Determination of the electrical characteristics of a commercially available yttria-stabilized zirconia electrolyte used in high-temperature thermodynamic studies

by M.J.U.T. VAN WIJNGAARDEN*, J.M.A. GELDENHUIS†, and R.J. DIPPENAAR‡

SYNOPSIS

The successful application of solid electrolytes in electrochemical cells for high-temperature thermodynamic studies depends to a large extent on an accurate knowledge of the P_e value of the electrolyte (the oxygen partial pressure at which the ionic conductivity and n-type electronic conductivity of the electrolyte are equal). Consequently, the P_e value of an electrolyte must be determined prior to its use in electrochemical cells.

This paper describes the successful application of a coulometric titration technique in the quantitative assessment of the P_e values of a commercially available yttria-stabilized zirconia electrolyte that has been used extensively by local investigators. The experimentally determined P_e values of the electrolyte are reported and compared with P_e values reported in the literature for a similar electrolyte.

SAMEVATTING

Die suksesvolle gebruik van vastestofelektroliete in elektrochemiese selle vir termodinamiese ondersoeke by hoë temperature is in 'n groot mate afhanklik van akkurate inligting ten opsigte van die P_e-waarde van die elektroliet (die suurstofdeeldruk waarby die ioongeleivermoë en die n-tipe elektroniese geleivermoë van die elektroliet gelyk is). Gevolglik moet die P_e-waarde van 'n elektroliet bepaal word voordat dit in elektrochemiese selle gebruik word.

Hierdie referaat bespreek die suksesvolle toepassing van 'n coulometriese titreertegniek vir die kwantitatiewe bepaling van die P_e-waardes van 'n yttriagestabiliseerde sirkonia-elektroliet wat in die handel beskikbaar is, en wat op groot skaal deur plaaslike navorsers gebruik word. Die eksperimenteel bepaalde P_e-waardes van die elektroliet word aangegee en met P_e-waardes van 'n soortgelyke elektroliet wat in die literatuur gerapporteer is, vergelyk.

Introduction

Interest in the use of stabilized zirconia, in particular of yttria-stabilized zirconia, as the solid electrolyte in electrochemical cells for the determination of the partial pressure of oxygen has increased markedly in South Africa since the 1980s. For example, solid zirconia electrolytes have been used in high-temperature thermodynamic studies of slag–metal systems typical of those used in the production of ferrochromium[1-5], iron[6-8], and steel[9].

Unfortunately, when zirconia electrolytes are exposed to the high temperatures and low oxygen potentials usually encountered in the slag–metal systems of practical importance, they exhibit mixed ionic and n-type electronic conduction. Under these conditions, the electrochemical cell generates an e.m.f. signal that is influenced by the electrical properties of the solid electrolyte. Schmalzried[10,11] analysed the contribution of electronic conduction in a solid oxide electrolyte to the measured e.m.f. of an electrochemical cell, and showed that, in the presence of n-type electronic conduction, the e.m.f. can

be expressed as

$$E = \frac{RT}{F} \ln \left[\frac{(P''_{O_2})^{1/4} + (P_e)^{1/4}}{(P'_{O_2})^{1/4} + (P_e)^{1/4}} \right], \quad \dots\dots\dots (1)$$

where P'_{O_2} and P''_{O_2} are the respective partial pressures of oxygen at the two electrolyte–electrode interfaces, R is the gas constant, F the Faraday constant, and T the absolute temperature. The parameter P_e describes the relation between the partial ionic and n-type electronic conductivity of the electrolyte, and is defined as the oxygen partial pressure at which the ionic conductivity and the n-type electronic conductivity of the electrolyte are equal. Since the work of Schmalzried, several investigators[7,9,12-15] have analysed and emphasized the importance of an accurate knowledge of the P_e value of the electrolytes used in electrochemical cells, and it is generally accepted that the P_e value of the electrolyte used must be consistent and must be known to a high degree of accuracy if precise and useful measurements are to be made.

However, until recently, no experimental technique was available locally for the determination of the P_e values of solid electrolytes. Consequently, several investigators used P_e values that had been reported in the literature[5,6], or even disregarded the P_e value altogether[1-3]. Clearly, the assumption of a negligible P_e value may result in erroneous electrochemical measurements in those cases where significant electronic conduction prevails.

* Associate Professor.
† Post-graduate student.
‡ Professor.
All the above of the Mintek Iron and Steel Research Group, c/o Department of Materials Science and Metallurgical Engineering, University of Pretoria, Hillcrest, Pretoria 0002.

The electrical properties of solid electrolytes are influenced by the type and concentration of the stabilizing oxide, the phase composition, the impurities in the electrolyte, and the microstructure of the electrolyte[16-18], and can therefore be influenced by the chemical and physical properties of the original raw materials, as well as by the heat treatment to which the electrolyte is exposed during fabrication. It is therefore not surprising to find that different P_e values have been reported for the same type of electrolyte[16,19,20]. For example, Iwase et al.[16] reported P_e values for an yttria-stabilized zirconia electrolyte (8 mol per cent Y_2O_3) that are up to 1,5 orders of magnitude higher than those determined by Swinkels[20] for essentially the same type of electrolyte (7 mol per cent Y_2O_3). Since commercially available solid electrolytes are usually specified only by the type and concentration of the stabilizing oxide, the use of published P_e values induces unnecessary uncertainty in the P_e value of the electrolyte, which may consequently lead to inaccurate electrochemical measurements. Hence, the P_e value of a particular electrolyte should be determined prior to its use in an electrochemical cell.

In view of these factors, a coulometric titration technique was developed that permits the P_e values of commercially available solid electrolytes to be determined to a higher degree of accuracy[17,18].

The present paper describes the application of this technique to the quantitative assessment of the P_e values of a commercially available yttria-stabilized zirconia electrolyte (supplied by Corning Glass, USA) commonly used by local researchers for high-temperature thermodynamic studies.

Theoretical Considerations

The parameter P_e, defined earlier, can be determined most effectively by the measurement of the e.m.f. in an electrochemical cell of the type

$$P'_{O_2} \mid \text{solid oxide electrolyte} \mid P''_{O_2},$$
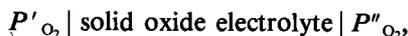
where

$$P'_{O_2} \ll P_e \ll P''_{O_2} \quad \text{.......................................} \quad (2)$$

When this relation between the P_e value of the solid electrolyte and the oxygen partial pressures on either side of the electrolyte applies, equation (1) can be simplified to

$$E = \frac{RT}{4F} \ln \frac{P''_{O_2}}{P_e} \quad \text{.......................................} \quad (3)$$

It is evident from equation (3) that, if the oxygen partial pressure, P''_{O_2}, is known, the parameter P_e can be determined by experimental measurement of the temperature and e.m.f. of the cell. However, it is extremely difficult to achieve experimentally the very low partial pressure of oxygen required at one of the electrolyte–electrode interfaces of the cell in order to satisfy equation (2). In the present investigation this low partial pressure of oxygen was established by the adoption of a coulometric titration technique[17]. The nature and purpose of the technique are briefly outlined below.

The experimental cell arrangement that was used can be expressed as

Mo | O_2 (in liquid silver) | ZrO_2-Y_2O_3 |
    O_2 (1 atm) | Pt .... (cell I)
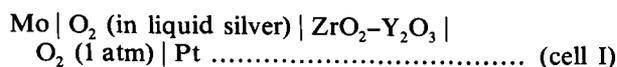
Oxygen can be removed electrolytically from the silver melt and transported to the Pt–O_2 electrode when a direct current is passed through the cell. At sufficiently high cell currents, liquid silver becomes polarized[21], and an oxygen concentration gradient is induced at the silver-electrolyte interface as illustrated schematically in Fig. 1. In this way, the oxygen partial pressure at the silver interface of the electrolyte can be sufficiently lowered to satisfy the condition

$$P'_{O_2} \ll P_e \quad \text{.......................................} \quad (4)$$
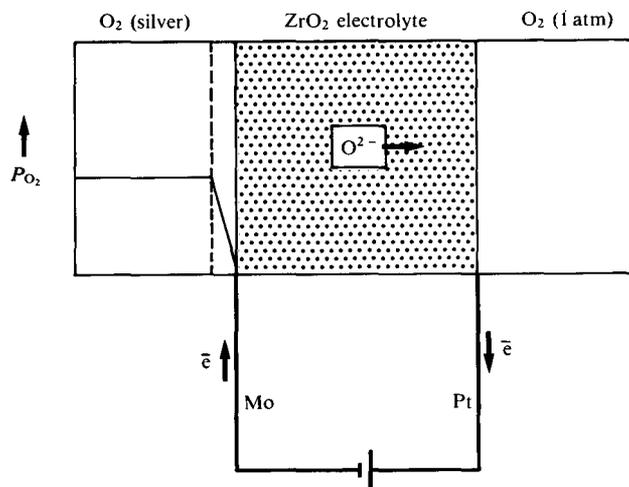

Fig. 1—Schematic representation of the cell arrangement used in the application of the coulometric titration technique

The Pt–O_2 (1 atm) reference electrode, on the other hand, is essentially non-polarizable[22], and the oxygen partial pressure at this interface remains at 1 atm, thus satisfying the requirement

$$P''_{O_2} \gg P_e \quad \text{.......................................} \quad (5)$$

Under the experimental conditions expressed in equations (4) and (5), the e.m.f. of cell I can be expressed as

$$E = E_t - \frac{RT}{4F} \ln P_e, \quad \text{.......................................} \quad (6)$$

where E_t denotes the thermal e.m.f. between the molybdenum-wire and platinum-wire electrical leads of cell I. Hence, the P_e value of the electrolyte incorporated in cell I can be determined by experimental measurement of the e.m.f. at any given temperature.

Experimental Apparatus

The experimental apparatus, which is illustrated schematically in Fig. 2, consisted essentially of a purification train (silica gel, magnesium perchlorate, and phosphorus pentoxide) for a gas mixture (argon containing 3 per cent hydrogen), and a vertical Super-Kanthal furnace containing an alumina reaction tube and equipped with a programmable proportional-integral derivative (PID) controller.

The reaction tube and cell assembly are shown schematically in Fig. 3. The cell arrangement consisted of an electrolyte tube (13 mm outer diameter, 9 mm inner diameter, 600 mm length) containing a silver electrode and having a porous platinum electrode on its outside surface. The
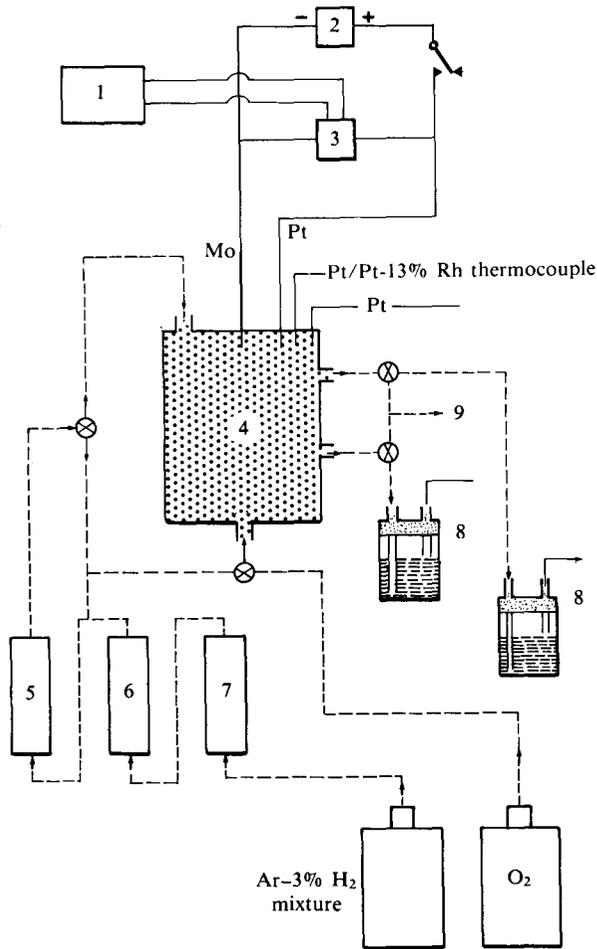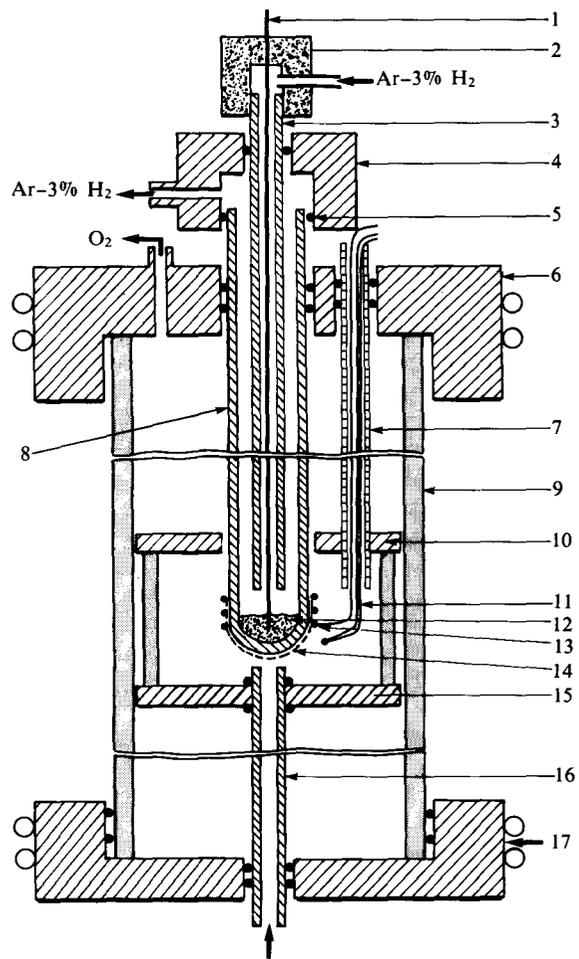
1	Recorder	5	Phosphorus pentoxide
2	Potentiostat	6	Magnesium perchlorate
3	Electrometer	7	Silica gel
4	Alumina reaction tube and furnace	8	Air trap
		9	Vacuum pump

Fig. 2—Schematic representation of the experimental apparatus

1	Molybdenum wire	10	Alumina guide disc
2	Rubber stopper	11	Pt/Pt-13% Rh thermocouple
3	Alumina tube	12	Liquid-silver electrode
4	Brass fitting	13	Platinum wire
5	Rubber O-ring	14	Platinized surface
6	Water-cooled brass fitting	15	Alumina guide disc
7	Alumina thermocouple sheath	16	Alumina oxygen inlet
8	Electrolyte tube	17	Water-cooled brass fitting
9	Alumina reaction tube		

Fig. 3—Reaction tube and crucible assembly

platinum electrode was prepared as follows. The surface at the closed end of the electrolyte tube was painted with platinum paste diluted with xylene. The paste was subsequently cured by being slowly heated to 1000°C, being held at that temperature for 6 hours, and being slowly cooled to room temperature. This procedure, which was usually repeated three times, ensured that the electrical resistance across the platinized surface would be sufficiently low. A molybdenum wire served as the electrical lead to the liquid-silver electrode. A platinum wire, wound round the platinized surface of the electrolyte tube, completed the electrical circuit of the cell.

A Pt/Pt-13%Rh thermocouple, which was placed against the platinized surface of the electrolyte tube, was used to measure the cell temperature. The temperature measurements indicated that the temperature gradient over a distance of 50 mm from the closed end of the electrolyte tube was less than 2°C. The temperature-measuring circuit was calibrated against the melting point of palladium, and it was found that the overall error was less than 3°C. An electrometer with an input impedance of $10^{14}\,\Omega$, coupled to a chart recorder with an accuracy of ± 2,5 mV, was used for measurements of the e.m.f.,

while a potensiostat was used to apply the external currents.

Experimental Procedure

The electrolyte tube (containing approximately 8 g of pure silver), electrical leads, inlet tubes, and thermocouple were positioned inside the reaction tube, as shown in Fig. 3. After the electrolyte and reaction tubes had been sealed and evacuated to ensure that they were gas-tight, purified argon–hydrogen gas mixture was introduced. The furnace was then heated to 1200°C at a rate of 80°C per hour.

The e.m.f. was measured during heating and cooling cycles in the temperature range 1200 to 1600°C. Immediately prior to the measurement of the e.m.f., the reaction tube was evacuated and flushed with oxygen. A direct polarizing current was applied to the cell by means of a potentiostat for approximately 5 minutes before being interrupted, and the open-circuit e.m.f. was measured immediately afterwards. This procedure was

repeated at increasing potentials until the measured open-circuit e.m.f. was independent of the magnitude of the applied potential, indicating that the condition represented in equation (4) was satisfied. As soon as the reproducibility of the open-circuit e.m.f. had been confirmed, the reaction tube was evacuated and flushed with the argon-hydrogen gas mixture, and the furnace was heated or cooled to the temperature at which the next measurement was to be taken.

A typical e.m.f. signal recorded during measurement of the e.m.f. is shown in Fig. 4. As soon as the polarizing current was interrupted, a stable e.m.f. plateau was obtained for a short period of time. However, it should be noted that a stable e.m.f. plateau is obtained only if the resistance of the cell, as well as the concentration of oxygen in the silver melt, are low. For this reason, every precaution was taken to prevent oxygen from leaking into the electrolyte tube (molecular diffusion as well as ionic transport due to electronic conduction in the electrolyte). To minimize the ionic transport of oxygen through the electrolyte, the electrolyte and reaction tubes were flushed with the same argon–hydrogen gas mixture during the heating and cooling cycles, and oxygen was introduced into the reaction tube only while the e.m.f. was being measured.

The zirconia electrolytes investigated in this study were supplied by Corning Glass, USA (4,5 mol per cent Y_2O_3). The consistency of the chemical compositions and the microstructures of the electrolytes were determined on samples of all the electrolytes used in the assessment of P_e values. This was done by chemical analysis, scanning electron microscopy, and electron-microprobe analysis. The chemical compositions of the electrolytes are presented in Table I, and were determined by atomic emission spectroscopy (AES) using inductively coupled plasma (ICP).

The thermal e.m.f. between Pt(+) and Mo(−) was determined experimentally[17] as

$$E_t = (23,2 \pm 1,0) - 0,04\ T, \quad\quad\quad (7)$$

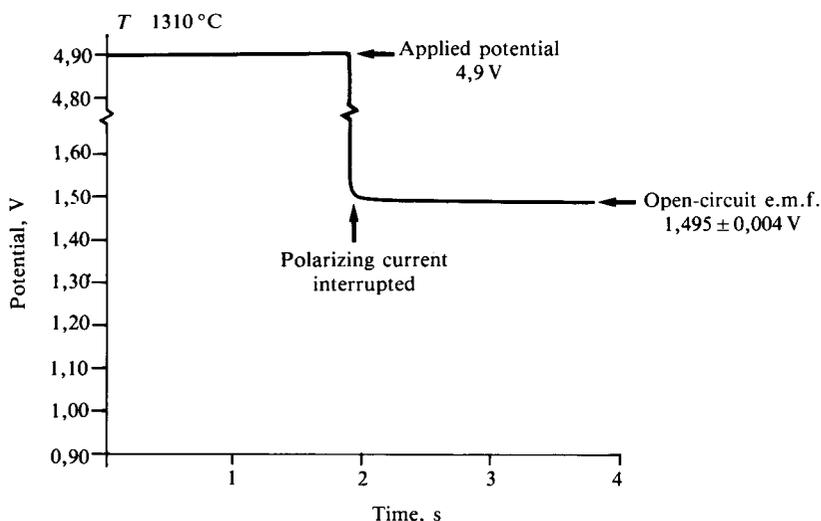where E_t and T are expressed in millivolts and kelvin respectively.

TABLE I
CHEMICAL COMPOSITIONS OF THE SOLID ELECTROLYTES* STUDIED

Sample no.	Analysis, % (by mass)								
	MgO	CaO	SiO₂	Al₂O₃	TiO₂	Fe₂O₃	Na₂O	K₂O	Y₂O₃
1	0,46	1,71	0,21	Trace	0,08	0,10	Trace	Trace	8,1
2	0,46	1,70	0,18	Trace	0,08	0,10	Trace	Trace	8,1
3	0,44	1,70	0,22	Trace	0,08	0,10	Trace	Trace	8,2

* As received

Results and Discussion

The experimentally determined P_e values of the yttria-stabilized zirconia studied are shown in Fig. 5, and the experimental results and associated uncertainties are summarized in Table II. The uncertainty in the P_e values was estimated from the differential of equation (6) as follows:

$$d(\log P_e) \leq \frac{4F}{2,3\ RT}[|dE| + |dE_t|] + \frac{4F}{2,3\ RT^2}[|E||dT|$$
$$+ |E_t||dT|], \quad\quad\quad\quad\quad\quad (8)$$

where $|dE_t|$, $|dT|$, and $|dE|$ denote the absolute values of the uncertainty in the thermal e.m.f. between molybdenum and platinum ($\pm$ 1 mV), the uncertainty in the temperature ($\pm$ 3°C), and the uncertainty in the measured e.m.f. of cell I respectively. It follows from the analyses shown in Table II that the uncertainty in log P_e of the individual measurements was always less than $\pm$ 0,15 atm.

It is evident from Fig. 5 that the P_e values determined during the heating and cooling of the electrolytes are in good agreement, indicating that equilibrium conditions were attained during the measurement of the these values. Hence, the P_e values can be expressed analytically as a function of temperature as

$$\log P_e \text{ (atm)} = 24,89 - 71\,970/T$$
$$(1200°C \leq T \leq 1600°C). \quad\quad\quad (9)$$

Also included in Fig. 5 are the results of Iwase et al.[16] for a solid yttria-stabilized electrolyte supplied by Nippon Kagaku Togyo, Japan (6 mol per cent Y_2O_3). It is evident

Fig. 4—A typical e.m.f. signal recorded during measurement of the e.m.f. in the determination of P_e values

TABLE II
EXPERIMENTAL RESULTS FOR THE YTTRIA-STABILIZED ZIRCONIA ELECTROLYTES SUPPLIED BY CORNING GLASS

| No.	Temperature, °C	E, V	E_1, V	$\log P_e$, atm
1.1	1206 (H)	1,705 ± 0,004	−0,036 ± 0,001	−23,73 ± 0,11
1.2	1303 (H)	1,590 ± 0,004	−0,040 ± 0,001	−20,85 ± 0,10
1.3	1351 (H)	1,529 ± 0,005	−0,042 ± 0,001	−19,50 ± 0,11
1.4	1401 (H)	1,465 ± 0,006	−0,044 ± 0,001	−18,17 ± 0,11
1.5	1451 (H)	1,398 ± 0,007	−0,046 ± 0,001	−16,89 ± 0,12
1.6	1522 (H)	1,300 ± 0,010	−0,049 ± 0,001	−15,15 ± 0,15
1.7	1484 (C)	1,350 ± 0,009	−0,047 ± 0,001	−16,03 ± 0,14
1.8	1422 (C)	1,429 ± 0,007	−0,045 ± 0,001	−17,53 ± 0,12
2.1	1208 (H)	1,702 ± 0,004	−0,036 ± 0,001	−23,66 ± 0,11
2.2	1276 (H)	1,616 ± 0,004	−0,039 ± 0,001	−21,54 ± 0,10
2.3	1303 (H)	1,600 ± 0,005	−0,040 ± 0,001	−20,98 ± 0,11
2.4	1408 (H)	1,450 ± 0,005	−0,044 ± 0,001	−17,92 ± 0,10
2.5	1594 (H)	1,210 ± 0,010	−0,051 ± 0,001	−13,62 ± 0,14
2.6	1553 (C)	1,264 ± 0,008	−0,050 ± 0,001	−14,51 ± 0,12
2.7	1374 (C)	1,494 ± 0,006	−0,043 ± 0,001	−18,81 ± 0,12
2.8	1324 (C)	1,558 ± 0,005	−0,041 ± 0,001	−20,18 ± 0,11
2.9	1249 (C)	1,640 ± 0,004	−0,038 ± 0,001	−22,23 ± 0,11

(H) Heating cycle
(C) Cooling cycle
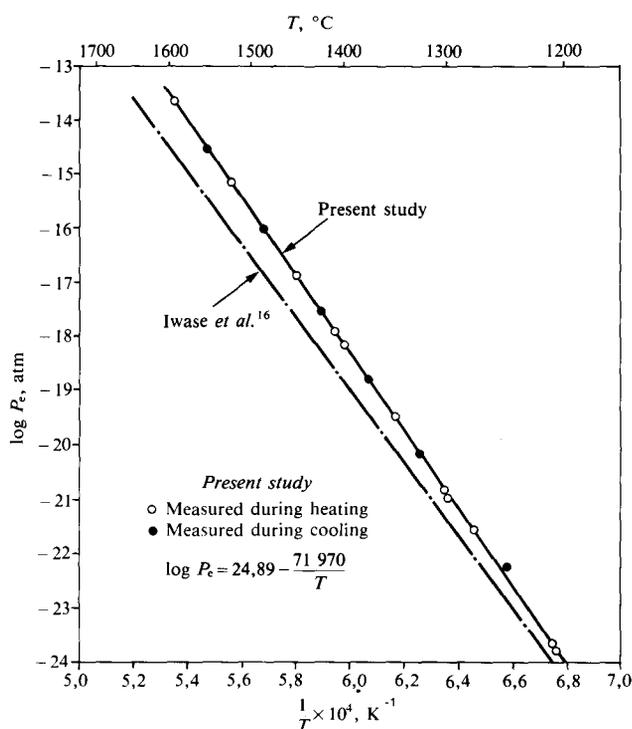
Fig. 5—The P_e values determined in the present study for the yttria-stabilized zirconia electrolyte supplied by Corning Glass, and those determined by Iwase et al.[16] for an yttria-stabilized zirconia electrolyte supplied by Nippon Kagaku Togyo

that the P_e values for the Corning electrolyte are consistently higher than those for the Nippon electrolyte. This can be explained by the equilibrium phase compositions of the electrolytes.

Yttria-stabilized zirconia can occur in three crystallographic modes, viz cubic, tetragonal, and monoclinic[23]. In the temperature range 1200 to 1600°C, the Corning and Nippon electrolytes under discussion (4,5 and 6 mol per cent Y_2O_3 respectively) consist of a mixture of cubic and tetragonal zirconia, as shown in Fig. 6. Phase equilibrium

considerations show that, at a given temperature in the range 1200 to 1600°C, the fraction of cubic zirconia increases with an increase in Y_2O_3 content from 4,5 to 6 mol per cent, implying that the Nippon electrolyte contains a much larger fraction of cubic zirconia (approximately 1,5 times more) than the Corning electrolyte. At these temperatures, the tetragonal zirconia contains less than 2 per cent Y_2O_3, suggesting that it has far fewer oxygen-ion vacancies in its crystal lattice and, accordingly, a lower ionic conductivity than the cubic phase, which contains more than 6 per cent Y_2O_3[24]. Hence, the tetragonal zirconia should exhibit a higher ratio of electronic-to-ionic conduction (and consequently a higher P_e value) than the cubic zirconia. The phase composition of the electrolytes under discussion should therefore have a pronounced influence on their P_e values, as was shown to be the case for magnesia-stabilized zirconia electrolytes[17,18]. Accordingly, a higher P_e value is to be expected for the Corning electrolytes than for the Nippon electrolytes, which is in agreement with the results presented in Fig. 5.

Yttria-stabilized zirconia electrolytes supplied by Corning Glass (4,5 mol per cent) have been used extensively by local researchers. For example, Finn and co-workers[1,2] and Wellbeloved[3] used this electrolyte in the cell

$$Cr + Cr_2O_2 \mid ZrO_2 - Y_2O_3 \mid (FeCr)_{alloy} + Cr_2O_3 \ldots \text{(cell II)}$$
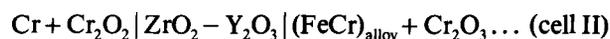
to determine the chromium activities in ferrochromium alloys at 1650°C. However, those investigators assumed that the P_e value was negligible under the prevailing experimental conditions, probably because the P_e value of the electrolyte used was not available. As the P_e value of this electrolyte was determined in the present investigation, this assumption can now be evaluated.

Fig. 7 illustrates the error in activity measurements that may be encountered if the P_e value of the solid electrolyte used in cell II is neglected. The diagram compares the 'true' chromium activity with the 'measured' chromium activity calculated from the e.m.f. of cell II when the P_e value of the electrolyte is neglected. The relation-
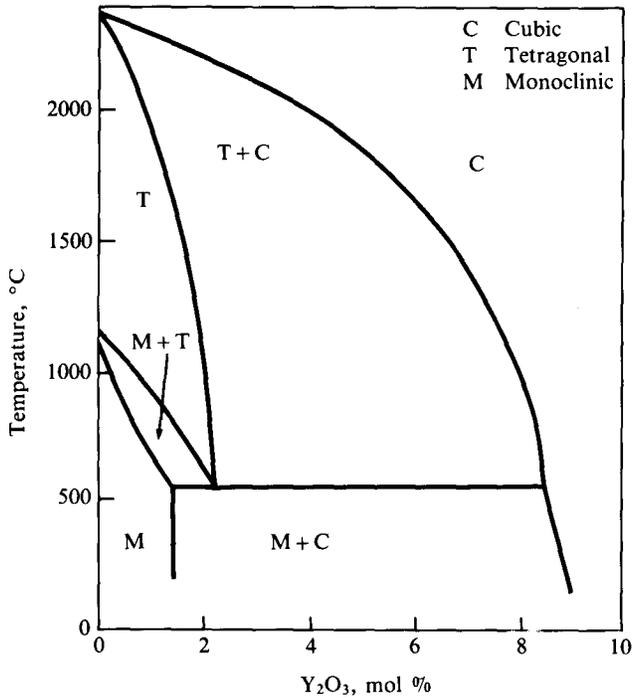
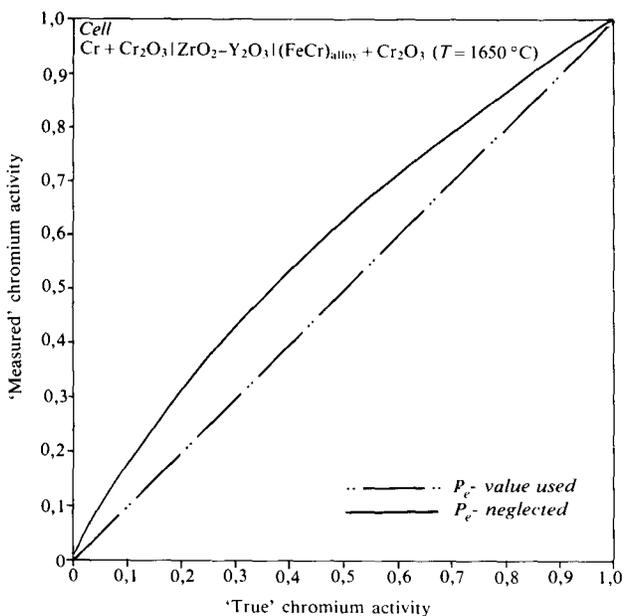**Fig. 6—Phase diagram of the ZrO₂–Y₂O₃ system (after Scott[23])**

Fig. 7—Comparison of the 'measured' chromium activity, calculated from the e.m.f. of the cell when the P_e value of the electrolyte is neglected, and the 'true' chromium activity, calculated by use of the applicable P_e value

ship between the 'true' activity and the 'measured' activity was derived as follows.

The theoretical e.m.f. of the cell was calculated for a given chromium activity ('true activity') according to equation (1), using the following relationship between chromium activity and oxygen partial pressure:

$$a_{Cr} = \left\{ \frac{P_{O_2}[Cr + Cr_2O_3]}{P_{O_2}[(FeCr)_{alloy} + Cr_2O_3]} \right\}^{\frac{3}{4}}, \quad \text{.................. (10)}$$

where a_{Cr} is the chromium activity relative to pure solid

chromium, $P_{O_2}[Cr + Cr_2O_3]$ is the oxygen partial pressure of pure solid chromium in equilibrium with pure Cr_2O_3 ($2,722.10^{-12}$ atm at 1650°C)[25,26], and $P_{O_2}[(FeCr)_{alloy} + Cr_2O_3]$ is the oxygen partial pressure of the ferrochromium alloy in equilibrium with pure Cr_2O_3.

A P_e value of $2,91 \cdot 10^{-13}$ (equation (9), 1923 K) was used for the calculations. The e.m.f. calculated in this way was then used for the re-calculation of the 'measured' chromium activity according to equations (1) and (10), but neglecting the P_e value in equation (1).

It is quite clear from Fig. 7 that there is a large difference between the 'measured' and the 'true' activities. For example, a 'true' activity of 0,50 corresponds to a 'measured' activity of approximately 0,63. This is a difference of 26 per cent, which is much higher than the usual experimental uncertainty in electrochemical measurements of activity. It is therefore evident that the assumption of a negligible P_e value in this particular case is not justified. This example clearly illustrates the importance of an accurate knowledge of the P_e values of the solid electrolytes used in high-temperature thermodynamic studies.

It is therefore recommended that the P_e values determined in the present study should be used in the calculation of the partial pressure of oxygen whenever the Corning ZrO₂–4,5 mol per cent Y₂O₃ electrolyte is used in electrochemical cells for high-temperature thermodynamic studies.

Summary and Conclusions

The successful application of solid electrolytes in electrochemical cells to the determination of the partial pressure of oxygen in high-temperature systems depends to a large extent on an accurate knowledge of the P_e value of the electrolyte employed. The P_e value of the solid electrolyte must therefore be determined prior to its use.

The experimentally determined P_e values of the commercially available ZrO₂–4,5 mol per cent Y₂O₃ electrolyte supplied by Corning Glass can be represented as a function of temperature as

$$\log P_e \text{ (atm)} = 24,89 - 71\,970/T,$$

for temperatures in the range 1200 to 1600°C.

It is recommended that the P_e values determined in the present study should be used in the calculation of the partial pressure of oxygen whenever the Corning ZrO₂–4,5 mol per cent Y₂O₃ electrolyte is used in electrochemical cells for high-temperature thermodynamic studies.

References

1. FINN, C.W.P., and WELLBELOVED, D.B. Solid State Ionics, vol. 2, pt 3/4. 1981. pp. 547–550.
2. FINN, C.W.P., WELLBELOVED, D.B., and ALGIE, S.H. Proceedings of the Third International Meeting on Chemical Sensors, Tokyo, 1983. pp. 300–305.
3. WELLBELOVED, D.B. M.Sc. dissertation, University of the Witwatersrand, 1982.
4. BRINKMANN, E.A. M.Sc. dissertation, University of the Witwatersrand, 1984.

5. PERRY, K.P.D. Ph.D. thesis, University of the Witwatersrand, 1987.
6. VAN WIJNGAARDEN, M.J.U.T., and DIPPENAAR, R.J. *J. S. Afr. Inst. Min. Metall.*, vol. 86. 1986. pp. 443–453.
7. VAN WIJNGAARDEN, M.J.U.T., and DIPPENAAR, R.J. A thermo-dynamic study of lime-based slags used for the external refining of hot metal. *Proceedings of the 71st Steelmaking Conference.* Toronto, Apr. 1988. (To be published.)
8. VAN WIJNGAARDEN, M.J.U.T., and DIPPENAAR, R.J. *Trans. Iron Steel Soc. AIME, Iron Steelmaker*, vol. 15, no. 2. 1988. pp. 49–56.
9. VAN WIJNGAARDEN, M.J.U.T., DIPPENAAR, R.J., and VAN DEN HEEVER, P.M. *J. S. Afr. Inst. Min. Metall.*, vol. 87. 1987. pp. 269–278.
10. SCHMALZRIED, H. *Ber. Bunsenges. Phys. Chem.*, vol. 66. 1962. pp. 572–576.
11. SCHMALZRIED, H. *Z. Phys. Chem.*, vol. 38. 1963. pp. 87–102.
12. JANKE, D. *Advances in Ceramics.* Heuer, A.H., and Hobbs, L.W. (eds.). American Ceramic Society, 1981. vol. 3, pp. 419–436.
13. JANKE, D., and RICHTER, H. *Arch. Eisenhüttenwes.*, vol. 50. 1979. pp. 93–99.
14. JANKE, D. *Proceedings of the Second International Conference on Clean Steel, Hungary, 1981.* London, The Metals Society, 1983. pp. 202–231.
15. ROMERO, A.R., HARKKI, J., and JANKE, D. *Steel Res.*, vol. 57. 1986. pp. 636–644.

16. IWASE, M., ICHISE, E., TAKEUCHI, M., and YAMASAKI, T. *Trans. Japan Inst. Metals*, vol. 25. 1984. pp. 43–52.
17. GELDENHUIS, J.M.A., VAN WIJNGAARDEN, M.J.U.T., and DIPPENAAR, R.J. Council for Mineral Technology (Mintek), Randburg. Private communication, 1987.
18. VAN WIJNGAARDEN, M.J.U.T., GELDENHUIS, J.M.A., and DIPPENAAR, R.J. *Trans. Iron Steel Soc. AIME, Iron Steelmaker*, vol. 15, no. 4. 1988.
19. JANKE, D., and RICHTER, H. *Arch. Eisenhüttenwes.*, vol. 50. 1979. pp. 93–99.
20. SWINKELS, D.A.J. *J. Electrochem. Soc.*, vol. 117. 1970. pp. 1267–1268.
21. GOTO, K., SOMENO, M., SANO, M., and NAGATA, K. *Metall. Trans.*, vol. 1. 1970. pp. 23–29.
22. ETSELL, T.H., and FLENGAS, S.N. *Metall. Trans.*, vol. 2. 1971. pp. 2829–2832.
23. SCOTT, H.G. *J. Mater. Sci.*, vol. 10. 1975. pp. 1527–1535.
24. IWASE, M., and MORI, T. *Trans. Iron Steel Inst. Jap.*, vol. 19. 1979. pp. 126–132.
25. ELLIOTT, J.F., and GLEISER, M. *Thermochemistry for steelmaking.* vol. 1. Mass., Addison Wesley, 1960. (Cited in reference 26.)
26. GOZZI, D., CIGNINI, E., STAMPA, E., ALFONSI, B., and PETRUCCI, M. *Trans. Iron Steel Inst. Jap.*, vol. 23. 1983. pp. 205–212.

SAIMM members win gold medals

Two members of the SAIMM were recently awarded the Order for Meritorious Service Class 1: Gold by the State President. They are Professor D.G. (Danie) Krige and Dr Louw Alberts. This Order is awarded to South African citizens who distinguish themselves by rendering exceptionally meritorious service in the general public interest.

Professor Danie Krige's citation referred to him as 'a brilliant mining engineer whose name has been linked for many years to important developments in South Africa as well as in international mining. Danie Krige's inventive initiatives have made a very important contribution to the stabilisation of the South African mining industry in particular, and the country's economy in general'. In the 1950s and 1960s, he developed a technique for the statistical evaluation of ores, which is known worldwide as *kriging*. After his retirement from the mining industry

in 1981, he accepted the first South African Chair of Mineral Economics in the Department of Mining Engineering at the University of the Witwatersrand. He is still a professor there, and also acts in a variety of capacities at several other universities.

Dr Louw Alberts has made a considerable contribution to South Africa as Professor of Physics, Vice President of the Atomic Energy Board, President of Mintek, Director General of Mineral and Energy Affairs and, in his present capacity, as Chairman of the C S I R. He is regarded as a world leader in physics research.

Both these men have received innumerable awards from South African and overseas organizations, and it is fitting that the State President should have conferred this honour on them. The South African Institute of Mining and Metallurgy is proud to number these distinguished gentlemen among its members.

Fire protection

The US Bureau of Mines will be presenting technology-transfer seminars and workshops this fall summarizing recent Bureau developments in fire protection for underground metal and non-metal mines. Each full-day seminar will address sulphide spontaneous combustion, fire detection and instrumentation, fire warning, fire suppression, diesel equipment, and toxicity analysis of combustion products. The half-day workshop will follow the seminar and will provide hands-on demonstrations of an advanced mine fire and ventilation computer model.

The seminars and workshops will be held in Denver on 18th and 19th October, Detroit on 20th and 21st October, Las Vegas on 1st and 2nd November, and Spokane

on 3rd and 4th November. The subject material covered in these cities will be identical. There is no cost for attendance at either the seminar or the workshop, but pre-registration is requested.

For further information, contact

Sheri Harris
Technology Transfer Office
Bureau of Mines
Columbia Plaza
2401 E Street NW
Washington, DC
20241 USA.