

Determination of mixed ionic and electronic conduction in commercial-grade magnesia-stabilized zirconia electrolyte

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Received 4 September 1985; revised 23 November 1985

The extent of mixed ionic and n-type electronic conduction in commercial-grade zirconia electrolyte has been determined by employing coulometric titration and open-circuit e.m.f. measurements. Impurities such as Al₂O₃, TiO₂ and Fe₂O₃ did not seriously affect the electronic conduction.

1. Introduction

Control of oxygen levels in molten steel is of critical importance in steelmaking from the stand point of proper deoxidation, steel cleanliness, good recovery of alloy additives and final product quality. In order to control the oxygen levels in steel, a knowledge of the oxygen concentrations or activities at various stages in the process is required. This can be most directly achieved by using a solid-state galvanic sensor equipped with a zirconia-based solid electrolyte and an appropriate reference electrode. Solid-electrolyte probes have been used extensively for the instantaneous determination of oxygen in steelmaking furnaces, ladles and tundishes. Industrial application of electrochemical sensors, however, has not been without problems. For example, Thomas [1] has reported that different types of commercial sensors would indicate different oxygen activities even though the deoxidation condition of the steel was the same for each measurement. In addition, Suitoh *et al.* [2] have shown that even the same oxygen probes can indicate different oxygen activities if the measurements were made in different steel-making vessels. The present authors [3-6] have analysed the factors influencing the measured cell potentials of commercial oxygen sensors and concluded that unsatisfactory performance of the electrochemical cell can be due to the incon-

sistent and unpredictable electrical properties of the solid electrolyte.

Zirconia-based electrolytes show a significant proportion of n-type electronic conduction at low oxygen potentials and high temperatures. In such cases, the open-circuit voltage of the probe is given by

$$E^* = \frac{RT}{F} \ln \left(\frac{P_{\theta}^{1/4} + P_{O_2}^{\prime 1/4}}{P_{\theta}^{1/4} + P_{O_2}^{\prime\prime 1/4}} \right) \quad (1)$$

where E^* is the cell potential, F the Faraday constant, R the gas constant, T temperature and $P_{O_2}^{\prime}$ and $P_{O_2}^{\prime\prime}$ are the oxygen partial pressures at each electrode. The parameter P_{θ} is the oxygen partial pressure at which the ionic conductivity is equal to the n-type electronic conductivity [7]. It should be anticipated that this parameter will vary from one commercial-grade zirconia electrolyte to another. In order to correlate the measured cell potentials of commercial oxygen probes to the oxygen activities in the molten steel, a knowledge of the parameters P_{θ} is therefore essential. The present study is aimed at determining this parameter for commercial-grade zirconia tubes which have been used practically for the instantaneous monitoring of oxygen activity in liquid steel.

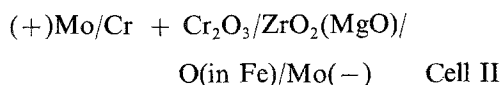
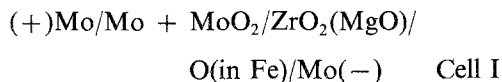
2. Experimental aspects

Two different experimental techniques were

employed for the determination of the parameter P_θ . These are open-circuit e.m.f. measurements and coulometric titration.

2.1. Open-circuit e.m.f. measurements

The open-circuit voltages of the following cells were measured at 1873 K.



A schematic diagram of the experimental apparatus is illustrated in Fig. 1. The design of the Cells I and II is essentially the same as that used in commercial oxygen probes. The details of the experimental apparatus and procedure are described elsewhere [8]. About 50 kg of low-carbon steel was melted in a high-frequency induction furnace under a stream of purified argon.

The oxygen probe consisted of a magnesia-stabilized zirconia tube, a Mo + MoO₂ or Cr + Cr₂O₃ reference electrode, and a molybdenum lead wire. The ZrO₂(MgO) tube, closed at one end, had an o.d. of 5.6 mm, an i.d. of

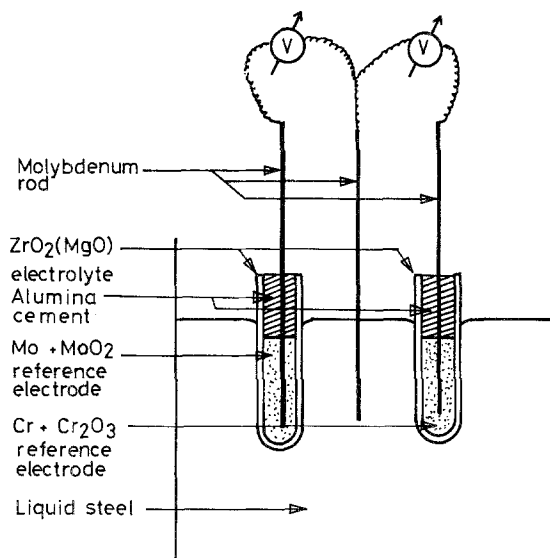


Fig. 1. Experimental apparatus employed for the determination of the parameter P_θ by open-circuit e.m.f. measurements at 1873 K.

3.6 mm, and a length of 35 mm. The oxygen content of the molten steel was changed by the addition of aluminium.

The open-circuit voltages of the Cells I and II are given by Equations 2 and 3, respectively.

$$E_{\text{MoO}_2} = \frac{RT}{F} \ln \left(\frac{P_\theta^{1/4} + P_{\text{O}_2}(\text{MoO}_2)^{1/4}}{P_\theta^{1/4} + P_{\text{O}_2}(\text{Fe})^{1/4}} \right) \quad (2)$$

$$E_{\text{Cr}_2\text{O}_3} = \frac{RT}{F} \ln \left(\frac{P_\theta^{1/4} + P_{\text{O}_2}(\text{Cr}_2\text{O}_3)^{1/4}}{P_\theta^{1/4} + P_{\text{O}_2}(\text{Fe})^{1/4}} \right) \quad (3)$$

where $P_{\text{O}_2}(\text{MoO}_2)$ and $P_{\text{O}_2}(\text{Cr}_2\text{O}_3)$ are the oxygen partial pressures of the reference electrodes, Mo + MoO₂ and Cr + Cr₂O₃, respectively [9], and $P_{\text{O}_2}(\text{Fe})$ is the oxygen potential of liquid steel. From Equations 2 and 3, one obtains

$$\begin{aligned} E_{\text{Cr}_2\text{O}_3} = E_{\text{MoO}_2} \\ + \frac{RT}{F} \ln \left(\frac{P_\theta^{1/4} + P_{\text{O}_2}(\text{Cr}_2\text{O}_3)^{1/4}}{P_\theta^{1/4} + P_{\text{O}_2}(\text{MoO}_2)^{1/4}} \right) \end{aligned} \quad (4)$$

Equation 4 can be used to determine the parameter P_θ ; a plot of $E_{\text{Cr}_2\text{O}_3}$ against E_{MoO_2} should be a straight line with the slope of unity and the intercept of $(RT/F) \ln[(P_\theta^{1/4} + P_{\text{O}_2}(\text{Cr}_2\text{O}_3)^{1/4}) / (P_\theta^{1/4} + P_{\text{O}_2}(\text{MoO}_2)^{1/4})]$.

For e.m.f. measurements, the Cells I and II were simultaneously dipped into the molten steel, and the open-circuit voltages were recorded on a strip-chart recorder of 2 M Ω internal impedance for a period of 10 to 20 s. All the experiments were conducted at 1873 K. After the present research project was initiated, however, the authors recognized that this technique did not have sufficient accuracy. Hence, open-circuit e.m.f. measurements were conducted with the specimen P9 only (see Table 1).

Table 1. Chemical compositions of zirconia specimens (wt %)

Sample code	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO
P2	0.07	0.36	0.07	0.14	0.24	3.0
P3	0.28	0.49	0.36	0.08	0.07	3.0
P4	0.20	0.50	0.10	0.08	0.07	3.3
P5	0.03	0.23	0.02	0.09	0.17	3.0
P6	<0.02	0.10	<0.02	0.03	0.03	3.0
P7	0.06	0.97	0.02	0.15	0.16	3.0
P8	0.07	0.11	0.03	0.13	0.16	3.3
P9	0.69	0.61	0.05	0.05	0.41	3.0

2.2. Coulometric titration

With the coulometric-titration technique, which was first described by Swinkels [10], an external current is applied to the cell;

Mo/Ag(O)/ZrO₂(MgO)/O₂($P_{O_2} = 101\ 300\ \text{Pa}$)/Pt

Cell III

Oxygen dissolved in liquid silver was electrochemically removed to the Pt/O₂(101 300 Pa) electrode, which was essentially non-polarized [11]. The open-circuit cell voltage, E_{oc} , was measured immediately after the circuit was opened. If the oxygen potential at the liquid-silver/electrolyte interface, $P_{O_2}(\text{Ag})$, is lowered sufficiently to satisfy the condition,

$$P_{O_2}(\text{Ag}) \ll P_{O_2} \quad (5)$$

then the open-circuit e.m.f. is given by Equation 6:

$$E_{oc} = -\frac{RT}{4F} \ln P_{O_2} \quad (6)$$

The details of the experimental apparatus and procedure are described elsewhere [12]. The experimental apparatus is shown in Fig. 2. The zirconia specimens used in these measurements were in the form of one closed-end tube with an o.d. of 12 mm, an i.d. of 8 mm and a length of 280 mm. About 6 g of pure silver was melted inside the zirconia tube under a stream of purified Ar + 3% H₂ gas mixture with a flow rate of 2.5×10^{-6} to $3.3 \times 10^{-6}\ \text{m}^3\ \text{s}^{-1}$. The electrical contact to the liquid silver was accomplished with a molybdenum rod of 3 mm diameter. The outer surface of the zirconia tube was platinumized

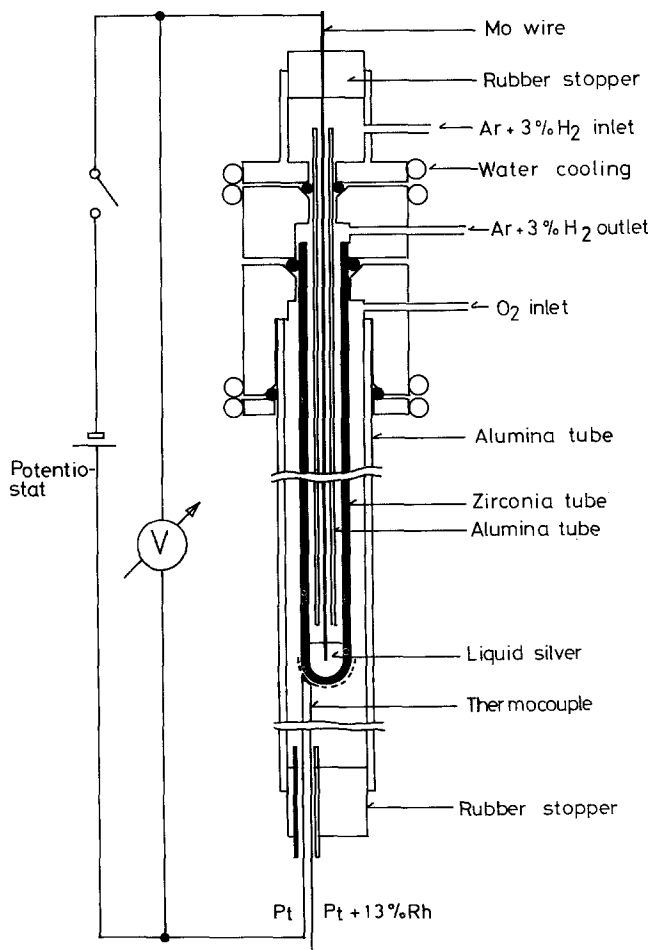


Fig. 2. Experimental apparatus employed for the determination of the parameter P_{O_2} by coulometric titration.

by applying platinum paste and platinum gauze and heating at 1273 K for 50 h. A Pt-PtRh13 thermocouple was used to serve as a conducting lead for establishing electrical contact with the platinized electrode. Open-circuit e.m.f.s between the platinum wire of the thermocouple and the molybdenum rod were measured with a strip-chart recorder of 2 M Ω internal impedance. The assembled cell was placed in a SiC resistance furnace, and the outside of the zirconia tube was flushed with pure oxygen at a rate of $5 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. The thermo-e.m.f. between molybdenum and platinum was corrected by using the authors' previous results [13].

The zirconia tubes with eight different compositions were supplied by Sumitomo Aluminum Smelting Co. Ltd. The chemical compositions of these specimens are given in Table 1. Two to three duplicate measurements were made for each composition.

3. Experimental results

3.1. Open-circuit e.m.f. measurements

The experimental results obtained with the open-circuit e.m.f. measurements are given in Fig. 3, where the measured voltages of Cell II, $E_{\text{Cr}_2\text{O}_3}$, are plotted against those of Cell I, E_{MoO_2} . As shown in Fig. 3, the slope is very close to

unity, which conforms to Equation 4. From the intercept of the straight line drawn in this diagram, the parameter P_θ was determined as $\log_1(P_\theta/\text{Pa}) = -9.0 \pm 0.7$ at 1873 K.

3.2. Coulometric titration

The values for the parameter P_θ determined for the commercial-grade zirconia tubes with eight different compositions are shown in Figs 4 to 6. The limits of accuracy in the determination of the parameter P_θ in the present study may be estimated by the following equation,

$$d(\ln P_\theta) \leq \left| \frac{4F}{RT} \right| |dE| + \left| \frac{4FE_{\text{oc}}}{RT^2} \right| |dT| \quad (7)$$

By using the average standard deviation for E_{oc} , which was less than ± 0.01 V, the uncertainty of $\log P_\theta$ was estimated to be approximately ± 0.1 to 0.2; better accuracy was obtainable with the coulometric-titration technique.

It is known that the temperature dependence of the parameter P_θ can be represented by the formula [12];

$$\log P_\theta = a + b/T \quad (8)$$

This formula could be well applied to the present results. In Table 2 the present values are expressed analytically along with the correlation factor, r^2 . As shown in this table, the P_θ value for the

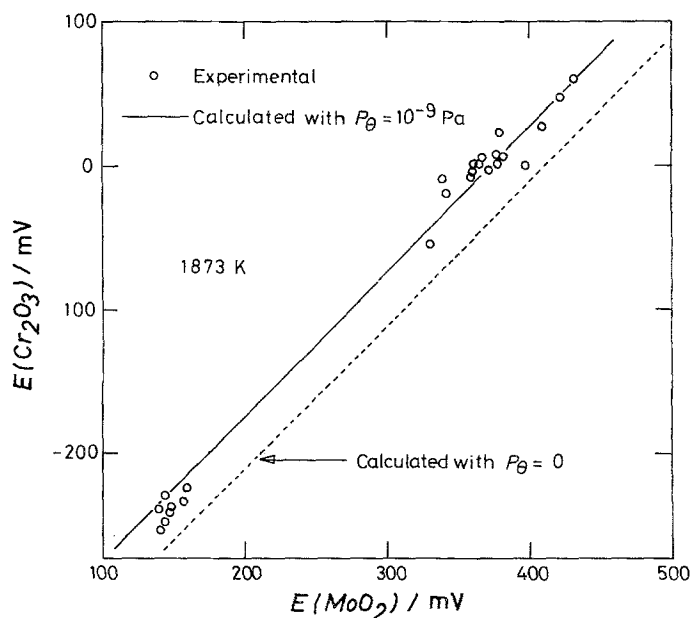


Fig. 3. Relation between the measured voltages of Cell I and those of Cell II at 1873 K.

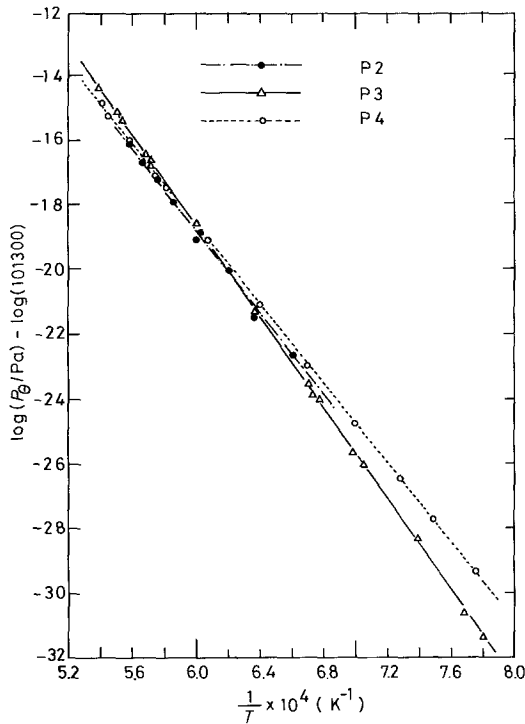


Fig. 4. Values for P_θ as a function of reciprocal temperature for the samples designated as P2, P3 and P4.

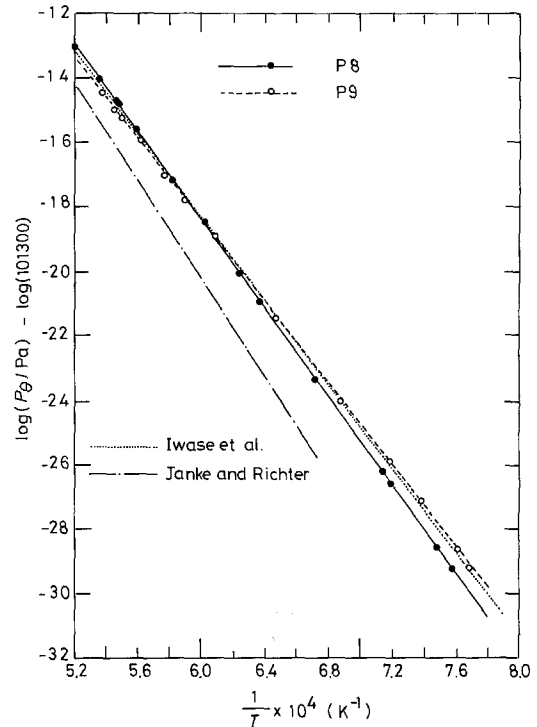


Fig. 6. Values for P_θ as a function of reciprocal temperature for the samples designated as P8 and P9 in comparison with literature data.

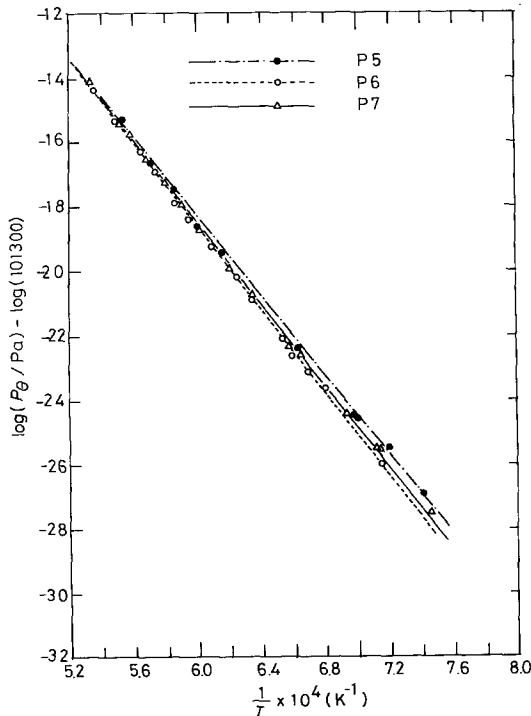


Fig. 5. Values for P_θ as a function of reciprocal temperature for the samples designated as P5, P6 and P7.

specimen P9 at 1873 K determined by the coulometric-titration technique ($10^{-9.2}$ Pa) is in very good agreement with that determined by the open-circuit e.m.f. measurements. It is also noted that the parameter P_θ did not show significant dependence upon the impurity levels.

4. Discussion

The present P_θ values are compared with those reported by Iwase *et al.* [12] in Fig. 6. The chemical composition of their specimen, $ZrO_2(MgO)$, is given in Table 3. Their values are fairly close to the present authors', again indicating that P_θ would not be seriously affected by the impurity levels.

In Fig. 6, comparison is also made with the P_θ values reported by Janke and Richter [14] for magnesia-stabilized zirconia. Their P_θ values are an order of magnitude lower than those of the present authors (Fig. 4), while the chemical composition of their specimen does not differ significantly from that of the present authors (see Table 4). Hence the difference cannot be

Table 2. P_θ values for various zirconia electrolytes as a function of temperature for the equation;
 $\log (P_\theta/\text{Pa}) - \log (1013200) = a + b/T$

Sample code	a	$b \times 10^{-4}$	Correlation factor, r^2	$\log (P_\theta/\text{Pa}) - \log (101300)$	
				at 1873 K	at 1273 K
P2	20.42	-6.534	0.991	-14.5	-30.9
P3	23.87	-7.085	0.999	-14.0	-31.8
P4	18.37	-6.161	0.999	-14.5	-30.0
P5	19.10	-6.233	0.997	-14.2	-29.9
P6	20.25	-6.476	0.998	-14.3	-30.6
P7	19.16	-6.282	0.998	-14.4	-30.2
P8	22.71	-6.863	0.999	-13.9	-31.2
P9	19.43	-6.303	0.999	-14.2	-30.1

attributed to the impurity levels. From the brief description of their experiments it appears that the maximum voltage after complete coulometric removal of oxygen from the liquid-copper electrode to the stirred iron electrode may be influenced by concentration polarization at the iron/electrolyte interface. Mechanical stirring may not have been sufficient to eliminate the polarization. Hence their values might be somewhat inaccurate.

In the initial stages of the present study, the authors anticipated that P_θ values would be significantly affected by the impurity content, especially by impurities such as transition-metal oxides. The Fe_2O_3 contents in the specimens P5, P6 and P7 were lowered to less than 0.02 wt % in the hope that considerably lower P_θ values might be obtained with these specimens. In general, a zirconia electrolyte of lower P_θ value is highly desirable in oxygen probes. The difference in $\log (P_\theta/\text{Pa})$ between these specimens and the relatively less pure material P3 is, however, only 0.2 to 0.4 at 1873 K. The authors confess that they were fairly disappointed with the present results. From an alternative point of view, however, the present results provide an important piece of information for the manufacture of zirconia

electrolytes, namely, it can now be said that, with respect to the n-type electronic conduction, impurities in zirconia such as Al_2O_3 , TiO_2 and Fe_2O_3 do not have to be carefully controlled. Such a statement could not have been made in the past.

With respect to the effect of SiO_2 as an impurity, a few words seem to be pertinent. The electrolyte tubes used in this study are of 'partially stabilized zirconia'. When these zirconia tubes are instantaneously dipped into liquid iron from ambient temperature, then the transformation of zirconia takes place. Yamada *et al.* [15] have found that at very low oxygen potentials, the e.m.f. values would be significantly influenced by the rate of this transformation which can be affected, in turn, by the concentration of SiO_2 impurities. In addition, at very low oxygen potentials, it is postulated that SiO_2 within the electrolyte would dissociate into silicon and oxygen, and this dissociation can change the oxygen concentration or activity at the electrolyte/liquid-steel interface. Hence, in practice, open-circuit e.m.fs would be affected by the SiO_2 content. As shown in Table 5, measured cell potentials decreased with increase in the SiO_2 content.

Table 3. Chemical composition (wt %) of the commercial-grade magnesia-stabilized zirconia electrolyte used by Iwase *et al.* [12]

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO
0.2	0.14	0.4	0.05	0.4	0.015	0.05	3.1

Table 4. Chemical composition (wt %) of magnesia-stabilized zirconia used by Janke and Richter [14]

MgO	CaO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ O	K ₂ O
2.40	0.20	0.15	0.30	<0.05	0.25	0.01

Acknowledgements

One of the authors (M.I.) would like to express his sincere appreciation to Professor Alex McLean of the Department of Metallurgy and Materials Science, University of Toronto, Canada for his constructive comments, suggestions, discussion and encouragement.

Table 5. Measured cell potentials with various zirconia electrolytes at 1873 K with aluminum-killed steel

	Sample code				
	P3	P5	P6	P7	P9
Measured cell potentials (mV)	560	598	601	615	532

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