

Sulphur potential measurements with a two-phase sulphide-oxide electrolyte

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The open circuit potentials of the galvanic cell, Pt (or Au)|(Ar + H₂S + H₂)'|CaS + ZrO₂(CaO)|| (Ar + H₂S + H₂)''|Pt (or Au) has been measured in the temperature range 1000 to 1660 K and P_{H₂S}:P_{H₂} ratios from 1.73 × 10⁻⁵ to 2.65 × 10⁻¹. The solid electrolyte consists of a dispersion of calcium sulphide in a matrix of calcia-stabilized zirconia. The surface of the electrolyte is coated with a thin layer of calcium sulphide to prevent the formation of water vapour by reaction of hydrogen sulphide with calcium oxide or zirconia present in the electrolyte. The use of a 'point electrode' with a catalytically active tip was necessary to obtain steady emfs. At low temperatures and high sulphur potentials the emf's agreed with the Nernst equation. Deviations were observed at high temperatures and low sulphur potentials, probably due to the onset of significant electronic conduction in the oxide matrix of the electrolyte. The values of oxygen and sulphur potentials at which the electronic conductivity is equal to ionic conductivity in the two-phase electrolyte have been evaluated from the emf response of the cell. The sulphide-oxide electrolyte is unsuitable for sulphur potential measurements in atmospheres with high oxygen potentials, where oxidation of calcium sulphide may be expected.

1. Introduction

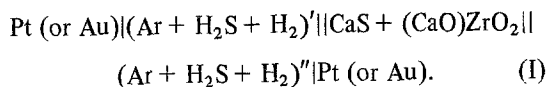
In recent times, enhanced use of sulphur containing fossil fuels has focused attention on the need for convenient methods for monitoring the partial pressure of sulphur or sulphur bearing species in a number of technologies. From an engineering point of view, *in situ* solid state sensors that measure directly the sulphur potential are preferable to devices that involve sampling of gases for low temperature analytical procedures. An advantage of solid state galvanic sensors is that the output is an electrical potential that can readily be used to actuate a control circuit. Solid state probes for sulphur are also useful in non-ferrous metallurgy involving sulphide melts.

A solid state galvanic sensor for sulphur may use either a sulphide or a non-sulphide material as the electrolyte. The use of calcium sulphide doped with higher valent transition metal sulphides as an electrolyte has been explored by a number of investigators [1-4]. These studies indicate that doped calcium sulphide becomes a predominantly ionic conductor only at low sulphur pressures, for example $P_{S_2} < 10^{-1}$ Pa at 1075 K. Taking an alternative approach Jacob *et. al.* [5] have used fluoride as the electrolyte in a solid state sensor, in which auxiliary electrodes of calcium sulphide were used to convert the sulphur potential of the gas to an equivalent fluorine potential. This paper reports studies on a two-phase solid electrolyte consisting of a dispersion of calcium sulphide in calcia-

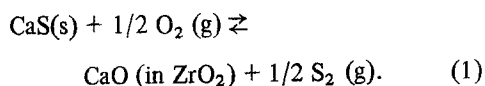
stabilized zirconia matrix for sulphur potential measurements. The concentration of calcia in the oxide matrix is 15 mol%. The technology for the manufacture of calcia-stabilized zirconia tubes is now well established and requires only minor modification to incorporate calcium sulphide as a second phase.

Calcia-stabilized zirconia is a predominantly ionic conductor because of its CaF_2 -type structure and the presence of a large number of oxygen vacancies [6]. The P_{O_2} -independence of the total conductivity and numerous excellent correlations of galvanic cell voltages to known Gibbs energy data have served as evidence that electrical conduction in this material is primarily due to the migration of oxygen ions. The open circuit emf of galvanic cells using calcia stabilized-zirconia is a measure of the oxygen potential difference across the electrolyte. The ionic conduction domain of stabilized zirconias in the oxygen potential-temperature space is well delineated. The effect of calcium sulphide dispersion on the ionic conduction domain cannot be predicted from information available. It is known [7] that dispersion of an insulator such as alumina in an ionic conductor like lithium iodide increases the ionic conductivity of the matrix. In the present case, however, the dispersed phase cannot be considered as an insulator relative to the matrix.

The galvanic cell used to study the bi-phase oxide-sulphide electrolyte system can be represented as;



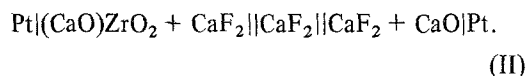
Since calcium sulphide coexists with dissolved calcium oxide in the zirconia electrolyte, the sulphur-oxygen exchange reaction must be considered;



It is apparent from this equilibrium that there is only one value for $P_{\text{S}_2}/P_{\text{O}_2}$ at a given temperature for which the composition of the electrolyte is

thermodynamically stable. To understand the behaviour of the bi-phase electrolyte, open circuit emf measurements were conducted at temperatures from 1000 to 1600 K and in $\text{Ar} + \text{H}_2\text{S} + \text{H}_2$ gas mixtures with ratios of H_2S to H_2 ranging from 1.73×10^{-5} to 0.265. Since oxygen or oxygen bearing species are not present in the gas mixtures used in this study, a thin coating of calcium sulphide was applied to the external surface of the electrolyte exposed to the gas mixtures in order to maintain the composition of the bi-phase electrolyte constant. The gas phase establishes the sulphur potential in the calcium sulphide coating and this is converted to an equivalent oxygen potential by virtue of reaction (1).

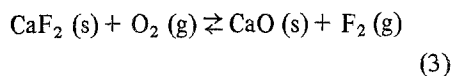
To compare the ionic conduction domain for the bi-phase electrolyte with known data for calcia-stabilized zirconia, the oxygen potentials established at the electrodes during emf measurements in $\text{Ar-H}_2\text{S-H}_2$ mixtures must be evaluated from the equilibrium (1). This requires information on the activity of calcium oxide in calcia-stabilized zirconia, in addition to the Gibbs energies of formation of CaO and CaS available in thermochemical tables. The activity of calcium oxide in the cubic zirconia-based solid solution, at a composition corresponding to 15 mol% calcium oxide, was determined from emf measurements on the cell;



The use of solid state electrochemical cells based on calcium fluoride electrolyte for determining the chemical potential of calcium oxide was initiated by Benz and Wagner [8]. Since the fluoride ions are the mobile species in calcium fluoride, the emf is given by

$$2FE = -(\mu'_{\text{F}_2} - \mu''_{\text{F}_2}), \quad (2)$$

where F is the Faraday constant, E is cell potential, and μ_{F_2} is the chemical potential of fluorine. The experimental conditions used in cell II fall within the electrolytic conduction domain ($t_{\text{ion}} > 0.99$) for CaF_2 . The fluorine potential at each electrode is established by the reaction;



When calcium fluoride is present at unit activity at the electrodes, dry oxygen gas at a pressure of 10^5 Pa is passed over the electrodes and the activity of CaO is fixed (either by having pure CaO or a CaO-ZrO₂ solid solution), the fluorine potentials and emf are unambiguously defined. The emf can be related directly to the chemical potential of CaO:

$$-2FE = \Delta\mu_{\text{CaO}} = RT \ln a_{\text{CaO}} \quad (4)$$

2. Experimental procedure

2.1. Sulphur potential measurement with bi-phasic electrolyte

2.1.1. Materials. A fine mixture of CaO and ZrO₂, containing 15 mol% CaO, was prepared from nitrate solution by evaporation to dryness and subsequent decomposition of the nitrate. This material was then mechanically mixed with 8 mol% CaS in a ball mill. The resulting powder was cold-pressed into a pellet of 15 mm diameter and 5 mm thickness in a steel die. Short rods of this material were also prepared by isostatic compaction. One end of the rods was tapered to a sharp point. The pellets and rods were then painted with a slurry of CaS. After drying they were packed in loose calcium sulphide powder and sintered under purified argon for 20 h at 2073 K and 4 h at 2273 K. The microstructure of the sintered product showed a coherent outer layer of CaS and a fine dispersion of CaS in (CaO)ZrO₂ solid solution matrix in the interior. X-ray diffraction also confirmed the presence of CaS and a cubic solid solution of (CaO)ZrO₂. Electron microprobe analysis indicated that the dissolved sulphur in the oxide solid solution was below detection limits. The microstructure was unaffected by prolonged exposure to Ar + H₂S + H₂ gas mixtures in the temperature range 1000 to 1600 K. The adhesion of the CaS coating to the substrate is at least in part due to its anchoring to the dispersed sulphide phase. Adhesion of the CaS coating deteriorated when the H₂S content of the gas was higher than that in test gas No. 7. A more detailed account of the microstructural engineering of this composite ceramic electrolyte will be published elsewhere.

High purity Ar + H₂S + H₂ gas mixtures and

their analysis were obtained from Matheson. A slight decrease in the H₂S concentration of the gas was observed over an extended storage period, presumably due to the reaction of H₂S with the gas cylinder. Correction factors for gas ratios were obtained by periodically observing the ion intensity ratios of H₂S to H₂ in a mass spectrometer. Table 1 summarizes the composition of the gas mixtures used in the study.

2.1.2. Apparatus. A schematic diagram of the experimental apparatus for electrochemical measurement of sulphur potential is shown in Fig. 1. The two-phase electrolyte pellet was pressed between two alumina tubes with metallic rings of platinum sandwiched in between. Before installation in the cell, the calcium sulphide coating on the vertical edge of the pellet was removed by grinding to prevent surface conduction through the coating during electrochemical measurements. The cell consisted of two electrode compartments. At the lower sulphur potential side, a 'point electrode' [9] was spring loaded against the electrolyte pellet by a system of springs and alumina supports. The 'point electrode' was made of the same material as the electrolyte pellet. Both the top end and the region near the tip of the point electrode were platinized by applying platinum paste and heating at 1300 K for 50 h. The function of the 'point electrode' is to dissipate the small electrochemical flux of oxygen [9–13] through the solid electrolyte near the tip, and prevent it from reaching the measuring electrode. The electrochemical flux of oxygen through the solid electrolyte is caused by small but finite electronic conductivity. Generally this flux causes polarization at the low potential electrode, although it can in principle cause polarization at both electrodes, especially when the flux is relatively large. The platinized band near the tip of the point electrode (see magnified insert in Fig. 1) was found to enhance the dissipation of the electrochemical flux near the tip by providing a catalytic surface. Although the use of 'point electrodes' for deflecting the electrochemical flux away from the measuring electrodes was pioneered by Fouletier *et al.* [9, 12], the use of catalytic surfaces near the tip

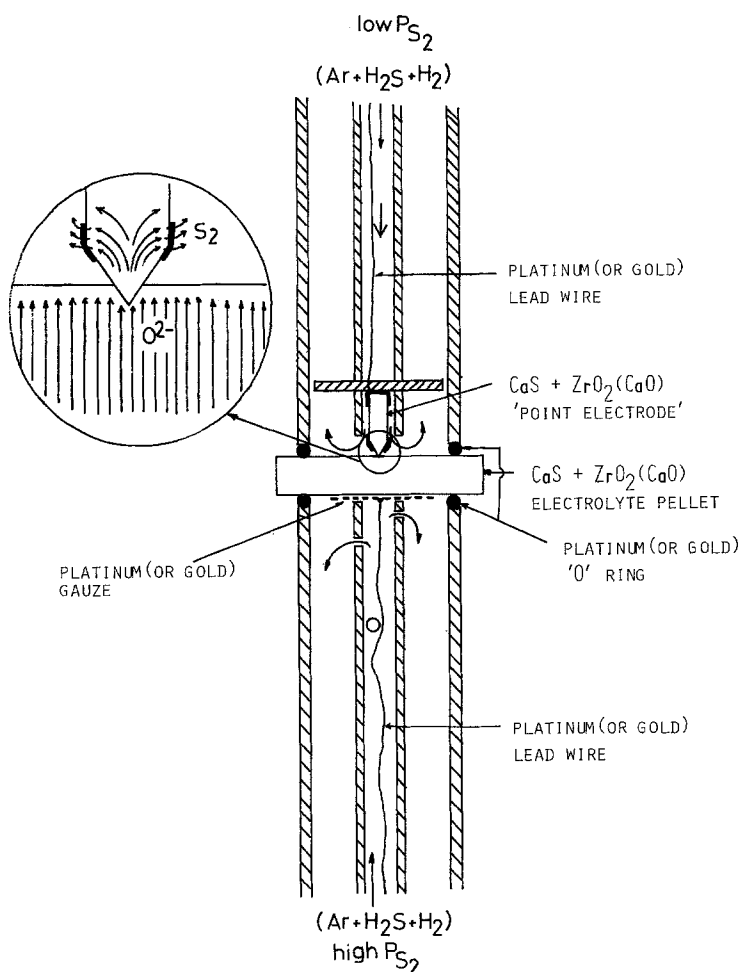


Fig. 1. Experimental apparatus for cell I.

does not appear in their design. The electrical contact to the 'point electrode' was made with a platinum wire connected to the platinized section at the top, as shown in Fig. 1. The electrode in the other compartment was formed by pressing a fine platinum mesh against the solid electrolyte pellet. A platinum lead was spot welded to the mesh.

The entire assembly shown in Fig. 1 was placed in a vertical alumina tube, through which purified argon gas was passed at the rate of $5 \text{ cm}^3 \text{ s}^{-1}$. A vertical resistance furnace surrounded the alumina tube. The temperature of the furnace was controlled to $\pm 1 \text{ K}$ by a stepless current-compensating controller. The temperature of the cell was measured by a separate Pt/Pt-13% Rh thermocouple placed within 5 mm of the solid electrolyte pellet.

Chemical attack of platinum by low sulphur potential gas mixtures (gases Nos. 1 to 5) was not observed in the hot zone of the furnace. At the colder ends, however, there was some evidence of reaction between platinum and hydrogen sulphide. Consequently the platinum wires were protected by alumina sheaths closed at both ends by alumina cement. At high sulphur potentials (gases Nos. 6 and 7) and lower temperatures ($T < 1300 \text{ K}$), platinum was replaced by gold, because of chemical reaction between platinum and hydrogen sulphide. The gold electrodes were found to work well at high sulphur potentials.

The flow of gases through the cell was arranged such that the chemical potential of sulphur at the 'point electrode' was always lower than that in the other compartment. The

Table 1. Composition of test gases and emf's of cell I measured over a range of temperatures from 1000–1600 K

Test gas No.	Gas composition (vol %)			emf (mV)												
	H ₂ S	H ₂	Ar	log (P _{H₂S} /P _{H₂})	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K					
1	1.03 × 10 ⁻³	59.40	40.60	-4.7069	-288	-315*	-339*	-361*	-380*	-396*	-408*					
2	6.80 × 10 ⁻³	52.41	47.58	-3.8869	-203	-222	-242*	-259*	-277*	-290*	-303*					
3	2.60 × 10 ⁻²	50.78	49.22	-3.2907	-144	-158	-172	-185	-198*	-210*	-220*					
4	1.80 × 10 ⁻¹	55.10	44.72	-2.4859	-65	-71	-78	-83	-91	-95	-100					
5†	7.90 × 10 ⁻¹	54.00	45.21	-1.8348	-0.20	-0.22	-0.26	-0.27	-0.28	-0.24	+0.24					
6	2.52	25.20	72.28	-1.0035	82	91	99	107	115	123	132					
7	9.21	34.77	56.02	-0.5770	125	137	149	162	174	186	199					

* emf was found to decay with time, due to polarization of the electrode. The values quoted correspond to plateau regions, or points of inflection on the decay curve after coulometric titration (see Fig. 3).

† Reference gas.

rate of flow of the Ar + H₂S + H₂ gas mixtures were measured by two capillary-type flow meters and were maintained at approximately 3 cm³ s⁻¹. Thermocouples attached to the solid electrolyte pellet in a preliminary experiment indicated the absence of a thermal gradient across the pellet with this flow rate. Gas No. 5 was selected for the reference electrode. The emf's were measured using a digital voltmeter with an input impedance of 10¹² Ω. All the measurements were conducted in the temperature range from 1000 to 1600 K at intervals of 50 K.

In general, when the emf remained constant with time for defined gas compositions at constant temperature, its reproducibility was checked by approaching the temperature from both higher and lower values. Reversibility of the emf was checked by passing small currents (5 μA) through the cell in both directions, and verifying that it returned to the same value after each titration. At high temperatures and low sulphur potentials in the test gas, the emf was found to decrease with time. This may be attributed to the polarization of the high oxygen (or sulphur) potential electrode due to significant n-type conduction in the electrolyte and consequent flux of oxygen. The 'point electrode' virtually eliminates polarization at the low oxygen (or sulphur) potential electrode by deflecting the flux away from the measuring platinum electrode. Traces of the time dependence of the emf's at 1000 and 1600 K for test gas No. 1 (see Table 1), after passing a current to titrate oxygen (or sulphur) up-hill against the chemical potential gradient, is shown in Fig. 3. The emf of the 'plateau' region was found to be independent (± 2 mV) of the amount of current passed in the range 5–100 μA for 15–60 min. Following the method of Diaz and Richardson [14] and Jacob and Alcock [15], the emf corresponding to the plateau can be considered as the true open circuit potential of the cell, free from polarization effects at the electrode.

2.2. Chemical potential of calcium oxide in 15 mol % CaO–ZrO₂ solid solution

2.2.1. Materials. The reference electrode in cell II was prepared by mixing high purity powders

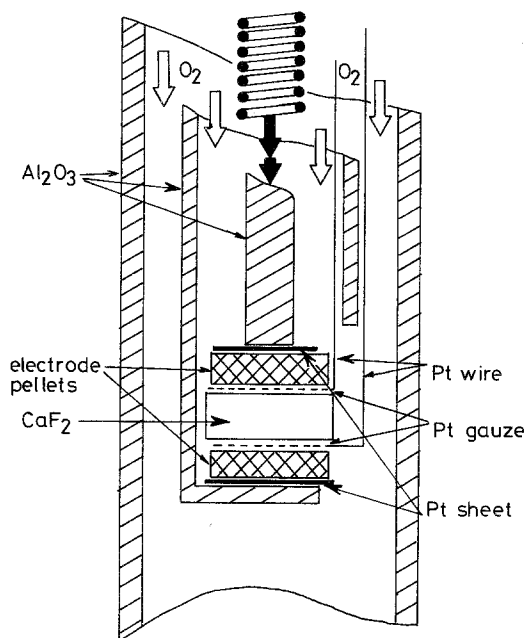


Fig. 2. Experimental apparatus for cell II.

of CaO and CaF₂ in the molar ratio 17:3. The mixture was compacted into pellets under pressure in a steel die and then sintered at 1300 K under dry argon. The measuring electrode was prepared in a similar manner starting from CaO–ZrO₂ solid solution containing 15 mol % CaO and pure CaF₂. The preparation of CaO–ZrO₂ solid solution is described in section 2.1.1.

2.2.2. Apparatus. A schematic diagram of the apparatus is shown in Fig. 2. The electrode pellets were spring loaded on either side of a transparent single crystal of CaF₂, with platinum gauzes placed between the electrodes and the solid electrolyte. Platinum leads, spot welded to the platinum gauze, provided electrical leads to a high input impedance digital voltmeter. The pellets were held together under pressure through a system consisting of springs, an alumina rod, and a flat-bottomed alumina tube with a section cut away parallel to its axis, as shown in the figure. Direct contact of the electrode pellets with the alumina rod or tube was prevented by inserting platinum foils between them. The cell was maintained under dry flowing oxygen at a pressure of 10⁵ Pa. In preliminary experiments, the transparent CaF₂ crystal (optical grade) became translucent during the run. Fine

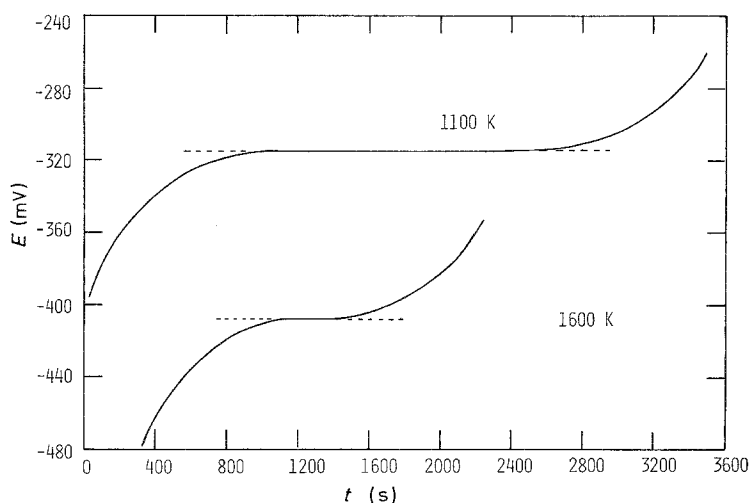
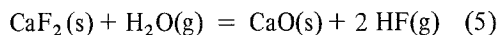


Fig. 3. Time dependence of open-circuit emf's of cell I after coulometric titration. For test gas number 1.

opaque precipitates appeared to have formed inside the CaF_2 crystal. These precipitates were identified as CaO by electron diffraction. They were apparently formed by reaction of the electrolyte crystal with residual moisture in the gas phase;



The CaO precipitation was minimized by degassing the alumina tubes and rod under vacuum and by using improved drying procedures for oxygen gas. The gas was first dried by two towers of anhydrous magnesium perchlorate and then over anhydrous phosphorus pentoxide. Since CaO , CaF_2 and O_2 gas must be in contact to fix the fluorine potential, the presence of a few internal precipitates of CaO in CaF_2 would not invalidate the emf results. It can be shown from thermodynamic considerations that CaF_2 will not react with dry oxygen to form CaO .

The emf measurements were conducted in the temperature range 1050–1280 K. The time required to attain steady emf's varied from 20 h at the lower temperature to 2 h at the highest temperature used in this study. The reversibility and reproducibility of the emf's were checked in the same manner as for Cell I. After the experiment, the electrode pellet was examined by X-ray diffraction. There was no significant change in the phase composition of the electrode during the emf measurement.

3. Results

3.1. Cell I

The emf's of Cell I obtained in this study for different test gases and temperatures are compiled in Table 1. The asterisks indicate that the emf was time dependent and the value was obtained using 'plateau technique'. All other emf's were constant with time for periods in excess of 30 min. The emf's are plotted as a function of temperature for each gas mixture in Fig. 4. Solid circles in this figure designate constant emf's, while the open circles denote values corresponding to a plateau or inflection in the emf variation with time after an up-hill coulometric titration.

3.2. Cell II

The emf of Cell II is plotted in Fig. 5 as a function of temperature. A linear relation is adequate for the representation of data:

$$E = 177 + 4.99 \times 10^{-2} T (\pm 1) \text{ mV} \quad (6)$$

The chemical potential of CaO in the CaO-ZrO_2 cubic solid solution, relative to pure CaO as the standard state is;

$$\begin{aligned} \Delta\mu_{\text{CaO}} &= RT \ln a_{\text{CaO}} \\ &= -34,160 - 8.66 T \text{ J mol}^{-1} \quad (7) \end{aligned}$$

The partial entropy of CaO in the solid solution at

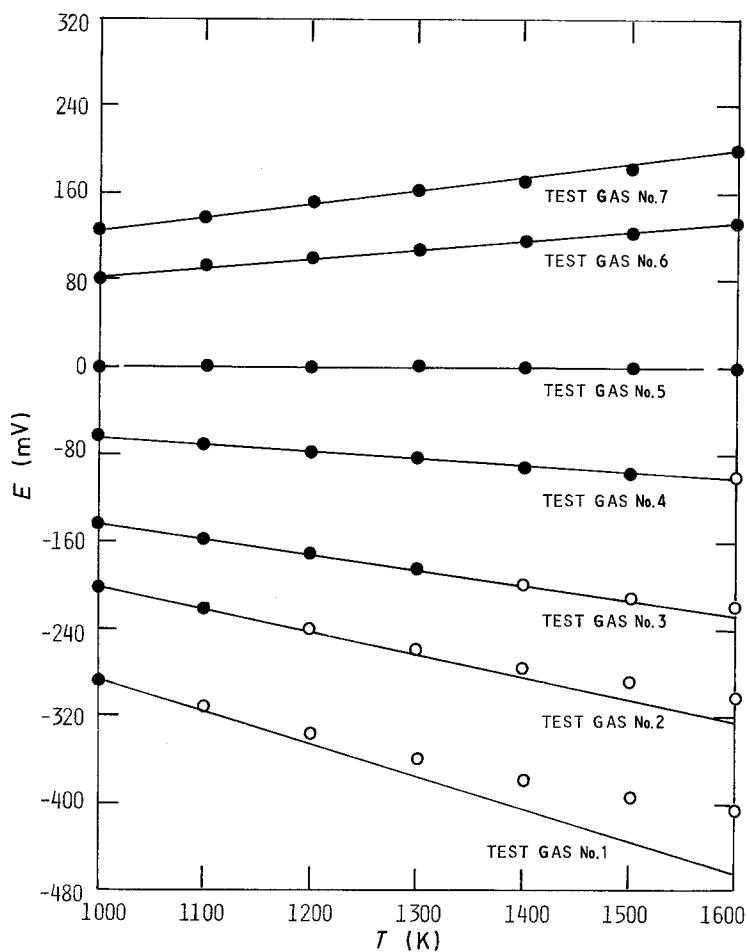


Fig. 4. Measured emf's of cell I as a function of temperature. ○, plateau emf after titration; ●, steady open circuit potential; —, theoretical (Equation 8).

$X_{\text{CaO}} = 0.15$ obtained from the emf data is $8.66 \text{ J mol}^{-1} \text{ K}^{-1}$ and compares with a value of $15.8 \text{ J mol}^{-1} \text{ K}^{-1}$ for an ideal solution. The negative excess partial entropy is consistent with the large negative partial enthalpy of CaO in the solid solution. These data indicate a tendency to form 'complexes' or associations between the end members of the solid solution.

4. Discussion

4.1. Calculation of sulphur and oxygen potentials

The gas phase containing Ar + H₂S + H₂ establishes a partial pressure of sulphur over the electrode, depending on the ratio of H₂S to H₂, by virtue of the reaction,

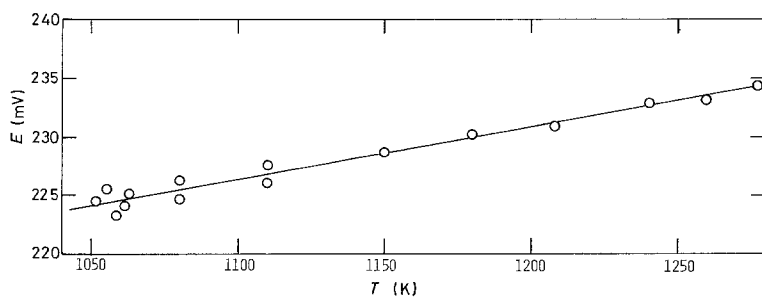
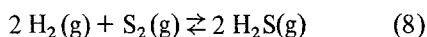


Fig. 5. Measured emf's of cell II as a function of temperature.



$$\Delta G^0(8) = -180.6 + 0.09878 T \text{ kJ} \quad (9)$$

$$RT \ln P_{\text{S}_2} = \Delta G^0(8) + 2 RT \ln (P_{\text{H}_2\text{S}}/P_{\text{H}_2}) \quad (10)$$

where $\Delta G^0(8)$, the standard Gibbs energy change for the reaction 8, is taken from reference [16]. The gas phase establishes the sulphur potential in the thin coating of CaS on the electrolyte. Because of mixed conduction in CaS, the coating rapidly equilibrates with the gas phase. The coating of CaS can be considered as a semi-conducting electrode that transmits the sulphur potential established by the gas mixture, while mechanically insulating the electrolyte from the gas. The sulphur potential transmitted through the coating is converted into a corresponding oxygen potential at the coating/electrolyte interface by the sulphur–oxygen exchange reaction 1. Therefore,

$$RT \ln P_{\text{O}_2} = 2(\Delta G_1^0 + \Delta\mu_{\text{CaO}}) + RT \ln P_{\text{S}_2} \quad (11)$$

where ΔG_1^0 is the standard Gibbs energy change for reaction 1 [17], and $\Delta\mu_{\text{CaO}}$ is the chemical potential of CaO in the solid electrolyte. If the two-phase electrolyte is a pure ionic conductor, the open-circuit emf is given by

$$\begin{aligned} E &= (RT/4F) \ln P_{\text{O}_2}^{\text{II}}/P_{\text{O}_2}^{\text{I}} \\ &= (RT/4F) \ln P_{\text{O}_2}^{\text{II}}/P_{\text{S}_2}^{\text{I}} \end{aligned} \quad (12)$$

where superscript I and II correspond to the reference and the test electrodes. Theoretical emf values calculated by Equation 12 are shown as straight lines in Fig. 4. At low temperatures and high sulphur potentials, there is reasonable agreement (± 1 to 3 mV) between theory and experiment.

4.2. *N-type electronic conduction in the biphasic electrolyte*

At high temperatures and low sulphur potentials, the emf's of cell I show significant deviations from theoretical lines corresponding to Equation 12. This may be attributed to the onset of n-type electronic conduction in the electrolyte. When the n-type electronic conduction in the solid elec-

trolyte becomes insignificant, the open-circuit emf is given by [18],

$$E = \frac{RT}{F} \ln ([P_{\text{O}_2}^{\text{II}/4} + P_{\theta}^{\text{I}/4}]/[P_{\text{O}_2}^{\text{I}/4} + P_{\theta}^{\text{II}/4}]) \quad (13)$$

where P_{θ} is a characteristic parameter of the electrolyte, and corresponds to the oxygen partial pressure at which the n-type electronic conductivity is equal to the ionic conductivity [18]. Because of the use of the 'point electrode' and the 'plateau emf technique', the emf values given in Table 1 are free from polarization effects and can be used for computing the values of P_{θ} based on Equation 13. Fig. 6 shows the relation between $\log P_{\theta}$ for the biphasic solid electrolyte and the reciprocal of absolute temperature, in comparison with data reported in the literature for calcia-stabilized zirconia.

In general, the values of P_{θ} for ZrO₂-based solid oxide electrolytes depends on; (a) the amount of monoclinic ZrO₂, and (b) the impurity level. According to Kumar *et al.* [19], monoclinic ZrO₂ is predominantly an electronic conductor. Friedman *et al.* [20] worked with ZrO₂ containing 3–4 wt % CaO. This probably consisted of a mixture of cubic ZrO₂-CaO solid solution and monoclinic ZrO₂. Their high values for P_{θ} could be attributed to the presence of monoclinic ZrO₂. Assuming that the mobilities of electrons are 1000 times higher than those of ions, Ramana-rayan and Worrell [21] have estimated that 60 mol ppm of an impurity which is compensated for by electrons would increase electronic conductivity by 1% in an oxide electrolyte with 3 mol % oxygen vacancies. The low P_{θ} values reported by Scaife *et al.* [22] are for high purity electrolytes, while values by Inouye *et al.* [23], Iwase and Mori [10–11], and Etsell and Flengas [24] are for commercial grade zirconia electrolyte.

In the present study, the electrolyte consisted of a mechanical mixture of 92 mol % of ZrO₂ solid solution and 8 mol % of pure CaS. The ZrO₂ solid solution contains 15 mol % CaO. The electrolytic domain of pure CaS has not yet been clearly identified. Egami *et al.* [25] have reported, however, that pure CaS exhibits significant hole conduction at 1473 K and sulphur partial pressure above 10⁻¹ Pa. The low sulphur potential limit of ionic domain for pure CaS has not yet been

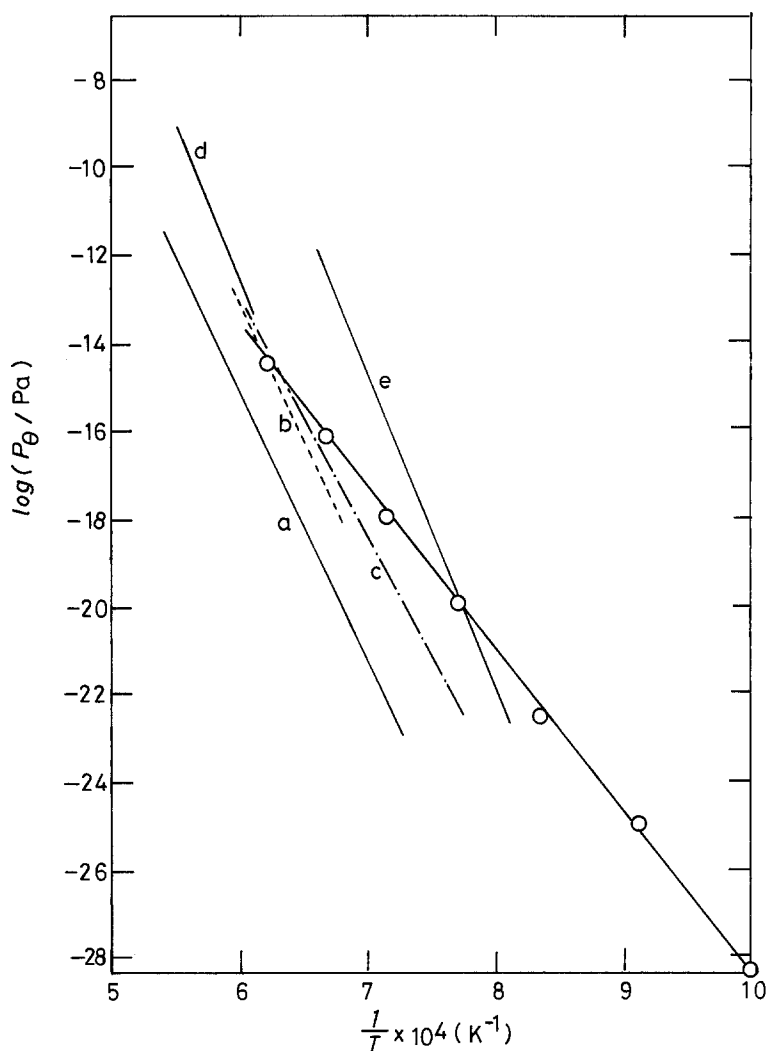


Fig. 6. The characteristic parameter, P_θ , for the two-phase sulphide-oxide electrolyte as a function of the reciprocal of absolute temperature. $-\circ-$, present study, $\text{CaS} + \text{ZrO}_2\text{-CaO}$ (15 mol %). a, Scaife *et al.* $\text{ZrO}_2\text{-CaO}$ (15 mol %); b, Inouye *et al.* $\text{ZrO}_2\text{-CaO}$ (11 mol %); c, Etsell and Flengas, $\text{ZrO}_2\text{-CaO}$ (10 mol %); d, Iwase and Mori, $\text{ZrO}_2\text{-CaO}$ (11 mol %); e, Friedman *et al.* $\text{ZrO}_2\text{-CaO}$ (3-4 wt %).

determined. Despite the presence of a dispersed phase of a mixed conducting material, the values of P_θ for the biphasic electrolyte are similar to those for calcia-stabilized zirconia. The values at the lower temperatures are not very accurate because the difference between the measured and theoretical emf's is small.

Since the sulphur and oxygen potentials in the biphasic electrolyte are interrelated, the condition under which the electronic conductivity is equal to ionic conductivity at any temperature can also be expressed in terms of a characteristic sulphur partial pressure, $P_{\text{S}_2}^\theta$. Table 2 summarizes these values.

Table 2. The characteristic parameters, P_θ and $P_{\text{S}_2}^\theta$, for $\text{CaS} + \text{ZrO}_2(\text{CaO})$ solid electrolyte

Parameter	Temperature (K)						
	1000	1100	1200	1300	1400	1500	1600
$\log(P_\theta/\text{Pa})$	-29.0 (± 0.5)	-25.5 (± 0.2)	-23.1 (± 0.3)	-20.4 (± 0.1)	-18.5 (± 0.2)	-16.6 (± 0.1)	-15.0 (± 0.1)
$\log(P_{\text{S}_2}^\theta/\text{Pa})$	-15.3 (± 0.5)	-13.0 (± 0.2)	-11.6 (± 0.3)	-9.8 (± 0.1)	-8.6 (± 0.2)	-7.4 (± 0.1)	-6.3 (± 0.1)

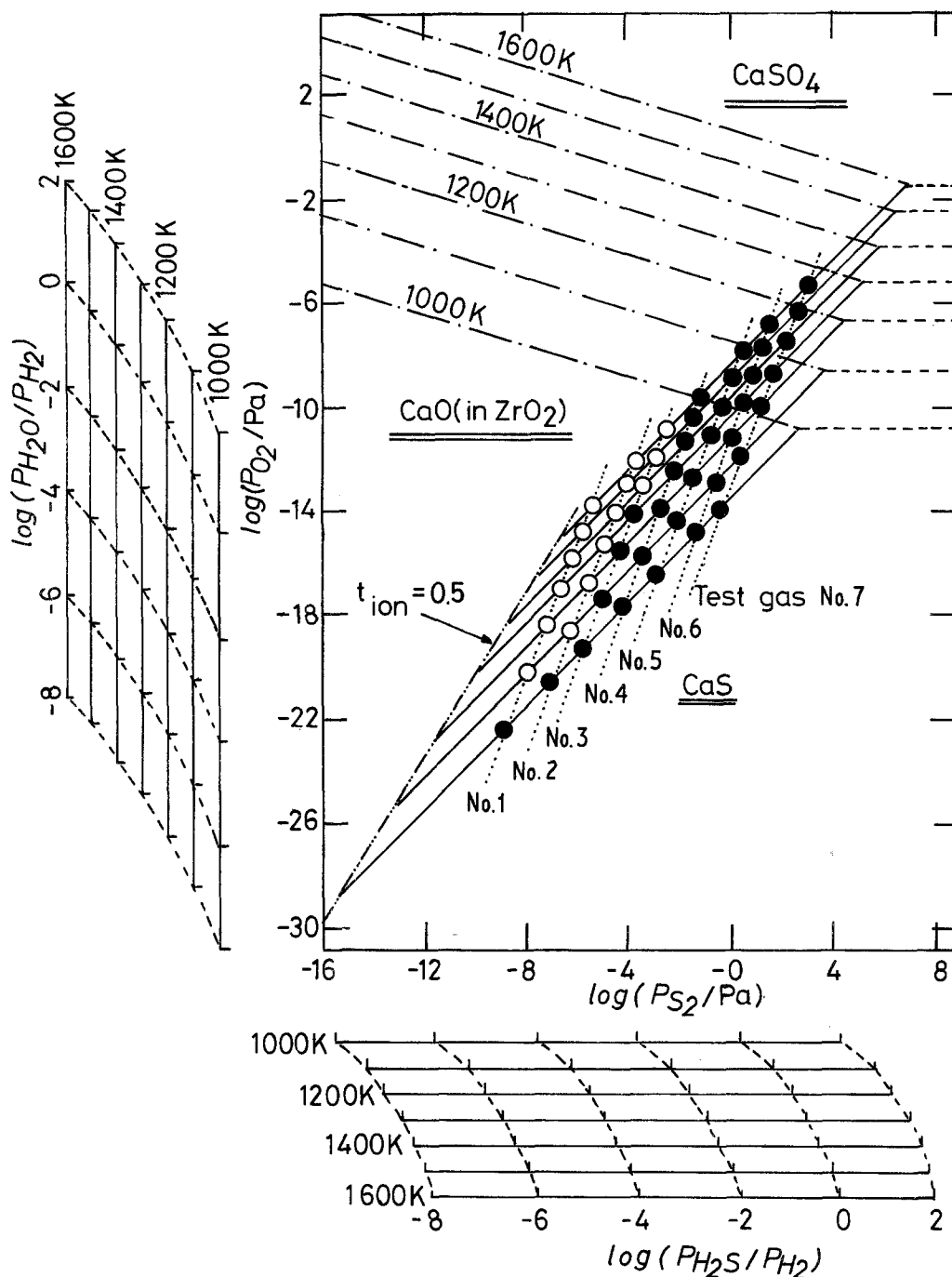


Fig. 7. Phase stability field for CaO (in ZrO₂), pure CaS and CaSO₄ as a function of oxygen and sulphur potentials. ○, plateau emf; ●, steady emf; ---, CaSO₄ + CaO (in ZrO₂); —, CaS + CaO (in ZrO₂); - - - , CaS + CaSO₄.

4.3. Limitations in the use of biphasic sulphide-oxide electrolytes

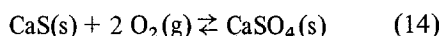
In sulphide-oxide electrolytes the presence of

exchange reactions of the type represented by reaction 1 must be considered. It follows, therefore, that there is only one value for P_{S_2}/P_{O_2} at any temperature for which the electrolyte is

thermodynamically stable. Relation between $\log P_{\text{O}_2}$ and $\log P_{\text{S}_2}$ calculated by Equation 11 is illustrated in Fig. 7. The corresponding $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ and $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratios at different temperatures are also shown in this figure in nomographic form. If the oxygen potentials in the gas phase were higher than those corresponding to these ratios, calcium sulphide will be oxidized to calcium oxide, causing a change in the composition of electrolyte matrix and depletion of CaS. There appears to be no solution to this problem.

If the oxygen potential in the gas phase is lower than that corresponding to the exchange reaction, the calcium oxide dissolved in zirconia will be converted to sulphide. This will result in gradual destabilization of the cubic structure and destruction of ionic conducting properties of the electrolyte. A solution to this problem, developed in this study, is to coat the biphasic electrolyte with CaS. With this modification the electrolyte can be used to measure sulphur potential when the oxygen potential of the ambient atmosphere is below values dictated by the sulphur–oxygen exchange reaction. If the sulphur partial pressure or $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratio in the gas, established by its own composition or via the sulphur–oxygen exchange reaction, are extremely low (say below 10^{-3} Pa), then the compositional change of the electrolyte may be small enough not to effect the cell performance. In such a case, the use of CaS coating may be unnecessary. More experimental studies in atmospheres containing both oxygen and sulphur are necessary before more precise recommendations can be formulated.

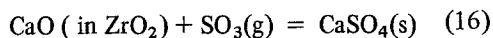
Another restriction on the permitted partial pressure of oxygen can arise from the reaction,



$$\Delta G^0(15) = -933.35 + 0.328 T \text{ kJ} \quad (15)$$

The equilibrium oxygen partial pressures for the above reaction vary from $10^{-10.8}$ Pa at 1000 K to $10^{-1.7}$ Pa at 1600 K [26].

The partial pressure of SO_3 must also be low enough to avoid the following reaction;



The equilibrium partial pressures of SO_3 for this

reaction are from $10^{-4.4}$ Pa at 1000 K to $10^{2.4}$ Pa at 1600 K.

5. Conclusions

A two-phase solid electrolyte containing a fine dispersion of pure calcium sulphide in a matrix of calcia-stabilized zirconia has been prepared. When the surfaces of this electrolyte are covered with a thin coating of calcium sulphide, it can be used in a galvanic sensor for measuring sulphur potentials. In atmospheres of low sulphur or oxygen potential, a limiting factor in the use of this electrolyte is the onset of electronic conduction in calcia-stabilized zirconia matrix. At high oxygen potential environments, the calcium sulphide is readily oxidized. Consequently cells containing the new two-phase electrolyte cannot be used for sulphur potential measurements under such conditions.

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