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SHORT COMMUNICATION

I. A chronopotentiometric study of iron in LiCl-KCl

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1. Introduction

The chemistry and electrochemistry of the compounds of iron in fused salts have not been extensively investigated. In an early study using $AlCl_3$–NaCl melts at 300° C, Delimarskii *et al.* [1] obtained two electrochemical reduction waves for Fe(III) ions, presumably successively to Fe(II) and Fe metal. Laitinen and Pankey [2], working with LiCl–KCl and platinum working electrodes at 400° C did not observe an electrochemical reduction wave for the step $Fe(III) + e \rightarrow Fe(II)$. The absence of the wave was explained in terms of the *chemical* reduction of Fe(III) ions by platinum. The model separation of the main components of the mineral (spinel) chromite in the form of a mixture of the oxides (FeO and Cr_2O_3) has been investigated [3]. The work described in this short communication formed part of the preliminary study of the chemistry and electrochemistry of the compounds of the component elements in molten LiCl–KCl. The main work on chromium itself has already been published [4].

2. Experimental

The apparatus and the procedure have been described in detail elsewhere [5]. Measurements were carried out in the temperature range 400° C –500° C.

3. Results and discussion

The Fe(II) ions were prepared *in situ* by anodic dissolution of the metal at a current density of 5×10^{-3} A cm^{-2} [5]. The electroreduction of these Fe(II) ions on a polished flat tungsten cathode gave rise to one chronopotentiometric wave. A typical chronopotentiogram is shown in Fig. 1. Measurements were made in the concentration range of $0{\cdot}399 \times 10^{-2}$–$3{\cdot}190 \times 10^{-2}$ mol l^{-1} at 500° C. The Sand's plots for $\tau^{1/2}$ versus $1/I$ (see, for example, Fig. 2) were straight lines which passed through the origin. (The small positive deviation at the larger transition times probably arises from the influence of convective mass transfer.) It was also noted that the quarter-time potentials ($e_{\tau/4}$) were virtually constant over the range of current densities employed. The plots of electrode potential versus $\log(\tau^{1/2} - t^{1/2}/\tau^{1/2})$ rather than versus $\log(\tau^{1/2} - t^{1/2}/t^{1/2})$ (Fig. 3) were linear. The slopes ranged from 76–82 mV per decade, corresponding to '*n*' values between 1·87 and 2·01 for various concentrations and applied currents. Thus the cathodic process is probably $Fe^{2+} + 2e \rightarrow Fe$ (solid). The values obtained for the diffusion coefficient are shown in Table 1.

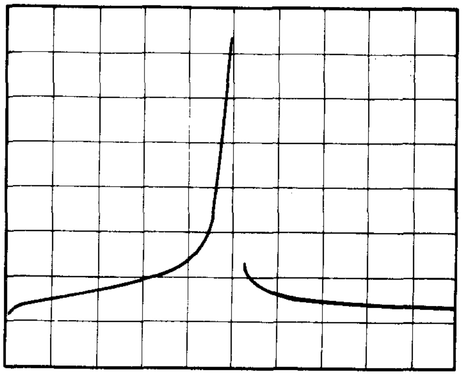

Fig. 1. Chronopotentiogram of cathodic reduction of Fe(II) in LiCl–KCl eutectic at 500° C; $i = 0{\cdot}2642$ mA; $Fe(II) = 1{\cdot}598 \times 10^{-2}$ mol l^{-1}; $x = 0{\cdot}5$ s cm^{-1}; $y = 100$ mV cm^{-1}; Micro electrode area (Tungsten) = 3·15 mm^2.

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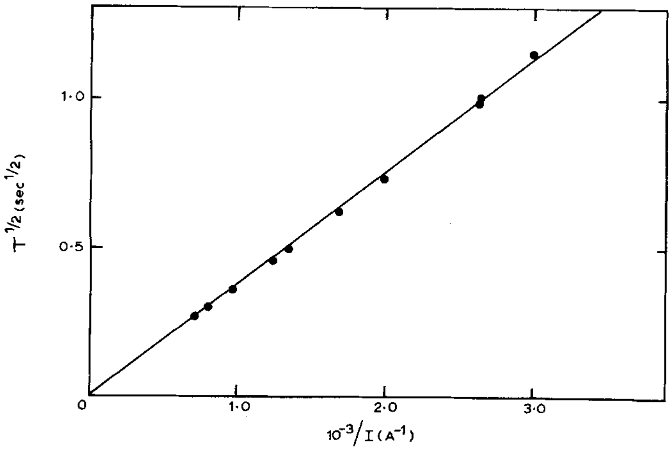

Fig. 2. Fe(II) ions in LiCl–KCl eutectic; Sand's Plot. Fe(II) = $1{\cdot}598 \times 10^{-2}$ mol l^{-1}; micro electrode area = $3{\cdot}15$ mm^2.

These results indicate that the electrochemical reduction of Fe(II) ions in the melt studied, under all conditions, is a diffusion-controlled process. This is in accord with the results of Poignet and Barbier [6] although the values for the diffusion coefficient of Fe(II) in LiCl–KCl are not in agreement (these authors cite a value of $1{\cdot}0 \times 10^{-5}$ cm^7 s^{-1} at 450° C).

In accordance with the potentiometric results reported by Jones [7], additions of fluoride ions up to concentrations of $0{\cdot}16$ mol l^{-1}, to melts containing $3{\cdot}190 \times 10^{-2}$ mol l^{-1} of Fe(II) ions, had no effect either on the equilibrium electrode potential or the chronopotentiograms. This indicates that fluoride ions do not form complexes with Fe(II) ions in this melt.

Attempts were made to obtain chronopotentiograms for the anodic oxidation of Fe(II) to Fe(III), using gold working electrodes which are more noble than those (platinum) employed by Laitinen and Pankey [2]. Examples of the results are shown in Figs. 4 (500° C) and 5 (400° C). At 500° C, there is no sign of a wave at potentials less positive than the anodic limit (gold dissolution/chlorine evolution). Although at 400° C, it was possible to obtain a poorly-defined anodic wave, it must be admitted that this result is rather perplexing as the anodic transition time observed is very much less than that expected on the basis of $D_{\mathrm{Fe}^{2+}}$ (determined *cathodically* in this work) and the other parameters of Sand's equation. Presumably the 400° C result is a less extreme example of the observation for 500° C, namely because of the volatility/instability of the product Fe(III) (this decomposition reaction may be catalysed by the electrode surface), the electrode process which would give rise to the chronopotentiometric wave is unpoised and therefore the potential changes directly to the anodic limit (gold dissolution/chlorine evolution). At 400° C,

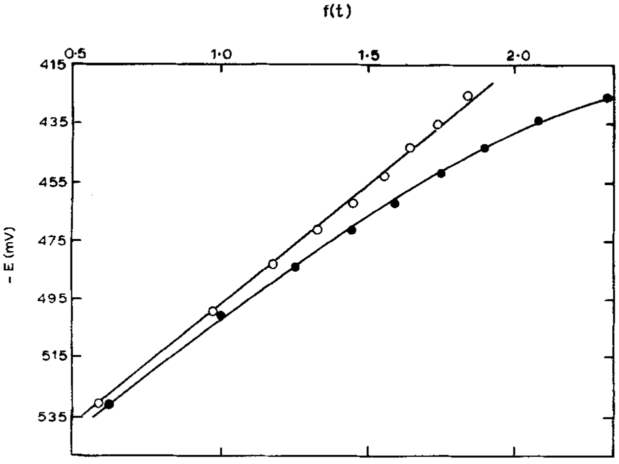

Fig. 3. Fe(II) ions in LiCl–KCl eutectic; Fe(II) = $1{\cdot}598 \times 10^{-2}$ mol l^{-1}; $\tau = 244$ ms.
○ $f_1(t) = [2 + \log(1 - t^{1/2}/\tau^{1/2})]$;
● $f_2(t) = [2 + \log(\tau^{1/2}/t^{1/2} - 1)]$;
$[\partial E/\partial f_1(t)] = 82$ mV.

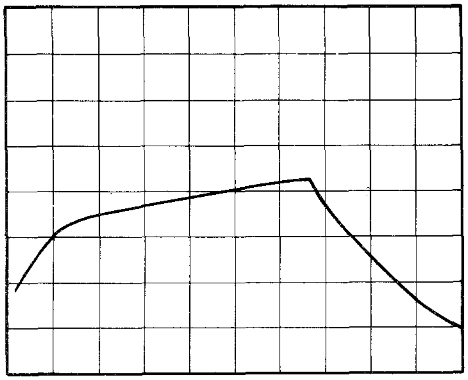

Fig. 4. Chronopotentiogram of anodic oxidation of Fe(II) in LiCl–KCl eutectic at 500° C; $i = 0{\cdot}5948$ mA; Fe(II) = $1{\cdot}440 \times 10^{-2}$ mol l^{-1}; $x = 0{\cdot}02$ s cm^{-1}; $y = 200$ mV cm^{-1}; micro electrode area (gold) = 7·9 mm^2.

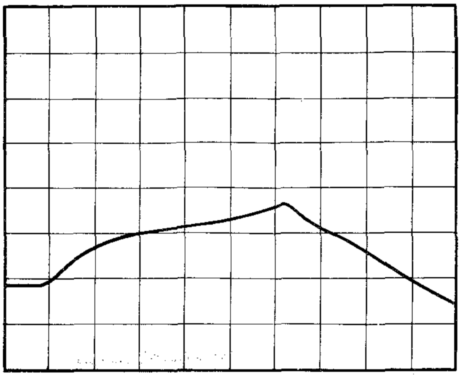

Fig. 5. Chronopotentiogram of anodic oxidation of Fe(II) in LiCl–KCl eutectic at 400° C; $i = 1{\cdot}038$ mA; Fe(II) = $1{\cdot}440 \times 10^{-2}$ mol l^{-1}; $x = 0{\cdot}005$ s cm^{-1}; $y =$ 200 mV cm^{-1}; micro electrode area (gold) = 7·9 mm^2.

it may just be possible for some 'transient poising' to take place before this occurs.

The *quantitative* anodic oxidation of melt containing Fe(II) on a graphite rod electrode at a current density of 5×10^{-3} A cm^{-2}, produced highly-coloured (reddish-brown) solutions although the colour of the melt became fainter with time. This was attributed to the formation of, albeit unstable, solutions of Fe(III) ions. Thus the open-circuit potential of the graphite electrode, which should correspond to the redox potential of the Fe(III)–Fe(II) couple, was not stable and slowly decreased with time. Cathodic chronopotentiograms (of these reddish-brown solutions) obtained using a gold working electrode were not reproducible. All these effects were more marked at 500° C than at 400° C as expected if the volatility of $FeCl_3$, as well as its tendency to decompose, increases with temperature. The extrapolated value of ΔG^0 calculated for the reaction $FeCl_3(s) \rightarrow FeCl_2(s) + 1/2\, Cl_2(g)$ at 500° C is -2 kcal [8]. Iwanec and Welch [9] gave the value $\Delta G^0 = +4{\cdot}5$ kcal for the same reaction, $FeCl_3(l) \rightarrow FeCl_2(l) + 1/2\, Cl_2(g)$, at 700 K. Thus $FeCl_3$ does not appear to be thermodynamically very stable at the working temperature. In order to suppress the decomposition reaction, a graphite rod was held at a sufficiently anodic potential to produce chlorine evolution in a melt containing Fe(III) ions at 500° C. Under these conditions, a yellow deposit, which was shown to be $FeCl_3$, appeared on the water-cooled head of the cell following its volatilization from the melt.

Table 1. Divalent iron in LiCl–KCl eutectic at 500° C: diffusion coefficients

Concentration (× 10^2) (mol l^{-1})	*Diffusion coefficient* ($D \times 10^5$) (cm^2 s^{-1})
0·399	2·16 ± 0·04
1·598	2·08 ± 0·10
2·399	2·13 ± 0·09
3·190	2·26 ± 0·20

Obviously further work on the anodic oxidation of Fe(II) in chloride melts is necessary, preferably using vitreous carbon working electrodes to avoid any possibility of product/electrode reactions.

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