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Irreversible behaviour of an electrochemical device for the monitoring of carbon in liquid sodium

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The use of a fused salt solution of calcium carbide as the electrolyte in an electrochemical cell for the monitoring of carbon in metal solutions is shown to be unsatisfactory due to partial electronic conductivity in the electrolyte.

The experimental results of Salzano *et al.* [1] using such a device with liquid sodium–carbon solutions are shown to correspond to a steady state situation in which a carbon flux, equivalent to the electron flux in the electrolyte, is established from the graphite electrode to the steel barrier separating the electrolyte from the liquid sodium. The cell e.m.f., calculated by assuming this carbon flux to be equal to the carbon flux by diffusion through the steel barrier to the liquid sodium, agrees within the uncertainty limits of the calculation, to the measured e.m.f.

1. Introduction

Salzano, Newman and Hobdell [1] have recently developed an electrochemical cell technique to monitor the concentration (activity) of carbon in liquid sodium. Two galvanic cells were constructed, and were represented as:

$$\mathrm{Na[C]}\left|\begin{array}{c}\text{iron}\\\text{barrier}\end{array}\right|\begin{array}{c}\text{electrolyte}\\\mathrm{Na_2CO_3,\ Li_2CO_3}\end{array}\left|\ \mathrm{C_{(graphite)}}\right. \qquad \mathrm{I}$$

and

$$\mathrm{Na[C]}\left|\begin{array}{c}\text{iron}\\\text{barrier}\end{array}\right|\begin{array}{c}\text{electrolyte}\\\mathrm{CaC_2,\ LiCl}\end{array}\left|\ \mathrm{C_{(graphite)}}\right. \qquad \mathrm{II}$$

where [C] represents carbon dissolved in liquid sodium. The iron barrier was used to separate the electrolyte from the liquid sodium and was assumed to be in equilibrium with the latter.

For the 'carbonate' cell I, the electrode reaction was assumed to be

$$\mathrm{C} + 3\mathrm{O}^{2-} \rightleftharpoons \mathrm{CO_3^{2-}} + 4\mathrm{e} \qquad (1)$$

The reversible cell electromotive force, E_{I}, is readily shown to be

$$E_{\mathrm{I}} = +\frac{RT}{4F}\ln a_{\mathrm{C}} \qquad (2)$$

where a_{C} is the activity of carbon in the sodium relative to the value unity assigned to pure carbon at the reference electrode, and R, T and F have their usual meaning.

Hawkes and Morris [2], in the study of the galvanic cell

$$\mathrm{Fe[C]}\,|\,\mathrm{CaC_2,\ CaCl_2}\,|\,\mathrm{C_{(graphite)}} \qquad \mathrm{III}$$

proposed the following electrode–electrolyte equilibrium

$$\mathrm{C} + \mathrm{e} \rightleftharpoons \tfrac{1}{2}\mathrm{C_2^{2-}} \qquad (3)$$

Hence, the reversible electromotive force of the 'carbide' cell E_{II} is readily shown to be

$$E_{\mathrm{II}} = -\frac{RT}{F}\ln a_{\mathrm{C}} \qquad (4)$$

It is apparent from Equations (2) and (4) that at a given carbon activity and temperature, one can write

$$E_{\mathrm{II}} = -4E_{\mathrm{I}} \qquad (5)$$

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Furthermore

$$\frac{\partial E_{\text{II}}}{\partial T} = -4\frac{\partial E_{\text{I}}}{\partial T} \qquad (6)$$

Salzano *et al.* [1] confirmed Equation (6) in the temperature range 600°–700°C but found that at a given temperature and carbon concentration in the liquid sodium, $E_{\text{II}} < | 4E_{\text{I}} |$. They suggested that the low e.m.f. of cell II was due to partial electronic conductivity of the electrolyte. In this paper we present quantitative support for this conclusion. It will be shown that the e.m.f. of cell II measured by Salzano *et al.* corresponds to a steady state situation determined by equality of the carbon flux from the graphite electrode to the inner surface of the iron barrier, to the carbon flux by diffusion through the iron barrier.

2. Theoretical

2.1. *Carbon flux to iron barrier*

The physicochemical and electrochemical properties of solutions of calcium carbide in calcium chloride have been studied by Aksaranan *et al.* [3] and by White *et al.* [4]. It was shown that calcium metal was present in the solution due to the dissociation of calcium carbide according to

$$Ca^{2+}C_2^{2-}{}_{(\text{soln})} \rightleftharpoons Ca_{(\text{soln})} + 2C \qquad (7)$$

It was also shown that the electrochemical behaviour of this solution was consistent with a model in which calcium metal was regarded as the electroactive species, according to

$$Ca_{(\text{soln})} \rightleftharpoons Ca^{2+} + 2e \qquad (8)$$

The presence of metal in its molten halides has been shown to increase the electrical conductivity of the halide due to the type of equilibrium 8 [5]. Galvanic cells involving partial electronic conductivity of the electrolyte are in principle irreversible.

Based upon equilibria 7 and 8, cell II is more accurately represented by

$$\underset{}{\text{Na[C]}}\,|\,\text{Fe[C]}\,|\,\underset{a'_M}{\text{M}},\ \text{CaC}_2,\ \text{LiCl},\ \underset{a''_M}{\text{M}}\,|\,\text{C} \qquad \text{IV}$$

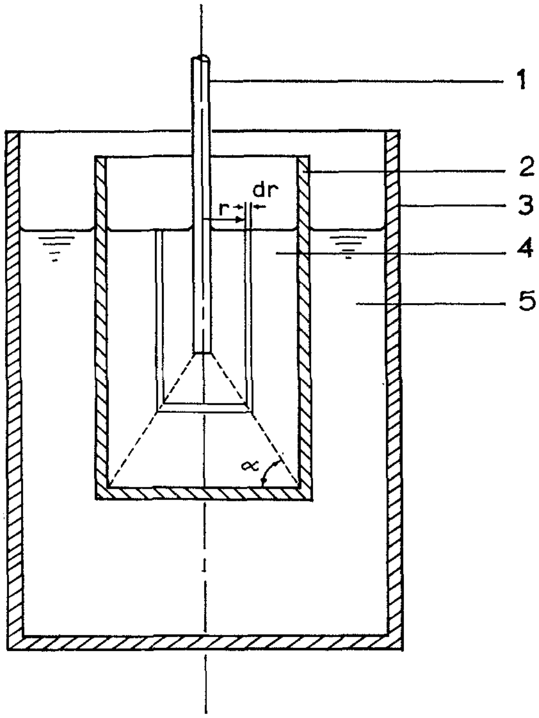

Fig. 1. Diagrammatic representation of cell IV.

1. Graphite electrode, radius r_1, depth of immersion l_1.
2. Fe[C] barrier, inner radius r_2, thickness Δr, depth of electrolyte l_2.
3. Stainless steel container for liquid sodium.
4. CaC_2–LiCl electrolyte.
5. Liquid sodium.

Location	*Carbon activity*	*Activity of metal in electrolyte phase*
$r = r_1$	1	a''_M
$r = r_2$	a'_C	a'_M
$r = r_2 + \Delta r$	a^o_C	—
Bulk of sodium	a^s_C	—

where Fe[C] represents the iron barrier, M is the metal in the solution and since the electrolyte consists of calcium carbide in lithium chloride, M ≡ Ca and Li. a'_M and a''_M are the metal activities at the Fe[C] surface and the graphite surface corresponding to equilibrium 7.

Fig. 1 shows a schematic diagram of cell IV used by Salzano *et al.* Let r_1, r_2 be the radii and l_1, l_2 be the depths of immersion into the electrolyte of the graphite electrode and Fe[C] barrier electrode respectively. Consider an elementary shell of electrolyte of thickness *dr* at a radius *r*. Assuming the electrolyte to be quiescent, that local equilibrium prevails, and that the electrolyte is of uniform composition in the metal carbide, the total electrical current density at the Fe[C] barrier, i_t and the electronic current density at the Fe[C] barrier, i_e are, for the isothermal case [6].

$$i_t = \frac{A}{A_b}\left[\frac{\sigma_t}{F}\operatorname{grad}\eta_e - \frac{\sigma_i}{nF}\operatorname{grad}\mu_M\right] = 0 \text{ (open circuit)} \quad (9)$$

$$i_e = \frac{A}{A_b}\frac{\sigma_e}{F}\operatorname{grad}\eta_e \quad (10)$$

where $\sigma_t = \sigma_e + \sigma_i$ and σ_e and σ_i are the electronic and ionic conductivities respectively. η_e and μ_M are respectively the electrochemical potential of electrons and the chemical potential of neutral metal atoms, n is the number of electrons involved in the electrochemical reaction. A and A_b are the areas of the elementary shell and the Fe[C] barrier, normal to the direction of flux.

Since $\sigma_e \ll \sigma_i$ (see Appendix), Equations (9) and (10) give for the cell e.m.f., E_{IV}, and for the electronic current density i_e

$$E_{IV} = -\frac{RT}{nF}\ln\left(\frac{a''_M}{a'_M}\right) \quad (11)$$

$$i_e = \frac{A}{A_b}\frac{\sigma_e}{nF}\operatorname{grad}\mu_M \quad (12)$$

The activities of metal at the electrode–electrolyte interfaces are determined by equilibrium 7, hence,

$$a''_M = Ka_{M_{2/n}C_2} \text{ at the graphite electrode} \quad (13)$$

$$a'_M = Ka_{M_{2/n}C_2}/(a'_C)^n \text{ at the Fe[C] barrier} \quad (14)$$

where K is the equilibrium constant. Equation (11) becomes

$$E_{IV} = -\frac{RT}{F}\ln a'_C = E_{II} \quad (15)$$

the same expression given earlier based upon equilibrium 3 as the assumed electrode–electrolyte process.

No electrical conductivity data are available for the Li/LiCl system [7]; the data for the $Ca/CaCl_2$ system due to Dworkin *et al.* [5] will be used. Thus the above equations will be developed with $M \equiv Ca$ and $n = 2$. The use of conductivity data pertaining to the $Ca/CaCl_2$ system is justified on the basis of the well known similarity of systems involving alkali metal/metal halides to those of alkaline earth metal/metal halides two periods removed [8]. This similarity is believed to be due to the near equality of the ion volume to charge ratio of the respective pairs.

Noting that the carbon flux to the Fe[C] barrier, $J_{C(e)} = i_e/F$;

$$\operatorname{grad}\mu_{Ca} \equiv \frac{d\mu_{Ca}}{dr} = \frac{RT}{a_{Ca}}\frac{da_{Ca}}{dr}, \quad (16)$$

and from equation 8,

$$\sigma_e = K_e\, a^{\frac{1}{2}}_{Ca} \quad (17)$$

where

$$K_e = \frac{2{\cdot}28\times10^5}{T}\exp\left(-\frac{4T_B}{T}\right), \text{(see Appendix)} \quad (18)$$

together with

$$A = \pi(\beta r^2 + \gamma r + \delta) \quad (19)$$

where $\beta = 2\tan\alpha + 1$, $\gamma = 2l_1 + 2r_1$ and $\delta = r_1^2$, Equation (12) may be integrated to give

$$J_{C(e)} = \frac{RT\,K_e}{BA_bF^2}\left(a'^{\frac{1}{2}}_{Ca} - a''^{\frac{1}{2}}_{Ca}\right)$$

$$= \frac{RT\,K_e}{BA_bF^2}K^{\frac{1}{2}}a^{\frac{1}{2}}_{CaC_2}\left(\frac{1}{a'_C} - 1\right) \quad (20)$$

in view of Equations (13) and (14) and where

$$B = \frac{1}{\pi(\gamma^2 - 4\delta\beta)^{\frac{1}{2}}}\left[\ln\left(\frac{2\beta r_2 + \gamma - (\gamma^2 - 4\delta\beta)^{\frac{1}{2}}}{2\beta r_2 + \gamma + (\gamma^2 - 4\delta\beta)^{\frac{1}{2}}}\right) - \ln\left(\frac{2\beta r_1 + \gamma - (\gamma^2 - 4\delta\beta)^{\frac{1}{2}}}{2\beta r_1 + \gamma + (\gamma^2 - 4\delta\beta)^{\frac{1}{2}}}\right)\right] \quad (21)$$

The equilibrium constant K for reaction 7 is related to the free energy change ΔG^0_T by

$$K = \exp(-\Delta G^0_T/RT) \quad (22)$$

where

$$\Delta G^0_T = (6820 + 0{\cdot}7T + 2{\cdot}76T\log T) \pm 2000 \text{ cal} \quad (23)\ [3]$$

Equation (20) should also include a term to account for the diffusion of neutral metal atoms. Calculations upon similar systems by Hesson *et al.* [9] and by Morris *et al.* [10] have shown the contribution by diffusional processes to the self discharge to be small relative to the electronic conduction process.

2.2. *Carbon flux through iron barrier*

The steady state carbon diffusion flux through the Fe[C] barrier is derived from the carbon activity gradient between the inner and outer surfaces of the wall. The measured e.m.f. of the 'carbonate' cell I, situated in the same bath of liquid sodium as the 'carbide' cell II, enables calculation of the carbon activity in the liquid sodium a_C^s which is maintained constant and assumed to be equal to the activity at the outer surface a_C^o of the Fe[C] barrier since the sodium is well stirred and the carbon activity is buffered by the stainless steel vessel [1]. Thus

$$a_C^o = a_C^s = \exp(4\,FE_I/RT) \qquad (24)$$

An empirical equation for E_I may be derived from the data given by Salzano *et al.* as

$$E_I = -1{\cdot}94\times10^{-4}t+8{\cdot}15\times10^{-2}\ \text{volts} \qquad (25)$$

where t is the temperature (°C).

The carbon diffusion flux $J_{C(D)}$ is given by Fick's first law as

$$J_{C(D)} = -D_C\frac{\Delta C_C}{\Delta r} = \left|\frac{D_C}{\gamma_C}\frac{(a_C' - a_C^s)}{\Delta r}\right| \qquad (26)$$

where D_C is the diffusion coefficient of carbon in iron, $\Delta C_C/\Delta r$ is the concentration gradient in the barrier of thickness Δr and γ_C is the activity coefficient of carbon in the iron assumed to be independent of concentration for the dilute solution of carbon in α-iron. Data on D_C are given by Homan [11] and data upon the saturation solubility of carbon in α-iron are due to Dunn and McLellan [12].

3. Results

At the steady state, $J_{C(e)} = J_{C(D)}$, Equations (20) and (26) may be equated and a_C' calculated. Hence E_{IV} ($\equiv E_{II}$) may be calculated. The results of these calculations are shown in Fig. 2 as a plot of E_{IV} vs. temperature including the limits of uncertainty in Equation (23), for an assumed $a_{CaC_2} = 0{\cdot}05$. This latter assumption was necessary as Salzano *et al.* do not state the composition of the electrolyte. The uncertainty in E_{IV} shown in Fig. 2 is approximately equal to the uncertainty deriving from an order of magnitude uncertainty in a_{CaC_2} (0·01 to 0·1).

Included in Fig. 2 are the data of Salzano *et al.* for E_I (Equation 25) and for E_{IV}. It is seen that the measured e.m.f. data of cell IV are within the uncertainty limits of the calculated values.

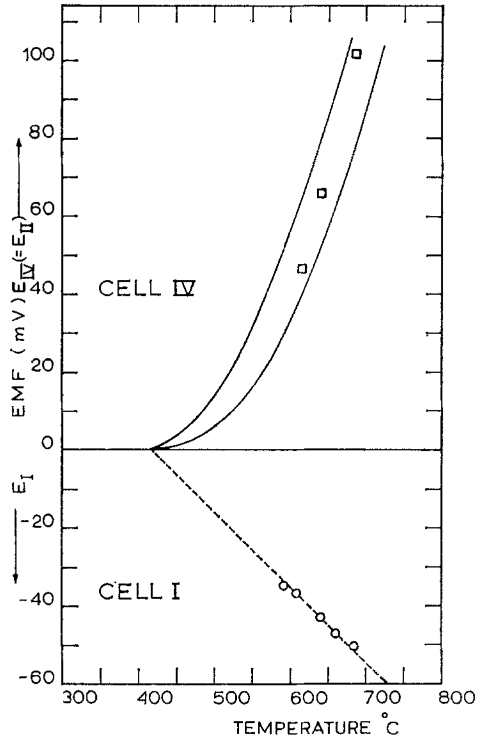

Fig. 2. Comparison of calculated with measured e.m.f. of cell IV (≡ cell II).
—— Calculated e.m.f. of cell IV with $a_{CaC_2} = 0{\cdot}05$; uncertainty limits due to Equation (23).
- - - - Plot of Equation (25) (e.m.f. of cell I).
□ Measured e.m.f., cell IV (ref. 1).
○ Measured e.m.f., cell I (ref. 1).

4. Conclusion

Salzano *et al.* [1] postulated that partial electronic conductivity in the electrolyte of the 'carbide' galvanic cell was the cause of the low e.m.f. values obtained. The calculations presented in this paper and summarized in Fig. 2 give good quantitative support for this conclusion. These calculations show the cell to be at a steady state condition in which the electron flux via the electrolyte phase is equivalent to a carbon flux to the inner side of the Fe[C] barrier, equal to the carbon flux by diffusion through the barrier to the liquid sodium.

Appendix

Estimation of the constant K_e

In order to calculate K_e it is assumed that conduction electrons are formed in the electrolyte by equilibrium 7 and hence

$$n_e = K' a_{Ca}^{\frac{1}{2}} \qquad \text{(A-1)}$$

where n_e is the electron concentration and K' is the equilibirum constant.

According to Rice [13] the electron motion occurs by a hopping mechanism akin to diffusion with activation energy $\Delta g = 4kT_B$ where T_B is the normal boiling point of metal and k the Boltzmann's constant. The diffusion coefficient of electrons D_e is then described by the equation

$$D_e = D_e^{\circ} \exp\left(-\frac{4T_B}{T}\right) \qquad \text{(A-2)}$$

where T is the absolute temperature, D_e° a constant.

From the Einstein relation

$$u_e = \frac{qD_e}{kT} = \frac{qD_e^{\circ}}{kT} \exp\left(-\frac{4T_B}{T}\right) \qquad \text{(A-3)}$$

where u_e and q are the electron mobility and charge respectively.

By definition, the electronic conductivity can be expressed as

$$\sigma_e = n_e q u_e \qquad \text{(A-4)}$$

Substituting for n_e and u_e in Equation (A-4) and from the data of Dworkin *et al.* [5] for the system Ca/CaCl$_2$ at 855°C for $a_{Ca} = 1$, $\sigma_e = 0{\cdot}40$ ohm^{-1} cm^{-1}, the following expression for the electronic conductivity is obtained.

$$\sigma_e = \frac{2{\cdot}28 \times 10^5}{T} a_{Ca}^{\frac{1}{2}} \exp\left(-\frac{4T_B}{T}\right) \qquad \text{(A-5)}$$

Hence

$$K_e = \frac{2{\cdot}28 \times 10^5}{T} \exp\left(-\frac{4T_B}{T}\right) \qquad \text{(A-6)}$$

At 600°C, $K_e = 0{\cdot}084$ (ohm . cm)$^{-1}$; from Equation (A-5), $\sigma_e \ngtr 0{\cdot}084$ (ohm . cm)$^{-1}$. From the compilations due to Janz [14], $\sigma_{LiCl} = 5{\cdot}64$ (ohm . cm)$^{-1}$, hence $\sigma_e \ll \sigma_i$ as stated earlier. This calculation assumes the influence of the C_2^{2-} ion upon the conductivity to be negligible.

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