

## SHORT COMMUNICATION

**Mechanisms of the discharge of porous-iron electrodes in alkaline medium**

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Received 18 August 1992; revised 1 December 1992

**1. Introduction**

The alkaline iron electrode forms the anode in both nickel-iron and iron-air secondary batteries. The iron electrode reaction in alkaline medium proceeds in two steps. The first step involves conversion of iron metal to  $\text{Fe}(\text{OH})_2$  which transforms to  $\delta\text{-FeOOH}$  during the second step. In the literature [1–5], several potentiostatic and galvanostatic polarization, as well as rotating disc, measurements have been conducted on the alkaline-iron electrode reaction in these two steps and it has been shown that, while the first step proceeds via a dissolution-precipitation process, the second step involves a solid-state mechanism. In this study we have measured steady-state, open circuit potentials (o.c.p.'s) at various state-of-charge (s.o.c.) values of porous-iron electrodes both with and without sulphide additives and have inferred that these measurements indicate the mechanisms involved during the two discharge steps of the alkaline iron electrode.

**2. Experimental details**

Iron electrodes were prepared as described elsewhere [6]. Iron oxalate was vacuum decomposed at  $500^\circ\text{C}$  and the resulting iron and magnetite powders (80 wt %) were mixed mechanically with appropriate amounts of graphite (10 wt %), polyethylene powder (9 wt %) and metal sulphide ( $\text{FeS}$  or  $\text{PbS}$  or  $\text{Bi}_2\text{S}_3$ ) additives (1 wt %). This mixture was hot pressed ( $118^\circ\text{C}$ ,  $125\text{ kg cm}^{-2}$ ) onto a degreased nickel grid to obtain porous iron electrodes of geometrical area  $2.8\text{ cm} \times 2.4\text{ cm}$  and thickness  $\sim 1\text{ mm}$ . The electrodes were subjected to continuous charge/discharge against nickel oxide counter electrodes positioned on both sides in 6 M KOH electrolyte containing 1 wt % LiOH, until their formation was complete. The temperature of the cell was maintained at  $27 \pm 1^\circ\text{C}$ .

The electrodes were discharged at a fixed current of 40 mA in flooded electrolyte (i.e. excess electrolyte) configuration over different intervals of time in both the discharge steps. Steady state, open-circuit potentials at different discharge intervals were recorded on a Philips PM-8043  $x-t$  Recorder against a pre-calibrated  $\text{Hg}/\text{HgO}$ ,  $\text{OH}^-$  (6 M KOH) reference electrode.

**3. Results and discussion**

Formation of the electrodes was found to be complete by the 35th charge-discharge cycle. The variations in the o.c.p. subsequent to the 10th charge-discharge cycle were within  $\pm 5\text{ mV}$  of the rest potential.

The steady state, open-circuit potential data as a function of s.o.c. values for iron electrodes, both with and without sulphide additives, are shown in Fig. 1. It is found that while little change is observed in the values of o.c.p. of the electrodes with decrease in their s.o.c. values in the first discharge step, there is a monotonic decrease in the o.c.p. values with the s.o.c. during the second step.

Under open-circuit conditions electrochemical reactions on porous alkaline-iron electrodes comprise the reversible iron electrode reaction, hydrogen evolution reaction, and oxygen reduction reaction; the respective reversible potentials ( $E^\dagger$ ) for these electrode reactions in 6 M KOH solution are  $-0.969\text{ V}$ ,  $-0.932\text{ V}$  and  $0.303\text{ V}$  ( $\text{Hg}/\text{HgO}$ ),  $\text{OH}^-$  (6 M KOH). The dissolution of atmospheric oxygen and its supply to the electrode surface by diffusion in the quiescent solution is a relatively slow process. Initially the electrolyte is also likely to be saturated with hydrogen. Therefore, the contribution from the oxygen-reduction reaction has been neglected. At state-of-charge close to unity, the contribution from the hydrogen evolution reaction (h.e.r.) is maximum, but decreases rapidly with decrease in s.o.c. value leaving the iron dissolution reaction to occur predominantly as the s.o.c. value approaches 0.9. The initial dip observed in the o.c.p. values of electrodes at s.o.c. about unity (i.e.  $\sim 1$ ) is due to the mixed potential arising from h.e.r. Although metal sulphide additives have been shown to affect the capacities of the iron electrodes [6–10], these seem to have little effect on the values of the open circuit potentials at various s.o.c. values in the first step. However, these additives do exhibit an effect in the second discharge step.

The o.c.p. data in the first step where iron-metal is in equilibrium with  $\text{Fe}^{2+}$ -ions ( $\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^-$ ) may be understood in the light of the behaviour of an electrode of the second kind, such as calomel. The rest potential of the electrode ( $E_1^\dagger$ ) can be represented as

$$E_1^\dagger = E_1^\circ - (RT/2F) \ln (a_{\text{Fe}}/a_{\text{Fe}^{2+}}) \quad (1)$$

where  $E_1^\circ$  is the standard potential,  $a_{\text{Fe}}$  and  $a_{\text{Fe}^{2+}}$  are the respective activities of the iron metal and  $\text{Fe}^{2+}$ -ions in the electrolyte, and  $R$ ,  $T$  and  $F$  have

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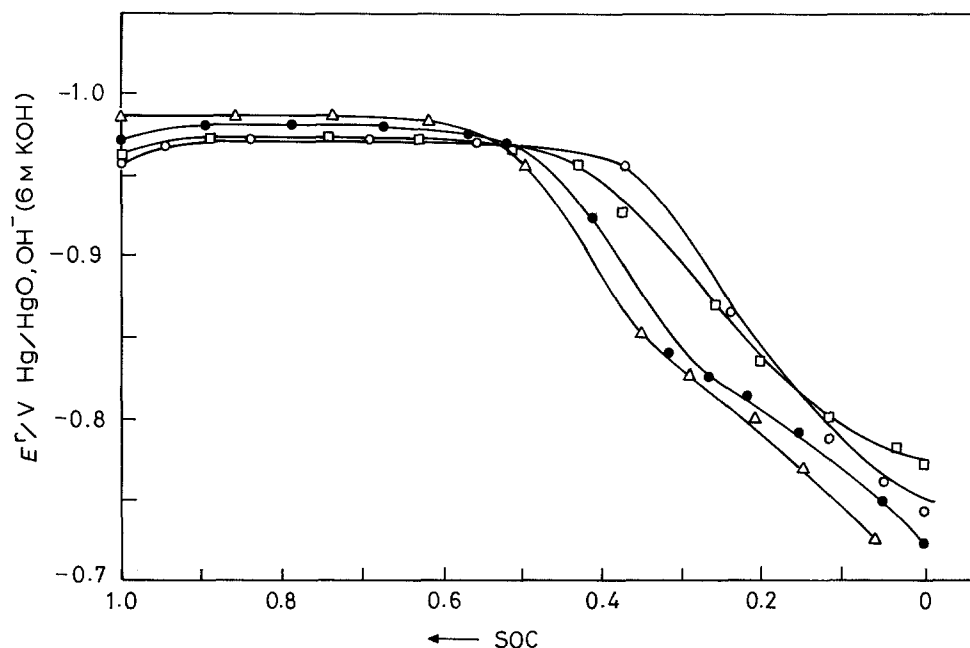


Fig. 1. Steady state, open circuit potentials at various states-of-charge for alkaline porous-iron electrodes both with and without sulphide additives during first and second discharge steps. Key: (O) no additive, (□) FeS-doped, (△) PbS-doped, (●) Bi<sub>2</sub>S<sub>3</sub>-doped.

their usual meaning. The overall reaction for the first discharge step may be written as  $\text{Fe} + 2\text{OH}^- \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{e}^-$ , with the solubility product of  $\text{Fe}(\text{OH})_2$ ,  $k_{\text{sp}} = a_{\text{Fe}} \cdot a_{\text{OH}^-}^2 = 1.65 \times 10^{-15}$  [11]. Consequently, Equation 1 may be written as

$$E_1^r = E_1^{\circ} - (RT/2F) \ln(k_{\text{sp}}/a_{\text{OH}^-}^2) \quad (2)$$

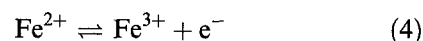
combining  $k_{\text{sp}}$  and  $E_1^{\circ}$  into a new constant  $(E_1^{\circ})'$  Equation 2 becomes

$$E_1^r = (E_1^{\circ})' + (RT/F) \ln a_{\text{OH}^-} \quad (3)$$

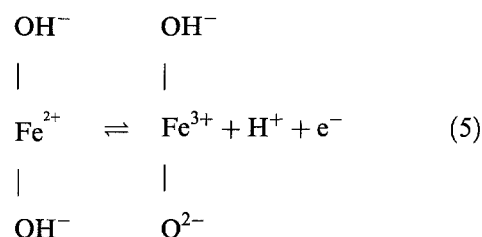
Since all the measurements were carried out in a concentrated (6 M KOH), as well as flooded, electrolyte and assuming that there is no electrolyte depletion within the electrode pores, the  $\text{OH}^-$ -ion concentration ( $a_{\text{OH}^-}$ ) may be considered to be virtually constant for all s.o.c. values and the corresponding rest potentials. This implies that the concentration of  $\text{Fe}^{2+}$ -ions is also constant at all s.o.c. values during the first step. This agrees with the experimental data. Thus the mechanism involved during this step is heterogeneous and proceeds through a dissolution-precipitation process.

During the second discharge step,  $\text{Fe}(\text{OH})_2$  is converted to  $\delta\text{-FeOOH}$  wherein  $\text{Fe}^{2+}$ -ions are oxidized

to  $\text{Fe}^{3+}$ -ions following the reaction



Alternatively, Equation 4 may be written



Reactions 4 and 5 may be compared to a redox electrode reaction with the difference that both the reduced and oxidized species exist in a dynamic equilibrium within the same solid phase. This situation is akin to the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  redox couple in the solid phase during the reduction of  $\text{MnO}_2$  to  $\text{MnOOH}$  in Leclanché cells [12]. Accordingly, the rest potential ( $E_2^r$ ) during this step may be expressed

$$E_2^r = E_2^{\circ} - (RT/F) \ln(a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}) \quad (6)$$

where  $E_2^{\circ}$  is the standard potential and  $a_{\text{Fe}^{3+}}$  is the concentration of  $\text{Fe}^{3+}$ -ions in the solution. Since the ratio  $a_{\text{Fe}^{2+}}/a_{\text{Fe}^{3+}}$  decreases continuously with

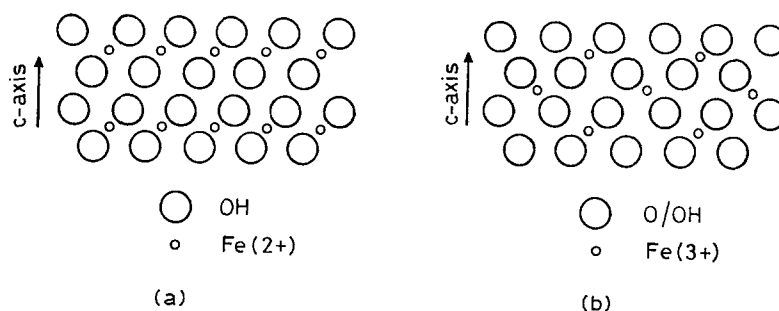


Fig. 2. Structures of (a)  $\text{Fe}(\text{OH})_2$  and (b)  $\delta\text{-FeOOH}$  [partly adopted from S. Okamoto, *J. Am. Ceram. Soc.* **51** (1968) 594].

discharge a concomitant change in rest potential occurs.

It is well known that rapid chemical oxidation of  $\text{Fe}(\text{OH})_2$  in alkali results in  $\delta\text{-FeOOH}$ , with a

structure consisting of hexagonally close-packed O/OH with  $\text{Fe}^{3+}$ -ions in certain interstices [13]. The structure of  $\delta\text{-FeOOH}$  is schematically shown in Fig. 2 and compared with  $\text{Fe}(\text{OH})_2$ . As this structural

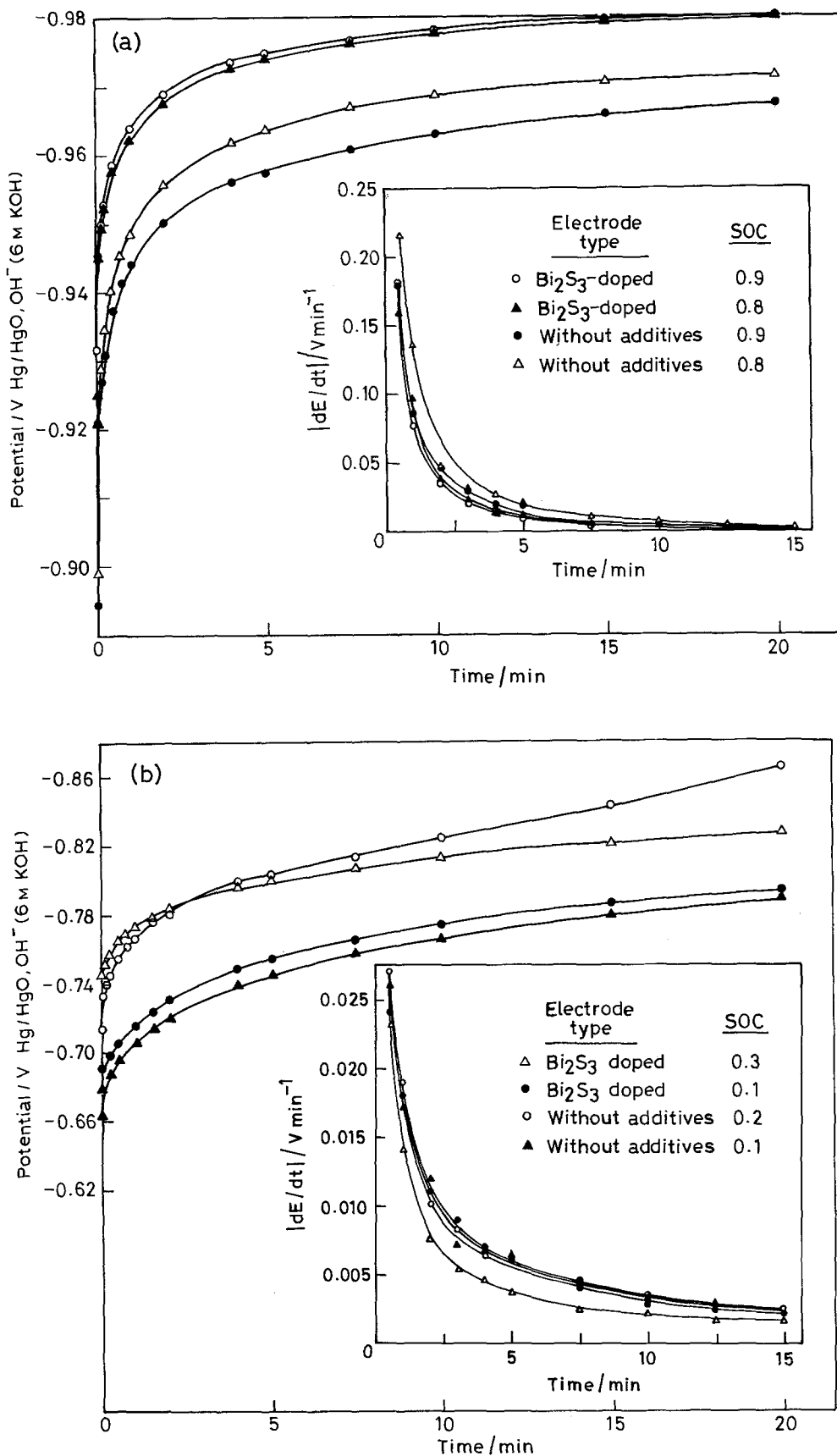


Fig. 3. Open circuit potential recovery transients for iron electrodes with  $\text{Bi}_2\text{S}_3$  additive and without additive in the first (a) and in the second (b) discharge steps. The rates of potential recovery,  $|dE/dt|$ , during the respective discharge steps are given in the insets.

transformation is a bulk feature, the mechanism involved during the second discharge step is homogeneous. Typical open circuit potential recovery transients both for an iron electrode with  $\text{Bi}_2\text{S}_3$  and an iron electrode without any additive at various state-of-charge values in the first and second discharge steps over a span of 20 min are shown in Fig. 3(a) and (b), respectively. It is obvious that the rate of potential recovery,  $|dE/dt|$ , is greater for the electrodes with s.o.c. values in the first step in relation to those of the second step. This agrees with the view that the bulk diffusion reactions are slower in relation to the surface processes.

#### 4. Conclusions

This study demonstrates that by measuring steady state, open circuit potentials of alkaline porous-iron electrodes as a function of state-of-charge, it is possible to determine the class of mechanisms involved during its discharge steps. It is inferred that, while the first discharge step is heterogeneous, the second step involves homogeneous solid-state oxidation of  $\text{Fe}(\text{OH})_2$  to  $\delta\text{-FeOOH}$ . As the measurements were made under equilibrium conditions, the conclusions are more reliable than those from polarization studies.

#### Acknowledgements

Thanks are due to Professor S. Sathyanarayana for helpful discussions. Financial assistance from the Department of Non-Conventional Energy Sources, Government of India, New Delhi is gratefully acknowledged.

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