

# Determination of electronic conductivity limits of mullite and $\text{ZrO}_2$ -9 mol% MgO solid electrolytes

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A coulometric titration technique was used for the determination of the parameter  $P_{\ominus}$ , defined as the oxygen partial pressure at which the ionic conductivity and n-type electronic conductivity of the electrolyte are equal, for mullite and 9 mol % MgO stabilized zirconia electrolytes in the temperature range 1674–1921 K. The results of  $P_{\ominus}$  for mullite and  $\text{ZrO}_2$ -9 mol % MgO were  $\log(P_{\ominus}/101\,325\text{ Pa}) = 54.32 - 137000/T$  and  $\log(P_{\ominus}/101\,325\text{ Pa}) = 27.16 - 75500/T$ , respectively. The results for low oxygen activities in liquid iron are discussed on the basis of the present results for  $P_{\ominus}$  values.

## 1. Introduction

Zirconia-based solid electrolyte has been successfully applied for high temperature thermodynamic studies. Unfortunately, when zirconia-based electrolytes are exposed to high temperatures and low oxygen potentials, they exhibit mixed ionic and n-type electronic conduction, which is influenced by the type and concentration of the stabilizing oxide, the phase composition, the impurities in the electrolyte, and the microstructure of the electrolyte. It is therefore imperative, if reproducible and accurate oxygen measurements are to be made, that the parameter  $P_{\ominus}$ , defined as the oxygen partial pressure at which the ionic and n-type electronic conductivities are equal, should be consistent and be known to a high degree of accuracy. However, a further problem concerning the polarization at the electrolyte-electrode interfaces is encountered, even if the  $P_{\ominus}$  values are accurately determined. This problem can be overcome by the use of the plug-type oxygen probe [1], which contains a magnesia-stabilized zirconia rod instead of a tube.

The mullite composition ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) was shown to vary within relatively wide limits of at least 59 to 62 mol %  $\text{Al}_2\text{O}_3$ , depending on temperature [2]. This compositional variation arises due to substitution of aluminium for silicon, accompanied by formation of oxygen vacancies [3, 4]. Schuh *et al.* [3] used mullite having an excess of  $\text{SiO}_2$  as a solid electrolyte in e.m.f. measurements on an oxygen concentration cell. Further detailed study was carried out by Fischer and Janke [5] who reported that lower oxygen activities could be measured by a mullite probe in comparison with a  $\text{ZrO}_2$ -CaO solid electrolyte. However, they used the mullite probe contained 3–6 mass % impurities and coated with porous zirconia.

Recently, the present authors [6] measured low oxygen activities in liquid iron deoxidized by aluminium using a tubular mullite probe manufactured from high purity materials coprecipitated by a sol-gel method. As a result, more accurate and reproducible measure-

ments of oxygen activity were possible with a mullite probe compared with a zirconia-based probe because of zero polarization at the electrolyte-electrode interfaces.

In the present work, the  $P_{\ominus}$  values for a mullite probe were measured in the temperature range 1676–1921 K by means of a coulometric titration technique introduced by Swinkels [7]. The  $P_{\ominus}$  values for  $\text{ZrO}_2$ -9 mol % MgO, which is commercially used in steel-making, were also measured. On the basis of the present  $P_{\ominus}$  values, low oxygen activities in liquid iron, which were previously measured [6] by a mullite and plug-type  $\text{ZrO}_2$ -9 mol % MgO probes, are discussed.

## 2. Basic considerations

Schmalzried [8] has analysed the contribution of electronic conduction in the solid electrolyte to the measured e.m.f. of an electrochemical oxygen probe. He proposed that the e.m.f. in the presence of n-type electronic conduction can be expressed as

$$E = \frac{RT}{F} \ln \frac{P_{\text{O}_2}^{1/4} + P_{\ominus}^{1/4}}{P'_{\text{O}_2}{}^{1/4} + P_{\ominus}^{1/4}} \quad (1)$$

where  $P_{\text{O}_2}$  and  $P'_{\text{O}_2}$  are the partial pressures of oxygen at the two electrolyte interfaces,  $R$  is the gas constant,  $F$  is the Faraday constant, and  $T$  is the absolute temperature

When the oxygen partial pressures satisfy the following condition,

$$P'_{\text{O}_2} \ll P_{\ominus} \ll P_{\text{O}_2} \quad (2)$$

Equation 1 can be simplified to

$$E = \frac{RT}{4F} \ln \frac{P_{\text{O}_2}}{P_{\ominus}} \quad (3)$$

It can be seen from Equation 3 that if the oxygen partial pressure,  $P_{\text{O}_2}$ , is known, the parameter  $P_{\ominus}$  can be determined experimentally. This very low partial pressure of oxygen,  $P'_{\text{O}_2}$ , can be established by a coulometric titration technique [9], which will be described in more detail.

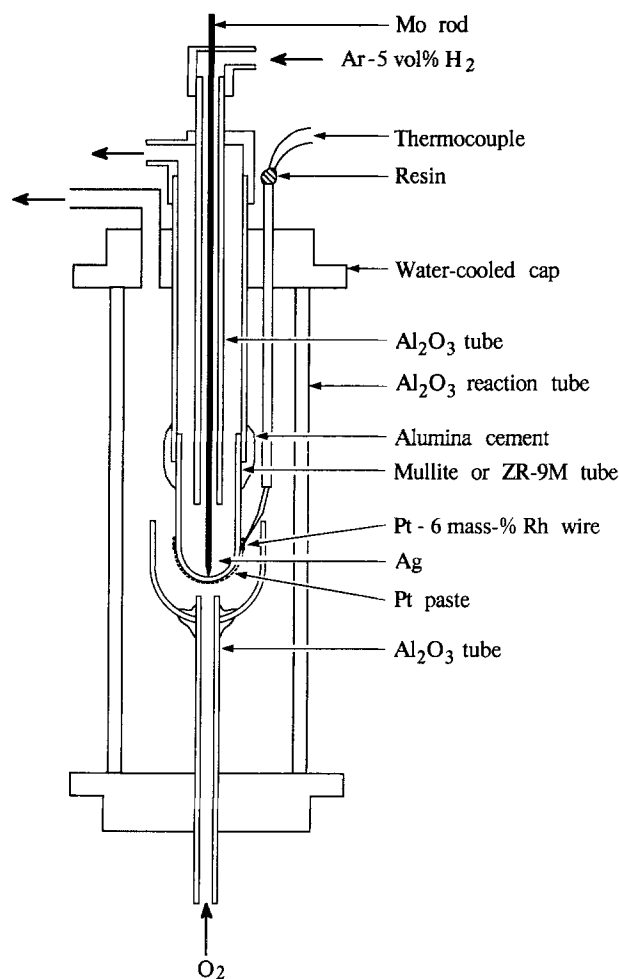


Fig. 1. Schematic diagram of experimental apparatus for measuring  $P_{\ominus}$  values.

### 3. Experimental details

#### 3.1. Apparatus

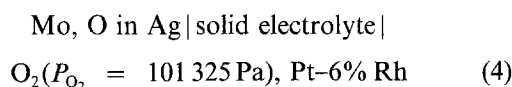
The apparatus is shown in Fig. 1. A mullite tube (ext. dia. 13 mm/int. dia. 9 mm  $\times$  200 mm) was made by the following method:  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  powder was coprecipitated by a sol-gel method and sintered at 1923 K for 3–5 h after slip casting. The apparent porosity was less than 0.2%. A  $\text{ZrO}_2$ -9 mol % MgO tube (ext. dia. 10 mm/int. dia. 7 mm  $\times$  100 mm, ZR-9M) was supplied from Nikkato. These tubes were fixed at the end of an alumina tube with alumina cement. The chemical compositions of mullite and  $\text{ZrO}_2$ -9 mol % MgO electrolytes are given in Table 1. That of mullite, except for sodium and potassium, was obtained by ICP spectrometric method after alkali-fusion technique. The contents of sodium and potassium were determined by atomic absorptiometry.

Six grams of pure silver (99.99 mass %) were melted in a dehydrated Ar-5%  $\text{H}_2$  gas mixture using a vertical resistance furnace ( $\text{LaCrO}_3$  heating element) with a 4 cm uniform temperature zone  $\pm 2$  K. A molybdenum wire (dia. 2 mm) was used for the electrical contact to liquid silver. The platinum electrode was prepared by painting with platinum paste (Furuya Metal Corp., No. 8103) on the surface at the closed end of the electrolyte tube. A Pt-6 mass % -Rh wire,

which was wound around the platinized surface of the electrolyte tube, was used for a contact lead. A Pt-6 mass % -Rh/Pt30 mass % -Rh thermocouple, which was placed against the platinized surface of the electrolyte tube, was used to measure the cell temperature. A memory-type electrometer with an input impedance of  $10^6 \Omega$ , coupled to a chart recorder with an accuracy of  $\pm 0.1\%$  was used for the e.m.f. measurements. The external direct currents were applied by a standard potentiostat.

#### 3.2. Procedure

The cell arrangement shown in Fig. 1 can be expressed as



Just before the measurement of the e.m.f., the reaction tube was flushed with pure oxygen with a flow rate of 100–700  $\text{ml min}^{-1}$ . A direct current was applied to the cell for 3–5 min before the electric circuit was opened. The open-circuit e.m.f. was measured immediately after interruption of the polarizing current.

When a direct current is passed in the appropriate direction, oxygen is transported to the Pt/ $\text{O}_2$  electrode from the silver melt. These measurements were repeated with the application of external potential, which was increased at intervals of 0.5 V, until the measured open-circuit e.m.f. became independent of the applied potential. This resulted in sufficiently low partial pressure of oxygen ( $P'_{\text{O}_2}$ ) at the silver interface of the electrolyte to satisfy the condition  $P'_{\text{O}_2} \ll P_{\ominus}$  (see Equation 2). Since the  $P_{\text{O}_2}$  value was 101 325 Pa in present experimental condition ( $P_{\text{O}_2} \gg P_{\ominus}$ ) and the Pt/ $\text{O}_2$  electrode was known to be non polarizable, the  $P_{\ominus}$  value can be obtained from Equation 3 by measuring the open-circuit e.m.f. of the cell given by Equation 4. The thermoelectromotive force between Pt-6 mass % Rh and Mo,  $E_t$  (mV) =  $20.5 - 0.0323 T$  (1668–1895 K), was used for the correction. The e.m.f. was measured during heating and cooling in the temperature range 1674–1921 K.

### 4. Results and discussion

#### 4.1. Effect of temperature on $P_{\ominus}$ values in mullite

In a preliminary experiment, the open-circuit e.m.f. at the applied potential of 6 V was measured at 1883 K as a function of flowrates of oxygen ( $V_{\text{O}_2}$ ) and Ar-5%  $\text{H}_2$  ( $V_{\text{Ar-5\% H}_2}$ ). As a result, the open-circuit e.m.f. was found to be independent of  $V_{\text{O}_2}$  ranging from 50 to 400  $\text{ml min}^{-1}$  at  $V_{\text{Ar-5\% H}_2} = 300 \text{ ml min}^{-1}$ , and of  $V_{\text{Ar-5\% H}_2}$  ranging from 100 to 700  $\text{ml min}^{-1}$  at  $V_{\text{O}_2} = 500 \text{ ml min}^{-1}$ . These results suggest that the rate of leakage of oxygen through the electrolyte assembly may have been minimal and the Pt/ $\text{O}_2$  electrode was not polarized. In the present work, the values of 300 and 500  $\text{ml min}^{-1}$  were selected for the flowrates of Ar-5%  $\text{H}_2$  gas mixture and pure oxygen, respectively.

Table 1. Chemical compositions of various solid electrolytes (in mass %)

	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	ZrO <sub>2</sub>	MgO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO
<i>Mullite</i>									
Stoichiometric	71.80	28.05	0.04	tr.	0.06	tr.	0.04	0.02	tr.
New mullite*	70.7	28.8	0.32	0.01	0.13	tr.	0.03	tr.	0.06
<i>Zirconia</i>									
ZrO <sub>2</sub> -9 mol % MgO*	0.67	0.07	96.18	2.7	0.1	0.1	tr.	-	0.09
ZrO <sub>2</sub> -9 mol % MgO <sup>12</sup>	1.0	0.5	94.8	3.1	0.1	0.1	tr.	tr.	0.4
ZrO <sub>2</sub> -7 mol % MgO <sup>13</sup>	0.15	0.3	96.7	2.4	-	tr.	0.25	0.01	0.2
ZrO <sub>2</sub> -9 mol % MgO <sup>14</sup>	0.4	0.2	95.6	3.1	0.14	0.05	0.015	0.05	0.4

\* analysed by Nikkato Co., Ltd.

A typical example of an e.m.f. signal obtained at 1871 K is shown in Fig. 2, indicating a stable open-circuit e.m.f. plateau.

It should be pointed out that the e.m.f. values were observed to be affected by the frequency caused by the a.c. power supply for the resistance furnace. However, a stable e.m.f. plateau was obtained in a zirconia probe, since the electrical resistivity of mullite is considerably higher than that of a zirconia-based electrolyte [10].

The values for open-circuit e.m.f. were measured at an interval of 0.5 V. A typical result for the open-circuit e.m.f. against applied potential obtained at 1830 K is shown in Fig. 3, in which the measured e.m.f. is independent of the applied potentials greater than 5 V. Since the critical applied potential is strongly affected by the gas-tightness of the electrolyte assembly, i.e. the rate of leakage of oxygen through the electrolyte assembly, the open-circuit e.m.f. measurements were repeated until the measured e.m.f. plateau was obtained. The values for  $\log P_{\ominus}$ , which were obtained by substituting these measured e.m.f. into Equation 3 and taking into account the thermoelectromotive force, are given in table 2 and plotted against reciprocal of temperature in Fig. 4, indicating

a straight line. The good reproducibility of  $P_{\ominus}$  values obtained by the measurements during the heating as well as the cooling of the two individual electrolytes indicates that phase equilibrium was attained during the experimental run. The  $P_{\ominus}$  values can be expressed as a function of absolute temperature for a mullite electrolyte (1676–1921 K):

$$\log (P_{\ominus}/101\,325\text{ Pa}) = 54.32 - 137000/T \quad (5)$$

and for a ZrO<sub>2</sub>-9 mol % MgO (1674–1904 K):

$$\log (P_{\ominus}/101\,325\text{ Pa}) = 27.16 - 75500/T \quad (6)$$

It can be seen from Fig. 4 that the  $P_{\ominus}$  value for a mullite electrolyte was significantly lower than that for a zirconia-based electrolyte. The commercially available mullite tube (new mullite, (ext. dia. 13.5 mm/int. dia. 9 mm × 600 mm) whose composition is given in Table 1 was used for the measurement of  $P_{\ominus}$  value. However, reproducible and consistent results for the open circuit e.m.f. could not be obtained by the present coulometric titration technique.

#### 4.2. Effect of temperature $P_{\ominus}$ values in ZrO<sub>2</sub>-9 mol % MgO

Magnesia-stabilized zirconia tubes, which have good

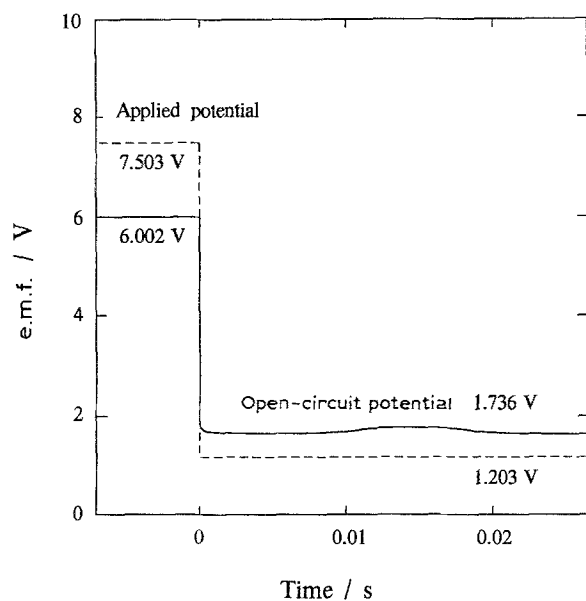


Fig. 2. A typical e.m.f. signal recorded during measurement of  $P_{\ominus}$  values of mullite and ZrO<sub>2</sub>-9 mol % MgO. (—) Mullite at 1871 K; (---) ZrO<sub>2</sub>-9 mol % MgO at 1876 K.

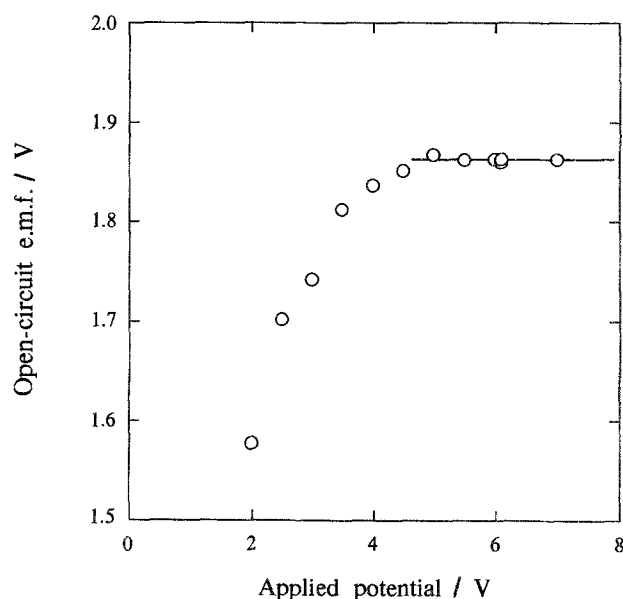


Fig. 3. Dependence of applied potential on open-circuit e.m.f. for mullite at 1830 K.

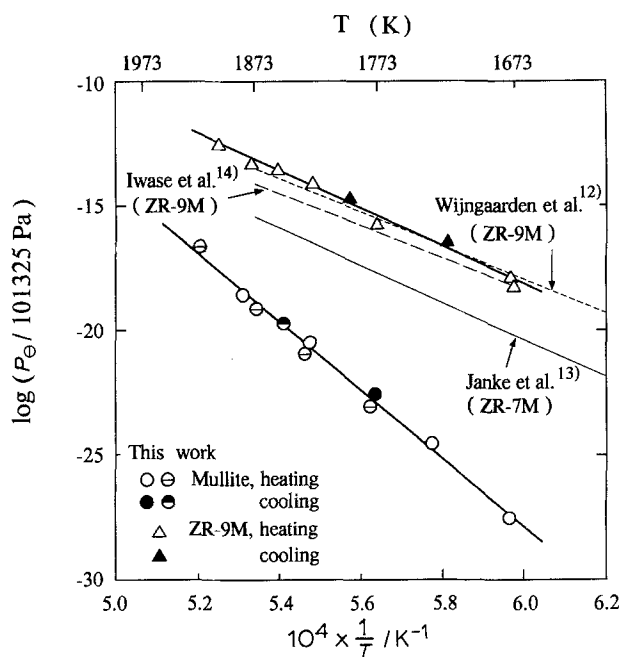


Fig. 4. Logarithms of  $P_{\ominus}$  as a function of reciprocal temperature.

thermal-shock resistance, are commonly used in commercial oxygen probes for the determination of the oxygen content of liquid steel. Successful application depends to a large extent on an accurate knowledge of the  $P_{\ominus}$  value of the electrolyte. Large differences in the  $P_{\ominus}$  values, as shown in Fig. 4, implies that materials, which different investigators have studied, differed in their chemical or physical properties. It was found by Wijngaarden, Geldenhuis, and Dippenaar [11] that magnesia-stabilized zirconia tended to destabilize (i.e. the fraction of the cubic phase decreases) if the electrolyte was exposed to working temperatures below 1673 K and that the  $P_{\ominus}$  values were strongly affected by the time-dependent destabilization.

For this reason, the  $P_{\ominus}$  values for magnesia (9 mol %)-stabilized zirconia whose chemical composition is given in Table 1, were measured at temperatures above 1674 K. A typical result of an open-circuit e.m.f. against time relationship is shown in Fig. 2, in which a stable e.m.f. plateau was obtained. The log  $P_{\ominus}$  values are plotted against reciprocal temperature and experimental conditions for this measurement are given in Table 2. The present results determined during heating and cooling were very close to those obtained by Wijngaarden *et al.* [12] who used the  $ZrO_2$ -9 mol % MgO electrolyte. The chemical composition of electrolytes used by other investigators [12-14] are given in Table 1.

The n-type electronic conductivity,  $\sigma_e$ , is obtained as a function of oxygen partial pressure by Equation 7, if the parameter,  $P_{\ominus}$ , and the ionic conductivity,  $\sigma_{ion}$ , are given [8].

$$\sigma_e = \left( \frac{\sigma_{ion}}{P_{\ominus}^{-1/4}} \right) P_{O_2}^{-1/4} \quad (7)$$

Hennicke and Meyer [15] measured the conductivity of mullite at 1073-1673 K under different oxygen partial pressures of  $(P_{O_2}/101325 \text{ Pa}) = 10^0$ - $10^{-22}$ . Their

results of conductivity, which are independent of oxygen partial pressure at a given temperature, are considered to be ionic ones. The conductivity of  $ZrO_2$ -9 mol % MgO was measured by Tinglian *et al.* [16] at 781-1730 K in air. The  $\sigma_e$  values for mullite and  $ZrO_2$ -9 mol % MgO were calculated at 1873 K as  $\sigma_e = 2.99 \times 10^{-9} P_{O_2}^{-1/4}$  and  $\sigma_e = 8.21 \times 10^{-5} P_{O_2}^{-1/4}$ , respectively using the  $\sigma_{ion}$  values obtained by extrapolating their values and the present values of  $P_{\ominus}$ . These results are shown in Fig. 5, indicating that the ionic transport numbers,  $t_{ion}$ , for mullite and  $ZrO_2$ -9 mol % MgO at  $\log(P_{O_2}/101325 \text{ Pa}) = -15$  (oxygen activity in liquid iron,  $a_O \approx 1$  p.p.m.) are 0.9 and 0.3 at 1873 K, respectively. It can thus be concluded that the n-type electronic contribution of  $ZrO_2$ -9 mol % MgO electrolyte is much greater than that of mullite.

#### 4.3. $P_{\ominus}$ values and low oxygen activities in Fe-Al-O melts

The  $a_O$  can be evaluated using the value for free energy of dissolution of oxygen into liquid iron:  $\Delta G_O^0 = -117200 - 2.89T \text{ J mol}^{-1}$  [17]. The relationship between e.m.f. and  $a_O$  can be derived from Equation 1 in which  $P_{O_2}$  is determined by the Cr-Cr<sub>2</sub>O<sub>3</sub> equilibrium. These results, obtained by using the values for free energy of formation of Cr<sub>2</sub>O<sub>3</sub> [18], and those of  $P_{\ominus}$  obtained in the present and previous works [12-14] at 1873 K are shown in Fig. 6. It can be seen that in the case of  $ZrO_2$ -based electrolyte, the dependence of  $a_O$  value on e.m.f. becomes larger with a decrease of the  $a_O$  value and tends to be more pronounced with an increase in  $P_{\ominus}$ . Therefore, it is important to note that the accurate determination of  $a_O$  values from e.m.f. values becomes difficult, since the small errors in e.m.f. measurement lead to large scattering of  $a_O$  values. If  $P'_{O_2}$  is much smaller than  $P_{\ominus}$  and  $P_{O_2}$ , Equation 1 is reduced to Equation 8 in which the measured e.m.f. becomes constant.

$$E = \frac{RT}{F} \ln \frac{P_{O_2}^{1/4} + P_{\ominus}^{1/4}}{P_{\oplus}^{1/4}} \quad (8)$$

The validity of the use of Equation 1 in the measurement of very low oxygen partial pressures is discussed below. Equation 1 is the approximate solution of Equation 9, which is derived under the condition that  $P_{\ominus}$  is much greater than  $P_{\oplus}$ ; that is, the parameter  $w$  given by Equation 10 is unity [8].

$$E = \frac{RT}{F} \frac{1}{w} \left\{ \ln \frac{1 - w + 2(P_{O_2}/P_{\oplus})^{1/4}}{1 - w + 2(P'_{O_2}/P_{\oplus})^{1/4}} + \ln \frac{1 + w + 2(P'_{O_2}/P_{\oplus})^{1/4}}{1 + w + 2(P_{O_2}/P_{\oplus})^{1/4}} \right\} \quad (9)$$

$$w = \left\{ 1 - 4 \left( \frac{P_{\ominus}}{P_{\oplus}} \right)^{1/4} \right\}^{1/2} = 1 - 2 \left( \frac{P_{\ominus}}{P_{\oplus}} \right)^{1/4} \quad (10)$$

The parameter  $P_{\oplus}$ , defined as the oxygen partial pressure at which the ionic and p-type electronic conductivities are equal, was measured in CaO-stabilized

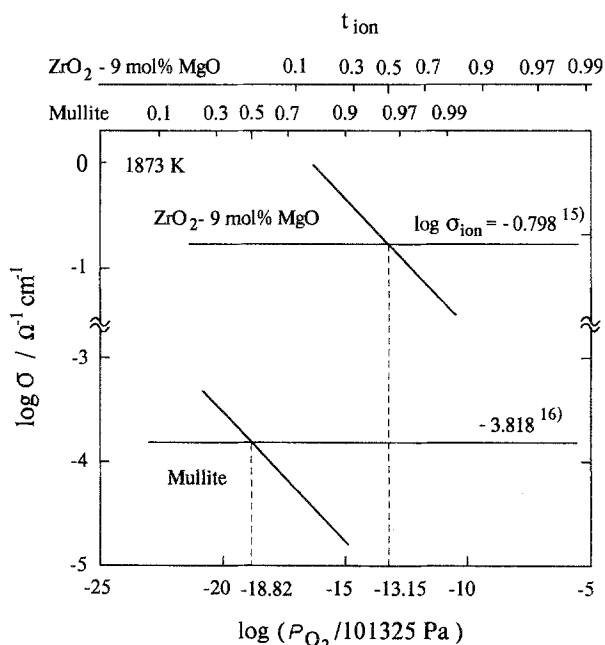
Table 2. Experimental results for  $P_{\ominus}$  values of mullite and ZrO<sub>2</sub>-9 mol % MgO

Ex. no.	Temp./K	$E/V$	$E_i/V$	$\log(P_{\ominus}/101\,325\text{ Pa})$
<b>Mullite</b>				
M-1	1778(H)	$1.999 \pm 0.005$	$-0.037 \pm 0.001$	$-23.09 \pm 0.056$
	1830(H)	$1.863 \pm 0.002$	$-0.039 \pm 0.001$	$-20.95 \pm 0.027$
	1871(H)	$1.734 \pm 0.007$	$-0.040 \pm 0.001$	$-19.11 \pm 0.079$
	1921(H)	$1.546 \pm 0.008$	$-0.042 \pm 0.001$	$-16.67 \pm 0.082$
	1848(C)	$1.767 \pm 0.009$	$-0.039 \pm 0.001$	$-19.70 \pm 0.099$
M-2	1676(H)	$2.254 \pm 0.007$	$-0.034 \pm 0.001$	$-27.52 \pm 0.080$
	1731(H)	$2.070 \pm 0.010$	$-0.036 \pm 0.001$	$-24.53 \pm 0.119$
	1826(H)	$1.819 \pm 0.008$	$-0.039 \pm 0.001$	$-20.51 \pm 0.087$
	1774(C)	$1.950 \pm 0.007$	$-0.037 \pm 0.001$	$-22.58 \pm 0.078$
	1883(H)	$1.696 \pm 0.005$	$-0.040 \pm 0.001$	$-18.59 \pm 0.054$
<b>ZrO<sub>2</sub>-9 mol % MgO</b>				
Z-1	1674(H)	$1.479 \pm 0.005$	$-0.034 \pm 0.001$	$-18.22 \pm 0.061$
	1676(H)	$1.454 \pm 0.002$	$-0.034 \pm 0.001$	$-17.90 \pm 0.048$
	1773(H)	$1.347 \pm 0.002$	$-0.037 \pm 0.001$	$-15.74 \pm 0.026$
	1825(H)	$1.239 \pm 0.003$	$-0.039 \pm 0.001$	$-14.12 \pm 0.033$
	1853(H)	$1.204 \pm 0.002$	$-0.039 \pm 0.001$	$-13.52 \pm 0.028$
	1876(H)	$1.199 \pm 0.005$	$-0.040 \pm 0.001$	$-13.31 \pm 0.056$
	1904(H)	$1.144 \pm 0.002$	$-0.041 \pm 0.001$	$-12.55 \pm 0.017$
	1795(C)	$1.268 \pm 0.002$	$-0.038 \pm 0.001$	$-14.67 \pm 0.022$
	1720(C)	$1.367 \pm 0.004$	$-0.035 \pm 0.001$	$-16.43 \pm 0.049$

(H): Heating cycle

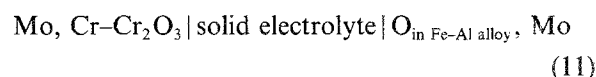
(C): Cooling cycle

ZrO<sub>2</sub> electrolyte [19–23]. The  $P_{\oplus}$  values at 1873 K were estimated as  $\log(P_{\oplus}/101\,325\text{ Pa}) = 6\text{--}11$  [20–23] by extrapolating those obtained at lower temperatures. The  $P_{\oplus}$  value obtained by Iwase and Mori ( $\log(P_{\oplus}/101\,325\text{ Pa}) = 6.12$  at 1873 K) [21] was used in the present work. The relationship between e.m.f. and  $a_{\text{O}}$  was calculated by using their value of  $P_{\oplus}$  and the  $P_{\ominus}$  value determined in the present work. It was found that these results were consistent with those calculated from Equation 1 in the range of low oxygen partial pressures down to  $a_{\text{O}} = 10^{-2}$  p.p.m. It can thus be concluded that Equation 1 is applicable to the e.m.f.

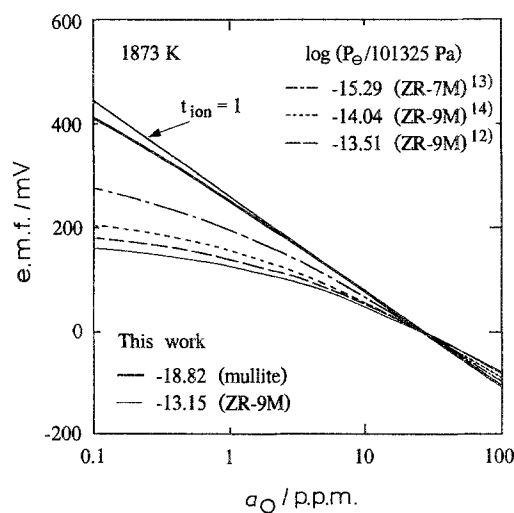
Fig. 5. Comparison of conductivity of mullite and ZrO<sub>2</sub>-9 mol % MgO with oxygen partial pressure in logarithmic form.

measurement of very low oxygen partial pressures.

The present authors [6] previously measured oxygen activities in liquid iron deoxidized with aluminium (0.0009–0.42 mass % total Al) at 1873 K in an alumina crucible, using a galvanic cell expressed as



The solid electrolyte was a stoichiometric mullite (ext. dia. 5.2 mm/int. dia. 3.5 mm × 40 mm, ext. dia. 4.9 mm/int. dia. 2.8 mm × 40 mm) and ZrO<sub>2</sub>-9 mol % MgO plug type (dia. 4 × 5–10 mm) probes. The values for oxygen activity calculated from analysed oxygen contents,  $a_{\text{O}}(\text{obs.})$ , using corresponding interaction parameters [17], are compared with those from measured e.m.f. by the two types of electrolyte in Fig. 7 in logarithmic form.

Fig. 6. Relationship between e.m.f. and oxygen activity at various  $P_{\ominus}$  values.

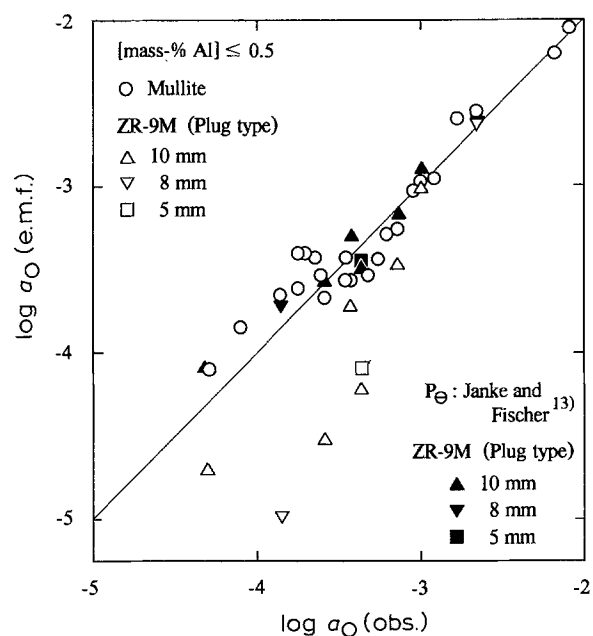


Fig. 7. Relationship between oxygen activity measured by various solid electrolytes and that calculated from analysed oxygen content in logarithmic form.

It is evident from Fig. 7 that the  $\log a_{\text{O}}(\text{e.m.f.})$  values obtained by using a mullite probe are in reasonable agreement with those of  $\log a_{\text{O}}(\text{obs.})$ . Oxygen activities from measured e.m.f. were not influenced by the  $P_{\text{O}_2}$  value in Equation 1 in the range of oxygen activities studied because of the considerably low values of  $P_{\text{O}_2}$  ( $\log (P_{\text{O}_2}/101\,325\text{ Pa}) = -18.82$ ). However, in the case of  $\text{ZrO}_2$ -9 mol % MgO plug-type probe ( $\log (P_{\text{O}_2}/101\,325\text{ Pa}) = -13.15$ ), the  $\log a_{\text{O}}(\text{e.m.f.})$  values below 5 p.p.m. are significantly different from those of  $\log a_{\text{O}}(\text{obs.})$ . This discrepancy is not within the limit of analytical error [24]. This may be explained by the fact that the scatter of  $a_{\text{O}}(\text{e.m.f.})$  due to the errors in e.m.f. measurements becomes greater in the range of  $a_{\text{O}} < 5\text{ p.p.m.}$ , as explained in Fig. 6. The results using the  $P_{\text{O}_2}$  value ( $\log (P_{\text{O}_2}/101\,325\text{ Pa}) = -15.29$ ) obtained by Janke and Fischer [13] are plotted by filled marks in Fig. 7 for purposes of comparison.

## 5. Conclusions

The parameter  $P_{\text{O}_2}$  values for mullite and  $\text{ZrO}_2$ -

9 mol % MgO solid electrolytes were measured in the temperature range 1674–1921 K, using a coulometric titration technique. The results obtained were

$$\log (P_{\text{O}_2}/101\,325\text{ Pa}) = 54.32 - 137000/T \text{ (mullite)}$$

and

$$\log (P_{\text{O}_2}(101\,325\text{ Pa})) = 27.16 - 75500/T$$

$$(\text{ZrO}_2\text{-9 mol \% MgO})$$

The accurate performance of a mullite electrolyte sensor at extremely low oxygen activities was observed to be possible.

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