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The use of alkali carbonates in carbon concentration cells

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The feasibility of using alkali carbonates as electrolytes in carbon concentration cells has been investigated. The following cell was set up:

environment with carbon of variable activity	α-Fe, C membrane	Na_2CO_3–Li_2CO_3 electrolyte	α-Fe, $C_{saturated}$ reference

The test electrode (LHS) was a carbon-permeable α-iron membrane in contact with a gaseous or liquid metal environment whose carbon activity could be varied. Experiments involving argon and liquid sodium environments at 970 K showed that the potential of the α-Fe test electrode was a function of its carbon activity.

The potential of the electrode, α-Fe, C | CO_3^{2-}, was also measured as a function of carbonate ion activity and current.

It was concluded that the predominant electrode reaction at the iron electrode was reversible and involved carbon and carbonate species or species with which they were in equilibrium.

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1. Introduction

The existence of carbon transfer in liquid sodium and helium-cooled reactors [1, 2] has led to the need to measure changes in carbon activities of steels and their liquid metal or gaseous environments at temperatures 570–970 K. Electrochemical carbon concentration cells provide an ideal means in principle, but there is no firmly established electrolyte for such devices. Calcium carbide solutions in molten calcium chloride [3] and alkali carbonates have both been used [4], but the latter were considered to be more suitable [4, 5].

The suitability of carbonate electrolytes has been investigated further using the electrode α-Fe, C | CO_3^{2-}. The variation of electrode potential with (1) carbon activity, (2) carbonate ion activity, and (3) current (micropolarization test) has been measured. These tests were performed to provide a basis for future electrochemical and thermodynamic studies.

2. Theory

A carbon concentration cell may be represented by:

test electrode, a_c	electrolyte with ionic form of carbon	reference electrode, a_c (ref)

The equilibrium e.m.f., E, is given by:

$$E = -\frac{RT}{n\mathrm{F}} \ln \frac{a_c}{a_c\,(\mathrm{ref})}, \qquad (1)$$

where n is the number of electrons involved per carbon atom in the electrode reaction, R the gas constant, F the Faraday constant and T the absolute temperature.

Equation 1 holds only if the cell is 'reversible' to carbon. This requires that the electrode potentials are determined by an electrode reaction involving carbon or some species in equilibrium with carbon, and that such a reaction is reversible;

it implies that the associated exchange current density greatly exceeds that of other reactions occurring at the electrode. Thus, if the electrode α-Fe, C$|$$CO_3^{2-}$ is a carbon electrode, α-iron will act as an 'inert' support for carbon, and the overall electrode reaction will be formally equivalent to: $C = C^{4+}(CO_3^{2-}) + 4e$. An increase in carbon activity is expected to increase the negative polarity (and vice versa) and n in Equation 1 will have a value of 4. The self-dissociation reaction in carbonate melts is: $CO_3^{2-} = O^{2-} + CO_2$; a possible overall electrode reaction is, therefore: $C + 3O^{2-} = CO_3^{2-} + 4e$.

3. Practical aspects

3.1. *Variation of carbon activity*

The following cell was set up:

$$\begin{array}{l|c|} \text{environment} & \\ \text{with C of} & \alpha\text{-Fe, C} \\ \text{variable } a_c & \text{membrane} \end{array}$$

$$\begin{array}{l|l} Na_2CO_3{-}Li_2CO_3 & \\ \text{electrolyte} & \alpha\text{-Fe, } C_{\text{saturated}} \end{array}$$

The test electrode (LHS) was a carbon permeable α-iron membrane, 0·25 mm thick (Ferrovat 'E', 3N+, Metals Research Ltd), in contact with a gas or liquid metal environment; the electrolyte was a mixture of sodium and lithium carbonates (equimolar m.p. ~775 K); a buffered saturated solution of carbon in α-iron acted as a reference electrode.

3.1.1. *Liquid sodium environment.* The carbon activity of the test electrode was varied in some experiments by using liquid sodium as a carbon transfer medium, bridging the iron membrane and a steel source or sink for carbon; the test electrode was:

$$\begin{array}{c|c|} \text{C source} & \\ \text{or sink} & \text{liquid Na, C} \end{array}$$

$$\begin{array}{c|l} & CO_3^{2-}, \\ \text{Fe membrane, C} & \text{electrolyte} \end{array}$$

Experience showed that liquid sodium and α-iron had the required carbon diffusivity, low carbon solubility ($\leqslant 100$ ppm) and absence of stable buffering carbides at the temperatures of interest (770–970 K) for the above technique to be suitable. The applicability of the cell to liquid sodium-steel systems was simultaneously assessed.

3.1.2. *Gaseous environment.* The decomposition [6] of carbon monoxide or methane at the iron electrode surface provided another method for varying the carbon activity of the test electrode. The test electrode was:

$$\begin{array}{c|c|l} Ar + CO & \text{Fe membrane, C} & CO_3^{2-} \\ \text{or } CH_4 & & \text{electrolyte} \end{array}$$

The reactions: $2CO = [C] + CO_2, CH_4 = [C] + 2H_2$ release carbon atoms which can diffuse across the iron membrane to the membrane/electrolyte interface.

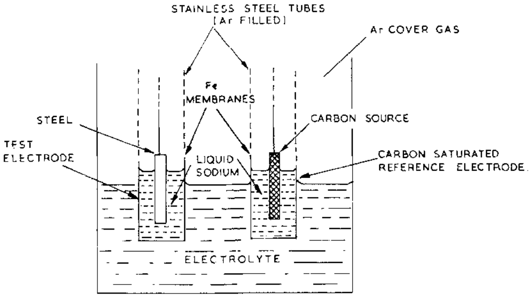

Fig. 1. Apparatus using sodium-filled electrodes.

3.1.3. *Apparatus and procedure.* Fig. 1 illustrates the salient features of the apparatus used in the sodium experiments. Further details are given elsewhere [7, 8]. The test electrode was in the form of a hollow iron capsule (wall thickness 0·25 mm, height 40 mm, diameter 10 mm) immersed in the electrolyte. An exactly similar iron capsule, but saturated with carbon, acted as the reference electrode. The hollow iron electrodes were welded to the bottom of stainless steel tubes. Liquid sodium (3 g, oxygen level ~ 10 ppm) was filtered directly into the electrode at 390 K under an argon cover gas. (The carbon content was typically 10–50 ppm, i.e. $\geqslant$ solubility limit in range 770–970 K.) The carbon activity was varied by adding a stainless steel tab (30 x 3 x 1 mm, 316L) as a carbon 'getter' and graphite or a carburized iron foil (30 x 3 x 0·03; 1·5 wt % C) as carbon sources.

The apparatus for use in gaseous environments was similar except that the test electrode was equipped with an internal stainless steel tube (3 mm diameter) to deliver gas to the inner membrane surface [8].

The reference electrode in some experiments was previously 'pack carburized', in others it contained liquid sodium equilibrated with excess carbon. A second reference electrode (not shown) consisting of a 'pack carburized' iron rod (6 mm diameter) was also employed to provide an independent check. Bias between reference electrodes did not exceed 2 mV.

The electrodes were suspended in the molten alkali carbonate previously dried under CO_2 at 670 K. The melt was contained in a stainless steel vessel with an argon cover gas. A separate argon cover gas was provided for electrodes containing sodium. The entire assembly was heated (970 K) in a pot furnace, and the voltage between electrodes measured with a high impedance electrometer (Keithley 610C) recorded continuously on a chart recorder.

3.2. *Variation of carbonate activity*

The potential of the $Fe, C|CO_3^{2-}$ electrode was measured as a function of carbonate ion activity using the cell:

$$C, \alpha\text{-}Fe\,|\,NaCl\text{–}KCl\text{–}Na_2CO_3\,||\,NaCl\text{–}KCl\text{–}AgCl\,|\,Ag.$$

3.2.1. *Apparatus and procedure.* A similar apparatus to that described above was used. The test electrode (LHS) was an interstitial solid solution of carbon in α-iron; the electrolyte consisted of an equimolar NaCl–KCl melt; the reference electrode (RHS) was a silver wire immersed in a solution of silver chloride in NaCl–KCl contained in a porous asbestos container. The reference electrode was thus irreversible to carbon. The entire assembly was kept under an inert cover gas of argon.

Two experiments at 970 K were performed; in one the α-iron electrode was saturated with carbon, while in the other the degree of saturation was ~0·1. Weighed pellets of dried sodium carbonate were successively added to the chloride electrolyte, and steady the e.m.f. value recorded after each addition.

3.3 *Micropolarization tests*

In a series of separate experiments with cells of the type:

$$\alpha\text{-}Fe, C\,|\,Na_2CO_3\text{–}Li_2CO_3\,|\,\alpha\text{-}Fe, C_{sat},$$

the electrode potentials of two iron electrodes (degree of carbon saturation unity and 0·1) were displaced (± few mV) from their equilibrium values by passing constant currents from a larger counter electrode. The change in potential of the electrode under study was measured with respect to a third (reference) electrode at equilibrium in the melt. Experiments were performed at temperatures from 820–970 K.

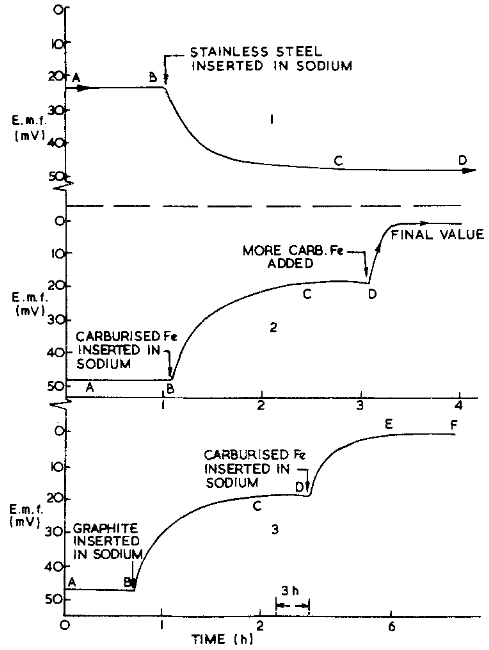

Fig. 2. E.m.f.-time profiles obtained in sodium environments at 970 K.

4. Results and discussion

4.1. *Variation of carbon activity*

4.1.1. *Results.* Fig. 2 (curves 1, 2 and 3) shows the e.m.f.-time profiles obtained at 970 K with test electrodes containing liquid sodium. The 'high carbon' reference electrode had negative polarity as predicted (Section 2). The initial part of curve 1, AB, represents the steady e.m.f. value (23 mV) established by filtered sodium alone; introduction of the stainless steel carbon getter, at B, caused the test electrode to become more positive with respect to the reference electrode and the magnitude of the e.m.f. increased (BCD). Subsequent metallographic examination of the stainless steel showed it to be carburized to a depth of 0·05 mm (Fig. 3a). It is well established that 316 stainless steel readily carburizes in sodium systems producing $(Fe,Cr)_7C_3$ and $(Fe,Cr)_{23}C_6$ type carbides. Curves 2 and 3 (Fig. 2) show the effect of adding carbon at B and D, as carburized iron or graphite, to 'gettered' sodium. The e.m.f. decreases (BC,DE) from the initial steady value AB of ~ 50 mV, i.e. an increase in carbon content of the test electrode caused a decrease in the positive value of its electrode potential with respect to the reference electrode. The carburized iron foils were found, on examination, to have lost carbon (Fig. 3b and c). Successive addition of more carbon had no further effect.

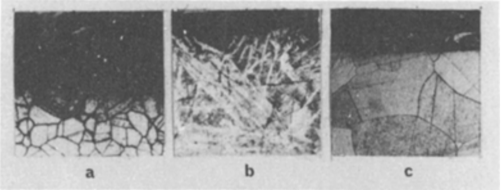

Fig. 3. (a) Carburized stainless steel after sodium exposure; (b) carburized iron, containing cementite, before sodium exposure; (c) decarburized iron after sodium exposure.

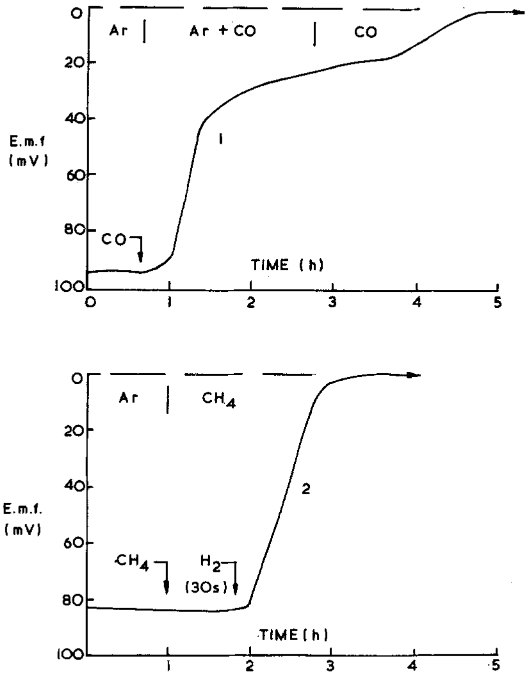

Fig. 4. E.m.f.-time profiles obtained in gaseous environments at 970 K.

Fig. 4 shows the results obtained when the inner surface of the test electrode was exposed to gaseous environments (flow rate 100 $mm^3 s^{-1}$) at 970 K. Argon (5–10 μatm H_2O,O_2) alone produced a high positive electrode potential (~ 90 mV), but the introduction, in separate experiments, of carbon monoxide (curve 1) or methane (curve 2) caused the e.m.f. magnitude to decrease, eventually to a constant value of zero, i.e. carburization of the test electrode caused its potential to become less positive until it became equal to that of the reference electrode (cf. Equation 1). Methane initially produced no change in potential. A transient addition of hydrogen was made to reduce any interfering surface oxides, and a decrease in cell e.m.f. was observed following this treatment.

4.1.2. *Discussion.* It is important to note that the basic cell in these experiments was symmetrical in all respects except electrode carbon level, and that its voltage was a direct measure of the potential difference between the surfaces of the α-iron electrodes in contact with the electrolyte. Changes in voltage, at constant temperature, were caused without physically disturbing the electrode-electrolyte interface. The voltage changes recorded with sodium-containing electrodes were accompanied by an increase or decrease in the carbon content of the carbon sink or source respectively. There must have occurred corresponding changes in the carbon content of the sodium and iron membrane since the total carbon content of the steel-sodium-iron system was fixed. This strongly suggests that the voltage profiles of Fig. 2 reflect changes in the carbon concentration at the outer surface of the α-iron electrode, i.e. that the electrode potential was a function of carbon concentration and hence activity. The results obtained in gaseous experiments support this conclusion. Thus argon, containing decarburizing impurities O_2 and H_2O, produce a relatively high cell voltage (low carbon activity) while exposure to the carburizing gases CO and CH_4 caused the cell voltages to decrease to zero (carbon saturation).

It is noteworthy that the continued *in situ* carburization of the test electrode in the above experiments produced a limiting e.m.f. value of zero; the polarity of the cell was never reversed. This observation again supports the conclusion that the electrode potential is determined predominantly by its carbon level; at zero voltage the test and reference electrodes had equal activities (Equation 1). The potential of the Fe,C|CO_3^{2-} electrode was thus the same whether carbon was added externally by pack-carburizing treatment, or *in situ*, from the inner surface; the electrode potential as a measure of carbon chemical potential, or activity, is expected to be independent of the path by which carbon is added.

4.2. *Kinetics of e.m.f. changes*

The increase and decrease in cell voltage occurred at a similar rate (cf. curves 1 and 2, Fig. 2). This suggested that carbon diffusion through the α-iron membrane to or from the iron/electrolyte interface was the rate-determining step. The relevant theoretical diffusion profiles can be constructed from the data provided by Crank [9]. It is found that $(C - C^0/C' - C^0) = 0{\cdot}89$ when $t = (L^2/D)$, where C, C^0, C' refer to surface concentrations at time t, initial and final concentration respectively, D is the diffusion coefficient of carbon in α-iron, and L the thickness of the membrane. Data for experimental diffusion profiles were obtained from the voltage values as follows: from Equation 1, putting $n = 4$, $T = 970$ K and assuming that carbon solutions in α-iron obey Henry's Law, one obtains:

$$E = -48{\cdot}2 \log_{10}(C/C_s),$$

where C is the carbon concentration in the variable electrode and C_s the terminal solubility of carbon in α-Fe at 970 K. Values of the function $(C - C^0/C' - C^0)$ computed from experimental e.m.f. data using Equation 2 are plotted as a function of time in Fig. 5 for increasing and decreasing e.m.f.; the curve corresponding to decreasing values is inverted to enable convenient comparison. The curves show that the concentration function has a value 0·89 when $t = 35$ min; hence $D = 3 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$. A theoretical curve is also shown in Fig. 5 corresponding to $D = 3 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$ and a membrane thickness 0·25 mm. Experimental and theoretical values are seen to be in good agreement over an extended range. The experimental results are thus consistent with carbon diffusion through the membrane controlling the rate of e.m.f. change, if the diffusion coefficient for carbon is given a value $3 \times 10^{-7}\,\text{cm}^2\,\text{s}^{-1}$ at 970 K. This is in good agreement with literature values [10]. The implication is that the cell e.m.f. changes at a rate governed by diffusion of carbon to or from the electrode-electrolyte interface. This is again consistent with the above conclusion that the electrode potential is a measure of carbon activity.

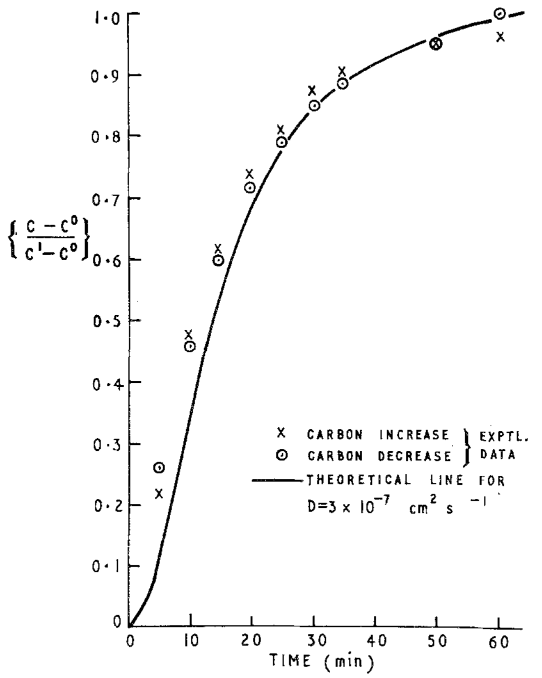

Fig. 5. Diffusion profiles for carbon in the iron membrane.

4.3. *The variation of carbonate activity*

Steady e.m.f. values were obtained only on addition of sodium carbonate to the chloride melt (Section 3.2). The results are presented in Fig. 6 where the sum of the incremental voltage $\sum_{i=1}^{i} \delta E_i$ is plotted against incremental increase in carbonate concentration, measured as $\log \sum_{i=1}^{i} m_i$, where m_i is the mass of the ith pellet. The lines 1 and 2 refer to the lower and higher carbon content electrodes respectively. (The relative position of these lines and their intercepts on the ordinate is not significant because of the random scatter in the e.m.f. values before carbonate addition.) The systematic increase in e.m.f. with added carbonate shows that the potential of the test electrode is a function of the carbonate ion activity of the melt. This implies that the dominant electrode process involves the CO_3^{2-} ion or some species with which it is in equilibrium.

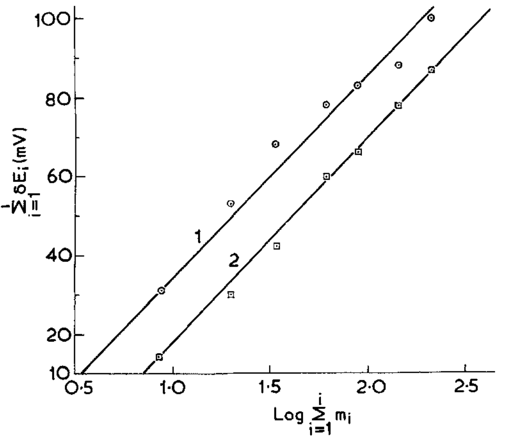

Fig. 6. Variation of e.m.f. with carbonate concentration in chloride melt at 970 K.

The linearity of the plots in Fig. 6 is of interest. Assuming the reaction at the test electrode to be: $C + 3O^{2-} = CO_3^{2-} + 4e$, then from the Nernst equation,

$$e = e^0 + \frac{RT}{4F} \ln \left[\frac{(CO_3^{2-})}{(C)(O^{2-})^3} \right].$$

It can be readily shown that the above linearity requires that the oxygen ion activity, in addition to carbon activity, be kept constant, specifically under these conditions:

$$\frac{\partial E}{\partial \ln \Sigma m_i} = \frac{\partial E}{\partial \ln [CO_3^{2-}]} = + \frac{RT}{nF},$$

assuming carbonate concentration $[CO_3^{2-}]$ is proportional to activity (CO_3^{2-}). The oxide ion activity may have been buffered by an oxide film on the iron electrode or on the stainless steel containment vessel in the present case. Interestingly, equating the slope of the lines in Fig. 6 with (RT/nF) gives $n = |3{\cdot}8| = 4$.

4.4. *Micropolarization test*

The current-voltage (i.e. displacement of voltage from equilibrium, or 'over-potential' η) curve shown in Fig. 7 for a low carbon electrode at 970 K typifies the results obtained. The curve is linear with no discontinuity at the origin, where $i = o = \eta$, i.e. where the cell voltage is equal to its open circuit equilibrium value. This implies that the electrode reaction determining the electrode potential is reversible, proceeding in either direction depending on the direction of current flow. A linear relationship between over-potential and current at small over-potentials is predicted by the theory of electrode kinetics.

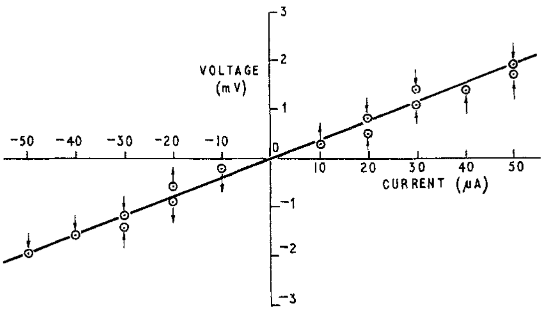

Fig. 7. Micropolarization test at 970 K. Points approached from high and low currents as shown.

5. Conclusions

(1) The cell

$$\alpha\text{-Fe,C} \,|\, CO_3^{2-} \,|\, \alpha\text{-Fe,C}_{sat}$$

functions as a carbon concentration cell at 970 K; with one iron electrode in the form of a thin membrane, the cell can monitor changes in carbon activity of carbon species in both liquid sodium and argon.

(2) The predominant reaction at the α-Fe,C$|CO_3^{2-}$ electrode is apparently reversible, involving C and CO_3^{2-} species or species with which they are in equilibrium.

(3) The results provide a basis for future quantitative studies; in particular, it should be possible to correlate carbon activities obtained from e.m.f. values and those calculated from CO/CO_2 mixtures simultaneously equilibrated with the iron membrane.

Acknowledgement

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