

An experimental technique employing a high-temperature gas-tight alumina seal for the assessment of the electrical properties of solid electrolytes

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A technique is described that permits the high-temperature gas-tight extension of short solid electrolyte tubes, discs or rods. It is demonstrated that this technique can be successfully used in the assessment, by coulometric titration, of mixed ionic and electronic conduction in the short solid electrolyte tubes that are commonly used in practical oxygen sensors.

1. Introduction

Solid electrolyte oxygen sensors are increasingly used in industry and research for the measurement of oxygen activities under conditions of low oxygen activities and high temperatures [1-4]. Under these conditions, the solid oxide (zirconia- and thoria-based) electrolytes that are commonly used in these sensors exhibit mixed ionic and *n*-type electronic conduction [5-8]. As a result, the calculation of the oxygen activity from the measured e.m.f. signal of the sensor requires an accurate knowledge of the electrical properties, in particular the P_e value (the partial pressure of oxygen at which the partial ionic and *n*-type electronic conductivities of the electrolyte are equal), of the electrolyte employed [1-4, 9]. Hence the P_e value of a particular type of electrolyte should be determined prior to its use in oxygen sensors.

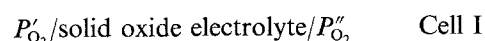
The P_e value of a solid oxide electrolyte can be determined most effectively by coulometric titration [5-8, 10, 11]. However, until now, the application of this technique to the assessment of the P_e values of the small electrolytes (short tubes, rods and discs) usually employed in practical oxygen sensors has been impeded by the difficulties encountered in the construction of the required gas-tight seal between the electrolyte and a suitable ceramic extension tube [6, 12]. For this reason, the coulometric titration technique is generally used only with long impervious electrolyte tubes, thereby overcoming the need for a gas-tight extension of the electrolyte [6-8]. However, long electrolyte tubes of the same type as the small electrolytes used in practical oxygen sensors are unfortunately not always available commercially. Also, whereas small electrolytes can be manufactured fairly easily in a research laboratory, the manufacturing of long impervious electrolyte tubes is difficult, and requires expensive isostatic pressing facilities, which are not always available in research laboratories.

A reliable method that can be used for making of high-temperature gas-tight seals to extensions of solid electrolytes would therefore permit the determination of the P_e values of the small solid electrolytes used in practical oxygen sensors by coulometric titration. This would contribute to an improvement in the reliability of electrochemical measurements of oxygen activity, and would be of considerable benefit to both the manufacturer and the users of solid electrolytes.

This paper reports the successful development of a slip-cast alumina coupling that can be fitted gas-tight between a small electrolyte tube, rod or disc and an alumina extension tube by means of shrinkage during heating. A feature of this coupling is that it retains its gas-tightness at operating temperatures up to approximately 1600°C. This makes the technique appropriate for a variety of applications. It is demonstrated that this seal can be successfully used in the assessment of the P_e values of the small magnesia-stabilized zirconia electrolyte tubes that are commonly used in electrochemical oxygen sensors.

2. Experimental determination of P_e

The P_e value of a solid electrolyte can be determined most effectively by the measurement of the e.m.f. in an electrochemical cell of the type [5-8, 10, 11]



where

$$P'_{O_2} \ll P_e \ll P''_{O_2} \quad (1)$$

When this relation between the P_e value of the solid electrolyte and the partial pressure of oxygen on both sides of the electrolyte applies, the open-circuit e.m.f. of Cell I, given [13, 14] by

$$E = \frac{RT}{F} \ln \left[\frac{(P'_{O_2})^{1/4} + (P_e)^{1/4}}{(P''_{O_2})^{1/4} + (P_e)^{1/4}} \right] \quad (2)$$

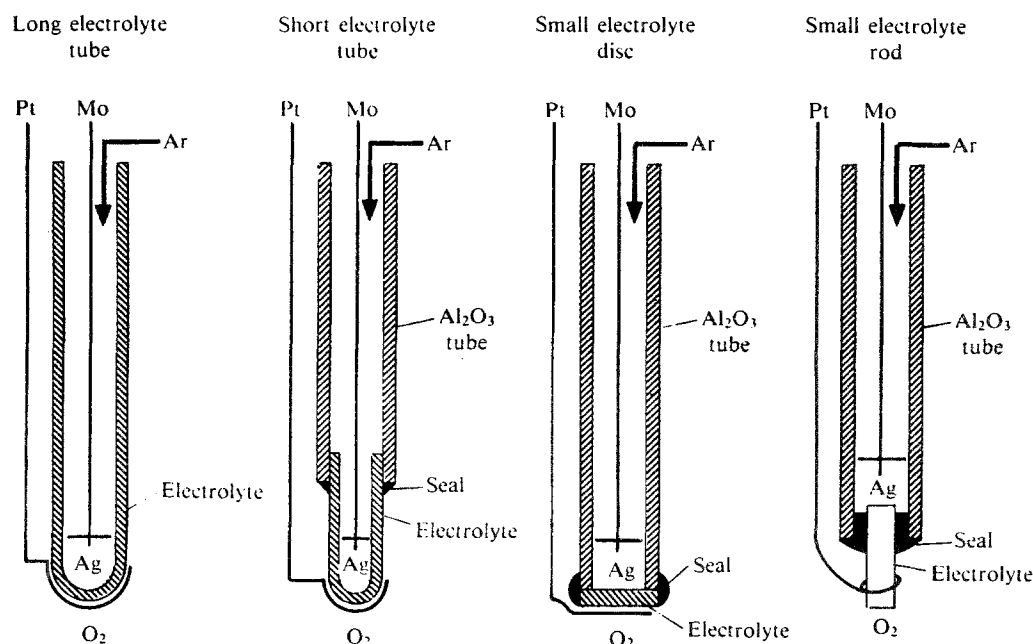


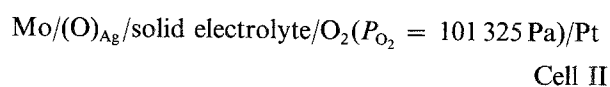
Fig. 1. Typical cell assemblies for use in the application of the coulometric titration technique.

can be simplified to

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

where P''_{O_2} and P_e 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. It is evident from Equation 3 that, if P''_{O_2} is known, the parameter P_e can be determined by measurement of the temperature and e.m.f. of the cell. Since thermodynamic considerations make it virtually impossible to attain the very low partial pressure of oxygen required at one of the electrolyte-electrode interfaces of Cell I in order to satisfy Equation 1, this low partial pressure of oxygen is usually achieved by the adoption of coulometric titration [5-8, 10, 11].

The cell arrangement commonly used in the determination of P_e by coulometric titration can be expressed as follows:



Typical cell assemblies that can be used are shown in Fig. 1. Oxygen is removed electrolytically from the silver melt and transported to the Pt/O₂ electrode when a direct current is passed in the appropriate direction through the cell. The molten silver becomes polarized to an extent determined by the rate of oxygen removal by the electrical current and by the rate of leakage of oxygen back into the melt from the argon cover gas or through the electrolyte assembly. In this way, the partial pressure of oxygen at the silver interface of the electrolyte can be sufficiently lowered to satisfy the condition $P''_{O_2} \ll P_e$. Since the Pt/O₂ reference electrode is essentially non-polarizable, the partial pressure of oxygen at this interface of the electrolyte remains at 101 325 Pa, thus satisfying the

condition $P''_{O_2} \gg P_e$. Under these experimental conditions, the e.m.f. of Cell II can be expressed as

$$E = E_t - \frac{RT}{4F} \ln \frac{P_e}{101\,325} \quad (4)$$

where E_t denotes the thermal e.m.f. between the platinum (+) and molybdenum (-) electrical leads. This value was determined previously [12] as

$$E_t = (23.2 \pm 1.0) - 0.04T \text{ (mV)} \quad (5)$$

Hence the P_e value of the solid electrolyte incorporated in Cell II can be determined at any given temperature by the measurement of the open-circuit e.m.f. of the cell immediately after interruption of the polarizing current.

Figure 2 depicts a typical example of an e.m.f. signal recorded during the application of the coulometric titration technique. As soon as the polarizing current is interrupted, a stable open-circuit e.m.f. plateau is obtained for a short period of time, after which the potential decays slowly. It should be noted, however, that this type of e.m.f. plateau is obtained only if the rate of leakage of oxygen back into the silver melt is sufficiently low. Furthermore, the rate at which the open-circuit e.m.f. decays is strongly affected by the gas-tightness of the electrolyte assembly [6, 12]. Since the accuracy of the measured P_e value is determined largely by the stability of this e.m.f. plateau, it is essential, if accurate and reliable P_e values are to be obtained, that the rate of leakage of oxygen through the electrolyte assembly should be minimized.

This important aspect was recently demonstrated by Iwase *et al.* [6], who used coulometric titration to determine the P_e values of small zirconia discs that were cemented onto an alumina extension tube. However, since they were unable to construct a fully gas-tight seal, gaseous oxygen leaked through the electrolyte assembly during the experimental runs, with

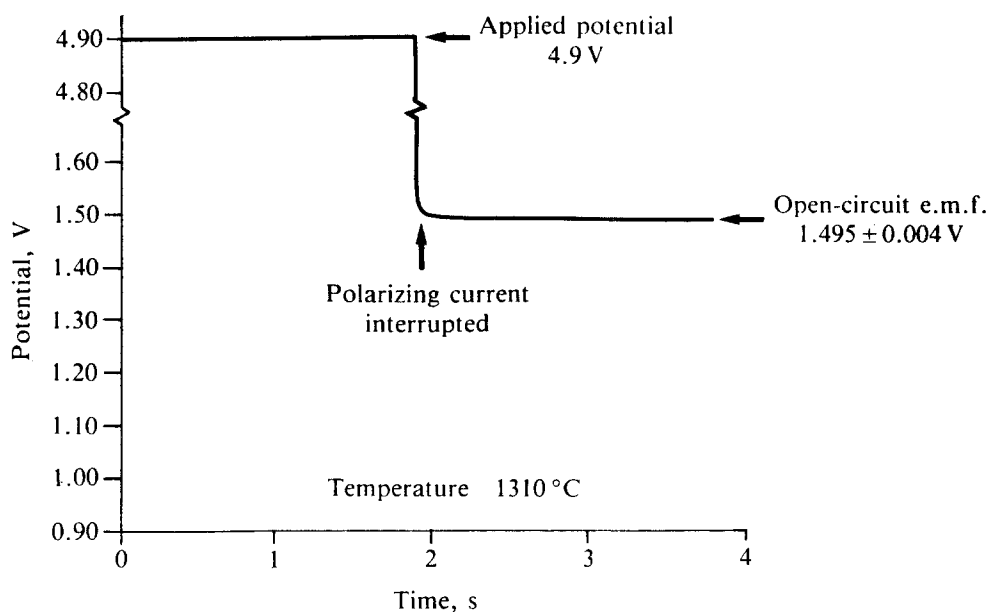


Fig. 2. Typical e.m.f. signal recorded during coulometric titration (after Geldenhuis [12]).

the result that the measured open-circuit e.m.f. values varied significantly with time. In an attempt to minimize this problem, they then measured the open-circuit e.m.f. within 20 ns after the interruption of the polarizing current. However, even with such rapid measurements, they were still unable to obtain reproducible e.m.f. values. Similar results were recently obtained by Geldenhuis [12]. Clearly, therefore, a gas-tight electrolyte assembly seems to be a prerequisite for the successful application of the coulometric titration technique.

In the present investigation, a slip-cast alumina coupling that can be used as a gas-tight seal between a short electrolyte tube and an alumina extension tube was developed. This sealing technique was used in the determination of the P_e values of short magnesia-stabilized zirconia electrolyte tubes (50 mm in length) by coulometric titration. As a check on the reliability of this sealing technique, the P_e values of this type of electrolyte were also determined on long impervious electrolyte tubes (600 mm in length).

3. Experimental details

3.1. Apparatus

The experimental apparatus and procedure used in the assessment of the P_e values of solid electrolytes have been fully described elsewhere [8]. Briefly, the apparatus consisted of a purification train (silica gel, magnesium perchlorate and phosphorus pentoxide) for a gas mixture of argon containing 3% 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 the cell assembly are shown in Fig. 3. The cell assembly consisted of an electrolyte tube (either a long electrolyte tube, or a short electrolyte tube coupled onto an alumina extension tube)

containing a silver electrode, and with a porous platinum electrode on the outside surface. A molybdenum wire served as the electrical lead to the liquid silver electrode. A platinum wire wound round the platinumized surface of the electrolyte tube completed the electrical circuit of the cell.

The short electrolyte tubes (6 mm outer diameter, 4 mm inner diameter and 50 mm length) were coupled onto an alumina extension tube (15 mm outer diameter, 12 mm inner diameter and 600 mm length) by means of a slip-cast alumina coupling. The construction of this assembly is shown in Fig. 4, and is described in detail elsewhere [12]. A slip-cast alumina disc (40 mm diameter and 30 mm height), supplied by MOH-9, South Africa, was used as the starting material for the alumina coupling. This disc was pre-sintered at 900°C for 2 h so as to strengthen it sufficiently for machining. The appropriate holes in the disc were then machined, and the electrolyte tube, extension tube and alumina coupling were assembled. The assembly was then slowly heated to 1550°C, held at that temperature for 2 h and slowly cooled to room temperature. During this heat treatment the slip-cast alumina disc shrinks and forms a strong seal round the surfaces of the electrolyte and the alumina tube. If after this heat treatment the assembly proved to be gas-tight under pressures of up to approximately 80 kPa above atmospheric pressure, it was considered sufficiently gas-tight for use in the coulometric titration technique.

However, it should be noted that the success rate of this sealing technique depends on several factors [12]. For example, the differences between the outer diameters of the electrolyte and the extension tubes and the diameters of the holes in the disc are of critical importance. Since the tightness of the seal depends on the shrinkage characteristics of the disc which, in turn, are affected by the properties of the alumina powder and the slip mixture, the pre-sintering temperature and the temperature of the final heat treatment, the

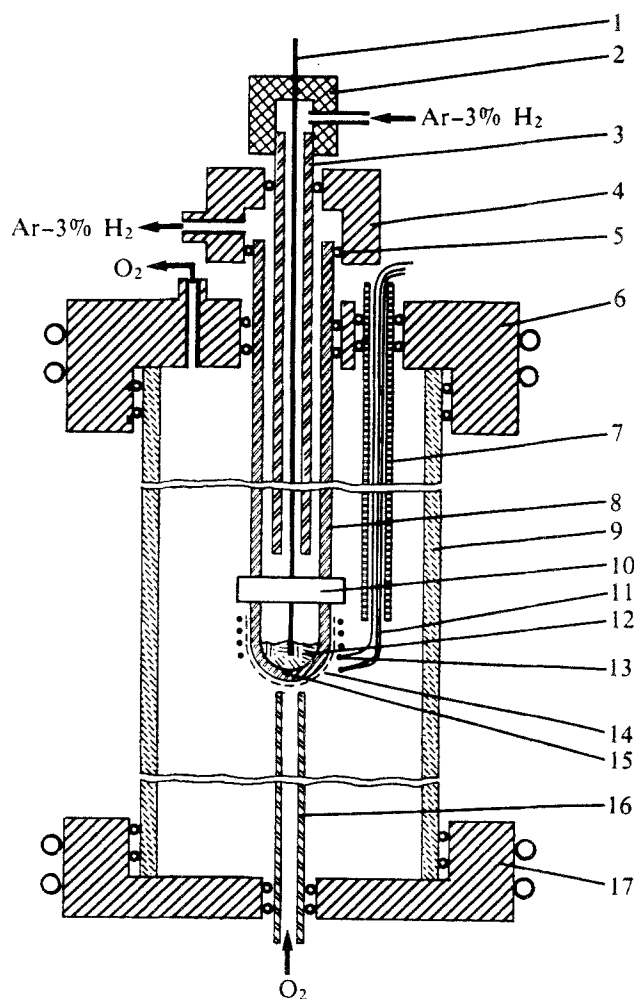


Fig. 3. Reaction tube and electrolyte assembly. 1, Molybdenum wire; 2, rubber stopper; 3, alumina tube; 4, brass fitting; 5, rubber O-ring; 6, water-cooled brass fitting; 7, alumina thermocouple sheath; 8, long electrolyte tube or alumina extension tube (used in combination with short electrolyte tube); 9, alumina reaction tube; 10, alumina coupling (used in combination with short electrolyte tube); 11, Pt/Pt-13% Rh thermocouple; 12, liquid-silver electrode; 13, platinum wire; 14, platinumized surface; 15, closed end of electrolyte tube; 16, alumina oxygen inlet; 17, water-cooled brass fitting.

construction of a reliable gas-tight seal is to a large extent a process of trial and error. Nevertheless, if sufficient care is exercised in the construction of the assembly and the shrinkage characteristics of the alumina disc are well controlled, strong gas-tight seals, able to withstand slow thermal cycling in the temperature range 25–1600°C, can be constructed with a high rate of success.

A Pt/Pt-13% Rh thermocouple, which was placed against the platinumized surface of the electrolyte tube, was used to measure the temperature. These measure-

ments 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 the overall error was found to be less than 3°C. An electrometer with an input impedance of 10^{14} ohm, coupled to a chart recorder with an accuracy of ± 2.5 mV, was used for the measurements of the e.m.f., while a standard potentiostat was used to apply the polarizing currents.

3.2. Experimental procedure

The electrolyte assembly, electrical leads, inlet tubes and thermocouple were positioned inside the reaction tube, as shown in Fig. 3. After the electrolyte tube (or extension tube) and the reaction tube had been sealed and evacuated to ensure that they were gas-tight, the purified argon-hydrogen gas mixture was introduced. The furnace was then heated to 1400°C at a rate of 60°C h^{-1} .

The open-circuit e.m.f. was measured during heating and cooling cycles in the temperature range 1400–1550°C. Immediately prior to each measurement, 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 min. The current was then interrupted, and the open-circuit e.m.f. was measured immediately. 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 $P_{\text{O}_2} \ll P_e$ 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 temperature of the furnace was then adjusted (at a rate of 60°C h^{-1}) to the level at which the next measurement was to be taken. Since oxygen was introduced into the reaction tube only during the measurement of the e.m.f., the leakage of oxygen through the electrolyte (the ionic transport of oxygen due to the presence of electronic conduction) was minimal.

The zirconia electrolytes were supplied by Nippon Kagaku Togyo, Japan. Two electrolytes of each type were investigated. The average chemical compositions are shown in Table 1.

4. Results and discussion

It was established in a previous investigation [8]

Table 1. Average chemical compositions of the solid electrolytes studied

Electrolyte type	Analysis (% by mass)							
	MgO	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	K ₂ O	Na ₂ O
Short tubes	3.1	0.3	0.6	1.3	0.1	0.1	tr	tr
Long tubes	3.1	0.4	0.5	1.0	0.1	0.1	tr	tr

tr = Trace.

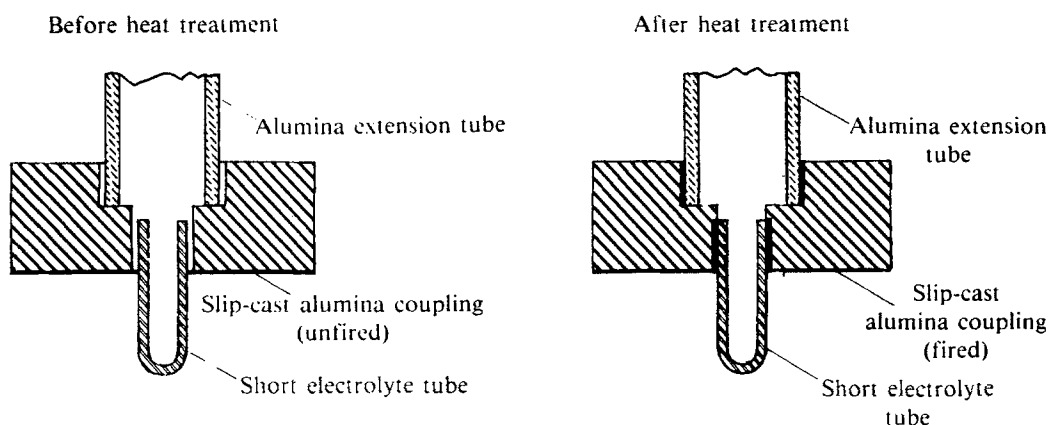


Fig. 4. Construction of the alumina coupling.

that magnesia-stabilized zirconia electrolytes tend to destabilize (i.e. the fraction of the cubic phase contained in the electrolyte decreases) rapidly when exposed to temperatures below 1400°C, and that their P_e values are strongly affected by this time-dependent destabilization. Accordingly, reproducible P_e values cannot be determined at temperatures below 1400°C, and the present investigation was therefore limited to the determination of P_e values at temperatures above 1400°C.

The P_e values determined on the short electrolyte tubes by the application of the sealing technique are shown in Fig. 5, and the experimental results and uncertainties are summarized in Table 2. The uncertainty in the P_e values was estimated from the differential of Equation 4 as follows.

$$d(\log P_e) \leq \frac{4F}{2.3RT} (|dE| + |dE_t|) + \frac{4F}{2.3RT^2} (|E||dT| + |E_t||dT|) \quad (6)$$

where $|dE_t|$, $|dT|$ and $|dE|$ denote the absolute values of the uncertainty in the thermal e.m.f. between molybdenum and platinum (± 1 mV), the uncertainty in

temperature (± 3 K) and the uncertainty in the measured open-circuit e.m.f. of Cell II, respectively. The results in Table 2 show that the uncertainty in individual measurements of $\log P_e$ was always less than ± 0.15 .

When a magnesia-stabilized zirconia electrolyte is heated or cooled, its phase composition (which significantly affects its P_e value) changes continuously until equilibrium is attained in the electrolyte [8]. Therefore, if the P_e values of these electrolytes are to be determined as a function of temperature, it is essential to confirm the attainment of equilibrium in the electrolyte during the measurement of P_e . In the present investigation this was done by the measurement of the P_e values during the heating as well as the cooling of the electrolyte. The good reproducibility of the P_e values obtained in this manner (Fig. 5) confirms that phase equilibrium was indeed attained during the experimental runs. Hence, the P_e values can be expressed analytically as a function of absolute temperature:

$$\log \frac{P_e}{101325} = 22.77 - \frac{67956}{T} \quad (7)$$

for temperatures in the range 1400–1600°C.

Table 2. Results for the short magnesia-stabilized zirconia electrolyte tubes supplied by Nippon Kagaku Togyo

Run No.	Temperature (°C)	E (V)	E_t (V)	$\log (P_e/101325)$ (Pa)
1.1	1404 (H)	1.425 ± 0.004	-0.044 ± 0.001	-17.66 ± 0.09
1.2	1424 (H)	1.410 ± 0.006	-0.045 ± 0.001	-17.29 ± 0.11
1.3	1474 (H)	1.350 ± 0.006	-0.047 ± 0.001	-16.12 ± 0.11
1.4	1500 (H)	1.320 ± 0.008	-0.048 ± 0.001	-15.56 ± 0.13
1.5	1525 (H)	1.292 ± 0.010	-0.049 ± 0.001	-15.04 ± 0.15
1.6	1550 (H)	1.265 ± 0.010	-0.050 ± 0.001	-14.54 ± 0.14
1.7	1487 (C)	1.340 ± 0.008	-0.047 ± 0.001	-15.89 ± 0.13
1.8	1434 (C)	1.405 ± 0.006	-0.045 ± 0.001	-17.13 ± 0.11
2.1	1412 (H)	1.420 ± 0.004	-0.044 ± 0.001	-17.52 ± 0.09
2.2	1446 (H)	1.380 ± 0.006	-0.046 ± 0.001	-16.73 ± 0.11
2.3	1510 (H)	1.305 ± 0.008	-0.048 ± 0.001	-15.30 ± 0.13
2.4	1536 (C)	1.270 ± 0.010	-0.049 ± 0.001	-14.70 ± 0.15
2.5	1462 (C)	1.372 ± 0.006	-0.046 ± 0.001	-16.48 ± 0.11
2.6	1412 (C)	1.425 ± 0.006	-0.044 ± 0.001	-17.58 ± 0.11

(H) Heating cycle.
(C) Cooling cycle.

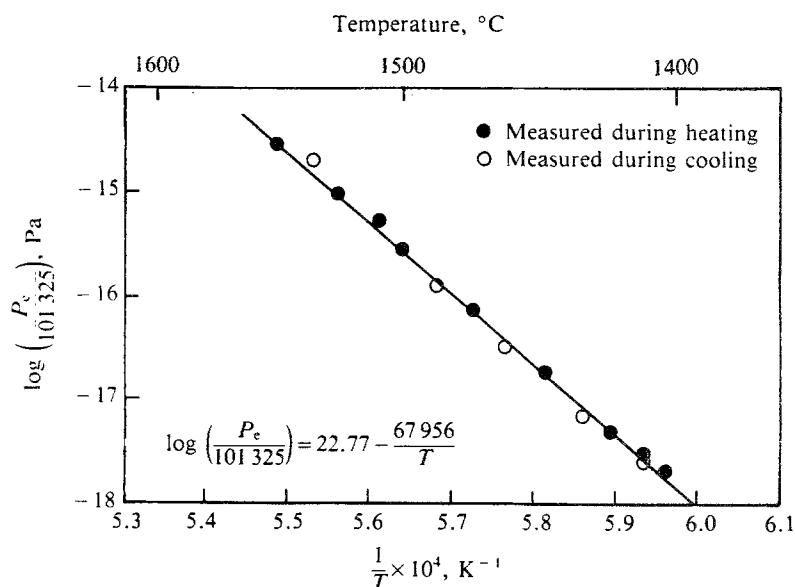


Fig. 5. P_e values as a function of temperature for the small magnesia-stabilized zirconia electrolyte tubes supplied by Nippon Kagaku Togyo.

The coulometric titration technique used in the present investigation was shown to be very sensitive and reliable when applied to the determination of the P_e values of long impervious electrolyte tubes [8]. Since previous studies [6–8] had shown that the P_e values of electrolytes with chemical compositions similar to those of the long and short electrolyte tubes supplied by Nippon Kagaku Togyo (Table 1) should be practically the same, the reliability of the new sealing technique in the application of the coulometric titration technique can be verified by a comparison of the P_e values determined on the long and short electrolyte tubes supplied by the manufacturer.

Figure 6 compares the P_e values determined on the long electrolyte tubes with those determined on the short electrolyte tubes (Equation 7). The experimental results and uncertainties of the measurements on the long electrolyte tubes are summarized in Table 3.

It is evident from Fig. 6 that the P_e values of the long and short electrolyte tubes are in excellent agreement.

Hence, on the basis of these results, it seems that the sealing technique can be used with a good measure of confidence in the application of the coulometric titration technique for the assessment of the P_e values of the short electrolyte tubes, rods or discs used in practical oxygen sensors.

5. Conclusions

In the past, the use of the coulometric titration technique in the measurement of the P_e values of the small electrolytes employed in practical oxygen sensors was impeded by the difficulties experienced in the construction of a gas-tight extension of the electrolyte. The use of the slip-cast alumina coupling developed in the present investigation overcomes this impediment, thus contributing to the improved reliability of electrochemical measurements of oxygen activity. This will be of considerable benefit to both the manufacturers and users of solid electrolytes.

Table 3. Experimental results for the long magnesia-stabilized zirconia electrolyte tubes supplied by Nippon Kagaku Togyo

Run No.	Temperature (°C)	E (V)	E_1 (V)	$\log(P_e/101325)$ (Pa)
1.1	1400 (H)	1.440 ± 0.005	-0.044 ± 0.001	-17.88 ± 0.10
1.2	1451 (H)	1.377 ± 0.006	-0.046 ± 0.001	-16.64 ± 0.11
1.3	1550 (H)	1.260 ± 0.009	-0.050 ± 0.001	-14.49 ± 0.13
1.4	1470 (C)	1.360 ± 0.010	-0.047 ± 0.001	-16.27 ± 0.15
1.5	1399 (C)	1.449 ± 0.005	-0.044 ± 0.001	-18.00 ± 0.10
2.1	1400 (H)	1.438 ± 0.004	-0.044 ± 0.001	-17.86 ± 0.09
2.2	1409 (H)	1.430 ± 0.006	-0.044 ± 0.001	-17.67 ± 0.11
2.3	1437 (H)	1.400 ± 0.006	-0.045 ± 0.001	-17.04 ± 0.11
2.4	1482 (H)	1.335 ± 0.007	-0.047 ± 0.001	-15.88 ± 0.12
2.5	1508 (H)	1.310 ± 0.008	-0.048 ± 0.001	-15.37 ± 0.13
2.6	1551 (C)	1.260 ± 0.008	-0.050 ± 0.001	-14.48 ± 0.12
2.7	1499 (C)	1.330 ± 0.006	-0.048 ± 0.001	-15.68 ± 0.10
2.8	1448 (C)	1.381 ± 0.004	-0.046 ± 0.001	-16.71 ± 0.09
2.9	1406 (C)	1.440 ± 0.005	-0.044 ± 0.001	-17.82 ± 0.10

(H) Heating cycle.

(C) Cooling cycle.

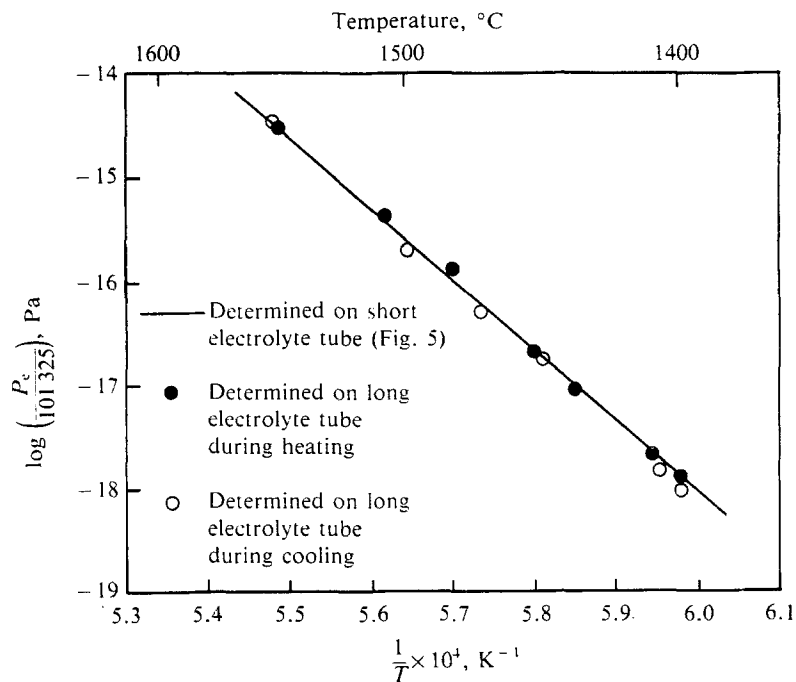


Fig. 6. Comparison of the P_c values for long and short electrolyte tubes.

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References

- [1] K. T. Jacob, J. P. Hajra and M. Iwase, *Arch. Eisenhüttenwes.* **55** (1984) 421.
- [2] A. R. Romero, J. Härki and D. Janke, *Steel Res.* **57** (1986) 636.
- [3] M. Iwase, N. Yamada, E. Ichise, H. Akizuki and M. Kuwahara, *Trans. Iron Steel Inst. AIME* **7** (1986) 45.
- [4] M. J. U. T. van Wijngaarden, R. J. Dippenaar and P. M. van den Heever, *J. S. Afr. Inst. Min. Metall.* **87** (1987) 269.
- [5] D. Janke and W. A. Fischer, *Arch. Eisenhüttenwes.* **45** (1975) 477.
- [6] M. Iwase, E. Ichise, M. Takeuchi and T. Yamasaki, *Trans. Jap. Inst. Met.* **25** (1984) 43.
- [7] K. Yamada, M. Murase and M. Iwase, *J. Appl. Electrochem.* **16** (1986) 712.
- [8] M. J. U. T. van Wijngaarden, J. M. A. Geldenhuis and R. J. Dippenaar, *Trans. Iron Steel Inst. AIME, Iron & Steelmaker* **4** (1988) 35.
- [9] D. Janke and H. Richter, *Arch. Eisenhüttenwes.* **50** (1979) 93.
- [10] D. A. J. Swinkels, *J. Electrochem. Soc.* **117**, (1970) 1267.
- [11] M. Iwase, E. Ichise and K. T. Jacob, in 'Advances in Ceramics' (edited by N. Claussen, M. Rühle and A. H. Heuer), American Ceramic Society (1984) Vol. 10, p. 646.
- [12] J. M. A. Geldenhuis, M. Eng. dissertation, University of Pretoria (1988).
- [13] H. Schmalzried, *Ber. Bunsenges. Phys. Chem.* **66** (1962) 572.
- [14] H. Schmalzried, *Z. Phys. Chem.* **38** (1963) 87.