mathrm{I}} \ll P_{O_2}^{\mathrm{II}} \ll P_{\oplus}$ was satisfied, where $P_{\oplus}$ and $P_{\ominus}$ represent those oxygen potentials at which ionic conductivity, $\sigma_{O^{2-}}$, is equal to the defect electron conductivity, $\sigma_{\oplus}$, and the excess electron conductivity, $\sigma_{\ominus}$,

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*Data taken from Kubaschewski *et al.* [15].
†Data taken from Pyun *et al.* [16].

TABLE II Ionic transference number of partially stabilized zirconia (PSZ), $Zr_{0.94}Ca_{0.06}O_{1.94}$, as a function of temperature and oxygen partial pressure for hot-kerosene dried specimen

Temperature (K)	Mixing ratio of O_2 to Ar gas or partial pressure ratio of H_2O to H_2	Oxygen partial pressure for mixed gas $P_{O_2}^{I}$ (O_2/Ar, H_2/H_2O) (bar)	Oxygen partial pressure for standard electrode $P_{O_2}^{II}$ (Ni/NiO) (bar)	e.m.f. E_0 estimated thermodynamically (V)	e.m.f. E measured (V)	Ionic transference number of oxygen (–)
1088	$V_{O_2} = 5\ cm^3\ min^{-1}$	1.013		0.734	0	0.212
	$V_{O_2}/V_{Ar} = 10^{-1}$	1.013×10^{-1}		0.680	0	0.317
	$V_{O_2}/V_{Ar} = 10^{-2}$	1.013×10^{-2}		0.626	0	0.445
	$V_{O_2}/V_{Ar} = 10^{-3}$	1.013×10^{-3}		0.572	0	0.581
	$P_{H_2O}/P_{H_2} = 1$	1.165×10^{-18}	2.545×10^{-14}	0.234	0.234	1.0
	$P_{H_2O}/P_{H_2} = 10^{-1}$	1.165×10^{-20}		0.342	0.341	1.0
	$P_{H_2O}/P_{H_2} = 2.36 \times 10^{-2}$	6.489×10^{-22}		0.410	0.412	1.0
	$P_{H_2O}/P_{H_2} = 1.12 \times 10^{-3}$	1.462×10^{-24}		0.553	0.560	1.0
1281	$V_{O_2} = 5\ cm^3\ min^{-1}$	1.013		0.649	0	0.193
	$V_{O_2}/V_{Ar} = 10^{-1}$	1.013×10^{-1}		0.585	0	0.272
	$V_{O_2}/V_{Ar} = 10^{-2}$	1.013×10^{-2}		0.522	0	0.369
	$V_{O_2}/V_{Ar} = 10^{-3}$	1.013×10^{-3}		0.458	0	0.478
	$P_{H_2O}/P_{H_2} = 1$	4.285×10^{-15}	6.257×10^{-11}	0.265	0.260	0.993
	$P_{H_2O}/P_{H_2} = 10^{-1}$	4.285×10^{-17}		0.392	0.387	0.997
	$P_{H_2O}/P_{H_2} = 2.36 \times 10^{-2}$	2.387×10^{-18}		0.472	0.468	0.998
	$P_{H_2O}/P_{H_2} = 1.12 \times 10^{-3}$	5.375×10^{-21}		0.640	0.621	1.0

respectively. He also derived the ionic transference number of oxygen $t_{O^{2-}}$ for PSZ solid electrolyte from the following equation:

$$t_{O^{2-}} = \left[1 + \left(\frac{P_{O_2}}{P_{\oplus}}\right)^{1/n} + \left(\frac{P_{O_2}}{P_{\ominus}}\right)^{-1/n}\right]^{-1}$$

where the exponent n is related to defect structure of the solid electrolyte.

3. Results and discussion

3.1. Electrical conductivity of PSZ

The measurement of the dependence of oxygen partial pressure on electrical conductivity of PSZ has not yet been reported. Though there are contributions from interface and grain boundary to bulk conductivity, it was beyond the scope of the present work to separate those effects. The total electrical conductivities of PSZ measured by the d.c. three-terminal technique are presented as a function of temperature and oxygen partial pressure in Fig. 5.

In the higher oxygen partial pressure range, 1 to 10^{-6} bar, and at temperatures of 1094 to 1285 K, the conductivity was found to be approximately proportional to $P_{O_2}^{+1/4}$ to $P_{O_2}^{+1/5}$ (exponents ranged between + 1/4 and 1/5),

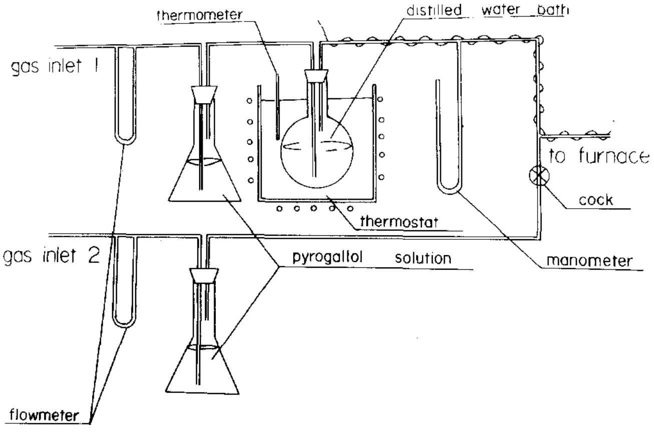

Figure 3 Apparatus for H_2/H_2O gas mixture.

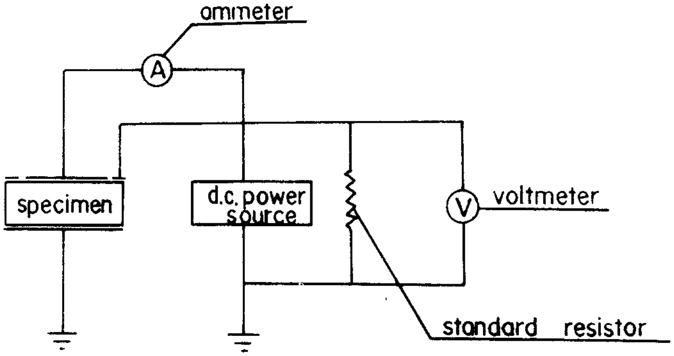

Figure 4 Circuit diagram for d.c. electrical conductivity measurements using three-terminal method.

indicative of p-type conduction; while in the lower oxygen partial pressure range, 10^{-6} to 10^{-24} bar, the conductivity was found to be virtually independent of oxygen partial pressure, indicative of oxygen-ion conduction.

It is suggested from this observation that the total conductivity at higher oxygen pressures is controlled by monoclinic-phase zirconia contained in PSZ, where singly ionized oxygen interstitials (O_i') or completely ionized zirconium vacancies (V_{Zr}'''') and defect electrons may prevail. Defect electrons mainly contribute to the total conductivity on account of their higher concentration and higher mobility compared with those of oxygen interstitials and zirconium vacancies. At lower oxygen pressures the total conductivity is nearly controlled by oxygen vacancy as a charge carrier in cubic-phase zirconia [8], hence PSZ could probably be used as a solid electrolyte at the lower oxygen potential.

The plots of log (ionic conductivity of PSZ) against reciprocal temperature, shown in Fig. 6, yielded an activation energy of 153.2 kJ mol^{-1}

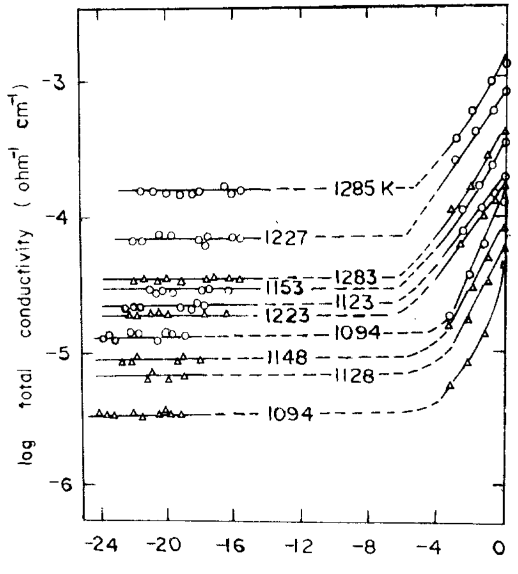

Figure 5 Total d.c. electrical conductivity for partially stabilized zirconia (PSZ), $Zr_{0.94}Ca_{0.06}O_{1.94}$, solid electrolyte prepared by hot-kerosene drying method (○) and conventional oxide wet-mixing method (△) against oxygen partial pressure for various temperatures. Numbers on the curves denote temperature (K).

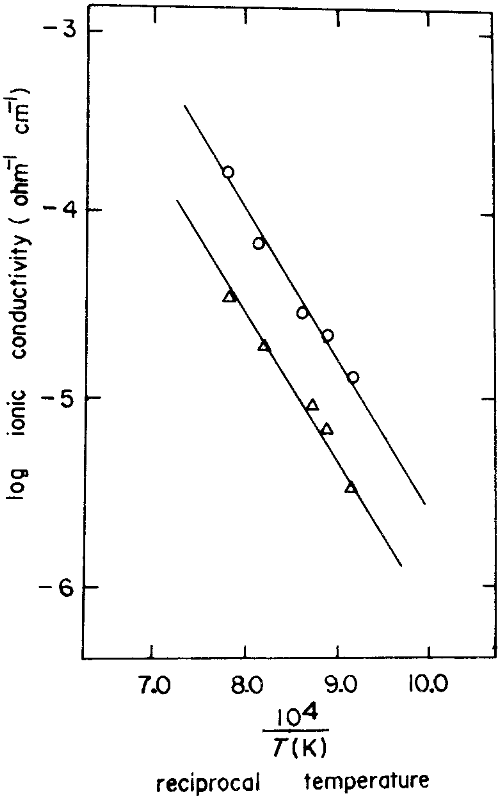

Figure 6 Arrhenius plots of ionic conductivity of partially stabilized zirconia (PSZ), $Zr_{0.94}Ca_{0.06}O_{1.94}$, prepared by hot-kerosene drying method (○) and conventional oxide wet-mixing method (△) at oxygen partial pressures in the range 10^{-6} to 10^{-24} bar.

for the hot-kerosene dried specimen as well as for the conventionally mixed specimen. The equality of the activation energy may possibly result from the approximate content of cubic-phase zirconia in PSZ within the probable error range. The activation energies for the ionic conduction of FSZ have been given as 112.9 [18], 116.8 [8] and 121.6 kJ mol^{-1} [10], which are in good agreement with one another. These values were less than the result of the present work. This may be due to the lower cubic content of the PSZ used in this work, 68 and 55 wt% in hot-kerosene dried and conventionally wet-mixed specimens, respectively.

The hot-kerosene dried specimens showed approximately 3.5 times higher ionic conductivity than the conventionally oxide-mixed specimens. This may be attributed either to the higher sintered density or to the lower contact resistance of hot-kerosene dried specimens.

Interpolating the ionic conductivity at 1273 K in Fig. 6, the hot-kerosene dried and conventionally oxide-mixed specimens showed values of 1.33×10^{-4} and 3.76×10^{-5} ohm^{-1} cm^{-1}, respectively. Comparing these values with $2\text{–}3 \times 10^{-2}$ ohm^{-1} cm^{-1} for cubic FSZ ($Zr_{0.85}Ca_{0.15}O_{1.85}$) [10, 18–20] and $2\text{–}3 \times 10^{-6}$ ohm^{-1} cm^{-1} for pure monoclinic zirconia [5, 7], the present data for pure monoclinic zirconia, PSZ and FSZ, give an account of the increased electrical conductivity with doped CaO content up to 12 mol% [20, 21]. The increase in conductivity is probably associated with the formation of the oxygen vacancy $V_{O^{2-}}$ with increasing concentration of doped CaO.

Experimental results for the total d.c. conductivity measured at an oxygen pressure of 0.2127 bar (air) as a function of reciprocal temperature are presented in Fig. 7. The activation energy of both hot-kerosene and conventionally mixed specimens was found to be ~ 130 kJ mol^{-1}. This is in good agreement with the result on monoclinic zirconia [7] of 127.7 kJ mol^{-1}. This may result from the fact that the total conductivity measured in air was caused by pure defect electron conduction in both cases.

The total d.c. conductivities of PSZ measured at 1273 K in air were 8.0×10^{-4} ohm^{-1} cm^{-1} for hot-kerosene dried specimen and 2.0×10^{-4} ohm^{-1} cm^{-1} for conventionally mixed specimen. The lower conductivity of the conventionally mixed specimen may be due to the higher porosity. In contrast with these d.c. data, the total a.c. conductivity of pure monoclinic zirconia measured by the three-terminal technique at 1273 K was given as 8×10^{-5} ohm^{-1} cm^{-1} by Vest *et al.* [5] and Kumar *et al.* [7]. The difference in the conductivity between these and the present work may possibly be attributed to contact resistance, in spite of a similar sintered density (90 to 95% theoretical). In the present work, the a.c. conductivity was conveniently obtained by extrapolating to the value at 1000 kHz and it was confirmed in a preliminary experiment of this work that the a.c. conductivity of PSZ determined by the two-terminal technique always showed a higher value than the d.c. conductivity determined by the three-terminal measurements, e.g. 1.1×10^{-3} ohm^{-1} cm^{-1} for a.c. and 8.0×10^{-4} ohm^{-1} cm^{-1} for d.c. conductivities of hot-kerosene dried PSZ at 1273 K in air. The a.c. conductivity measured at frequencies below 5 kHz remained nearly the same as the d.c. conductivity, but it increased inverse-linearly as the frequency increased from 10 to 100 kHz.

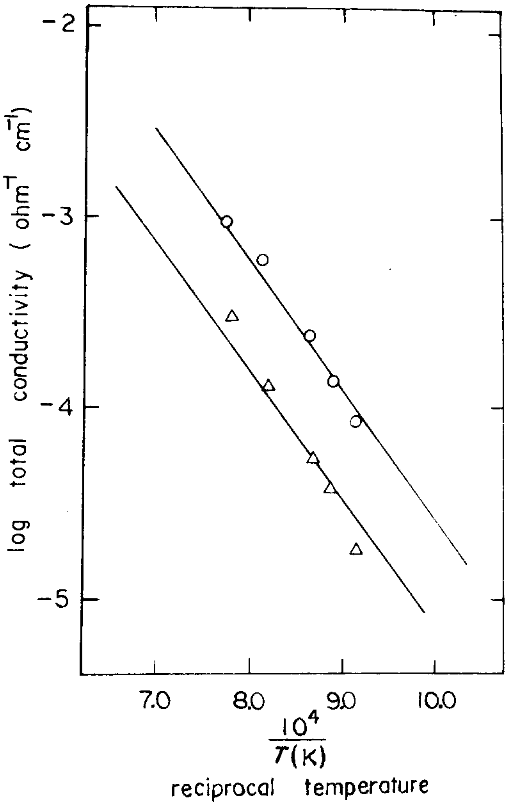

Figure 7 Arrhenius plots of total d.c. conductivity (pure electron-hole conduction) of partially stabilized zirconia (PSZ), $Zr_{0.94}Ca_{0.06}O_{1.94}$, prepared by hot-kerosene drying method (○) and conventional oxide wet-mixing method (△) at oxygen partial pressure $P_{O_2} = 0.2127$ bar.

3.2. Oxygen ion transference number $t_{O^{2-}}$ of PSZ

In the present work, $P_{\oplus}$ for PSZ was calculated from Figs 5 and 6 to be 4×10^{-3} to 6×10^{-4} bar, whereas $P_{\ominus}$ was assumed to be below 10^{-24} bar; hence the term $(P_{O_2}/P_{\ominus})^{-1/n}$ in the expression for $t_{O^{2-}}$ was insignificant in the temperature range $T = 1094$ to 1285 K and oxygen partial pressure range $P_{O_2} = 1$ to 10^{-24} bar. Table II presents the oxygen ion transference number $t_{O^{2-}}$ as a function of temperature and oxygen partial pressure for the hot-kerosene dried specimen. The values of $t_{O^{2-}}$ and e.m.f. at the temperatures 1088 and 1281 K for oxygen partial pressures of 1 to 10^{-3} bar were less than unity and zero, respectively. Relating this fact to the proceeding result of the electrical conductivity, it is suggested that PSZ shows a mixed conduction due to oxygen-ion and defect-electron, i.e. p-type, conduction at the given temperatures and oxygen pressures. Any positive hole contribution to the total conductivity would ensure a "short-circuit" flux through the PSZ electrolyte which would rapidly polarize the Ni/NiO electrode because of the very slow kinetics associated with this electrode. Moreover, any molecular permeability through the electrolyte would also result in zero e.m.f. values.

The transference number, however, remained nearly unity at the two temperatures and oxygen partial pressures of 4×10^{-15} to 10^{-24} bar, and additionally decreased slightly as temperature increased from 1088 to 1281 K. An association of these transference number data with the proceeding data on the oxygen pressure dependence of conductivity leads to the suggestion that PSZ shows nearly an oxygen ion conduction at temperatures of 1088 and 1281 K, and in the oxygen partial pressure ranges 10^{-6} to 10^{-24} and 10^{-6} to 10^{-21} bar, respectively. Therefore, PSZ would be available as an oxygen sensor. But at the higher oxygen partial pressure of 1 to 10^{-3} bar, PSZ would not be a suitable solid electrolyte because of its mixed conduction by the electron hole mechanism. Compared with this PSZ electrolyte, FSZ used as a solid electrolyte exhibits nearly an oxygen ion conduction at temperatures of 1143 and 1273 K, in the oxygen partial pressure range 1 to 4×10^{-22} bar [9] and 1 to 10^{-15} bar [11, 12], respectively.

4. Conclusions

(1) The hot-kerosene dried PSZ specimen showed near oxygen ion conduction with approximately four times higher conductivity than conventionally oxide-mixed specimens at $T = 1088$ to 1285 K and $P_{O_2} = 10^{-6}$ to 10^{-24} bar.

(2) At higher oxygen pressures (1 to 10^{-6} bar) the conductivity was approximately proportional to $P_{O_2}^{+1/4}$ to $P_{O_2}^{+1/5}$, indicative of a defect electron conduction of PSZ, while at lower oxygen pressures (10^{-6} to 10^{-24} bar) the conductivity was virtually independent of oxygen pressure at $T = 1088$ to 1285 K, indicative of an oxygen-ion conduction of PSZ.

(3) The activation energy of both hot-kerosene dried and conventionally oxide-mixed specimens was found to be 130 kJ mol^{-1} at $T = 1088$ to 1285 K and $P_{O_2} = 0.2127$ bar (air) for the pure electron-hole conduction, and 153 kJ mol^{-1} at $T = 1088$ to 1285 K for the oxygen-ion conduction.

Acknowledgements

The authors are indebted to Professor Dr H. C. Kim of Korea Advanced Institute of Science and Technology (KAIST) for many helpful discussions and to KAIST for financial support of this work.

References

1. B. C. H. STEELE, in "Electromotive Force Measurements in High Temperature Systems", edited by C. B. Alcock, (The Institution of Mining and Metallurgy, London, 1968) p. 3.
2. H. SCHMALZRIED, in "Proceedings of a Symposium on Metallurgical Chemistry, 14–16 July 1971", edited by O. Kubaschewski (Her Majesty's Stationary Office, London, 1972) p. 39.
3. J. D. TRETYAKOW, *Inorg. Mater. (USSR)* **2** (1966) 432.
4. J. W. PATTERSON, E. C. BOGREN and R. A. RAPP, *J. Electrochem. Soc.* **114** (1967) 752.
5. R. W. VEST, N. M. TALLAN and W. C. TRIPP, *J. Amer. Ceram. Soc.* 47 (1964) 635.
6. D. L. DOUGLASS and C. WAGNER, *J. Electrochem. Soc.* **113** (1966) 671.
7. A. KUMAR, D. RAJDEV and D. L. DOUGLASS, *J. Amer. Ceram. Soc.* 55 (1972) 439.
8. F. HUND, *Z. Phys. Chem.* **199** (1952) 142.
9. K. KIUKKOLA and C. WAGNER, *J. Electrochem. Soc.* **104** (1957) 379.
10. W. D. KINGERY, J. PAPPIS, M. E. DOTY and D. C. HILL, *J. Amer. Ceram. Soc.* 42 (1959) 393.
11. H. SCHMALZRIED, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.* 66 (1962) 572.
12. B. C. H. STEELE and C. B. ALCOCK, *Trans. Met. Soc. AIME* 233 (1965) 1359.
13. P. REYNEN and H. BASTIUS, *Powder Met. Intern.* 8 (1976) 91.
14. P. REYNEN, H. BASTIUS, M. FAIZULLAH and

H. v. KAMPTZ, *Ber. Dtsch. Keram. Ges.* **54** (1977) 63.

15. O. KUBASCHEWSKI, E. LL. EVANS and C. B. ALCOCK, "Metallurgical Thermochemistry" (Pergamon Press, London, 1967) (thermochemical tables).
16. S. I. PYUN and F. MÜLLER, *High Temp.-High Press.* **9** (1977) 111.
17. H. SCHMALZRIED, *Z. Phys. Chem. N. F.* **38** (1963) 87; also "Proceedings of a Symposium on Thermodynamics, Vol. I, 22–27 July 1965" (IAEA, Wien, 1966) p. 97.
18. T. Y. TIEN and E. C. SUBBARAO, *J. Chem. Phys.* **39** (1963) 1041.
19. W. H. RHODES and R. E. CARTER, presented at the Amer. Ceram. Soc. Meeting, April 1962, abstract in *Amer. Ceram. Soc. Bull.* **41** (1962) 283.
20. J. M. DIXON, L. D. LaGRANGE, U. MERTEN, C. F. MILLER and J. T. PORTER II, *J. Electrochem. Soc.* **110** (1963) 276.
21. H. A. JOHANSEN and J. G. CLEARY, *ibid.* **111** (1964) 100.

Received 12 August 1981
and accepted 1 February 1982