

A Quantitative Assessment of Mixed Ionic and Electronic Conduction in Some Commercially Available Magnesia-Stabilized Zirconia Electrolytes

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ABSTRACT

A coulometric titration technique has been successfully applied in the quantitative assessment of the electrical characteristics of two commercially available magnesia-stabilized solid electrolytes. Experimentally determined values of P_{O_2} (the oxygen partial pressure at which the ionic conductivity and the n-type electronic conductivity of the electrolyte are equal) of the electrolytes are reported and discussed.

It is shown that magnesia-stabilized zirconia may destabilize if the electrolyte is exposed for long periods to working temperatures below 1,400 °C, and that this destabilization significantly affects the P_{O_2} -value. The practical implications of this finding are discussed briefly. Some conclusions are presented regarding the influence of the impurity content, phase composition and the microstructure of magnesia-stabilized zirconia on their P_{O_2} -values.

INTRODUCTION

Interest in the use of magnesia-stabilized zirconia as the solid electrolyte in electrochemical cells for the determination of oxygen partial pressure, has increased markedly since the 1980s.^{1,2} For example, it has become standard practice for steelmaking plants to use electrochemical oxygen probes, equipped with magnesia-stabilized zirconia electrolytes, to determine the oxygen activity in liquid steel.^{1,2} In research applications, these electrolytes have also been used extensively in high temperature thermodynamic studies of slag-metal systems typical of those encountered in the production of copper,^{3,4} ferrochromium,⁵ iron^{6,8} and steel.⁹

Unfortunately, zirconia solid electrolytes exhibit mixed ionic and electronic conduction when exposed to the high temperatures and low oxygen potentials usually prevalent in slag-metal systems of practical importance. This mixed conduction has been shown

the electrical properties of the solid electrolyte. Schmalzried^{10, 11} analyzed the contribution of the electronic conduction in a solid oxide electrolyte to the measured emf of an electrochemical cell, and showed that, in the presence of n-type electronic conduction, the emf can be expressed as:

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

where P''_{O_2} and P'_O are the 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_{O_2} , describes the relation between the partial ionic and n-type electronic conductivity of the solid 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 investigators¹²⁻¹⁵ have analyzed and emphasized the importance of an accurate knowledge of the P_{O_2} -value of the electrolytes used in electrochemical cells, and it is generally accepted that the P_{O_2} -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.

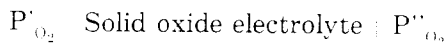
Although P_{O_2} -values for magnesia-stabilized zirconia electrolytes have been published,¹²⁻¹⁵ there are large differences in the reported data. For example, Iwase et al.¹³ reported P_{O_2} -values for a magnesia-stabilized zirconia electrolyte (9 mol percent MgO) that are between 1 and 2 orders of magnitude (depending on the temperature) higher than those determined by Janke and Richter¹² for essentially the same type of electrolyte (7 mol percent MgO). Moreover, this apparent discrepancy cannot be explained by a consideration of the various factors which influence the P_{O_2} -value of zirconia solid electrolytes.¹³ Hence

the P_e -values of magnesia-stabilized zirconia. Clearly, this leads to unnecessary uncertainties in the experimentally determined data in those cases where significant electronic conduction prevails. It was considered necessary, therefore, to study the P_e -values of magnesia-stabilized zirconia solid electrolytes in more detail.

This paper describes the application of a coulometric titration technique in the quantitative assessment of the P_e -values of some commercially available magnesia-stabilized zirconia electrolytes. A preliminary investigation showed an irreversibility in the P_e -values determined during heating as opposed to cooling. In an attempt to investigate this phenomenon, the experimental work was extended to a determination of the phase compositions of the electrolytes as a function of time and temperature. These results allowed a semi-quantitative assessment to be made of the effect of the destabilization (decrease in the volume fraction of cubic zirconia) of magnesia-stabilized zirconia on their P_e -values.

EXPERIMENTAL

The parameter, P_e , defined earlier, can be determined most effectively by the measurement of the emf in an electrochemical cell of the type:



where:

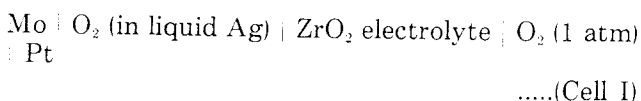
$$P'_{O_2} \ll P_e \ll P''_{O_2} \quad \dots(2)$$

When this relation between the P_e -value of the solid electrolyte and the oxygen partial pressures on both sides of the electrolyte applies, Equation (1) can be simplified to:

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

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 emf of the cell. However, it is extremely difficult to achieve experimentally the very low oxygen partial pressure required at one of the electrolyte-electrode interfaces of the cell in order to satisfy Equation (2). In the present investigation, this low oxygen partial pressure was established by the adoption of a coulometric titration technique,^{13, 16} the nature and purpose of which are briefly outlined here.

The experimental cell arrangement used in the present study, can be expressed as:



Oxygen is removed electrolytically from the silver melt and transported to the Pt/O₂ electrode when a direct current is passed through the cell. At sufficiently high cell currents, liquid silver is polarized,¹⁷ and an oxygen concentration gradient is established

oxygen partial pressure at the silver interface electrolyte can be lowered sufficiently to satisfy condition:

$$P_{O_2} \text{ (silver)} \ll P_e$$

The Pt/O₂ (1 atm) reference electrode, on the other hand, is essentially non-polarizable,¹⁸ and the oxygen partial pressure at this interface remains at 1 atm, thus satisfying the requirement:

$$P''_{O_2} \gg P_e$$

Under the experimental conditions expressed in Equations (4) and (5), the emf of Cell I can be expressed as:

$$E = E_t - \frac{RT}{4F} \ln P_e$$

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

Experimental Apparatus

The experimental apparatus consists essentially of a purification train (silica gel, magnesium perchlorate and phosphorus pentoxide) for a gas mixture (air containing 3 percent hydrogen), and a vertical stainless steel Kanthal furnace containing an alumina reaction chamber and equipped with a programmable proportional-integral-derivative (PID) controller.

The reaction tube and cell assembly are shown schematically in Figure 1. The cell arrangement consisted of an electrolyte tube (13 mm outer diameter, 9 mm inner diameter; 500 to 600 mm length) containing a silver electrode and having a porous platinum electrode on its outside surface. The platinum electrode was prepared as follows. The surface at the closed end of the electrolyte tube was painted with platinum paste diluted with xylene, which was subsequently cured by being heated slowly to 1,000°C at this temperature for 6 h and 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, and a platinum wire, wound around 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 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-measurement 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 10¹⁴ ohm, coupled to a chart recorder with an accuracy of ±2.5 mV, was

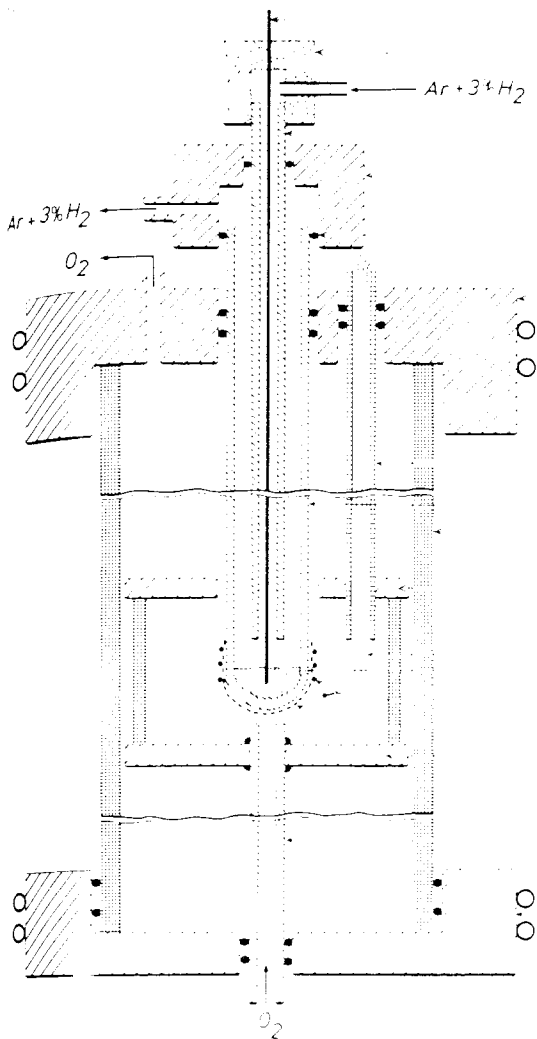


Fig. 1 — Reaction tube and crucible assembly

- 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 — Electrolyte tube
- 9 — Alumina reaction tube
- 10 — Alumina guide disc
- 11 — Pt/Pt-13% Rh thermocouple
- 12 — Liquid-silver electrode
- 13 — Platinum wire
- 14 — Platinized surface
- 15 — Alumina guide disc
- 16 — Alumina oxygen inlet
- 17 — Water-cooled brass fitting

Experimental Procedure

The electrolyte tube (containing approximately 8 g of pure silver), electrical leads, inlet tubes and the thermocouple were positioned inside the reaction tube, as shown in Figure 1. After the electrolyte and reaction tubes 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 1,200°C at a rate of 80°C/h.

The emf was measured during heating and cooling cycles in the temperature range 1,200 to 1,600°C. Immediately prior to measurement of the emf, 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 before being interrupted, and the open-circuit emf was measured immediately. This procedure was repeated at increasing potentials until the measured open-circuit emf was independent of the magnitude of the applied potential, indicating that the conditions expressed in Equation (4) were satisfied. As soon as the reproducibility of the open-circuit emf 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. (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 heating or cooling cycles, and oxygen was introduced into the reaction only while the emf was being measured.)

The zirconia electrolytes investigated in this study were supplied by Nippon Kagaku Togyo, Japan (9 mol percent MgO) and Corning Glass, USA (3 percent MgO by mass). Three electrolytes of each type were investigated. The consistency of the chemical and phase compositions, and the microstructures of the electrolytes were determined on samples of all the electrolytes by chemical analysis, X-ray diffraction, scanning electron microscopy and microprobe analysis. The chemical compositions and degrees of stabilization of the electrolytes are presented in Table I. The chemical composition was determined by atomic emission spectroscopy (AES) using an inductively coupled plasma (ICP). The degree of stabilization, i.e., the volume fraction of cubic zirconia contained in the electrolyte, was estimated by the use of X-ray powder diffractometry,^{13, 19, 20} for which pieces of the electrolytes were reduced to smaller than 40 μm by crushing, which transforms any metastable tetragonal zirconia

Table I — Chemical Composition and Degree of Stabilization of the Solid Electrolytes^a Studied

Electrolyte	Analysis, % (by Mass)										
	Type	No.	MgO	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	Na ₂ O	K ₂ O	Y ₂ O ₃
ZrO ₂ -MgO (Nippon)	1	3.09	0.36	0.44	0.98	0.14	0.09	tr	tr	—	26
	2	3.08	0.36	0.49	1.01	0.14	0.09	tr	tr	—	24
	3	3.08	0.35	0.48	0.99	0.14	0.10	tr	tr	—	25
ZrO ₂ -MgO (Corning)	1	2.80	0.31	0.31	0.10	0.09	0.09	tr	tr	—	32
	2	2.79	0.33	0.32	0.09	0.09	0.10	tr	tr	—	33
	3	2.79	0.32	0.35	0.10	0.09	0.10	tr	tr	—	32

tr = Trace

contained in the electrolyte, to monoclinic symmetry.^{19, 21, 22} The relative amount of cubic phase present was determined by the ratio of the diffraction intensities of cubic and monoclinic zirconia, as expressed in Equation (7):

$$X = \frac{I_c(111)}{I_c(111) + I_m(11\bar{1})} \quad \dots(7)$$

where $I_c(111)$ and $I_m(11\bar{1})$ denote the peak heights of the diffraction patterns of the (111) plane of cubic zirconia and the (11 $\bar{1}$) plane of monoclinic zirconia respectively. The intensity ratio so obtained was converted to the volume fraction of cubic zirconia (V_c) by the use of a calibration curve given by Nakamura and Moriya.¹⁹

The thermal emf between platinum (+) and molybdenum (-) has been determined experimentally as:

$$E_t = (23.2 \pm 1.0) - 0.04 T \quad \dots(8)$$

where E_t and T are expressed as millivolts and kelvin, respectively.

RESULTS AND DISCUSSION

The uncertainty in the experimentally determined P_p -values can be estimated from the differential of Equation (6) as follows:

$$d(\log P_p) \leq \frac{4F}{2.3 RT} [dE_{t1} + dE_{t2}] + \frac{4F}{2.3 RT^2} [E_{t1} dT + E_{t2} dT] \quad \dots(9)$$

where E_{t1} , dT and dE_{t1} denote the absolute values of the uncertainty in the thermal emf between molybdenum and platinum (± 1 mV), the uncertainty in the temperature ($\pm 3^\circ\text{C}$) and the uncertainty in the measured emf of Cell I respectively. The uncertainty in $\log P_p$ of the individual measurements was always less than ± 0.15 , when these were calculated according to Equation (9).

Effects of Temperature and Phase Composition

The P_p -values determined for the magnesia-stabilized zirconia supplied by Nippon Kagaku Togyo and Corning Glass are shown in Figures 2 and 3, respectively. It is evident from these diagrams that, at temperatures below 1,400°C, the P_p -values determined during heating and cooling of the electrolytes differ significantly, indicating that non-equilibrium conditions existed in both the Nippon and Corning electrolytes. At temperatures above 1,400°C, on the other hand, the P_p -values determined during heating and cooling are in good agreement, indicating that equilibrium conditions were attained.

Zirconia may exist in three crystallographic modes, namely cubic, tetragonal and monoclinic.²³ At temperatures above 1,400°C, the magnesia-stabilized zirconia studied (8 to 9 mol percent MgO) consists of a mixture of cubic and tetragonal zirconia, as shown in Figure 4.²⁴ Although phase-equilibrium considerations indicate that cubic zirconia should be subjected to eutectoid decomposition on being cooled from high temperatures, rapid cooling may suppress this rather sluggish reaction.²³ The martensitic tetragonal-mono-

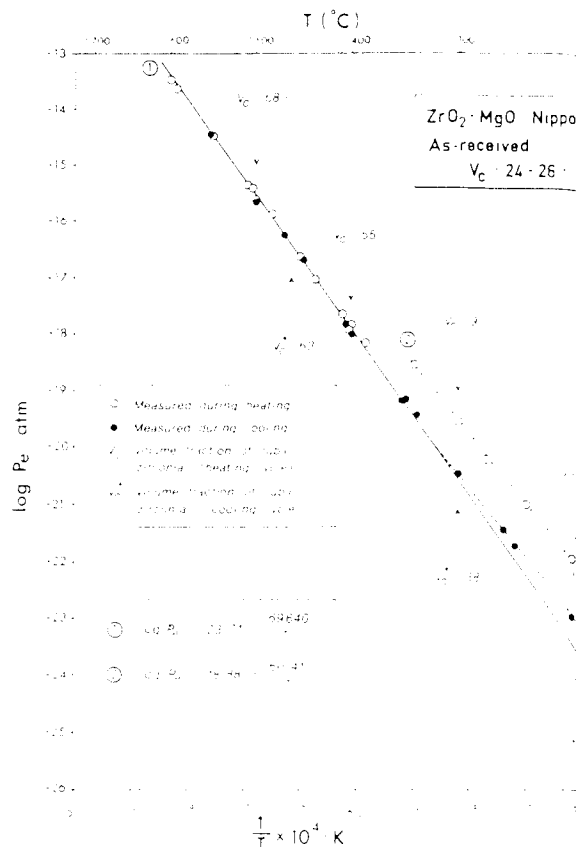


Fig. 2 - The P_p -values and phase compositions (in volume fraction of cubic zirconia) as a function of temperature for the magnesia-stabilized zirconia electrolyte supplied by Nippon Kagaku Togyo.

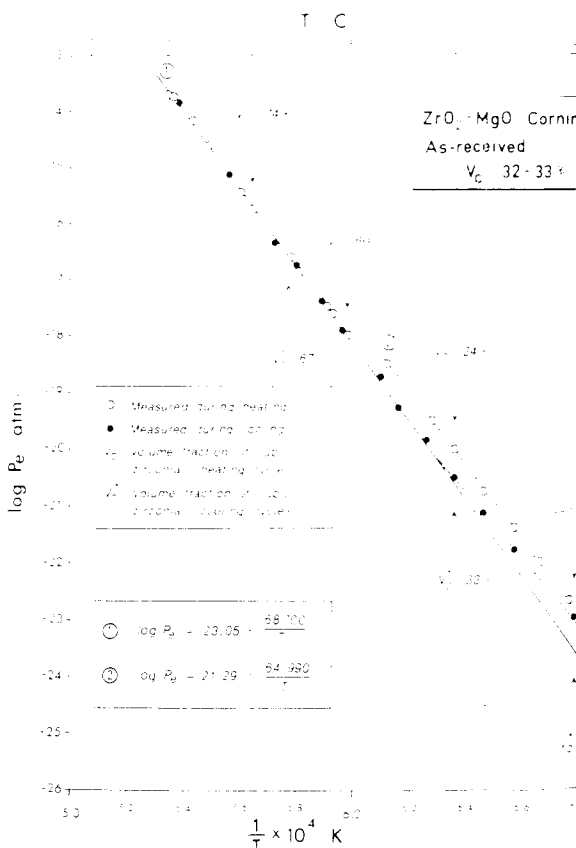


Fig. 3 - The P_p -values and phase compositions (in volume fraction of cubic zirconia) as a function of temperature for the magnesia-stabilized zirconia electrolyte supplied by Corning Glass.

tetragonal zirconia is present as very small particles.²⁰ Since the eutectoid decomposition of cubic zirconia involves the interdiffusion of magnesium and zirconium cations, the phase composition of magnesia-stabilized zirconia at temperatures below 1,400°C will be influenced by the thermal history of the electrolyte. The phase composition of the electrolyte is therefore likely to be different during heating (as opposed to cooling) at temperatures below 1,400°C. Since cubic zirconia exhibits primarily ionic conduction, whereas monoclinic and tetragonal zirconia exhibit essentially electronic conduction and virtually no ionic conduction,^{25, 26} the phase composition of an electrolyte should have a pronounced influence on its P_{e} -value. Hence, the observed irreversibility in the P_{e} -values in Figures 2 and 3 is considered to be related to the phase compositions of the electrolytes.

In an effort to substantiate this premise experimentally, the change in the volume fraction of cubic zirconia present in the electrolytes at different temperatures was determined during heating and cooling cycles. Samples of the electrolytes were exposed to a temperature cycle approximately the same as that used during the determination of the P_{e} -values, and were subsequently water-quenched from various temperatures. The phase composition of the electrolytes was then determined by the use of an X-ray diffraction technique. The results are summarized in Table II and are also shown in Figures 2 and 3 as a function of temperature for the Nippon and Corning electrolytes respectively. It was not possible to simulate exactly the temperature cycle to which the electrolytes had been exposed during the determination of the P_{e} -values. However, this procedure did provide an estimate of the phase composition of an electrolyte as a function of time and temperature.

From the results presented in Table II and Figures 2 and 3, it is evident that the phase composition of the magnesia-stabilized zirconia electrolytes investigated, does indeed depend on their thermal history.

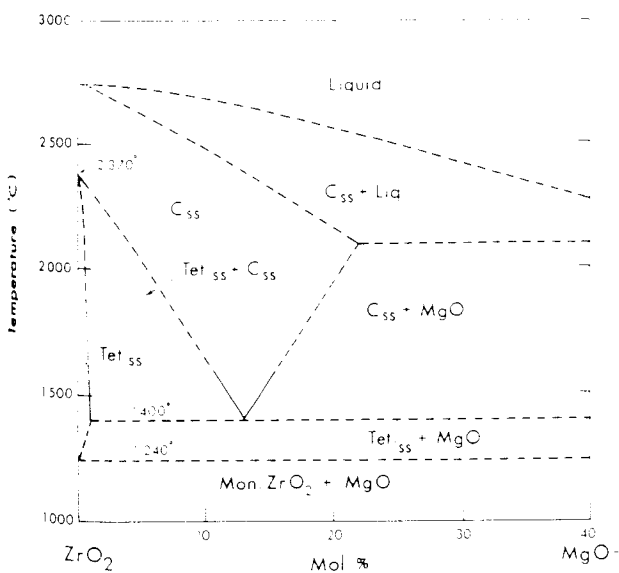


Fig. 4 - Phase diagram of the ZrO₂-MgO system. (After Grain²⁴)

C_{ss} Cubic solid solution
Tet_{ss} Tetragonal solid solution

If the electrolyte is slowly heated from room temperature (24 to 33 percent cubic zirconia), destabilization, i.e., a decrease in the fraction of cubic zirconia, ensues. At approximately 1,400°C, the eutectoid reaction occurs, and the fraction of cubic zirconia suddenly increases to approximately 60 percent. At temperatures above 1,400°C, cubic zirconia is thermodynamically stable, and the fraction of cubic zirconia is fixed by the temperature and chemical composition of the electrolyte. During slow cooling through 1,400°C, a large amount of cubic zirconia is retained in a metastable condition but, during further cooling, the fraction of cubic zirconia decreases continuously owing to eutectoid decomposition. As a result, the phase composition of the electrolyte is different following heating or cooling cycles in the temperature range 1,200 to 1,400°C, suggesting that the observed irreversibility in the P_{e} -value is indeed related to the phase composition of the electrolyte. The influence of phase composition on the parameter, P_{e} , is further evident from the sudden increase in the volume fraction of cubic zirconia at approximately 1,400°C and the associated decrease in the P_{e} -value.

During the experimental runs it was noted that, when the Nippon and Corning electrolytes were held at a constant temperature in the range 1,200 to 1,350°C, the P_{e} -values increased with time. In an attempt to find further proof that this increase in the P_{e} -value is related to a change in the phase composition of the electrolytes, the volume fraction of cubic zirconia in the electrolytes was determined as a function of time at 1,350°C. (Prior to this destabilization treatment, the electrolytes had been treated at 1,460°C for 1 h to ensure that they contained a high fraction of cubic zirconia.) The results are summarized in Table III, and clearly show that the fraction of cubic zirconia in the electrolytes decreased rapidly with time. There is therefore convincing experimental evidence that the P_{e} -value is strongly influenced by the amount of cubic zirconia present in the electrolyte.

All of these results show clearly that, with the experimental technique used, very small changes in the P_{e} -value, associated with changes in the phase composition of the electrolyte, can be detected, and illustrate the sensitivity of the technique to changes in the parameter P_{e} . Hence, the experimental technique can be used with a good measure of confidence for the accurate measurement of the P_{e} -values of solid electrolytes.

The experimentally determined P_{e} -values of the Nippon and Corning electrolytes shown in Figures 2 and 3, respectively, can be analytically expressed as a function of temperature as follows:

For the Nippon electrolyte:

$$\log P_{\text{e}} (\text{atm}) = 23.71 - 69\,640/T \quad (1,400^\circ\text{C} \leq T \leq 1,600^\circ\text{C}) \quad \dots(10)$$

and

$$23.71 - 69\,640/T \leq \log P_{\text{e}} (\text{atm}) \leq 18.88 - 60\,410/T \quad (1,200^\circ\text{C} \leq T \leq 1,399^\circ\text{C}) \quad \dots(11)$$

Table II -- Phase Composition of the Nippon and Corning Magnesia-Stabilized Zirconia Electrolytes as a Function of the Temperature During Heating and Cooling Cycles

Temperature (°C)	Heat Treatment ^a	Phase Composition of Electrolyte ^b	
		Nippon	Corning
As received	None	24 to 26	32 to 33
1,200 (H)	Heated to and held for 1 h at 1,200°C, water-quenched from 1,200°C	9	27
1,300 (H)	Heated to and held for 1 h at 1,200°C, heated to and held for 1 h at 1,300°C, water-quenched from 1,300°C	9	24
1,400 (H)	Heated to and held for 1 h at 1,200°C, heated to and held for 1 h at 1,300°C, heated to and held for 1 h at 1,400°C, water-quenched from 1,400°C	55	60
1,500 (H)	Heated to and held for 1 h at 1,500°C, water-quenched from 1,500°C	68	74
1,460 (C)	Heated to and held for 1 h at 1,500°C, cooled to and held for 1 h at 1,450°C, water-quenched from 1,450°C	63	67
1,300 (C)	Heated to and held for 1 h at 1,450°C, cooled to and held for 1 h at 1,300°C, water-quenched from 1,300°C	38	32
1,200 (C)	Heated to and held for 1 h at 1,450°C, cooled to and held for 1 h at 1,300°C, cooled to and held for 1 h at 1,200°C, water-quenched from 1,200°C	25	22

^aHeating and cooling rates 80°C/min throughout

^bAs cubic zirconia, % (by volume)

(H) Heating cycle

(C) Cooling cycle

$$\log P_{\text{O}_2} \text{ (atm)} = 23.05 - 68\,700/T \quad (1.400^\circ\text{C} \leq T \leq 1.600^\circ\text{C}) \quad \dots(12)$$

and

$$23.05 - 68\,700/T \leq \log P_{\text{O}_2} \text{ (atm)} \leq 21.29 - 64\,990/T \quad (1.200^\circ\text{C} \leq T \leq 1.399^\circ\text{C}) \quad \dots(13)$$

It is important to note that the P_{O_2} -values of these electrolytes are time-dependent at temperatures below 1,400°C, and that long exposure of the electrolyte to these temperatures may result in higher P_{O_2} -values than those given by Equations (11) and (13). This is especially true for the Corning electrolyte, since the upper limit of Equation (13), namely line 2 in Figure 3, represents P_{O_2} -values associated with 20 to 30 percent cubic zirconia, and further destabilization of this electrolyte may yet occur.

Practical Implications of Destabilization

The time-dependent destabilization of magnesia-stabilized zirconia electrolytes has important implications for their practical application. If these electrolytes are used in electrochemical cells (for the determination of oxygen partial pressure) that are exposed for long periods to temperatures below 1,400°C, the P_{O_2} -value of the electrolyte, and therefore the emf of the cell, will change with time and inaccurate measurements will be obtained. Further

Table III -- Phase Composition of the Nippon and Corning Magnesia-Stabilized Zirconia Electrolytes as a Function of Exposure-Time at 1,350°C

Exposure-Time (h)	Phase Composition of Electrolyte ^a	
	Nippon	Corning
0	62	68
5	44	54
10	38	52

^aAs cubic zirconia, % (by volume)

amount of electronic conduction in the electrolyte which may result in polarization of the cell and, consequently, in erroneous measurements.¹¹⁻¹² When emf is to be measured in this temperature range it is therefore essential to minimize the degree of destabilization of the electrolyte. This can be done if the cell is designed in such a way as to allow the electrolyte to be heated rapidly to the measurement temperature.⁸

Comparison of Different Electrolytes

Figure 5 compares the P_{O_2} -values of the magnesia-stabilized electrolytes as expressed in Equations (11) to (13). Also included in the diagram are the results of Iwase et al.¹³ for a magnesia-stabilized electrolyte supplied by Nippon Kagaku Togyo which has approximately 10 percent cubic zirconia. The data

and the P_c -values of a ZrO_2 -7 mol percent MgO electrolyte reported by Janke and Richter.¹² The results of the present investigation show that, at temperatures below 1,400°C, the P_c -values of the Nippon electrolyte during heating are higher than the corresponding values for the Corning electrolyte. This can be explained by the lower content of cubic zirconia in the Nippon electrolyte, which, as discussed previously, results from a relatively high rate of destabilization.

The small difference in the P_c -values of the Nippon and Corning electrolytes observed at temperatures above 1,400°C can be ascribed to the phase compositions and microstructures of the electrolytes, as well as the impurities they contain. The chemical compositions in Table I, show that the Nippon electrolyte has a higher MgO content than the Corning electrolyte, indicating that the former should contain a slightly higher fraction of cubic zirconia at temperatures above 1,400°C. On the other hand, the phase compositions of the electrolytes (Table II) show that the opposite is true. However, both electrolytes contain impurities, which, when present in relatively large concentrations, segregate to the grain boundaries and precipitate as magnesia or magnesia-alumina silicates, or both, thereby effectively reducing the MgO available for stabilization. Since the Nippon electrolyte contains more silica and especially more alumina than the Corning electrolyte, a larger concentration of segregated MgO is to be expected in the Nippon electrolyte. Figures 6 to 11 present typical examples of the microstructures of the Nippon and Corning electrolytes studied. Figures 8 and 9 show the MgO distribution in the electrolytes as the

magnesium distribution and Figures 10 and 11 show the silica distribution in the electrolytes as the silicon distribution. The white areas in these photographs represent high concentrations of magnesium and silicon respectively, and indicate that segregated phases



Fig. 6 — Back-scattered electron image of the magnesia-stabilized zirconia electrolyte supplied by Nippon Kagaku Togyo.

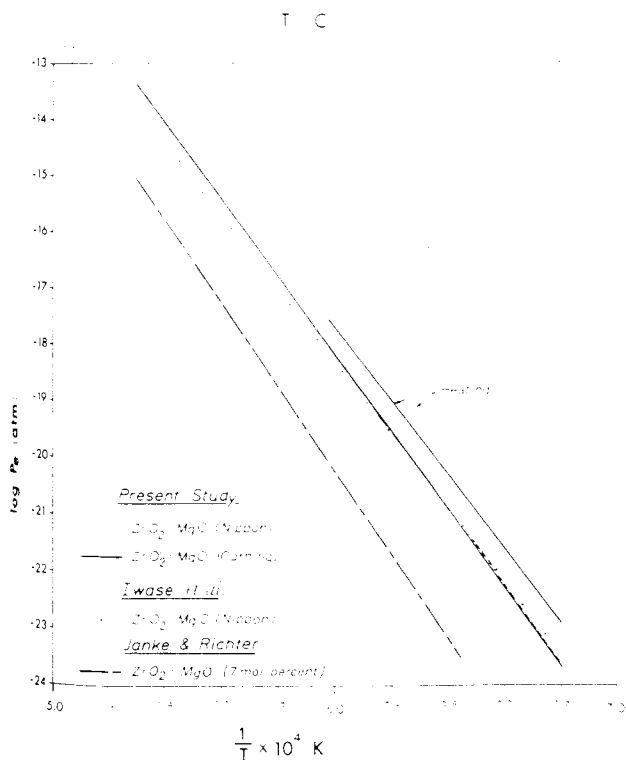


Fig. 5 — Comparison of the P_c -values for the magnesia-stabilized zirconia electrolytes determined in this study and



Fig. 7 — Back-scattered electron image of the magnesia-

containing MgO are indeed present in both electrolytes. Although the average grain size of the Nippon electrolyte is approximately half that of the Corning electrolyte, the phase distributions of the two electrolytes are essentially the same. The microstructures

of both electrolytes consist of a relatively coarse-grained, MgO-rich cubic matrix and finer-grained, MgO-lean, intergranular monoclinic zirconia. Some intragranular monoclinic, and probably some tetragonal, precipitates are also present within the



Fig. 8 — Characteristic X-ray image of the magnesia-stabilized zirconia electrolyte from Nippon showing the distribution of magnesium.

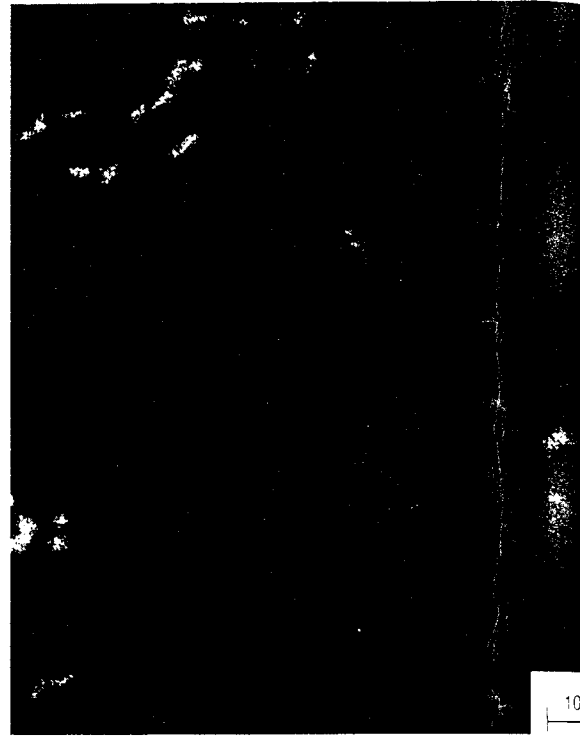


Fig. 10 — Characteristic X-ray image of the magnesia-stabilized zirconia electrolyte from Nippon showing the distribution of silicon.



Fig. 9 — Characteristic X-ray image of the magnesia-stabilized zirconia electrolyte from Corning showing the distribution of magnesium.

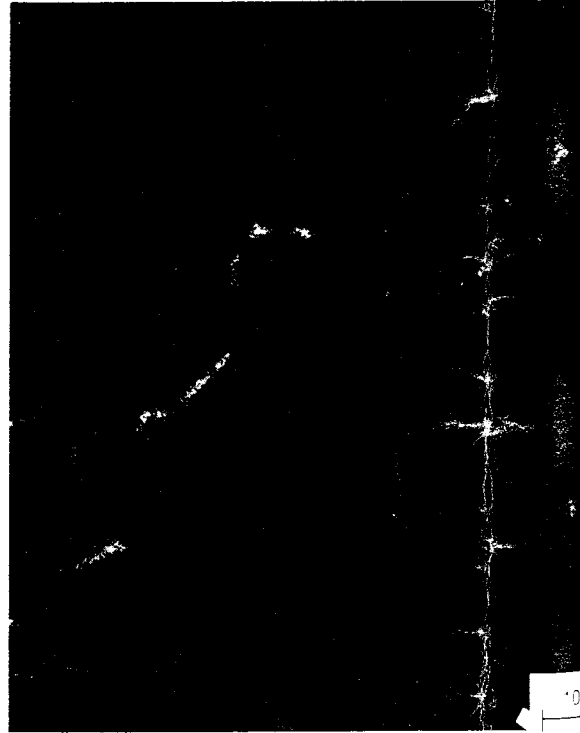


Fig. 11 — Characteristic X-ray image of the magnesia-stabilized zirconia electrolyte from Corning showing the distribution of silicon.

matrix. The development of the microstructures of these magnesia-partially stabilized zirconia electrolytes has been described in detail by Porter and Heuer.²⁶ Although not clearly discernible at the magnifications of Figures 8 and 9, examination of the microstructure of the electrolytes at lower magnifications showed that the Nippon electrolyte contained more segregated MgO than the Corning electrolyte. This may explain the lower fraction cubic zirconia present in the Nippon electrolyte at temperatures above 1,400°C. Accordingly, the Nippon electrolyte should have a slightly higher P_c -value than the Corning electrolyte, which is in agreement with the results of the present investigation.

Impurities may also increase the P_c -value of a solid electrolyte because they influence its electronic and ionic conductivity.^{13, 27, 28} If the impurities are dissolved in the zirconia matrix, the electronic conduction should increase as a result of the introduction of excess electrons.²⁷ Beekmans and Heyne²⁸ and Iwase et al.¹³ have suggested that segregated impurities primarily influence the ionic conductivity of an electrolyte, since the segregated phase behaves as an ionic insulator. This results in a lower ratio of ionic-to-electronic conduction, and consequently, in a higher P_c -value. The P_c -value of an electrolyte that does not contain segregated impurities will therefore increase significantly if an increase in the amount of impurities results in the formation of segregated phases.¹³ However, Iwase et al.¹³ have shown experimentally that the addition of impurities such as silica and alumina (up to 1.5 percent) to an electrolyte that already contains segregated impurity phases, does not significantly influence its P_c -value. From the microprobe analyses in Figures 6 to 11, it is evident that the impurities occur primarily as segregated phases in both electrolytes. The agreement in the P_c -values of the Nippon and Corning electrolytes obtained in the present study at temperatures above 1,400°C, notwithstanding significant differences in the impurity content, is therefore evidence in support of the conclusions of Iwase et al.¹³

It is apparent from Figure 5 that, at high temperatures, the P_c -values determined in the present investigation are higher than those determined by Iwase et al.¹³ and Janke and Richter.¹² From the chemical compositions in Tables I and IV, it is evident that the electrolytes studied by Iwase et al. and Janke and Richter were of much higher purity than those of the present study. Since Iwase and his co-workers reported that the electrolyte they investigated did not contain segregated impurities, and since the same is to be expected for the high purity electrolyte

studied by Janke and Richter, the higher P_c -values obtained in the present study can most likely be explained by the presence of segregated impurities. However, the reason why the P_c -values obtained by Janke and Richter are also much lower than those of Iwase et al. cannot be explained by a consideration of the various factors which influence the P_c -value. Moreover, since the electrolyte studied by Janke and Richter had a lower magnesia content than that investigated by Iwase et al., and since apparently neither electrolyte contained segregated impurities, the P_c -values of the former should be slightly higher than those determined by Iwase et al.

It is further interesting to note that neither Iwase et al.¹³ nor Janke and Richter¹² mentioned any irreversibility in the P_c -values of the electrolytes that they studied. Since they did not indicate whether their P_c -values were determined during heating or cooling cycles, the reason for this apparent anomaly is not clear. However, it is most likely that their P_c -values were determined during cooling of the electrolyte, in which case a linear relationship between the P_c -value and temperature is expected, as was shown by the results of the present investigation.

SUMMARY AND CONCLUSIONS

The coulometric titration technique used in the present investigation allows small changes in the P_c -values to be detected, and the P_c -values of solid electrolytes to be measured accurately.

Commercially available magnesia-stabilized zirconia electrolytes may destabilize if the electrolyte is exposed for long periods to working temperatures below 1,400°C. This destabilization increases the amount of electronic conduction in the electrolyte, and undesirably high P_c -values result.

Provided that the impurities in the electrolyte are present as segregated phases, small variations in the silica content (up to 0.2 percent) and alumina content (up to 1.0 percent) do not significantly influence the P_c -value of magnesia-stabilized zirconia electrolytes. However, the P_c -value is strongly influenced by the electrolyte's phase composition, and a large fraction of cubic zirconia is a prerequisite for a low P_c -value.

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Table IV - Chemical Composition of the Solid Electrolytes Investigated by Iwase et al.¹³ and Janke and Richter¹²

Investigators	Electrolyte Type	Analysis, % (by Mass)							
		MgO	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	Na ₂ O	K ₂ O
Iwase et al.	ZrO ₂ -MgO (Nippon)	3.1	0.4	0.2	0.4	0.14	0.05	0.015	0.05
Janke and Richter	ZrO ₂ -MgO	2.4	0.2	0.3	0.15	n.a.	0.05	0.25	0.01

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Published by Kawata Publicity, Inc., Hatori Bldg., 5-6, Koishikawa 5-chome, Bunkyo-ku, Tokyo 112, Japan; 219 pages; paper; \$36; no ISBN

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- Trade in steel in 1986
- Overview of the Kansai International Airport Project
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Field Metallography, Failure Analysis and Metallography. Proceedings of the 19th Annual Technical Meeting of the International Metallographic Society, Boston, MA, August 5-6, 1986. (Microstructural Science Volume 15)

Edited by Michael E. Blinn et al., published by International Metallographic Society, Columbus, OH & ASM International, 9275 Kinsman Rd., Metals Park, OH 44137, 1987; 584 pages; bound; ISBN 0-87170-299-

The papers presented provide information on a broad range of microstructural topics. Twelve of the papers discuss microstructural characterization of a broad range of materials while another five papers are devoted to microstructural studies of stainless steels. Six papers describe metallographic preparation methods and related topics. Five other papers cover field metallographic techniques, which are important techniques for evaluating the remnant life of power plant components. The remaining conference papers cover various topics of interest to the failure analyst; five papers are on case histories, four on fractographic studies, three on corrosion problems and two on hydrogen embrittlement studies.

Plastic Design of Steel Structures

Edited by Augustin Mrazik et al., published by Ellis Horwood Ltd., distributors: John Wiley & Sons, 605 Third Avenue, New York, NY 10016; 1987; 637 pages; bound; \$110.00; ISBN 0-85312-381-0; (Ellis Horwood) 9420-20132-0 (Halsted Press)

This book describes the design of steel structures based on plasticity theory. The authors depict all aspects of per-

formed by flexural effects and the corresponding plastic limit load, they also deal with other effects, e.g., internal forces, buckling phenomena, deformations and the design of connections. Practical applications are suggested by way of numerical examples that are chosen to comply with current standards. Tables, charts and graphs list the factors and formulae necessary to simplify the calculations; also, an abundant list of references is included.

Iron Ore Symposium, 5th, Monaco, April 26-28, 1987

Published by Meta-Bulletin Inc., 708 Third Avenue, New York, NY 10017, 1987; 11 papers; paper; price not given; no ISBN

Papers include: the iron ore price outlook; the threatened North American iron ore industry; the current situation and the outlook for small-scale iron ore mines; the impact of direct reduction developments on iron

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International Conference on Isostatic Pressing, 3rd, London, November 10-12, 1986, 2 volumes

Published by MPR Publishing Services Ltd., Old Bank Buildings, Bellstone, Shrewsbury, England SY1 1HU, 1986; paper; price not given; no ISBN

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Pig Iron Production (thousand metric tons)

U.S.A.

January 1988.....	4,100
January 1987.....	2,916
Percent change 1988 vs. 1987.....	40.6

Canada

January 1988.....	795
January 1987.....	879
Percent change 1988 vs. 1987.....	-9.6

Source: International Iron and Steel Institute

