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Cathodic polarization of pure iron in concentrated alkaline solution

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The potentiostatic pulse method was used to study the electrochemical evolution of hydrogen on polycrystalline iron electrodes in concentrated KOH solutions. It was found that in pure KOH solutions there appeared to be two reaction mechanisms for hydrogen evolution, one at high the other at low overpotentials. The addition of Li^+, at constant hydroxide ion concentration, altered the kinetic parameters of these two mechanisms. Furthermore in pure LiOH only one reaction mechanism for all overpotentials was observed.

1. Introduction

Of the negative electrodes which may be used in alkaline cells, the iron electrode is of especial interest due to its reasonable energy density and economic advantages.

It has long been known that the addition of LiOH to the electrolyte adds stability to, and prolongs the life of, alkaline cells. However, little work has been reported concerning the participation of the Li^+ ion in the electrode reaction. Foester [1] has suggested that the mechanism involves adsorption of Li^+ on the 'oxide active material' present on the electrode surface.

There has also been some inconsistent evidence reported concerning the nature of the products produced at the electrode surface. Faust [2] reported that the iron was converted directly to $Fe(OH)_3$, while Faizullin, Kochmann and Turashev [3] favoured conversion via $Fe(OH)_2$ to $Fe(OH)_3$. More recently, Fe_3O_4 and FeOOH have been identified by X-ray diffraction after complete oxidation [4, 5], but the mechanism has remained unsolved. Labat, Jarrousseau and Laurent [6], using the dissolution-precipitation theory of Flerov and Pavlova [7], have postulated that the oxidation of iron to $Fe(OH)_2$ and magnetite takes place in two stages involving the intermediate formation of the soluble species $HFeO_2^-$ and FeO_2^-.

In the present experiments, it was decided to investigate:

(i) The effects of OH^- concentrations using KOH solutions.

(ii) The effects of the addition of various concentrations of LiOH solutions to the electrolyte, keeping the OH^- concentration constant.

(iii) The results of reducing the holding potential* to a value within the likely oxidation/reduction region as defined by a potential sweep.

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[*] The holding potential was that potential applied to the cell from which all pulsing was made.

2. Experimental

2.1 *Electrolytic system*

The cell used has been described previously [8].

2.2 *Electrode pretreatment*

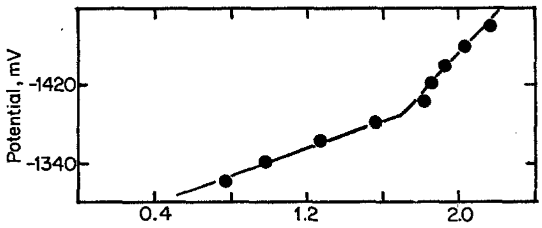
The electrode was constructed from 99·999% iron wire ($3{\cdot}14 \times 10^{-2}$ cm^2) supplied by Johnson Matthey Co. The electrode was first polished on roughened glass and then electropolished in 20:1 glacial acetic acid/70% perchloric acid for 10 seconds [9].

2.3 *Electrical equipment*

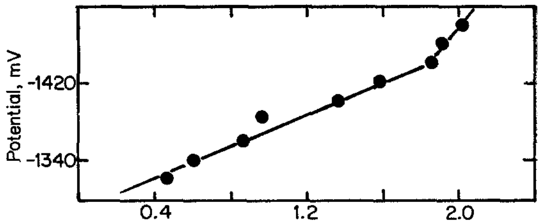
Cyclic potential sweep [10–11] and potentiostatic pulse [12] experiments were made using a potentiostat (Chemical Electronics, Type TR70–2A) and ancillary equipment. Transients were recorded photographically from an oscilloscope (Hewlett-Packard 130C). All potentials are quoted versus S.C.E.

3. Results

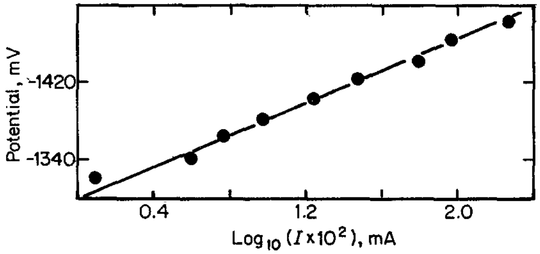
For 4·25 M KOH solutions, a typical cyclic potential sweep experiment, starting from −1380 mV, showed oxidation peaks at −1142, −955 and −595 mV, and a reduction peak at −1280 mV (Fig. 1). In contrast, using 4·5 M LiOH solution, the reduction peak was produced at a more positive potential of −1248 mV (Fig. 1). In order to ensure that as little oxide as possible was present on the electrode surface, it was decided that pulsing should start from a holding potential of −1300 mV.



(a) 6 mol l^{-1} KOH



(b) 3.5 mol l^{-1} Li$^+$ in 5.0 mol l^{-1} OH$^-$



(c) 4.5 mol l^{-1} LiOH

Fig. 2. Tafel plots of evolution rate as a function of potential. Electrode area (geometric) = $3{\cdot}14 \times 10^{-2}$ cm^2.

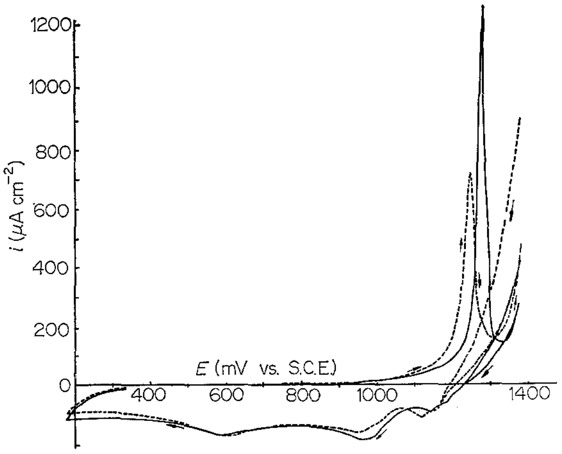


Fig. 1. Potentiodynamic sweep curve for pure iron. (———) in 4·25 M KOH. (– – – –) in 4·5 M LiOH. Sweep rate 20 mV sec^{-1}.

Current-time transients had an initial steeply-falling region extending for 0·4 ms followed by a horizontal linear region which was extrapolated to zero time. In this case (a slow reaction and therefore not limited by solution mass transport) no advantage was obtained by plotting i versus $t^{\frac{1}{2}}$.

Fig. 2a shows a typical Tafel plot of the hydrogen currents at zero time as a function of potential. Two linear portions are evident, one at potentials more negative than about −1400 mV,

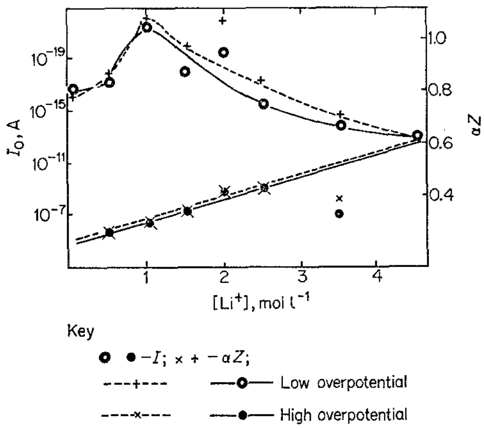


Fig. 3. I_0, αZ versus [Li⁺].

the other at potentials positive to this value. Apparent exchange currents obtained by extrapolating each of these linear regions back to the reversible potential are shown in Fig. 3.

The addition of LiOH modified the twin slopes of the Tafel plots (Fig. 2b) and thus changed the values of apparent exchange current, I_0, and transfer coefficient, α. The effect of using pure 4·5 M LiOH (Fig. 1c), was markedly different from that using the KOH solution. In this case only one Tafel slope was observed. An attempt was made to repeat these observations using a more positive holding potential, but it was found that, due to the distorted *i-t* curves produced (Fig. 4), extrapolations of the current to zero time were not valid.

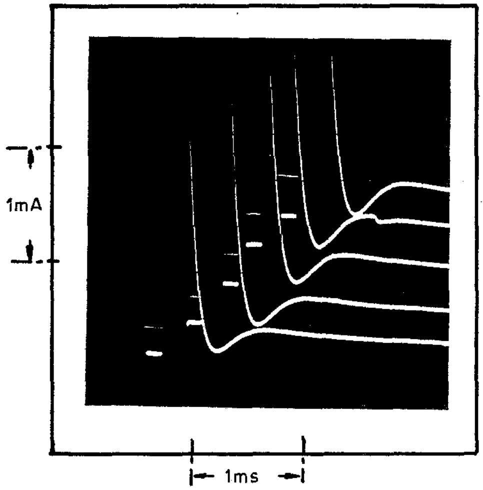


Fig. 4. *I–t* transient on pulsing potential from −1000 mV into h.e.r. region. Vertical scale; *I* (0·45 mA cm⁻¹). Horizontal scale: *t* (0·45 ms cm⁻¹).

However, some qualitative observations were made at this more positive potential of −1·1 V. The results showed that the distortion seems to increase with time at 1·1 V when using 4·5 M LiOH solution but there was little change when using 5 M KOH solution.

4. Discussion

4.1 *Potential sweeps*

Cyclic sweep results (Fig. 1) obtained in this investigation in pure KOH solutions, compare well with those found by Labat, Jarrousseau and Laurent [6].

Similar results were obtained with 4·5 M LiOH, but the reduction peak was broader and the peak potential 32 mV more positive than that for the KOH electrolyte.

The results suggest that the Li^+ initially hinders formation of the oxides but allows their reduction at more positive potentials. It is likely that the lithium ions are preferentially absorbed on to the electrode surface thereby hindering oxide growth. In addition the ions could be incorporated into the growing oxide layer.

4.2 *Tafel plots*

The inclusion of Li^+ in the KOH electrolyte apparently produced a considerable change in the kinetics of the hydrogen evolution reaction (h.e.r.). The effect of increasing the proportion of the Li^+ is both important and fundamental. Plots of exchange current, I_0 and αZ against Li^+ concentration are shown in Fig. 3.

At less negative potentials −1300 to −1400 mV, a maximum in αZ, and a corresponding minimum in I_0, occurs at approximately 1 M Li^+ concentration before a more general trend towards the values obtained for 4·5 M LiOH is obtained. It is evident that there is an initial decrease in the h.e.r. rate followed by a subsequent increase as Li^+ concentration is increased at constant total OH^- concentration. An explanation would be that at low Li^+ concentrations its presence alters the oxide-solution interfacial structure and hinders hydrogen evolution. As the Li^+ concentration is increased this ion becomes incorporated into the defect oxide lattice. The resultant increase in electronic conductivity allows the hydrogen evolution rate to rise.

At more negative potentials -1400 to -1480 mV, the electrode surface is assumed to be covered with little or no oxide. It is found that, in this case, there is a steady decrease in the h.e.r. rate. This may be explained using the Volmer-Heyrovsky [13–14] mechanism, where an essential intermediate in the h.e.r. is adsorption of hydrogen on to the electrode surface. The Li^+ would then be preferentially adsorbed on to the surface and thus inhibit the h.e.r.

The measured value of I_0 in pure 4·5 M KOH calculated from Figure 3 was $6{\cdot}3 \times 10^{-4}$ A cm^{-2}. This is considerably higher than the previously observed values of Bockris *et al.* [15] of $8{\cdot}7 \times 10^{-7}$ A cm^{-2} in 0·1N NaOH and 1×10^{-8} A cm^{-2} in 6 M KOH [16]. This may be compared with a directly determined value of I_0, using LiOH-free KOH, of $\sim 10^{-7}$Acm^{-2}; however, it should be noted that results of experiments with LiOH-free systems were subject to much more dispersion than those containing Li^+. Further work is required to resolve these differences but previous values are from steady state measurements using mechanically polished specimens in [16] and with doubts expressed by the authors on the stability of the overpotential values in [15].

4.3 *Altering holding potential to a more positive value* ($-1{\cdot}0$ V)

It was found that extrapolations of the linear portion of the transient were not valid due to a distortion. The formation of this distortion is probably a function of the reduction of the oxides on the surface. In the case of 4·5 M LiOH the growth of this hump appears to be a function of time. This may again be explained by the Li^+ incorporating into the oxide lattice.

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