

# *Experimental problems in the use of solid oxide electrolytes*

B. HESHMATPOUR<sup>†</sup>, D. A. STEVENSON*Department of Materials Science and Engineering, Stanford, California 94305, USA*

Received 4 August 1980

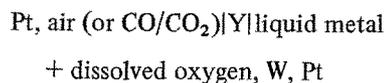
Several observations are described concerning the use of solid oxide electrolytes in kinetic and thermodynamic studies in liquid-metal-oxygen systems. These observations include: degradation of commercially available oxide electrolytes, degradation of electrodes and contamination from conventionally purified argon protective atmospheres. The conductivity of commercially available calcia-stabilized zirconia (CSZ) and yttria-stabilized zirconia (YSZ) decreased with use at elevated temperatures in contact with liquid metals. This decrease causes discrepancies in the values of oxygen diffusivity unless appropriate correction factors are used. Tungsten-wire-liquid-metal electrodes were observed to oxidize even when the average oxygen activity in the liquid metal was below the threshold level for tungsten oxidation; however, rhenium and tungsten-rhenium alloys performed satisfactorily. A low residual oxygen level in purified argon introduces large errors in oxygen solubility measurements. The rate of absorption of the residual oxygen in argon by liquid indium was studied and a rate constant established. A method for oxygen solubility measurements which avoids these sources of error is discussed.

## 1. Introduction

Recent activity in solid-state electrochemistry has established a valuable research tool, as illustrated by the following representative examples. Galvanic cells using solid oxide electrolytes are used for a number of scientific and technological applications and these applications can be classified according to the mode of operation of the electrochemical cells [1, 2]. In some applications, the cells are operated in an equilibrium mode: the electrodes are both at equilibrium, and the open circuit cell e.m.f. is measured. Cells operating in this mode have been used for such applications as direct oxygen sensors in combustion processes [3], closed-loop fuel/air control systems in some automobiles, oxygen probes for liquid metal processing, measurement of the Gibbs energies of formation of metal oxides [4] and the determination of the activities of alloy components [5]. In other applications, a dynamic mode of operation is employed; the electrodes are both at equilibrium, and the cell current or voltage is measured as a function of time. Cells operating in this manner have been used in such applications as: fuel cells [6], measuring the rate of gas-solid reactions

involving oxygen [7] and measuring the diffusion rates of oxygen in metals [8].

The research reported here concerns specifically the use of solid oxide electrochemical cells to study thermodynamic and kinetic properties of oxygen in liquid-metal-oxygen systems, but the results relate more broadly to the use of solid electrolytes in general. The electrochemical cells used had one electrode composed of oxygen dissolved in a liquid metal with either calcia-stabilized zirconia (CSZ), yttria-stabilized zirconia (YSZ), or yttria-doped thoria (YDT) as the electrolyte. Several techniques employing combinations of measurements of potentials and currents in these cells are used to measure the oxygen solubility, the oxygen activity, the Gibbs free energy of formation of relevant oxides and the diffusion coefficient of oxygen in liquid metals and alloys. A typical cell is:



where Y represents the solid oxide electrolyte.

The reliable performance of the solid electrolyte and associated electrodes is crucial to these

<sup>†</sup> Present address: Oak Ridge National Laboratory, PO Box X, Oak Ridge, TN 37830, USA.

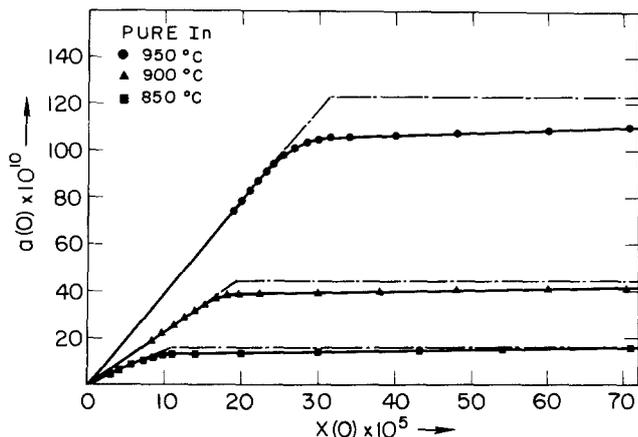


Fig. 1.  $a(O)$  versus  $X(O)$  for pure In at 850, 900 and 950°C. — experimental results; - - - - - extrapolation lines.

studies. We describe here some observations on the degradation of electrodes and electrolytes and on the interaction of protective atmospheres used in the conventional operation of these cells that lead to significant errors. This paper outlines the experimental problems, gives methods for correcting experimental results and describes improvements in the experimental procedures.

## 2. Degradation of electrodes in electrochemical studies of liquid-metal-oxygen systems

Various refractory materials have been used as electrodes in contact with liquid and solid metals and slags for electrochemical studies. The most commonly used are Pt, W, Ir, Ni, Mo and chromel [9-12]. Tungsten has been used most extensively, often spot-welded to Pt. We have observed that tungsten oxidizes even when the average oxygen activity in the liquid metal is below the threshold level for tungsten oxidation, apparently the result of transient oxygen activity gradients in the melt. This problem is particularly severe for coulometric titration experiments used to determine oxygen solubility. In these experiments, small amounts of oxygen are titrated into the melt coulometrically and the activity of oxygen is calculated by measuring the open-circuit e.m.f. of the cell using the Nernst relation after a few hours of equilibration. The number of gram atoms of oxygen which are titrated in the melt,  $n(O)$ , is related to the number of coulombs by Faraday's law:  $n(O) = \int Idt/zF$ . Oxygen which is used to oxidize tungsten is incorrectly considered as dissolved oxygen and leads to calculated oxygen solubilities that are too

high. Fig. 1 represents the oxygen activity,  $a(O)$ , versus the atomic fraction of oxygen,  $X(O)$ , in pure liquid In at 850 to 950°C. The broken lines show the expected behaviour while the full lines represent the experimental results using tungsten as the negative electrode. The results suggest that tungsten oxidizes prior to liquid In even though tungsten oxide is slightly less stable than indium oxide. The slow rate of oxygen transport in liquid indium does not remove the localized high oxygen concentrations for relatively long times, resulting in the oxidation of tungsten. At lower indium activities, as in the case for indium alloys, tungsten oxides are relatively more stable than indium oxides, and tungsten oxidation is even more likely. The sublimation of tungsten oxides at prevailing temperatures continuously removes the oxidation product from the melt which, in turn, accelerates the rate of oxidation.

The amount of oxygen consumed in oxidizing tungsten and the corresponding weight loss of tungsten can be calculated from Fig. 1. The difference  $a(O) - X(O)$  between the ideal and the observed curves (broken and full respectively), is the amount of oxygen used to oxidize the tungsten. Fig. 2 displays the observed weight in grams of tungsten that is oxidized in a run,  $m(W)$ , versus the temperature and Fig. 3 gives the oxygen ratio,  $r(O)$  (the number of moles of oxygen consumed in oxidizing tungsten,  $n(O)^W$ , divided by the oxygen that is dissolved in liquid In,  $n(O)^{In}$ ). It is assumed that tungsten is oxidized to  $WO_2$  which is the stable oxide in this temperature range. The following are least-square expressions for  $m(W)$  and  $r(O)$  as a function of temperature:

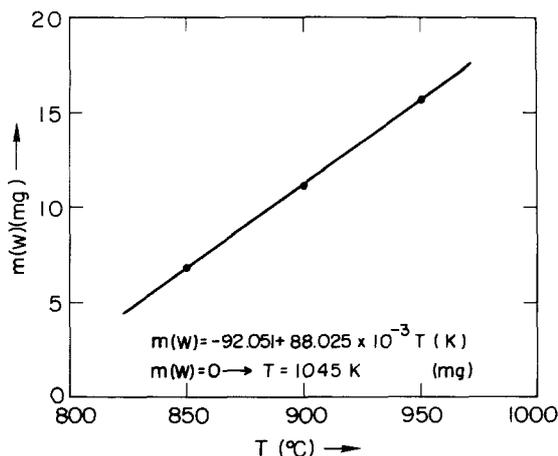


Fig. 2. The dependence of the mass loss of tungsten,  $m(W)$ , upon temperature  $T$ , for oxidation of tungsten wire in liquid indium.

$$m(W) = -68.02 + 88.025 \times 10^{-3} T \quad (1)$$

$$r(O) = 18.059 - 1.115 \times 10^{-2} T, \quad 850 < T < 950 \quad (2)$$

where the weights are in milligrams and the temperature in degrees centigrade.

The surface area of tungsten wire in contact with liquid metal was  $\sim 0.2 \text{ cm}^2$ , and thus the weight of oxidized tungsten per unit surface area,  $m^*(W)$ , is

$$m^*(W) = m(W)/0.2 = -340.1 + 440.1 \times 10^{-3} T.$$

From these equations, it may be deduced that

$$m(W) = 0 \quad \text{for } T \leq 772^\circ \text{C} \quad (3)$$

and

$$r(O) = 0 \quad \text{at } T \geq 1347^\circ \text{C}. \quad (4)$$

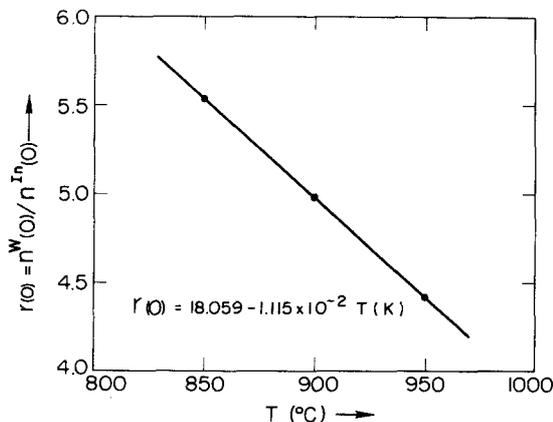


Fig. 3.  $r(O)$  versus  $T$  for oxidation of tungsten in liquid In.

This implies that the oxidation of tungsten is negligible below  $772^\circ \text{C}$  for thermodynamic reasons and above  $1347^\circ \text{C}$  for kinetic reasons. The decrease in  $r(O)$  with increasing temperature indicates that at higher temperatures the localized high oxygen concentrations are diluted more rapidly, resulting in less tungsten oxidation.

Metallographic examination of the tungsten wire, before and after use, indicated other failure mechanisms also. For short-time use, no change was observed in the microstructure of tungsten wire except for a decrease in its diameter due to oxidation; however, for intermediate times, the samples were recrystallized and embrittled at unusually low temperatures ( $850\text{--}950^\circ \text{C}$ ) with the low recrystallization temperature being attributed to dissolution of indium and/or oxygen in the tungsten. The sintering cavities originally in the tungsten were spheroidized and coalesced to form larger pores. After use for long times, the diameter of the tungsten wire was extensively reduced and a relatively uniform dispersion of other phases, probably trapped tungsten oxides or some In-W intermetallics, was observed in the microstructure. Cavities often enlarge and reach the surface of the wire allowing liquid In to penetrate into the interior of the wire, thus contributing further to the failure of tungsten wire. In summary, the following are some of the important mechanisms responsible for failure of the tungsten electrode in liquid indium: oxidation by the dissolved oxygen in liquid metal; liquid-metal corrosion and embrittlement; growth of sintering voids; and dissolution of oxygen and liquid metal in tungsten and the resulting formation of intermetallics and compounds.

To find a better alternative to tungsten, the following inert or refractory metals were evaluated in liquid In and Bi at  $1000^\circ \text{C}$ : Pt, Rh, Ir, Re, Ta, Mo, chromel, constantan, alumel, Pt-13%Rh, W-5%Re and W-26%Re. Among these materials, Ta and Mo were severely oxidized and embrittled and Pt, Pt-13%Rh, Rh, chromel, constantan and alumel dissolved rapidly in the melt. Iridium dissolves slowly, but does not oxidize. An intermetallic compound forms on the surface of Ir causing it to embrittle and fail in a few hours. The best electrode material for use in liquid-metal environments was found to be rhenium. It neither dissolves nor is oxidized and is only slightly

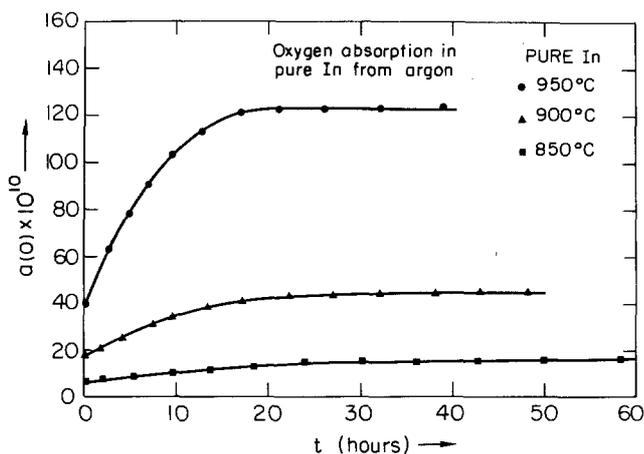


Fig. 4.  $a(O)$  versus  $t$  for absorption of oxygen from argon in pure liquid In at 850, 900 and 950°C.

embrittled. Tungsten-rhenium alloys, W-5%Re, and W-26%Re are superior to pure tungsten but are not as good as Re. Depending on the nature of the liquid metal, the oxygen potential and the temperature, the following are possible choices for electrode materials in liquid-metal environments at high temperatures: Re, W-26%Re, W-5%Re and W. Other promising electrode materials which were not considered in this study are: SiC-refractory metal composites, semiconductor-refractory metal composites, LaCrO<sub>3</sub> and zirconized platinum.

### 3. Argon purification and related problems

The use of an oxide electrolyte to measure thermodynamic and kinetic quantities utilizes the difference in the equilibrium oxygen partial pressures at the two cell electrodes. These partial pressures may be as low as  $10^{-30}$  atm especially for metal-metal-oxide electrodes and special care must be taken to ensure that these equilibrium partial pressures are not altered by the cell surroundings [6]. The usual practice is to protect both electrodes with a purified inert gas, such as argon, so that the oxygen partial pressure in the gas is negligible compared with the electrode. In this investigation argon was purified by conventional procedures by passing it through two columns of activated Linde 3A molecular sieve at room temperature (dehydrating agent), through a column of copper gauze at 500°C (primary deoxidizing agent) and finally through a titanium chip trap at 850°C (secondary deoxidizing agent). Necessary steps were taken to prevent oxygen leaks from the environment.

This particular arrangement of purification system was reported to purify argon to as low as  $10^{-25}$  atm of oxygen [13, 14], using a solid oxide electrochemical probe to measure this level of purity. However, as discussed below, it appears that the electrochemical probe is not reliable at such low oxygen pressures. Theoretically it requires  $10^{-15.8}$  atm oxygen partial pressure to saturate pure liquid indium at 950°C [15, 16]. Thus, it was expected that purified argon would not introduce oxygen contamination in liquid indium. Fig. 4 represents the observed  $a(O)$  versus time response when purified argon is passed over pure liquid indium at temperatures of 850, 900 and 950°C. No oxygen was titrated in the melt coulometrically. Obviously the oxygen content of purified argon was high enough to saturate liquid In, i.e.,  $p_{O_2}(\text{Ar})$  was larger than  $10^{-15.8}$  atm. The residual oxygen in argon will introduce significant errors in oxygen solubility obtained by coulometric titration methods since oxygen will be concurrently absorbed from argon and produce measured solubilities that are too low. This is probably responsible for the disparity in the values reported by various investigators for oxygen solubility for the same liquid metals.

The absorption of oxygen from the argon atmosphere also introduces small errors in diffusivity measurements. In diffusion experiments the residual current after a long-time potentiostatic titration was traditionally taken as the electronic current. This current is subtracted from the total measured current to yield the ionic current  $I$  and the diffusivity of oxygen is then calculated from the slope of  $\log I$  versus time plots. The continu-

ous absorption of oxygen by liquid metal from the purified argon under potentiostatic conditions produces a residual ionic current which may be incorrectly taken to be the electronic current and leads to calculated diffusivity values for oxygen that are high.

The discrepancy between the observed oxygen uptake by indium and the measured oxygen pressure using an electrochemical probe is probably explained by the extremely low number density of oxygen molecules at these low oxygen pressures. Under these conditions the flux of oxygen molecules incident to the platinum electrode surface is extremely low and the total electrode reaction may not be well defined<sup>†</sup>. In order to obtain more reliable measurements, we prepared an oxygen probe using a YDT tube with relatively large electrode areas and using a  $p_{\text{CO}_2}/p_{\text{CO}} = 10.25$  reference gas electrode. With this oxygen probe, the following observations were made:

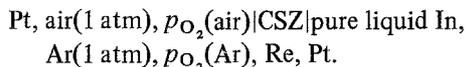
(a) For argon taken directly from the tank  $p_{\text{O}_2}(\text{Ar}) = 1.214 \times 10^{-8}$  atm. No substantial change in  $p_{\text{O}_2}(\text{Ar})$  was observed with a change in the argon flow rate.

(b) For argon flowing through a fresh purification system at a low flow rate  $p_{\text{O}_2}(\text{Ar}) = 3.401 \times 10^{-9}$  atm; at high flow rate  $p_{\text{O}_2}(\text{Ar}) = 7.349 \times 10^{-9}$  atm.

(c) For argon flowing through a purification system after two weeks' use: at a low flow rate,  $p_{\text{O}_2}(\text{Ar}) = 1.115 \times 10^{-7}$  atm; at high flow rate,  $p_{\text{O}_2}(\text{Ar}) = 9.047 \times 10^{-8}$  atm.

From these observations, it appears that the purification was relatively inefficient and the oxygen content of argon was even increased for an aged purification system.

In order to establish the influence on electrochemical measurements, we measured the rate of absorption of oxygen from the argon gas using the following cell:



The open-circuit e.m.f. was measured in 3-hour intervals with no oxygen titrated coulometrically in liquid indium during that time interval. Since

<sup>†</sup> One should distinguish between low oxygen pressures arising from such couples as  $\text{H}_2/\text{H}_2\text{O}$  or  $\text{CO}/\text{CO}_2$ , where the number density of oxygen-containing species is high, and gases containing only  $\text{O}_2$  as oxygen species.

there is an oxygen concentration gradient along the liquid metal column, the measured value of e.m.f. will correspond to average activities  $a(\text{O})^{\text{av}}$ . The variation of  $a(\text{O})^{\text{av}}$  versus  $t$  was presented in Fig. 4 for pure liquid indium. The surface area available for absorption of oxygen, the top surface of the cylindrical liquid column, is  $0.4 \text{ cm}^2$ . The number of gram atoms of adsorbed oxygen,  $n(\text{O})^{\text{ad}}$ , and the corresponding atomic fraction,  $X(\text{O})^{\text{ad}}$ , could be calculated from  $n(\text{O})^{\text{av}}$  and the initial gram atoms of oxygen in liquid indium  $n(\text{O})^{\text{i}}$  as follows:

$$n(\text{O})^{\text{ad}} = n(\text{O})^{\text{av}} - n(\text{O})^{\text{i}} \quad (5)$$

and

$$X(\text{O})^{\text{ad}} = X(\text{O})^{\text{av}} - X(\text{O})^{\text{i}} \quad (6)$$

where

$$X(\text{O}) = a(\text{O})/\gamma(\text{O}) \quad (7)$$

and

$$n(\text{O}) = \frac{n(\text{In})X(\text{O})}{1 - X(\text{O})} \cong n(\text{In})X(\text{O}) \quad (8)$$

where  $\gamma(\text{O})$  is the oxygen activity coefficient in liquid indium which was previously measured for pure liquid In as a function of temperature, and  $n(\text{In})$  in the gram atoms of liquid In used for this particular study.

We define  $n(\text{O})^{\text{s}}$  as

$$n(\text{O})^{\text{s}} = n(\text{O})^{\text{sat}} - n(\text{O})^{\text{i}} \quad (9)$$

where  $n(\text{O})^{\text{sat}}$  is the gram atoms of oxygen required to saturate liquid In at a given temperature, which has also been previously measured. For unidirectional nonsteady-state diffusion of a solute into the surface (in the  $x$  direction) of a single-phase slab of thickness  $h$ , the mathematical solution of Fick's second law results in the following expression for the long-time solution [17]:

$$\frac{n(\text{O})^{\text{s}} - n(\text{O})^{\text{ad}}}{n(\text{O})^{\text{s}}} = \exp\left(\frac{4D(\text{O})t}{h^2} + 0.21\right) \quad (10)$$

where  $D(\text{O})$  is the diffusivity of oxygen ( $\text{cm}^2\text{s}^{-1}$ ) and  $t$  is the time (s). The boundary conditions are:

$$X(\text{O}) = X(\text{O})^{\text{i}} \quad \text{at } t = 0 \text{ and } 0 < x < h,$$

$$X(\text{O}) = X(\text{O})^{\text{sat}} \quad \text{at } x = 0 \text{ and } 0 < t < \infty.$$

It is assumed that the surface ( $x = 0$ ) is saturated with oxygen for a surface concentration of  $X(\text{O})^{\text{sat}}$ . Values of  $h$  are obtained from the grams of liquid In, the inside diameter of the electrolyte tube and the literature value of the density of liquid In at the temperature of interest [18]. Sub-

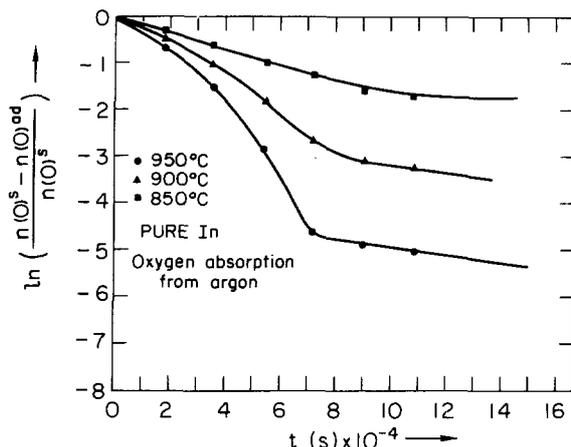


Fig. 5.  $\ln [(n^s(\text{O}) - n(\text{O})^{\text{ad}})/n(\text{O})^s]$  versus  $t$  for absorption of oxygen from argon in pure liquid indium at 850, 900 and 950°C.

stituting the respective values of  $h$  in Equation 10, the coefficient for  $D(\text{O})t$  becomes  $-0.280$ ,  $-0.283$  and  $-0.287$  for the respective temperatures of 950, 900 and 850°C. Fig. 5 shows the plot of  $\ln [(n(\text{O})^s - n(\text{O})^{\text{ad}})/n(\text{O})^s]$  versus  $t$ . The observed nonlinear behaviour is inconsistent with diffusion control. Furthermore, if we equate the initial slopes of these curves (for less than 10 hours' absorption) with the appropriate coefficient in Equation 10, we obtain values for  $D(\text{O})$  which are 20 to 30 times larger than previously measured  $D(\text{O})$  values. This suggests that the absorption is not exclusively controlled by diffusion. This higher rate of absorption may arise from convection in the liquid metal or from transfer of oxygen from the reference compartment through the tube due to partial electronic conductivity.

Fig. 6 is a plot of  $X(\text{O})^{\text{ad}}$  versus  $t$  for the

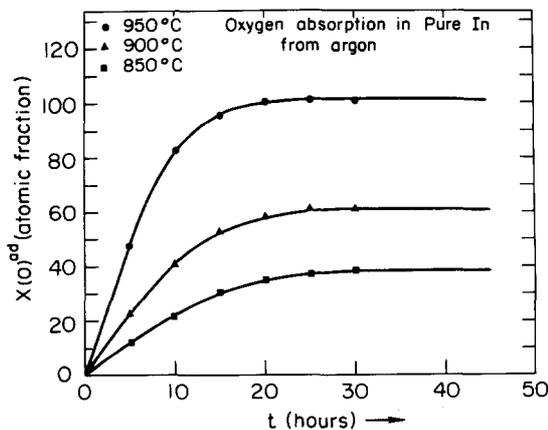


Fig. 6.  $X(\text{O})^{\text{ad}}$  versus  $t$  for absorption of oxygen from argon in pure liquid indium at 850, 900 and 950°C.

absorption of oxygen in liquid indium from argon and may be used to correct for the oxygen pick-up in coulometric titration experiments. The curves are described by the following equations:

$$\begin{aligned} X(\text{O})^{\text{ad}} &= 101.9 [1 - \exp(-0.153t)] && 950^\circ\text{C} \\ &= 63.6 [1 - \exp(-0.103t)] && 900^\circ\text{C} \\ &= 47.5 [1 - \exp(-0.065t)] && 850^\circ\text{C}. \end{aligned}$$

Taking the derivative of  $X(\text{O})^{\text{ad}}$  with respect to  $t$  and dividing by the surface area available for absorption ( $A = 0.4 \text{ cm}^2$ ) and substituting for the exponents, we obtain for the three temperatures:

$$\begin{aligned} dX(\text{O})/Adt &= 0.383 [101.9 - X(\text{O})^{\text{ad}}] && 950^\circ\text{C} \\ &= 0.258 [63.6 - X(\text{O})^{\text{ad}}] && 900^\circ\text{C} \\ &= 0.163 [47.5 - X(\text{O})^{\text{ad}}] && 850^\circ\text{C}. \end{aligned}$$

This indicates that the absorption is a first-order reaction of the form

$$\frac{dX(\text{O})}{Adt} = K[B - X(\text{O})]$$

where the rate constants  $K$  are:  $0.383 \text{ h}^{-1} \text{ cm}^{-2}$  at 950°C,  $0.258 \text{ h}^{-1} \text{ cm}^{-2}$  at 900°C and  $0.163 \text{ h}^{-1} \text{ cm}^{-2}$  at 850°C.

Fig. 7 shows  $\ln K$  versus  $1/T$  for the absorption of oxygen in liquid indium from argon, and least-squares fit of the data gives the following expression for  $K$  ( $R$  is in calories):

$$K = 7675 \exp \left[ \frac{-24 \times 10^3}{RT} \right] \quad 850 < T < 950^\circ\text{C}. \quad (11)$$

It is obvious that improved argon purification

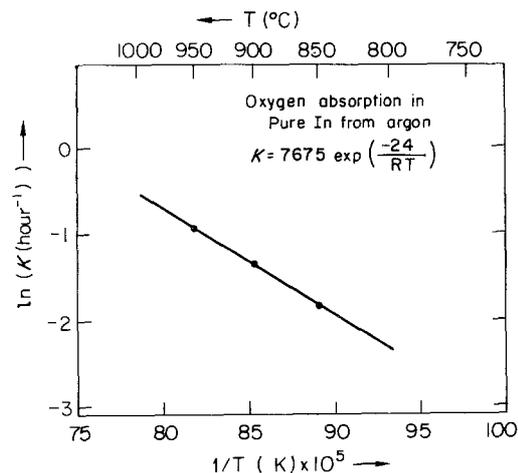


Fig. 7.  $\ln K$  versus  $1/T$  for absorption of oxygen from argon in pure liquid indium at 850, 900 and 950°C.

would improve the experimental methods and there are a number of alternative purification systems. A two-column calcium-tungsten trap (the first column at 600–650°C and the second at 350°C) is an effective system; the first column removes all gaseous impurities but hydrogen, whereas the second removes hydrogen in the form of calcium hydride. Activated charcoal at liquid nitrogen temperature may also be used for argon purification [19]. Other materials such as Ba, Ta, Zr, Th, Nb and alloys such as cerium-misch metal-aluminium-thorium, Zr-Al, Zr-Al-Ti and Zr-Ti may also be used as efficient getters for oxygen and other impurities [20, 21].

#### 4. Ageing of commercially available solid oxide electrolytes

In using electrochemical cells for kinetic and thermodynamic studies, it is important to select the best electrolyte. A major concern is the dependence of the fractional ionic and electronic conductivities upon temperature and the ambient oxygen partial pressure. In order for the Nernst equation and Faraday's law to apply, the ionic transference number  $t_{\text{ion}}$  must be close to unity. Any appreciable electronic conductivity has the effect of shorting out the cell, thus causing the measured cell voltages to be smaller than those corresponding to the Nernst equation. There are also the considerations of mechanical strength and thermal shock resistance. We report on the ageing

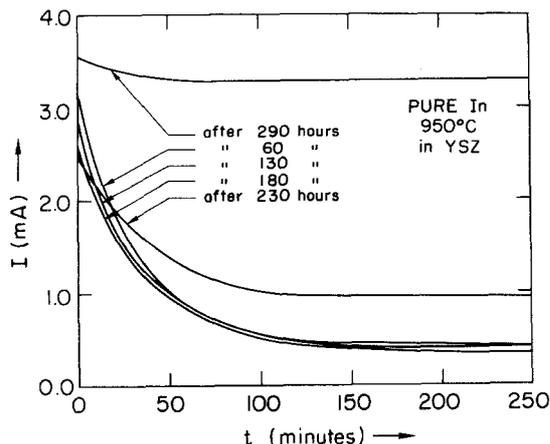


Fig. 8.  $I$  versus  $t$  for potentiostatic titration experiments on pure In at 950°C for 60, 130, 230 and 290 h ageing of a YSZ solid electrolyte.

of CSZ and YSZ electrolytes and the effect on the measured values of oxygen diffusivity.

The d.c. conductivity, as obtained from the potentiostatic current-time ( $I-t$ ) characteristic, showed a decrease in conductivity with the time of ageing. Fig. 8 shows the exponential decay of current versus time in a conventional potentiostatic diffusivity measurement in pure liquid In at 950°C using a YSZ solid electrolyte. Measurements were made after the sample was maintained at 950°C for 60, 130, 180, 230 and 290 h.

For each experimental run, the liquid metal was initially deoxidized by applying a voltage  $E_1$ , which corresponded to an oxygen activity several orders of magnitude lower than the metal-metal-oxide equilibrium. The voltage was then changed to  $E_2$ , corresponding to an oxygen activity in the metal slightly lower than that at which the most stable oxide of the metal forms. After the cell had equilibrated at the applied e.m.f. value, the e.m.f. was instantaneously changed to a value  $E_3$ , corresponding to an oxygen activity in the metal between  $10^{-1}$  and  $10^{-3}$  times the equilibrium value, and the resulting diffusion-controlled current was recorded until only a constant residual electronic current remained. Further details of the experimental methods are given in previous publications [22, 23]. Ageing of the electrolyte tube is quite obvious from Fig. 8; under exactly the same conditions (temperature, applied potential step and the liquid metal), the  $I$  versus  $t$  characteristics were significantly different.

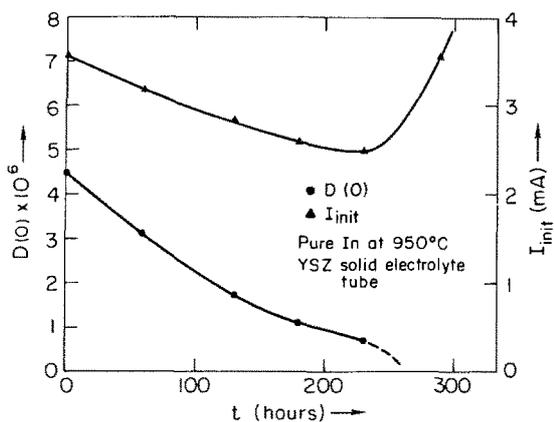


Fig. 9.  $D(O)$  and  $I_{init}$  versus ageing time  $t$  for pure In at 950°C in a YSZ solid electrolyte tube.

The solution of the diffusion equation for potentiostatic conditions for radial geometry gives the following  $I-t$  characteristic [22]:

$$I = \frac{8FD(O)M_{\infty}}{a^2} \exp\left[\frac{-\alpha_1^2 D(O)t}{a^2}\right] \quad (12)$$

where  $M_{\infty}$  is the number of gram atoms of oxygen that would be removed from the liquid metal at infinite time for the applied potential step,  $\alpha_1$  is the first root of the Bessel function of zero order (2.405),  $D(O)$  is the diffusivity of oxygen,  $F$  is the Faraday constant and  $a$  is the sample radius. The value of  $D(O)$  can thus be calculated from a plot of the observed  $\log I$  versus  $t$ .

The change in the initial current  $I_{init}$  (the value of  $I$  at  $t = 0$  in Fig. 8) and  $D(O)$  in liquid In, calculated from the slope of  $\log I$  versus  $t$ , are shown in Fig. 9. As is seen from this graph, the measured values of  $D(O)$  and  $I_{init}$  have decreased due to the ageing of the YSZ electrolyte. For ageing times longer than about 230 h, there is a sharp increase in  $I_{init}$  which arises from cracks in the electrolyte and the intrusion of liquid metal which short circuits the electrolyte.

For times shorter than 200 h, the following equation was developed from Fig. 9 to calculate the true value of oxygen diffusivity in liquid indium,  $D(O)$ , from the measured values of oxygen diffusivity,  $D(O)_m$ , and the time of the ageing of the YSZ electrolyte:

$$D(O) = D(O)_m + 2.1 \times 10^{-8} t$$

where  $D(O)$  is in  $\text{cm}^2 \text{s}^{-1}$  and the time is in hours.

The current through the cell is controlled by

the following three steps in series: transport of the oxygen to the electrolyte-liquid-metal interface; reaction at the interface electrode to form oxide ions; and transport of ions through the electrolyte. For a series process such as this, the slow step is rate-controlling. At longer times of potentiostatic polarization the transport of oxygen in the liquid metal has been established as the rate-limiting step; however, when the cell is initially polarized, oxygen is present in sufficient quantity at the electrode interface and the current will be controlled either by the interface reaction or the transport through the electrolyte. Assuming the latter to be rate-controlling, one may calculate the electrolyte conductivity from  $I_{init}$ , the applied potential step (20 mV) and the dimensions of the electrolyte. From the slope of  $I_{init}$  versus  $t$ , the rate of decrease in specific conductivity of the YSZ due to ageing was calculated at  $d\sigma/dt = 2.11 \times 10^{-6} \Omega^{-1} \text{cm}^{-1} \text{h}^{-1}$ . The ionic conductivity  $\sigma_{\text{ionic}}$  is calculated in a similar manner by subtracting the residual current from  $I_{init}$ . The residual current is the value of  $I$  in Fig. 9 for  $t = \infty$  and is attributed to the electronic current. The specific ionic conductivity (in  $\Omega^{-1} \text{cm}^{-1}$ ) of YSZ electrolyte tubes can be expressed as a function of ageing as:

$$\sigma_{\text{(ionic, YSZ, 950°C)}} = 1.23 \times 10^{-3} - 2.11 \times 10^{-6} t$$

with  $t$  in hours. The initial value of  $1.23 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$  is about an order of magnitude smaller than the value determined from a.c. impedance measurements [23]; however, we have assumed that there is no activation polarization. The disparity in the apparent conductivity implies, therefore, that there is a slow activation step at the liquid-metal-oxygen electrode.

Similar results were also obtained with CSZ solid oxide electrolytes and are reported elsewhere [23]. From a comparison of the two electrolytes, it appears that the decrease in conductivity of the YSZ electrolyte is slower than that of CSZ for relatively short times of application in liquid-metal environments. On the other hand, for long-time applications, the YSZ electrolyte has a shorter life because of crack development. For both electrolytes, the relatively large decrease of ionic conductivity, compared with the electronic conductivity, results in underestimating the ionic cell current and consequently the measured oxygen

diffusivity values. It is not yet clear whether the small increase in residual current is due to an increase in electronic conductivity because of the ageing of the electrolyte or the decrease in efficiency of argon purification which gives rise to increasing absorption of oxygen from argon gas by the melt. The extent to which each of these factors contributes to the residual current remains to be determined.

### 5. Measurement of oxygen solubility by the potentiostatic titration method

The absorption of residual oxygen in purified argon causes the oxygen solubility to be underestimated if appropriate corrections are not made. On the other hand, simultaneous oxidation of tungsten electrodes in liquid metals less reactive than Ga, such as In, Sb, Bi, Sn and Pb, results in overestimating the oxygen solubility. Ageing problems in commercially available solid oxide electrolytes and the resulting increase in the electronic contributions tend to underestimate the oxygen diffusivities and overestimate the oxygen solubilities measured by the coulometric titration method. The existence of these three sources of errors suggests that one should consider alternative techniques for oxygen solubility measurements. The intercept method, previously used by several investigators [9, 10, 24], obviates many of these problems. In this method the maximum oxygen solubility,  $S_m(\text{O})$ , is expressed as:

$$S_m(\text{O}) = \frac{Aa^2a(\text{O})^{\text{sat}}}{8FD(\text{O})n_{\text{metal}}(a(\text{O})_1 - a(\text{O})_2)} \quad (13)$$

where  $A$  is the pre-exponential in Equation 12,  $a(\text{O})^{\text{sat}}$ ,  $a(\text{O})_1$ , and  $a(\text{O})_2$  are oxygen activities, evaluated from the Nernst equation, which correspond to  $E^{\text{sat}}$ ,  $E_1$  and  $E_2$  ( $E_1$  and  $E_2$  being used for the diffusion measurements), and  $n_{\text{metal}}$  is the gram atoms of liquid metal. The quantity  $M_\infty$  is related to the oxygen solubilities  $X(\text{O})_1$  and  $X(\text{O})_2$  by the expression:

$$M_\infty = (X(\text{O})_1 - X(\text{O})_2)n_{\text{metal}}.$$

For the Henrian behaviour of oxygen in liquid metal, we may write:

$$S_m(\text{O}) = \frac{a(\text{O})^{\text{sat}}(X(\text{O})_1 - X(\text{O})_2)}{(a(\text{O})_1 - a(\text{O})_2)}.$$

for the atomic fraction of oxygen.

Values of  $E^{\text{sat}}$  are calculated from the Gibbs free energy of formation of the respective oxides. The activity coefficient of oxygen,  $\gamma(\text{O})$ , could be calculated from:

$$\gamma(\text{O}) = \frac{a(\text{O})^{\text{sat}}}{S_m(\text{O})}.$$

We have measured oxygen solubilities in liquid In, Ga, Sb and Bi using the intercept method and have found large differences compared with the results of solubility measurements made by the coulometric titration. This confirms our predictions of the influence of experimental problems that we previously discussed. One must, of course, correct the errors in the measured values of  $D(\text{O})$  arising from the ageing of electrolyte prior to the evaluation of the solubility by the intercept method. The intercept method, when carefully corrected for the relevant errors, is a rapid and accurate alternative to the coulometric titration technique.

### 6. Summary

Observations were made on the degradation of tungsten electrodes during coulometric titration. It was found that tungsten oxidizes even when the average oxygen activity in the liquid metal is below the threshold level for tungsten oxidation. This is presumably caused by transient oxygen activity gradients in the melt. This oxidation also introduces errors in electrochemical measurements. Mechanisms of the failure and qualitative analysis of oxidation were studied. Several other alternative materials were investigated and rhenium and tungsten-rhenium alloys were found to be satisfactory in liquid-metal environments.

It was found that protective atmospheres of argon, purified by conventional techniques, still contain sufficient oxygen to cause significant errors in electrochemical measurements, particularly of oxygen solubility using coulometric titration techniques. Study of the rate of absorption of oxygen in liquid In from argon indicated a combination of diffusion and interface reaction control. A first-order reaction was found to describe the absorption process and the corresponding rate constant was calculated as a function of temperature.

The conductivity of the electrolyte tubes was found to decrease with use at high temperatures and in contact with liquid metals. This decrease causes differences in the calculated values of oxygen diffusivity measured at different times. Correction factors were developed for the diffusivity values when either calcia-stabilized zirconia or yttria-stabilized zirconia electrolyte tubes are used. The measurement of the solubility by the analysis of the current-time response under potentiostatic polarization was discussed and concluded to have advantages.

## References

- [1] W. L. Worrell, in 'Solid Electrolytes: Topics in Applied Physics', Vol. 21 (edited by S. Geller) Springer-Verlag, New York (1977) pp. 143-68.
- [2] T. H. Etsell and S. N. Flengas, *Chem. Rev.* **70** (1970) 339.
- [3] J. Weissbart and R. Ruka, *J. Electrochem. Soc.* **109** (1962) 723.
- [4] *Idem*, *Rev. Sci. Instrum.* **32** (1961) 593.
- [5] K. Kiukkola and C. Wagner, *J. Electrochem. Soc.* **104** (1957) 379.
- [6] R. A. Rapp and F. Maak, *Acta Metallogr.* **10** (1962) 63.
- [7] V. B. Tare and H. Schmalzried, *Trans. Met. Soc. AIME* **236** (1966) 444.
- [8] H. Rickert and A. A. El Miligy, in 'Reactivity of Solids', (edited by J. W. Mitchell) Wiley-Interscience, New York (1969) p. 17.
- [9] K. E. Oberg, L. M. Friedman, W. M. Boorstein and R. A. Rapp, *Met. Trans.* **4** (1973) 61.
- [10] T. A. Ramaranaganam and R. A. Rapp, *ibid* **3** (1972) 3239.
- [11] K. A. Klinedinst and D. A. Stevenson, *J. Chem. Thermodyn.* **4** (1972) 565.
- [12] M. Iwase, M. O. Yasuda and T. Mori, *Electrochim. Acta* **24** (1979) 261.
- [13] S. K. Hahn, PhD Thesis, Stanford University (August 1978).
- [14] K. A. Klinedinst, PhD Thesis, Stanford University (May 1972).
- [15] K. A. Klinedinst and D. A. Stevenson, *J. Chem. Thermodyn.* **5** (1973) 21.
- [16] J. P. Coughlin, 'Bureau of Mines Bulletin', US Government Printing Office, Washington, DC, (1954) p. 24.
- [17] F. D. Richardson, 'Physical Chemistry of Melts in Metallurgy', Academic Press, London (1974) p. 398.
- [18] D. D. Williams and R. R. Miller, *J. Amer. Chem. Soc.* **72** (1950) 3821.
- [19] A. U. Seybolt and J. E. Burke, 'Experimental Metallurgy', John Wiley, New York (1953) p. 113.
- [20] S. Dushman, 'Scientific Foundations of Vacuum Technique', John Wiley, New York (1962) pp. 620-45.
- [21] W. Espe, *Powder Met. Bull.* **3** (1956) 100.
- [22] H. Rickert and A. El Miligy, *Z. Metallkde* **59** (1968) 635.
- [23] D. A. Stevenson, B. Heshmatpour and F. K. Moghadam, 'Fast Ion Transport in Solids', (edited by P. Vashishta, J. N. Mundy and G. K. Shenoy) Elsevier, Amsterdam (1979) p. 117.
- [24] R. Szwarc, K. E. Oberg and R. A. Rapp, *J. High Temp. Sci.* **4** (1972) 347.