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A study of the $Ag(s)/Ag_2SO_4 + Na_2SO_4(l)$ reference electrode

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The high temperature electrode $Ag(s)/Ag_2SO_4 + Na_2SO_4(l)$ contained in a mullite membrane is a suitable reference electrode for measuring sodium activities in Na_2SO_4 melts. Several Na concentration cells have been studied at 900° C to establish the thermodynamic basis for the $Ag(s)/10$ mol% $Ag_2SO_4 + Na_2SO_4$ electrode. Part of this work involved the determination of the ratio of activity coefficients of Ag_2SO_4 and Na_2SO_4 in melts that were dilute in Ag_2SO_4. When the non-ideal solution behaviour was taken into account, very good agreement was obtained between predicted and measured cell voltages for acidic Na_2SO_4 melts.

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1. Introduction

Many studies of redox reactions and corrosion reactions at high temperatures in fused alkali sulphates have used a reference electrode based on a silver wire in contact with a Na_2SO_4–Ag_2SO_4 melt [1–5]. The popularity of this electrode is due to its long-term stability, low polarizability, reproducibility and simplicity of construction [6–8]. However, it has not previously been placed on a thermodynamically meaningful e.m.f. scale, but rather E_0 has been assigned a value of zero so that only relative measurements were possible. This report summarizes an experimental study to establish the thermodynamic basis of the electrode $Ag(s)/Na_2SO_4$–10 mol% $Ag_2SO_4(l)$ contained in a mullite membrane.

2. Thermodynamic considerations

Consider the following cell:

$$\underset{\text{electrode [A]}}{\text{Ag(s), Na}_2\text{SO}_4\text{–10 mol\% Ag}_2\text{SO}_4} \left| \underset{\text{mullite}}{\text{Na}^+ \rightleftharpoons} \right| \underset{\text{electrode [B]}}{\text{Na}_2\text{SO}_4(l), \text{O}_2, \text{SO}_3, \text{Pt(or Au)}.} \qquad \text{(I)}$$

Mullite is a two-phase ceramic consisting of mullite grains ($2\ Al_2O_3$–SiO_2) enveloped by silica. At high temperatures dissolved alkali metal compounds in the silica film allow transport of alkali metal cations under an electrochemical driving force with essentially no electronic conduction [9, 10]. Similar behaviour has been observed for SiO_2 glasses [6, 11, 12]. The mullite grains are inert and thereby contribute to the chemical stability of the solid electrolyte.

According to Wagner [13], the galvanic potential for Cell I can be calculated from the thermodynamic properties of the electrodes and the transport properties of the electrolyte. Since this cell involves essentially only cation transport, the voltage is given by:

$$E_I = 1/F(\mu_{Na}[B] - \mu_{Na}[A]) \qquad (1)$$

The equilibrium of interest in the left-hand electrode (electrode A) is:

$$2Na + Ag_2SO_4 \rightleftharpoons 2Ag + Na_2SO_4. \qquad (2)$$

With solid Ag present at unit activity, and identifying Na_2SO_4 as component 1 and Ag_2SO_4 as component 2, the chemical potential of Na in the left-hand electrode is:

$$\mu_{Na}[A] = 1/2\,[\Delta G_1^0 - \Delta G_2^0 + RT \ln (a_1/a_2)] \qquad (3)$$

where ΔG_1^0 and ΔG_2^0 are the standard free energies

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of formation of components 1 and 2, a_1 and a_2 are the activities of components 1 and 2. R and T have their usual meanings. Similarly, for the right-hand electrode (electrode B):

$$2\text{Na} + \text{SO}_3 + 1/2\ \text{O}_2 \rightleftharpoons \text{Na}_2\text{SO}_4. \qquad (4)$$

For pure Na_2SO_4 the chemical potential of Na at the platinum electrode is given by

$$\mu_{\text{Na}}[\text{B}] = 1/2[\Delta G_1^0 - \Delta G_{\text{SO}_3}^0 - RT\ln(P_{\text{SO}_3}P_{\text{O}_2}^{1/2})] \qquad (5)$$

Substituting Equations 3 and 5 into Equation 1:

$$E_{\text{I}} = 1/2F\{\Delta G_{\text{SO}_3}^0 - \Delta G_2^0 + RT\ln(a_1[\text{A}]/a_2[\text{A}]) + RT\ln(P_{\text{SO}_3}P_{\text{O}_2}^{1/2})[\text{B}]\}. \qquad (6)$$

Equation 6 may be rewritten in the form:

$$E_{\text{I}} = E_0 + RT/2F\ln(P_{\text{SO}_3}P_{\text{O}_2}^{1/2})[\text{B}] \qquad (7)$$

where E_0 is comprised of terms which are constant for a given temperature, pressure and reference electrode composition:

$$E_0 = 1/2F\{\Delta G_{\text{SO}_3}^0 - \Delta G_2^0 + RT\ln(a_1[\text{A}]/a_2[\text{A}])\}. \qquad (8)$$

Alternatively, Equation 7 may be expressed in terms of P_{SO_2} and P_{O_2}:

$$E_{\text{I}} = E_0' + (RT/2F)\ln(P_{\text{SO}_2}P_{\text{O}_2}) \qquad (9)$$

with

$$E_0' = 1/2F\{\Delta G_{\text{SO}_2}^0 - \Delta G_2^0 + RT\ln(a_1[\text{A}]/a_2[\text{A}])\} \qquad (10)$$

or in terms of P_{O_2} and activity of Na_2O:

$$E_{\text{I}} = E_0'' - (RT/2F)\ln(a_{\text{Na}_2\text{O}}/P_{\text{O}_2}^{1/2}) \qquad (11)$$

where

$$E_0'' = 1/2F\{\Delta G_1^0 - \Delta G_{\text{Na}_2\text{O}}^0 - \Delta G_2^0 + RT\ln(a_1[\text{A}]/a_2[\text{A}])\}. \qquad (12)$$

If Na_2SO_4 is present at less than unit activity in the right-hand electrode, then the term $(RT/2F) \times \ln(a_1[\text{B}])$ must be subtracted from Equations 7 and 9 and added to Equation 11.

To evaluate E_0 in Equations 8–12 it is necessary to determine the ratio of the activity coefficients of Na_2SO_4 and Ag_2SO_4 in the left-hand electrode, since

$$a_{\text{i}} = N_{\text{i}}\gamma_{\text{i}} \qquad (13)$$

where N_i is the mole fraction of component i, and γ_i is its activity coefficient.

Consider the following series of cells:

$$\begin{array}{c|c|l} \text{Ag, Na}_2\text{SO}_4\text{–10 mol\% Ag}_2\text{SO}_4 & \text{Na}^+ \rightleftharpoons & \\ [\text{A}] & \text{mullite} & \\ \end{array}$$
$$\begin{array}{c} \text{Na}_2\text{SO}_4\text{–}N\text{ mol\% Ag}_2\text{SO}_4\text{, Ag} \\ [\text{B}] \end{array} \qquad \text{(II)}$$

The voltages of Cell II are given by:

$$E_{\text{II}} = -1/2F(RT\ln a_1[\text{B}]/a_2[\text{B}] - RT\ln a_1[\text{A}]/a_2[\text{A}]) \qquad (14)$$

or

$$E_{\text{II}} = E^* - (RT/2F)\ln\left\{\left(\frac{1-N_2[\text{B}]}{N_2[\text{B}]}\right)\frac{\gamma_1[\text{B}]}{\gamma_2[\text{B}]}\right\} \qquad (15)$$

where

$$E^* = -(RT/2F) \times \ln\{N_2[\text{A}](\gamma_2[\text{A}]/N_1[\text{A}])(\gamma_1[\text{A}])\} \qquad (16)$$

With the assumption of regular solution behaviour for Na_2SO_4–Ag_2SO_4 melts, it may be shown that [14]:

$$RT\ln\gamma_1 = \alpha N_2^2 \qquad (17)$$

$$RT\ln\gamma_2 = \alpha N_1^2 \qquad (18)$$

where α is a constant. Subtracting Equation 18 from 17 and substituting into Equation 15

$$E_{\text{II}} = E^* - (RT/2F)\ln\frac{(1-N_2[\text{B}])}{N_2[\text{B}]} - 1/2F\alpha(2N_2[\text{B}] - 1). \qquad (19)$$

Since E^* is independent of electrode B, a plot of $E_{II} + (RT/2F)\ln\{(1 - N_2[B])/N_2[B]\}$ versus $(2N_2[B] - 1)$ for a series of cells with different $N_2[B]$ should yield a straight line whose slope is $-\alpha/2F$. From Equations 17 and 18

$$\frac{\gamma_1}{\gamma_2} = \exp\left[\frac{\alpha(N_2^2 - N_1^2)}{RT}\right]. \qquad (20)$$

The value of γ_2/γ_1 for 10 mol% Ag_2SO_4 may then be incorporated in Equations 8–11.

All of the standard free energies in Equations 8–11 were considered to be well established from recent measurements with the possible exception of ΔG_f^0 Ag_2SO_4 [15]. The following cell allows this quantity to be evaluated:

$$\begin{array}{c|c|c} W, WS_2, Na_2S & Na^+ \leftrightharpoons & \\ [A] & \text{mullite} & \end{array} \quad \begin{array}{c} Na_2SO_4\text{–}10\,\text{mol\%}\ Ag_2SO_4, Ag \\ [B] \end{array} \qquad \text{(III)}$$

The left-hand electrode has been used recently by Liang and Elliott [16, 17] to measure ΔG^0_f of Na_2SO_4 and the activity of Na_2O in Na_2SO_4. The chemical potential of Na in electrode [A] is:

$$\mu_{Na}[A] = 1/2(\Delta G^0_{Na_2S} - 1/2\, \Delta G^0_{WS_2}) \qquad (21)$$

and

$$E_{III} = -1/F(\mu_{Na}[B] - \mu_{Na}[A]) \qquad (22)$$

Substituting Equations 21 and 3 into Equation 22 and re-arranging, yields the standard Gibbs free energy of formation of Ag_2SO_4

$$\Delta G^0_2 = 2FE_{III} + \Delta G^0_1 - \Delta G^0_{Na_2S} + 1/2\, \Delta G^0_{WS_2} + RT \ln (a_1[B]/a_2[B]) - E_{W\text{–}Pt} \qquad (23)$$

where the last term is the thermoelectric e.m.f. of the W–Pt thermocouple.

3. Experimental procedure

The voltages of a variety of cells have been obtained with the experimental apparatus illustrated in Fig. 1. The cells were held at 900° C ± 1.5° C within a 4.5 cm inner diameter mullite tube fitted with a gas-tight brass flange. The following electrodes were contained in 0.9 cm outer diameter mullite tubes, which served as ionic conducting membranes: $Ag(s)/Na_2SO_4\text{–}Ag_2SO_4(l)$; W, WS_2, Na_2S (all solid); and W(s), Sn–Ag(l). Reagent grade chemicals were used without further purification except for dehydration. Because of the non-trivial P_{SO_3} over the $Na_2SO_4\text{–}Ag_2SO_4$ melt, a plug was placed in the end of the mullite tube to retard a slow drift in potential owing to a loss of SO_3. A short piece of Ag wire dipped into the melt and was connected to a Pt wire. Oxygen and water vapour were excluded from the W, WS_2, Na_2S and the W, Sn–30 mol% Ag(l) electrodes. The latter electrode was kept under a slow flow of dry Ar when in use. The W, WS_2, Na_2S electrode was first baked out at 400° C overnight under vacuum, then the mullite tube was sealed under vacuum with a short glass extension at the top. With both of these electrodes it was necessary to correct the measured voltages for the Pt–W thermoelectric e.m.f. Three different kinds of mullite tubes, Morganite grade H5, McDanel MV30 and McDanel MV33†, were used with no discernible differences in cell voltages.

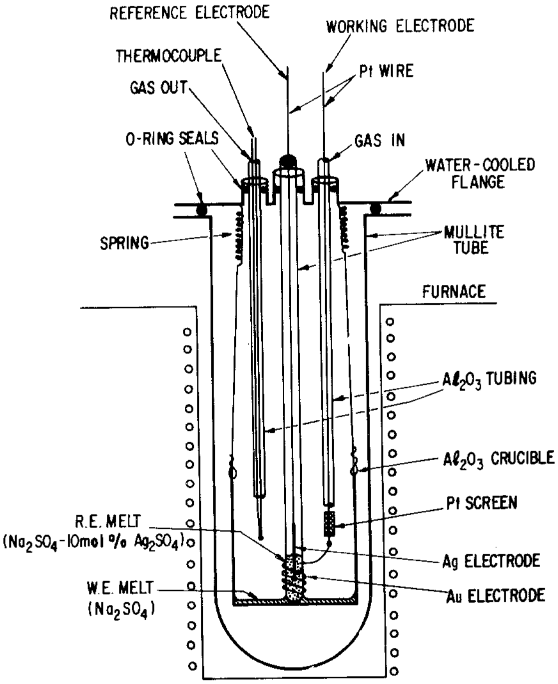

Fig. 1. Schematic diagram of experimental cell arrangement.

The other electrode consisted of a small amount of Na_2SO_4 contained in the Al_2O_3 crucible and equilibrated with various $O_2\text{–}SO_2\text{–}SO_3$ gas mixtures. A Pt screen or several turns of Au wire were wrapped around the mullite electrode tube, and this served as the contact to the Na_2SO_4 melt. Only a thin layer of salt infiltrated the screen or Au wire, which helped to insure rapid equilibration between the salt and gas. A separate Pt screen was placed near the gas inlet tube to make sure the equilibrium P_{SO_3} was achieved. The Au and Pt electrodes served equally well under the acidic conditions; others, however, have shown that Pt is unsuitable in basic Na_2SO_4 melts [17]. In some cells the Na_2SO_4 melt served only as a salt bridge between two electrodes contained in mullite tubes. In some preliminary experiments, cell voltages

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[*] H5 is a trade name of Morganite, Inc. MV30 and MV33 are trade names of McDanel Refractory Porcelain Co.

were found to be independent of gas flow rate from 2 to 6 $cm^3 s^{-1}$. All voltages were measured at 3 $cm^3 s^{-1}$. The cell potential was measured with a digital voltmeter having an impedance of $10^7\,\Omega$ after allowing several hours for equilibration.

The following cells have been investigated, not all of which proved to be successful:

$$\text{Au or Pt}, O_2, SO_3\ Na_2SO_4 \left| \begin{matrix} Na^+ \rightleftharpoons \\ \text{mullite} \end{matrix} \right| Na_2SO_4\text{–}10\,\text{mol\%}\ Ag_2SO_4, Ag \qquad (I)$$

The gas atmosphere over the Au or Pt/Na_2SO_4 electrode was varied over the range $P_{SO_3} P_{O_2}^{1/2} =$ 1.3×10^{-15} to 1.6×10^{-4} (pressure in atm). Analyzed gas mixtures containing O_2–0.15% SO_2, O_2–2% SO_2, O_2–10% SO_2 and Ar–0.10% O_2–0.11% SO_2 were obtained from Linde Division of Union Carbide. Intermediate compositons were prepared by mixing these gases with high purity O_2 with the use of calibrated flow meters.

$$Ag, Na_2SO_4\text{–}10\,\text{mol\%}\ Ag_2SO_4 \left| \begin{matrix} Na^+ \rightleftharpoons \\ \text{mullite} \end{matrix} \right| Na_2SO_4 \left| \begin{matrix} Na^+ \rightleftharpoons \\ \text{mullite} \end{matrix} \right| Na_2SO_4\text{–}N\,\text{mol\%}\ Ag_2SO_4, Ag \qquad (II)$$

where $N = 5, 20, 30$ and 40.

$$W, WS_2, Na_2S \left| \begin{matrix} Na^+ \rightleftharpoons \\ \text{mullite} \end{matrix} \right| Na_2SO_4\text{–}10\,\text{mol\%}\ Ag_2SO_4, Ag \qquad (III)$$

$$W, WS_2, Na_2S \left| \begin{matrix} Na^+ \rightleftharpoons \\ \text{mullite} \end{matrix} \right| Na_2SO_4, O_2, SO_3, \text{Pt or Au} \qquad (IV)$$

$$W, Sn\text{–}30\,\text{mol\%}\ Ag(l) \left| \begin{matrix} Ag^+ \rightleftharpoons \\ \text{mullite} \end{matrix} \right| Ag_2SO_4, O_2, SO_3, Au. \qquad (V)$$

This last cell was unsuccessful, apparently because the mullite did not function as an Ag ion conductor.

4. Results and discussion

Table 1. Thermodynamic data

Compound	*ΔG°(formation) at 900° C*	*Reference*
SO_3(g)	− 63 350 cal/mole	18
SO_2(g)	− 66 050	18
1/2 WS_2(s)	− 18 260	19
Ag_2SO_4(l)	− 81 730	15
Na_2S(s)	− 69 230	18
Na_2SO_4(l)	− 220 080	16
Na_2O(l)	− 59 560	18
Na_2O_2(s)	− 62 760	18
$Na_2S_2O_7$(l)	− 278 670	24
Al_2S_3(s)	− 141 230	25
$Al_2(SO_4)_3$(s)	− 484 210	26
Al_2O_3(s)	− 311 530	18
$NaAlO_2$(s)	− 208 820	11
$Na_2O\cdot 11Al_2O_3$(s)	− 3540 285	29
Na_2CrO_4(l)	− 223 770	27
$NaCrO_2$(s)	− 150 240	30
$Cr_2(SO_4)_3$	− 378 500	28
Cr_2O_3(s)	− 197 390	18
CrS(s)	− 14 350	25

In Cells I–IV the equilibrium cell voltage may be calculated from the well established thermodynamic properties of the electrode components. A comparison of the thermodynamic voltage with the measured voltage provides a basis for evaluating the performance of the cell. The voltage of Cell IV, which is equivalent to Cell III minus Cell I, is given by:

$$E = 1/2F[\Delta G^0_{SO_3} + \Delta G^0_{Na_2S} - \Delta G^0_{Na_2SO_4} - 1/2\Delta G^0_{WS_2} + RT \ln (P_{SO_3} P_{O_2}^{1/2})] \qquad (24)$$

Using the free energy data in Table 1, Equation 24 becomes:

$$E = 2.292 + (RT/2F) \ln (P_{SO_3} P_{O_2}^{1/2}). \qquad (25)$$

In Fig. 2 the measured voltages for Cell IV are plotted as a function of ln $(P_{SO_3} P_{O_2}^{1/2})$. The experimental values agree quite well with the thermodynamic voltages calculated from Equation 25, which confirms that mullite functions as a Na ion membrane under the present experimental conditions. Previous studies of a similar cell with a β-Al_2O_3 membrane, which is a well-known solid electrolyte for Na ions, established that the electrodes behave reversibly when Na_2SO_4 is maintained sufficiently acidic; in basic melts a buffering reaction such as the formation of sodium platinate limits the usefulness of this cell [17]. Cell voltages at the lowest value of $(P_{SO_3} P_{O_2}^{1/2})$, see Fig. 2, did not conform to Equation 25, presumably because of this limitation.

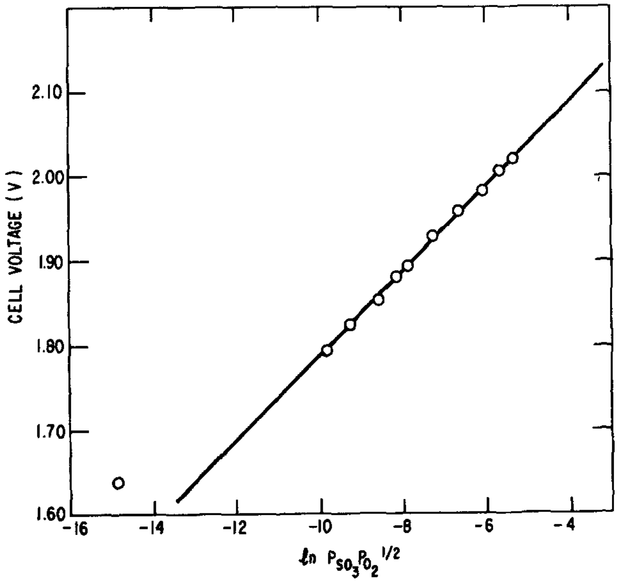

Fig. 2. Voltage of Cell IV as a function of $\ln(P_{SO_3}P_{O_2}^{1/2})$ at 900° C. The solid line corresponds to Equation 25 (see text).

The voltage of Cell II is proportional to the ratio of the activity coefficients of Na_2SO_4 and Ag_2SO_4 at shown previously by Equation 15. A series of cells with a reference electrode containing 10 mol% Ag_2SO_4 and the working electrodes containing 5, 20, 30 or 40 mol% Ag_2SO_4 have been measured, and the data are presented in Table 2. These data are shown in Fig. 3 as a plot of $E_{II} + (RT/2F) \ln [(1 - N_2)/N_2]$ versus $2N_2 - 1$. Although there is some scatter, the data can be represented by a straight line whose slope is equal to $-\alpha/2F$. Least squares analysis of the data yields a value of α equal to -3441 cal mol^{-1}, which corresponds to the interaction energy between Ag and Na ions in the Na_2SO_4–Ag_2SO_4 melts [14]. Values of the ratio of activity coefficients calculated from Equation 20 are also presented in Table 2.

Table 2. Cell voltages and calculated activity coefficients from Cell II

Mol% Ag_2SO_4 in electrode II	*e.m.f.* (V)	γ_1/γ_2*
5	-0.073	3.78
10	0	3.26
20	0.047, 0.056	2.42
30	0.089, 0.080	1.80
40	0.120	1.34

* Calculated from Equation 20

Cell III was constructed to check the value of the standard Gibbs free energy of formation of Ag_2SO_4 at 900° C. Two determinations yielded cell voltages of 1.721 V and 1.738 V, after correction for the W–Pt thermoelectric e.m.f. From Equation 23 and using $\gamma_1/\gamma_2 = 3.26$, ΔG_f^0 of Ag_2SO_4 was found to be $-81\,839$ and $-81\,060$ cal mol^{-1}. These values were considered as confirming the value of $-81\,730$ cal mol^{-1} from Kellogg [15], and the literature value was used in subsequent calculations.

Using the thermodynamic data in Table 1 and the ratio $\gamma_1/\gamma_2 = 3.26$, the voltage of Cell I may be calculated from Equation 6:

$$E_I = 0.569 + 0.0505 \ln (P_{SO_3} P_{O_2}^{1/2}) \quad (26)$$

Several examples of Cell I have been investigated and the cell voltages are plotted in Fig. 4 as a function of $\ln (P_{SO_3} P_{O_2}^{1/2})$. Except at the lowest $P_{SO_3} \times P_{O_2}^{1/2}$, the data were found to agree quite well with Equation 26 (average measured value of $E_0 = 0.580$). Voltages predicted on the basis of ideal solution behaviour of Na_2SO_4–Ag_2SO_4 melts, shown as a dashed line on Fig. 4, underestimate the measured voltages by about 70 mV. Clearly, the non-ideal behaviour of Ag_2SO_4–Na_2SO_4 solutions must be taken into account. If other than 10% Ag_2SO_4 is used, then the corresponding E_0 may be calculated from Equations 8, 13 and 20; for example, E_0 for 1 molal Ag_2SO_4 is 0.553 at 900° C.

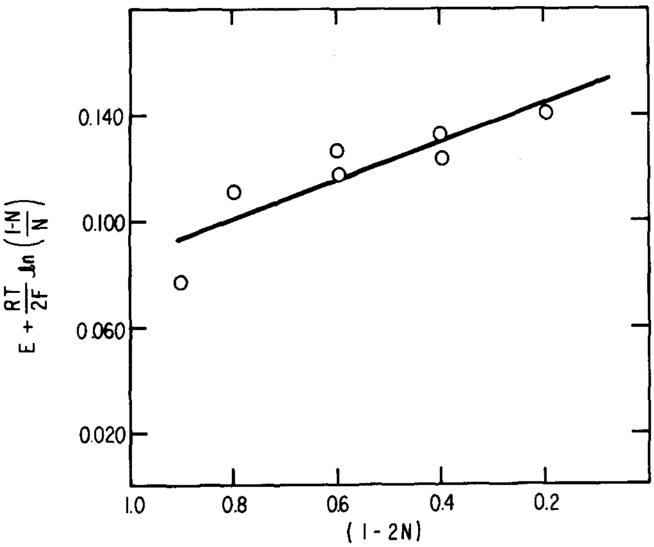

Fig. 3. Plot of data from a series of cells represented by Cell II.

Sequeira and Hocking [20] studied a cell similar to Cell I, but with the apparent difference that their noble metal electrodes were submerged in a deep melt of Na_2SO_4. Their cell voltages were ~ 0.3 V negative of our values in the same environment, and they found that their cell, unlike our cells, responded relatively slowly to changes in the environment. To try to resolve these differences a cell was constructed with an Ag/Na_2SO_4–10 mol% Ag_2SO_4 reference electrode and two gold electrodes in Na_2SO_4, one held at the bottom of the ~ 1 cm deep Na_2SO_4 melt, and the other extending into the gas phase, but just touching the melt surface. The connecting wires were routed through a piece of two-hole Al_2O_3 tubing, the end of which was submerged in the melt. Thus, the melt rising by capillarity into the tubing froze, forming a plug which effectively eliminated the gas/liquid/metal interface on the submerged wire. The initial voltages of the two electrodes were very different: after 3 h in O_2–2% SO_2 at 900° C, the submerged electrode yielded − 0.201 V, whereas the electrode exposed to the gas phase yielded 0.277 V (which may be compared with an expected voltage of

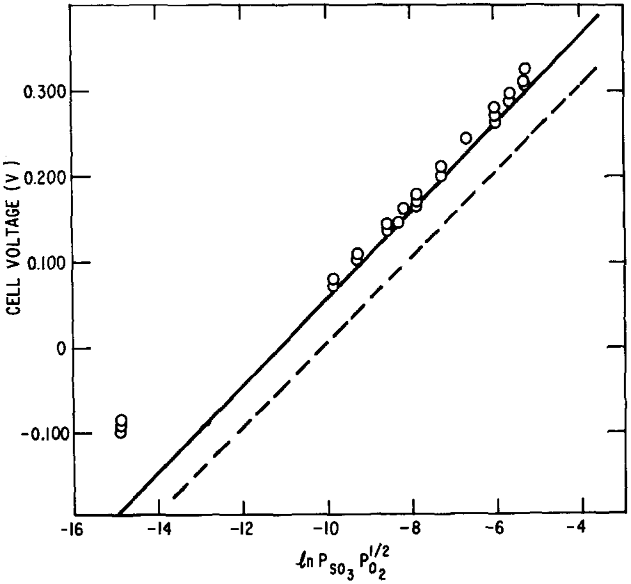

Fig. 4. Voltage of Cell I as a function of ln (P_{SO_3} $P_{O_2}^{1/2}$) at 900° C. The solid line corresponds to Equation 26 based on thermodynamic data with the ratio of activity coefficients γ_1/γ_2 as determined from Cells II. The broken line corresponds to the assumption of ideal solution behaviour for Na_2SO_4–Ag_2SO_4 liquids.

0.299 V from Equation 26). After further equilibration for 63 h, the submerged electrode yielded 0.259 V and the gas/salt electrode yielded 0.280 V. Next, the gas was quickly changed to O_2–10% SO_2, and the cell voltages were monitored for 24 h. The gas/salt electrode responded rather rapidly: 50% of the change in voltage occurred in 1 min and 90% in 1.1 h. As expected, the submerged electrode responded much more slowly: 50% of the change occurred in 150 min and 90% in 10.4 h. From this rather cursory experiment, it appears that at least some of the differences between the work of Sequeira and Hocking [20] and the present study may be attributed to the differing geometries of the salt/noble metal electrodes used in the two studies. The two-electrode experiment just described illustrates the additional point, however, that a partly submerged electrode will produce a mixed potential unless the melt is well equilibrated with the environment.

The use of the Ag/Na_2SO_4–Ag_2SO_4 reference electode for the measurement of Na activities in fused salts has a few limitations. The mullite tube or other Na ion conducting membrane should be chemically stable in the system of interest. Mullite is stable in molten Na_2SO_4 and other sulphate mixtures [8]. However, after about 250 h operation, Ag was found to have penetrated ~ 1 mm into the mullite tube; this may compromise the mechanical stability and thermal shock resistance of the tube. Although the present studies were carried out at 900° C, operation of the reference electrode at either higher or lower temperatures should be possible with an attendant re-evaluation of Equation 3. Below about 865° C Na_2SO_4–10 mol% Ag_2SO_4 will freeze, and the performance of the electrode may be adversely affected by easy polarization. However, the use of compositions richer in Ag_2SO_4 could extend the temperature range to considerably lower temperatures, perhaps approaching the melting point of Ag_2SO_4 at 651° C [21]. Above the melting point of Ag, 960° C, E_0 must be modified by adding the heat of fusion divided by F to reflect the change in standard state. At temperatures other than 900° C and with Na_2SO_4–Ag_2SO_4 mixtures outside the range considered in the present study, the activity coefficient ratio, γ_1/γ_2, must be re-evaluated.

For many applications, for example in studies of the corrosion of alloys in fused salts, the activity of Na_2O, not Na, is of interest. Measurements of Cell I, in conjunction with a knowledge of the oxygen activity, can be used to calculate the activity of Na_2O in a sulphate mixture from Equation 11. Because of the low solubility of O_2 in many fused salts, the possibility of oxygen

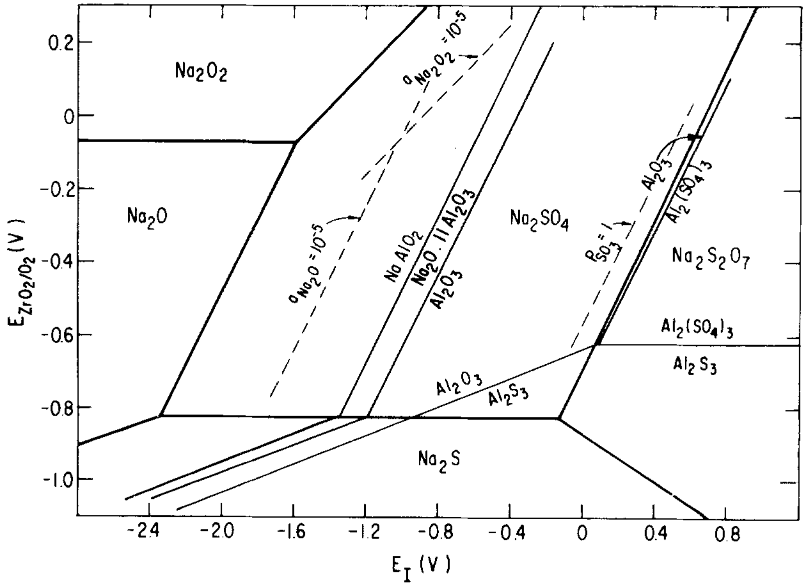

Fig. 5. Superimposed stability diagrams of the systems Na–S–O and Al–Na–S–O at 900° C represented in terms of the voltages of a cell to measure oxygen activity (reference P_{O_2} = 1 atm) versus Cell I.

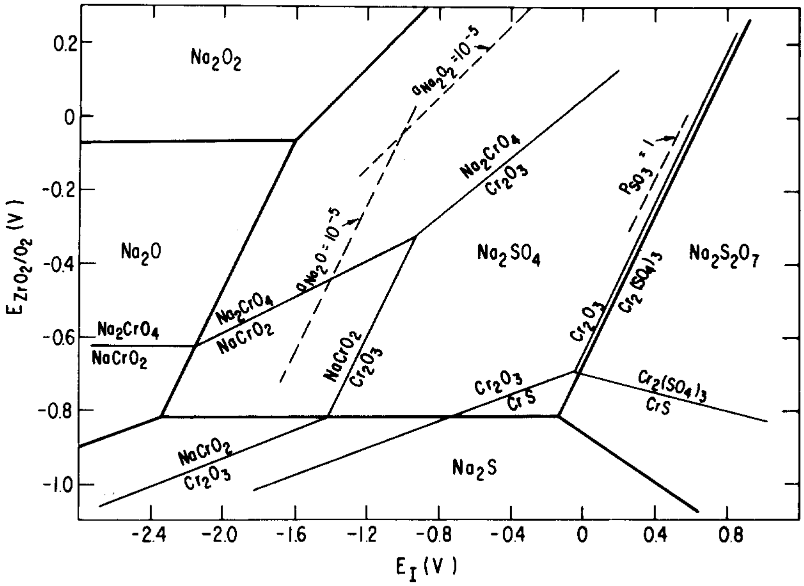

Fig. 6. Superimposed stability diagrams of the systems Na–S–O and Cr–Na–S–O at 900° C represented in terms of the voltages of a cell to measure oxygen activity (reference $P_{O_2} = 1$ atm) versus Cell I.

gradients in a reactive system must not be discounted. For example, oxygen gradients (and SO_3 gradients) were encountered during the hot corrosion of a nickel-base superalloy under a film of Na_2SO_4 only 0.01 cm thick [22]. As pointed out by Erdos and Altorfer [8] and more recently by Watt *et al.* [23], a dual electrode arrangement, involving both the Ag/Na_2SO_4–Ag_2SO_4 (mullite electrode and a Pt, O_2 (stabilized zirconia) electrode, may be used to unambiguously measure P_{SO_3} and P_{O_2}, and hence the activity of Na_2O at the surface of a corroding alloy may be calculated. Such measurements may be referred to a Pourbaix-type stability diagram to infer the stable species or phases of corrosion products at the corroding surface. Two such diagrams, having as co-ordinates the voltages of Cell I and a cell to measure oxygen, are shown in Figs. 5 and 6 for the systems Na–Al–S–O and Na–Cr–S–O.

5. Summary

The high temperature electrode $Ag(s)/Na_2SO_4 + Ag_2SO_4(l)$ contained in the Na ion conducting membrane, mullite, has been studied in several cells involving Na_2SO_4 melts. The ratios of activity coefficients of Na_2SO_4 and Ag_2SO_4 in Na_2SO_4-rich melts at 900° C were determined from a series of concentration cell measurements with the aid of a simple regular solution model. By assigning the value zero to the $Ag(s)/Na_2SO_4$–$Ag_2SO_4(l)$ reference electrode, the standard electrode potential of the Pt/Na_2SO_4, O_2, SO_3 electrode was calculated from free energy data and the measured ratio of activity coefficients. That is, at 900° C for the cell:

$$\mathrm{Ag(s), Na_2SO_4\text{–}10\,mol\%\ Ag_2SO_4} \left| \mathrm{mullite} \right| \mathrm{Na_2SO_4, O_2, SO_3, Pt\ (or\ Au)}$$

the voltage is

$$E = 0.569 + 0.0505 \ln (P_{SO_3} P_{O_2}^{1/2})$$

or

$$E = 0.511 + 0.0505 \ln (P_{SO_2} P_{O_2})$$

or

$$E = -1.537 - 0.0505 \ln (a_{Na_2O}/P_{O_2}^{1/2})$$

Measured and calculated voltages agreed very well for acidic Na_2SO_4 melts. In combination with a knowledge or separate measurement of oxygen activity, the $Ag(s)/Na_2SO_4$–$Ag_2SO_4(l)$ reference electrode may be used to determine the activity of Na_2O, which is relevant, for example, to high temperature corrosion studies.

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