

## An insight into the self-discharge of $\text{Fe}_3\text{O}_4$ electrodes in alkali solutions

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**Abstract.** Iron oxide development is necessary as the Iron electrodes exhibit high self discharge and poor charging efficiency in alkaline batteries. Pressed electrodes containing electrolytic iron powder with varying amounts of  $\text{Fe}_3\text{O}_4$  have been used. The variation of open circuit potential and self discharge currents with alkali concentration is followed. For better understanding of these variations, cyclic polarisation ( $-1.3$  V to  $+0.4$  V vs Hg/HgO) and hydrogen evolution studies are carried out. Beyond  $-0.5$  V vs Hg/HgO, the surface is covered by hydrolysed layer and the protons diffuse away from this layer. The hydrogen evolution takes place with the discharge of  $\text{K}^+$  ions as the rate determining step.

**Keywords.** Corrosion; cyclic voltammetry; iron oxide electrodes.

### 1. Introduction

The electrochemical behaviour of iron oxide is extensively researched in strong alkaline media because of its practical applications in alkaline Ni–Fe accumulators (Galushko *et al* 1960, 1961; Flerov *et al* 1964, 1965; Lishanski *et al* 1982; Falk and Salkind 1969). Iron oxide added to sintered iron electrode was found to increase reversibility with increasing  $\text{Fe}_3\text{O}_4$  content, the mixed potential shifted towards noble direction and was attributed to the depolarisation of  $\text{Fe}(\text{OH})_2$  to  $\text{FeOOH}$  (Paruthimal Kalaigyan *et al* 1987). The behaviour of iron oxide electrodes in presence of various dopants was already reported (Micka and Zabransky 1987). When magnetite was mixed with copper, the electrode exhibited 90% efficiency in strong alkali but the capacity is limited on discharge (Labat *et al* 1970). The present work deals with the self discharge behaviour of  $\text{Fe}_3\text{O}_4$  electrodes in 0.1 to 10 M KOH solutions.

### 2. Experimental

The pressed iron oxide electrodes were prepared by mixing electrolytic iron powder with varying amounts of  $\alpha\text{-Fe}_3\text{O}_4$ . The electrode was in the form of a pellet of 10 mm diameter and 3 mm thickness and prepared by pressing the mix at  $2.1\text{--}3.5 \times 10^3$  kgm<sup>2</sup>. The pellets were pressed into teflon sockets and electrical connections were made. The details of the electrode preparation and composition are given (table 1).

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Table 1. Composition of iron electrodes.

Electrode	Composition (%)		
	Fe	Fe <sup>2+</sup>	Fe <sup>3+</sup>
Fe	91.1	—	—
Fe + 10% Fe <sub>3</sub> O <sub>4</sub>	92	4	3
Fe + 30% Fe <sub>3</sub> O <sub>4</sub>	78	12	9
Fe + 40% Fe <sub>3</sub> O <sub>4</sub>	69	16	12

Triangular potential sweep voltammetry was carried out on these electrodes in a three electrode cell assembly using BAS (Model 100A). Potentiodynamic polarisation had been carried out from the open circuit potential (100 mV/s) and  $E - \log i$  curves were obtained. The potentials were measured using Hg/HgO electrode as reference electrode and no corrections were made for liquid junction potentials. Various mixtures (6 M KOH + YMKCL with 0.1 M <Y> 0.5 M) were used to study the reaction order with respect to K<sup>+</sup> ion for hydrogen evolution reaction.

### 3. Results

The open circuit potentials for pressed iron and iron oxide electrodes varied with time and became steady after sometime (30 min). The variation of steady open circuit potential with KOH concentration is presented (figure 1). The potential becomes more noble with increase in alkali concentration and Fe<sub>3</sub>O<sub>4</sub> content in the electrode. For 10 M KOH solution, the steady state values for iron electrode (without Fe<sub>3</sub>O<sub>4</sub>) lie in the passive region. A linear relationship with a slope of 180 mV per decade concentration of KOH is observed for iron and found to decrease with oxide content.

The self discharge current increases with alkali concentration for iron while increase of Fe<sub>3</sub>O<sub>4</sub> content decreased it. Negligible discharge was found to occur at higher KOH concentration (table 2).

In order to understand the significance of self discharge or corrosion currents, detailed investigation was carried out.

#### 3.1 TPSV studies

When polarised from -1.3 to 0.4 V vs Hg/HgO for the pressed iron, the forward scan revealed a peak at -0.662 V(I) and a broad peak at -0.146 V(II) while the reverse scan exhibited three peaks at -0.052 V(III) at -0.5 V(IV) and -1.02 V(V) respectively (figure 2). The scan rate increased the charge flowing under the peak and at the scan rate above 20 mVs<sup>-1</sup>, cathodic peak at -0.052 V disappeared. Zero current crossing potential (ZCP) occurred at -0.7 V in the forward scan and at -0.2 V in the reverse scan.

Introduction of Fe<sub>3</sub>O<sub>4</sub> changed the electrochemical spectrum. On 10% Fe<sub>3</sub>O<sub>4</sub> electrodes in the forward scan, anodic peaks appear at -0.85 V(I), -0.672 V(II), -0.51 V(III) and -0.380 V(IV) while the reverse scan presented a shoulder around -0.760 V(V) and a sharp peak at -1.02 V(VI) followed by hydrogen evolution

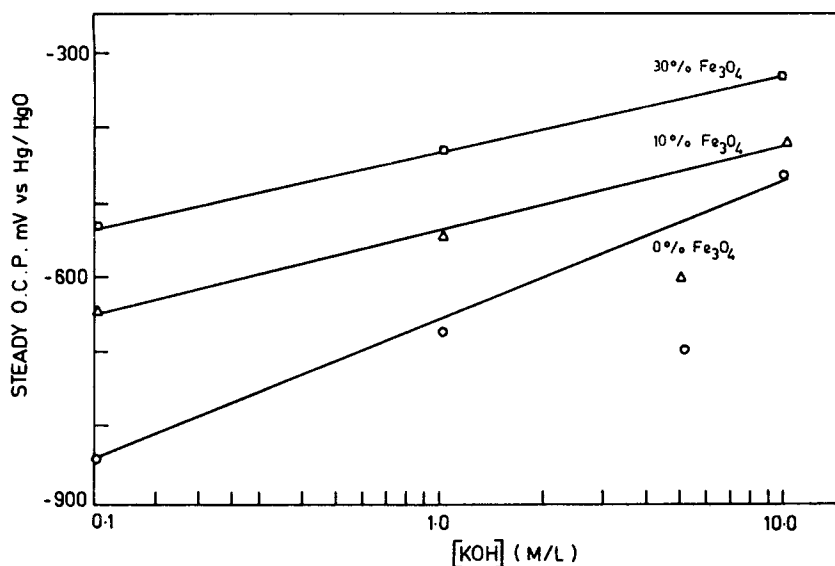


Figure 1. Variation of steady OCP values with KOH concentration.

Table 2. Variation of corrosion current with oxide content.

Electrode	Corrosion (self-discharge) current (A)			
	0.1 N	1.0 N	6.0 N	10.0 N
Fe	$10 \times 10^{-3}$	$27 \times 10^{-3}$	$34 \times 10^{-3}$	$29 \times 10^{-3}$
Fe + 10% $Fe_3O_4$	$8.5 \times 10^{-3}$	—	$1.7 \times 10^{-3}$	$0.5 \times 10^{-3}$
Fe + 30% $Fe_3O_4$	$3 \times 10^{-3}$	$0.7 \times 10^{-3}$	$2 \times 10^{-3}$	$1.2 \times 10^{-3}$
Fe + 40% $Fe_3O_4$	$2 \times 10^{-3}$	$1.6 \times 10^{-3}$	$0.2 \times 10^{-3}$	—

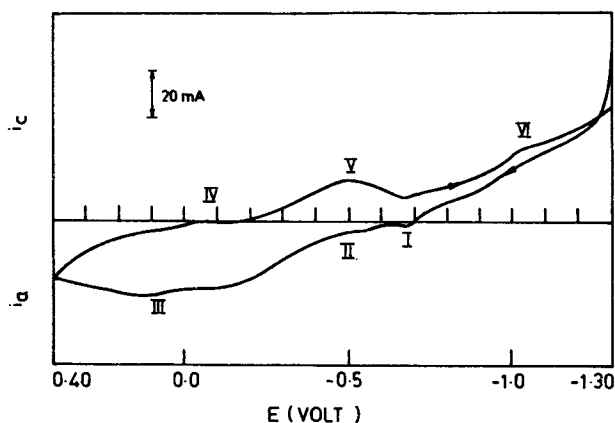


Figure 2. Cyclic voltammetric curves for pressed iron in 6.0 M KOH,  $E_{\lambda,c} = -1.30$  v;  $E_{\lambda,a} = 0.4$  v;  $v = 5$  m Vs $^{-1}$ .

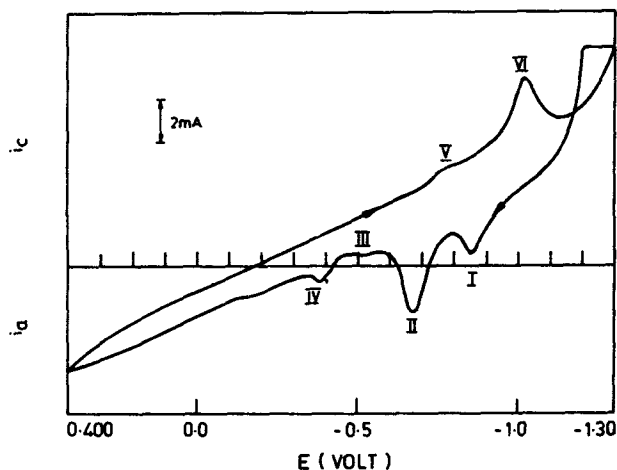


Figure 3. Cyclic voltammetric curves for pressed iron + 10%  $\text{Fe}_3\text{O}_4$  in 6.0M KOH,  $E_{\lambda,c} = -1.3$  v;  $E_{\lambda,a} = 0.4$  v;  $v = 5$  m  $\text{Vs}^{-1}$ .

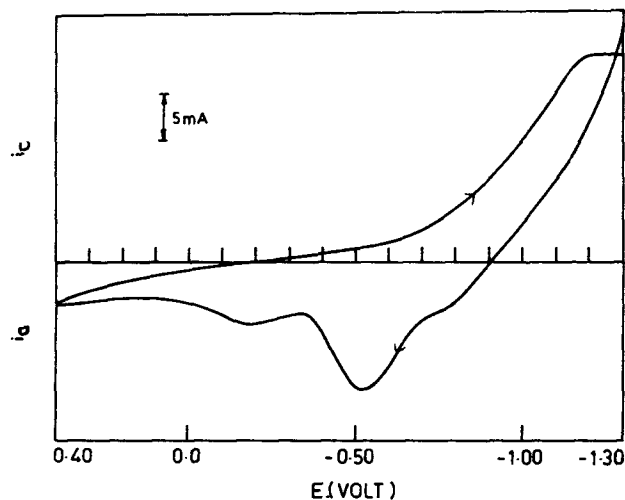


Figure 4. Cyclic voltammetric curves for pressed iron + 10%  $\text{Fe}_3\text{O}_4$  in 6.0M KOH,  $E_{\lambda,c} = -1.3$  v;  $E_{\lambda,a} = 0.4$  v;  $v = 5$  m  $\text{Vs}^{-1}$ .

(figure 3). With increase of sweep rate, all the peak potentials shifted towards noble direction. At sweep rate above  $20$  m  $\text{Vs}^{-1}$ , there is no cathodic peak and the anodic peak at  $-0.672$  V is found to shift in the noble direction where as the peak (III) disappeared (figure 4). ZCP occurred at  $-0.9$  V in the forward scan while it was observed at  $-0.3$  V in the reverse scan.

Increase of oxide content beyond 10% exhibited (figure 5) a large peak at  $0.0$  V(I) with a sharp increase in current beyond  $0.1$  V. The reverse scan displayed a shoulder at  $-0.25$  V(II) and a peak at  $-0.4$  V(III). Near hydrogen evolution a broad peak was observed at  $-1.2$  V. Increase of sweep rate decreased the cathodic peak current while the anodic peak completely disappeared.

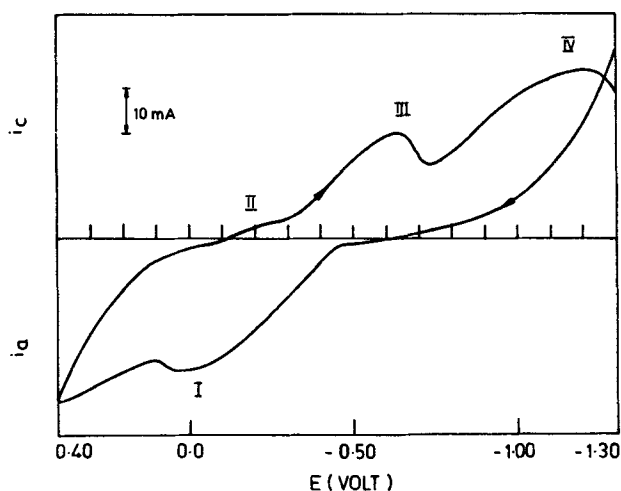


Figure 5. Cyclic voltammetric curves for pressed iron + 40%  $Fe_3O_4$  in 6.0 M KOH,  $E_{\lambda,c} = -1.3$  v;  $E_{\lambda,a} = 0.4$  v;  $v = 2$  m  $Vs^{-1}$ .

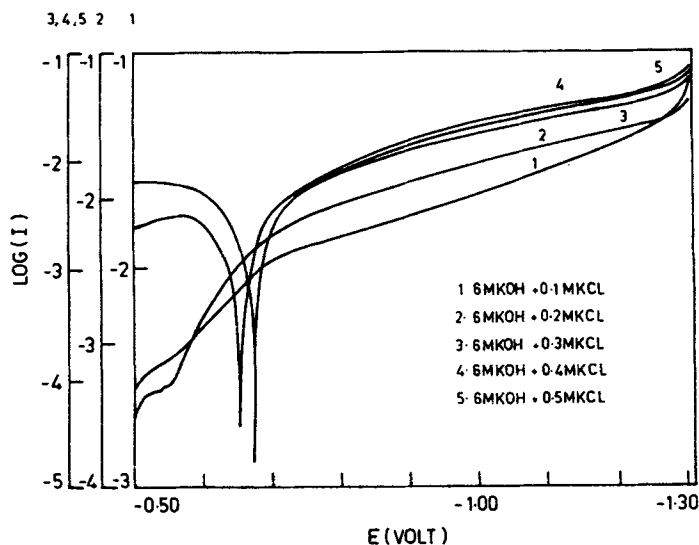


Figure 6.  $E - \log i$  plot for pressed iron in 6.0 M KOH containing different concentrations of KCl—(1) 0.1 M, (2) 0.2 M, (3) 0.3 M, (4) 0.4 M and (5) 0.6 M.

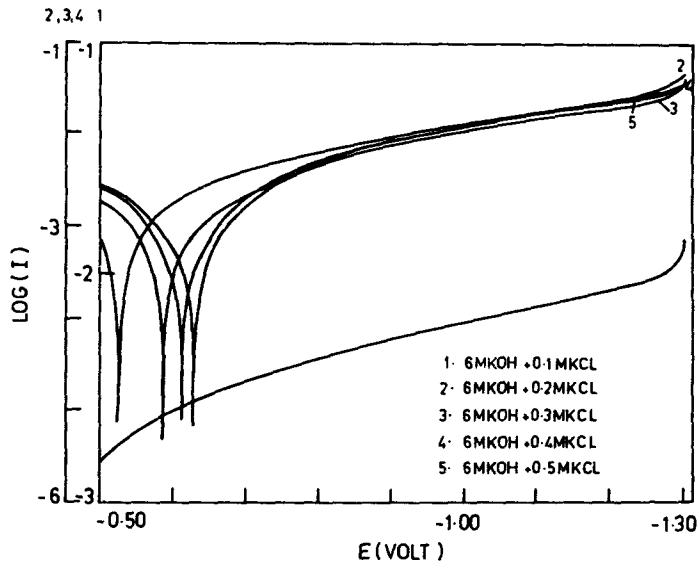
### 3.2 $E - \log i$ studies

For better understanding the significance of steady open circuit potentials, anodic and cathodic potentiodynamic polarisation studies were made. The investigation of mechanism of hydrogen evolution requires the measurement of cathodic current density at constant potential as a function of  $K^+$  ions and water activity.

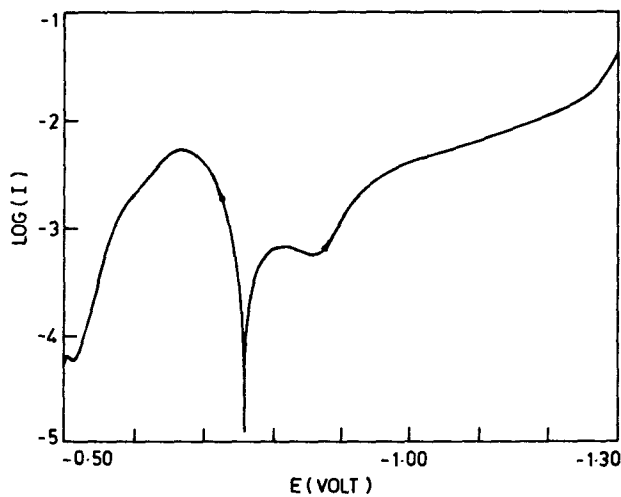
Figure 6 presents the  $E - \log i$  curves for pressed iron in 6 M KOH solution containing various KCl concentrations. KCl concentration in solution has no effect on the cathodic current beyond  $-1.0$  V. The cathodic Tafel slope for hydrogen

evolution (obtained in the potential range  $-1.10$  V to  $-1.30$  V) was found to be  $120$  mV/decade in the KOH range  $0.1$  M to  $1.0$  M KOH.

In  $10\%$   $\text{Fe}_3\text{O}_4$  electrode, single anodic and cathodic segments were found. Below  $6$  M KOH, a bend appeared around  $-0.86$  V (figure 7) in the cathodic curve. Increase of KCl concentration increased the cathodic current. Only above  $6$  M KOH two separate segments appeared in the cathodic polarisation curve. A  $30\%$  iron oxide electrode in  $10$  M KOH solution exhibited two distinct cathodic peaks at  $-0.67$  V



**Figure 7.**  $E - \log i$  plot for pressed iron +  $10\%$   $\text{Fe}_3\text{O}_4$  in  $6.0$  M KOH containing different concentrations of KCl, numbered as in figure 6.



**Figure 8.**  $E - \log i$  plot for pressed iron +  $30\%$   $\text{Fe}_3\text{O}_4$  in  $10.0$  M KOH  $E_{1,a} = -0.5$  v;  $E_{2,c} = -1.3$  v.

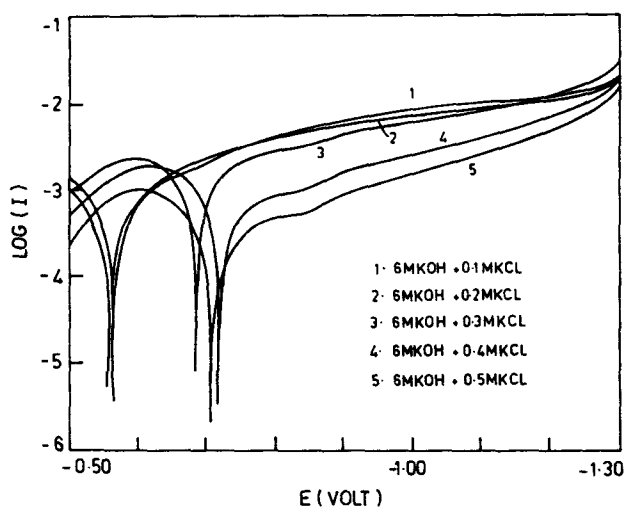


Figure 9.  $E - \log i$  plot for pressed iron + 30%  $Fe_3O_4$  in 6.0 M KOH containing different concentrations of KCl, as in figure 6,7.

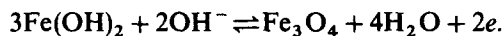
and  $-0.86$  V (figure 8). Increase of KCl concentration in solution decreased the cathodic currents beyond  $-1.0$  V (figure 9).

#### 4. Discussion

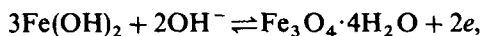
The voltammetric behaviour and the oxidation and reduction processes occurring on an iron electrode surface in alkaline media is reviewed recently (Cerny and Micka 1989). The oxidation of iron proceeds in two steps the first of which is



The second oxidation step of the iron electrode involves the formation of  $\delta$ -FeOOH and further to magnetite on cycling (Teplinskaya *et al* 1964).

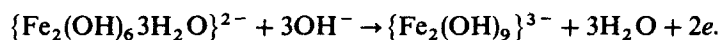


According to Dibrov *et al* (1980) magnetite appears in hydrated form



The hydrated magnetite is less stable than natural magnetite and it can be well reduced before the evolution of hydrogen. The cyclic sweeping between the switching potentials of  $-1.3$  and  $-0.5$  V on sintered iron and 10% iron oxide electrodes showed that at  $-0.5$  V the surface is covered by  $Fe_3O_4 \cdot H_2O$  (Muralidharan and Veerashunmugamani 1985; Paruthimal Kalaignan *et al* 1987).  $Fe_3O_4$  formation is due to the transformation of  $\beta$ -FeOOH via  $FeO_2^-$ , a soluble Fe(III) species. The appearance of peaks beyond

– 0.5 V at pH14 and the corresponding reduction peaks were discussed earlier (Burke and Lyons 1986). It was assumed to be due to a Fe(II)/Fe(III) transition in a polymeric hydrous oxide layer formed initially by hydration of the outer regions of the Fe(OH)<sub>2</sub>. The process involved may be represented as follows:



The composition of the oxidised state suggested is similar to that of gold. Water acts as a base to Fe<sup>2+</sup> ions and also as an oxidising agent to Fe. This is due, not only to the relative energies of the filled and empty orbitals, but also to their large energy separation which prevents their orbitals from interacting with each other. Anodic polarisation leads to the hydration of iron ions due to lowering of the Fermi level of Fe. The hydration of iron ions results from the frontier orbital interaction due to the configurational coordination of water molecules which act as Lewis bases around iron ions which act on a Lewis acid leading to the formation of bonding and anti-bonding molecular orbitals. The valence electrons of water occupy the bonding orbitals and a stable aquo complex of metal ion is formed (Sato 1989).

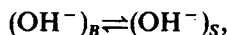
The appearance of peaks on iron at – 0.146 V(III) and – 0.52 V(IV) may belong to the redox process of this hydrous oxy species.

The appearance of a cathodic peak at – 0.500 V(V) may be due to the reduction of FeOOH to Fe(OH)<sub>2</sub>. This process is assumed to take place in the compact film close to the metal (Burke and Lyons 1986). Further reduction of Fe(OH)<sub>2</sub> to Fe takes place along with hydrogen evolution.

On the inclusion of 10% Fe<sub>3</sub>O<sub>4</sub>, earlier appearance of peak (III) (figure 2) suggests that the oxide favours the oxidation of Fe(II) to Fe(III). Specific adsorption of anion on α-FeOOH is known (Sigg and Stumm 1980, 1981) and it resembles a surface complex on a metal oxide. The appearance of a single broad anodic peak on oxide electrodes may be due to the oxidation of a species found on the surface which undergoes subsequent reduction in the reverse scan and hydrogen evolution takes place along with the reduction of divalent oxides to iron.

Increase of Fe<sub>3</sub>O<sub>4</sub> increases the ferric content (table 1) in the mixture and on α-Fe<sub>2</sub>O<sub>3</sub> not only the chemisorbed water molecules but also the physisorbed molecules are utterly immobile even with any intra molecular rotation hindered. These water molecules can be considered as “frozen” on the surface of the oxide. The actual picture of oxide solution interphase is complex. The physisorbed water molecules may be bound to positive sites probably through the oxygen atoms, water molecules may be hydrogen-bonded to neutral surface sites. Water molecules can be bound to two OH<sup>–</sup> groups. Doubly hydrogen bonded molecules on oxides are also known (Schindler *et al* 1976). The structure of hydrous films on iron is not known. It is shown that (Muralidharan 1988) on electrodeposited Ni(OH)<sub>2</sub> and nickel oxy hydroxides, the electrocatalytic activity can be explained in terms of the existence of hydrous layer. The dual transport of H<sup>+</sup> ions from the interior of the film and OH<sup>–</sup> ions from the solution into the solid phase is inferred.

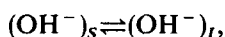
On anodic polarisation of OH<sup>–</sup> ions move towards the film/solution interface.



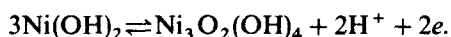
where *B* is the bulk of solution and *S* is the surface of the film. Depending on the local electrical field and thickness, diffusion of OH<sup>–</sup> ions from the surface to some site



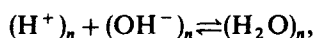
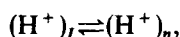
in the interior of the film.



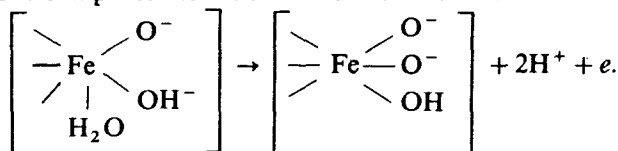
where  $I$  is some site in the interior of the film. On oxidation  $Ni(OH)_2$  releases a proton.



The protons released from the interior of the film diffuses to a site where it combines with an  $OH^-$  ion to form water.



where  $n$  is the neutralisation site. As the oxidation proceeds the neutralisation site moves towards the solution side. The progress of the neutralisation site ceases as it reaches the solution phase. Similarly on an iron oxide surface, with increase of potential, loss of protons from coordinated water molecules can take place. Protons being smaller can penetrate the film and move towards the solution,



The negative charge is neutralised by the presence of  $K^+$  ions in the film. The corresponding replacement of co-ordinated water (Paruthimal Kalaignan *et al* 1987) by  $OH^-$  was earlier envisaged. Replacement by anion of  $H_2O$  or  $OH^-$  group on the first coordinated shell of metal complexes are known. The slow changes of pH in aqueous  $Fe_2O_3$  suspensions is due both to the ion exchange mechanism and also partly to a diffusion of protons in the solid phase of the hydrated  $Fe_2O_3$  (Blok and deBrugn 1970).

**Hydrogen evolution reaction:** On solid iron electrodes in alkaline solutions it was found earlier (Paruthimal Kalaignan *et al* 1985) that  $Fe + H_2O + e \rightarrow Fe \cdot H_{ads} + OH^-$  is the slow step. The observed 120 mV/decade on pressed iron electrode and independency of cathodic current on  $K^+$  ion concentration ( $-1.1$  to  $-1.3$  V) suggests that (figure 10)  $K^+$  ion is not undergoing a discharge on the iron electrode.

When cathodically polarised the 10% iron oxide exhibited a peak at  $-0.86$  V and two distinct cathodic segments in solutions above 6 M KOH. The trivalent oxides undergo successive reduction to divalent oxides and then to iron. Hydrogen evolution takes place above  $-1.1$  V.

Iron oxide electrodes adsorb alkali metal ions from alkaline solutions (Ahmed 1969). For hydrated ferric oxide the isoelectric point in KCl is 8.6 (PZc of the oxide) and 6 M KOH solutions have ( $pH > 14$ )  $OH^-$  ions from the solution as a first step would neutralise the surface  $H^+$  ions to form water molecules which are initially adsorbed on the surface.

The  $K^+$  ions from the solution subsequently replace the water molecules and specifically adsorb on the oxide. This "specifically" adsorbed  $K^+$  ion (should not be misunderstood in terms of specific adsorption on metal) undergoes reduction.

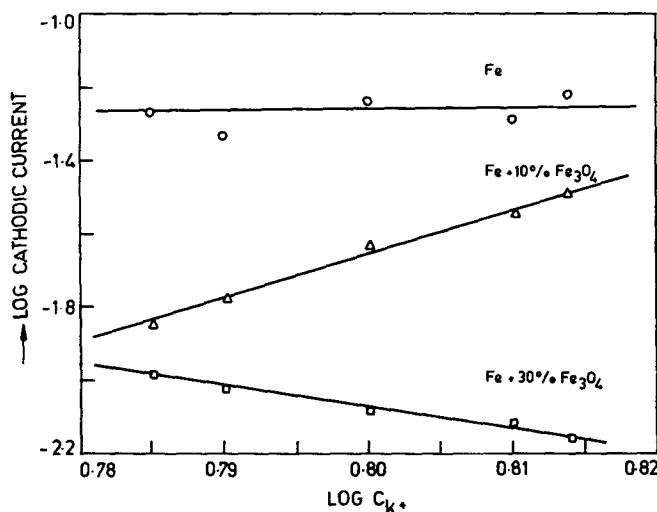
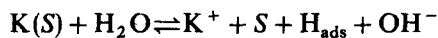
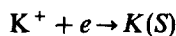


Figure 10. Variation of log cathodic current density with log  $K^+$  ions concentrations at constant  $OH^-$  (6.0 M KOH) at  $-1.1$  V for different electrodes.

On zinc and tin, hydrogen evolution reaction involves the discharge of alkali metal ions as the slow step from alkali solutions (Muralidharan and Rajagopalan 1978; Thangavel *et al* 1982). The observed 120 mV/decade and  $\{d \log i_c / d \log C_{K^+}\} = 0.98$ .

On 10%  $Fe_3O_4$  electrodes suggest that  $K^+ + e \rightarrow K(S)$  where (S) is the oxide surface site.



The negative dependence of cathodic current on  $K^+$  ions (slope of  $-0.5$ ) on 30%  $Fe_3O_4$  electrodes may be due to (i) the fact that with increase of  $K^+$  ion concentration, there is decrease in  $\Delta G^\circ$  for the specific adsorption of  $K^+$  ions in  $KNO_3$  solution (Ahmed 1969, 1972) and the adsorption of  $K^+$  ions becomes increasingly difficult with increasing  $K^+$  ion concentration; (ii) There may be a decrease in effective negative potential on the inner Helmholtz plane i.e. the potential which the  $K^+$  ion encounters as it approaches the surface due to the previous surface coverage by  $K^+$  ion or a repulsive potential between adsorbed  $K^+$  ions and the  $K^+$  ions about to be adsorbed.

The observed decrease in self discharge or corrosion with increase of  $Fe_3O_4$  content and  $OH^-$  ion concentration may be due to decrease in exchange current density of hydrogen evolution.

## 5. Conclusions

$Fe_3O_4$  electrode surface, beyond  $-0.5$  V, is found to be covered by hydrolysed layer and proton diffusion away from this layer is inferred. Reduction of these oxides takes place along with hydrogen evolution. Hydrogen evolution proceeds with these oxides

with the discharge of  $K^+$  ions. Increase of  $Fe_3O_4$  content decreases the cathodic current because of the repulsion of specifically adsorbed  $K^+$  ion.

### Acknowledgement

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