Short Communication

Role of activation on the performance of the iron negative electrode in nickel/iron cells

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Abstract

Activated iron electrodes have been prepared by electrochemical impregnation with both mercury and sulfur. The performance of such electrodes in 10 A h nickel/iron cells has revealed that the activation exerts only a marginal influence on the discharge capacity. By contrast, ageing of the activated electrodes is harmful to discharge performance.

Introduction

The iron electrode employed in nickel/iron alkaline cells is receiving renewed attention due to the abundance of iron in nature, non-toxicity, inexpensive design and marginal cost. Iron electrodes have been prepared either by introducing additives into the iron powder before sintering or by incorporating additives after sintering by electrochemical methods [1, 2]. Sintered iron electrodes are 'activated' by cathodic treatment in alkali-sulphur solutions [3]. Chronopotentiometric and open-circuit potential recovery studies have revealed [4] that additions of mercury and sulfur benefit the electrode. In particular, these additives minimize [5] the self-discharge of the iron electrode. The present work investigates the charge/discharge behaviour of nickel/iron cells containing either sintered or activated sintered iron electrodes. The activation has been carried out by electrochemical impregnation of mercury and sulfur into sintered iron electrodes.

Experimental

Preparation of sintered iron electrodes
Loose-sintered iron electrodes ($16 \times 11 \times 0.2$ cm) were prepared using nickel-plated steel sheets as current collectors. Electrolytic iron powder of composition 99.95 wt.% Fe, 0.01 wt.% Pb, 0.008 wt.% Zn, 0.001 wt.% As, 0.025 wt.% Mn and 0.006 wt.% Cu was used. Before sintering at 1173 K for 1 h under hydrogen atmosphere, the

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electrolytic iron powder was mixed with various additives. The major additives in the active material were 10 wt.% iron oxide, 5 wt.% copper and 2 wt.% FeS. The minor constituents were 0.5 wt.% As_2O_3, 0.5 wt.% Sb_2O_3, 1 wt.% zinc and 0.1 wt.% acetylene black. The overall mixture of the active material after sintering produced iron plaque of porosity 60 to 70%.

Activation of sintered iron electrodes

Porous sintered iron electrodes were further treated cathodically in 6.0 M KOH solutions containing 3.2 g l^{-1} of elemental sulfur with 1.8 g l^{-1} of mercury salt by passage of a current of 10 mA cm^{-2} for 4 h at 303 K using stainless steel anodes. The incorporation of mercury takes place, along with sulfur, during the cathodic treatment.

Preparation of sintered nickel electrodes

Details of the preparation of loose-sintered nickel anodes have been presented elsewhere [6].

Charge/discharge studies

Nickel/iron cells of 10 A h capacity were assembled with a single iron electrode and a nickel electrode on either side. Prior to use, the activated electrodes were kept idle for 30 days for ageing. Three different types of iron electrodes were used, namely, loose-sintered unactivated, activated and aged electrodes. All the cells were charged at the C rate and discharged at C/50, C/35 and C/20 rates. During discharge, the potential of the iron electrode was monitored with a Hg/HgO reference electrode. All potentials are reported with respect to this electrode.

Reactivation of a dead electrode

After very deep discharge, the activated iron electrode was virtually dead and efforts to recharge it were unsuccessful. The dead electrode was reactivated by cathodic treatment in KOH solution containing both mercury and sulfur at a current density of 10 mA cm^{-2} for 14 h. The electrode was found to accept charge; its performance is discussed below.

Results and discussion

Performance of activated electrode

An ideal reversible battery requires the positive and negative plates to be electrodes of the second kind [7], i.e., a metal in contact with its sparingly soluble salt and a solution saturated with the salt. The reaction can be represented by:

$$O + X + ne^- \rightleftharpoons R + Y \tag{1}$$

where O and R are, respectively, the oxidant and the reductant present in the solid phase, and X and Y are species from the electrolyte. For the iron electrode, the storage (charge) reaction is:

$$Fe(OH)_2 + 2e^- \rightleftharpoons Fe + 2OH^- \tag{2}$$

During discharge, the slope of the open-circuit potential versus the state-of-discharge curve (E_- versus Q) should be zero in the absence of activation overpotential,

diffusion overpotential, internal resistance and other complications arising from the electrode design. (Note, E_- is used to denote the open-circuit potential of the negative electrode.) Figure 1 presents the potential versus delivered capacity curves for different iron electrodes. There is a rapid initial decrease in potential from -1030 to -920 mV due to oxidation of adsorbed hydrogen and partial oxidation of the iron surface [8, 9]. The change in potential (dE_-/dt), which is a measure of exchange current density of hydrogen evolution on iron, is found to be greater for aged, reactivated and unactivated electrodes than for the activated electrode. This is due to the incorporation of sulfur. It was shown earlier [5] that sulfur incorporation hinders the hydrogen evolution reaction by increasing the Fe–H bond energy. The appearance of a potential plateau around -910 ± 10 mV for these electrodes is due to the oxidation of iron to $Fe(OH)_2$. This region accounts for 50 to 60% of the capacity. The limiting region, from -875 to -800 mV, is due to the diffusion of OH^- ions inside the pores and other transport limitations. Table 1 presents values of dE_-/dQ at 50% state-of-
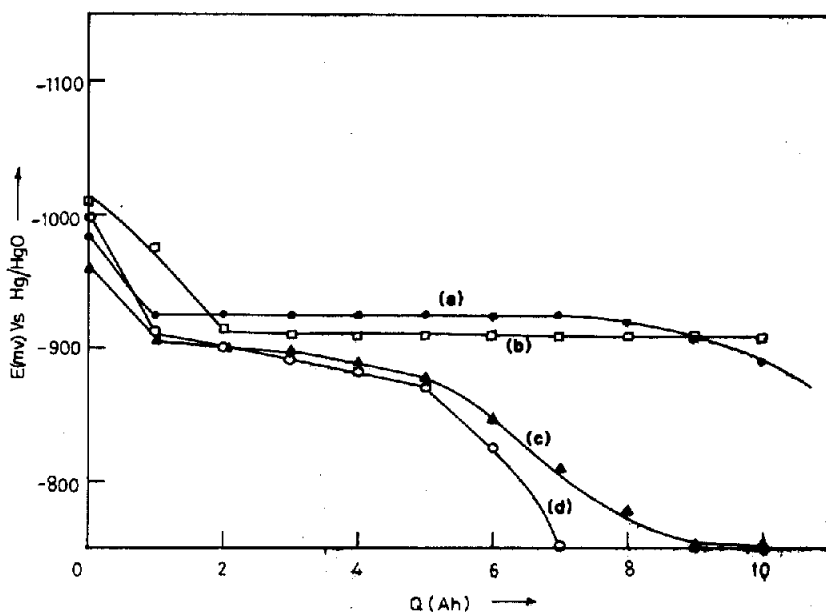

Fig. 1. Potential of iron electrode vs. delivered capacity for different iron electrodes: (a) unactivated; (b) activated; (c) reactivated; (d) aged-activated.

TABLE 1

Parameters derived from discharge curves for different iron electrodes at the C/25 rate

Electrode	dE/dQ $\times 10^{-6}$ (V C^{-1})
Unactivated	0
Activated	0
Reactivated	12.5
Aged-activated	24.3

charge. As mentioned above, an ideal electrode requires the value of dE_-/dQ to be zero. It can be seen, therefore, that both unactivated and activated electrodes exhibit better reversibility than reactivated and aged electrodes.

Performance of 10 A h nickel/iron cell

The discharge characteristics of cells using activated iron electrodes at different discharge rates (Fig. 2) reveal that the latter increase the dV/dQ at 50% state-of-discharge (Table 2). At high rates of discharge, this is due to: (i) the nucleation and growth of smaller nuclei of FeS at the mouth of the pores that causes an enhancement of overvoltage for iron oxidation; (ii) hinderance to the diffusion of OH^- ions inside the pores that, in turn, reduces the conductivity of the electrode.

At the $C/35$ rate, the discharge characteristics for different iron electrodes showed (Fig. 3), that dV/dQ at $Q = 50\%$ is greater for aged-activated and activated electrodes than for unactivated electrodes. This is because: (i) the oxidation of iron to FeS occurs before the formation of $Fe(OH)_2$; (ii) the porosity of the activated electrodes is less compared to unactivated electrodes. Ageing will cause surface oxidation of the iron and thus the electrodes will possess fewer pores than the other two electrodes. Activation
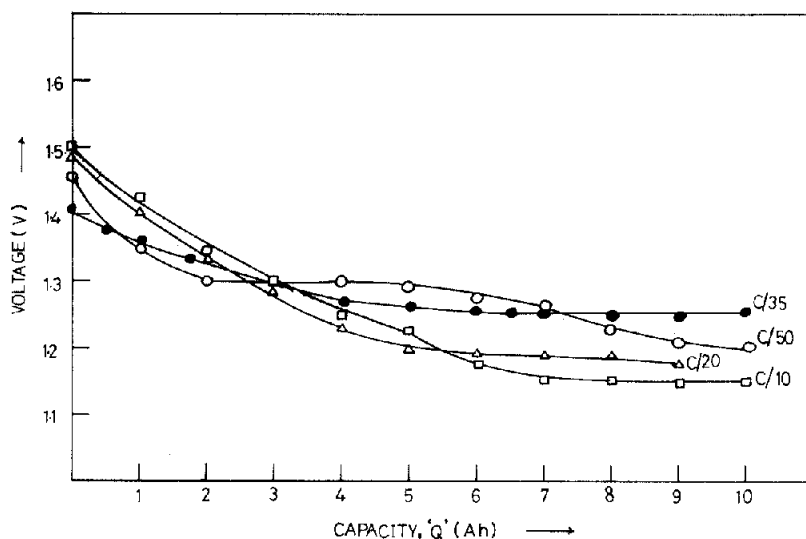

Fig. 2. Discharge behaviour of 10 A h nickel/iron cell at different discharge rates as shown.

TABLE 2

Parameters derived from discharge curves obtained at different discharge rates

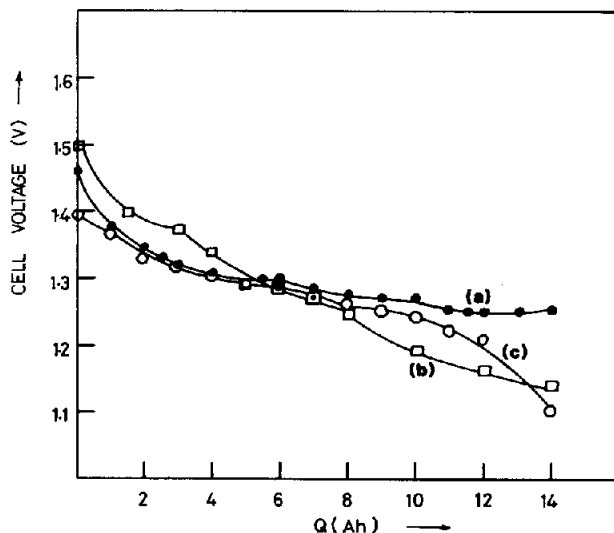| Discharge rate	dV/dQ $\times 10^{-6}$ (V C^{-1})
$C/50$	2.77
$C/35$	3.0
$C/20$	6.94
$C/10$	8.33

Fig. 3. Discharge characteristics of 10 A h cell at $C/35$ rate for different iron electrodes: (a) unactivated; (b) activated; (c) aged-activated.

TABLE 3

Parameters derived from discharge curves at the $C/35$ rate

Electrode	dV/dQ $\times 10^{-6}$ (V C^{-1})
Unactivated	2.7
Activated	3.0
Aged-activated	4.8

of the electrode exerted only a marginal influence on the dV/dQ value. By contrast, ageing nearly doubled the dV/dQ value (Table 3).

Polarity reversal of activated iron electrodes

The potential of the activated iron electrode was followed at the $C/25$ rate until the cell voltage became 0.2 V (Fig. 4). When the capacity has fallen to 3.2 A h, initial oxidation of the surface, along with ionization of adsorbed hydrogen, has taken place (region A). The complete conversion to divalent hydroxide has been accomplished (region B) when the capacity has fallen to 8.8 A h. Further drain of power causes the oxidation of divalent iron to a mixture of FeOOH and FeO (region C). At this stage, the iron electrode polarity is reversed, i.e., it becomes more active in the region D. The shift of the electrode potential to more negative values must be discussed in terms of the behaviour of the nickel electrode. When the cell voltage has declined to 0.2 V, the nickel electrode experiences a potential of about -0.9 V. At this potential, cyclic voltammetric studies [10, 11] on nickel and electrodeposited nickel hydroxide have revealed that nickel hydroxide is converted nickel. This corresponds to a situation where the nickel surface is covered by bare metal that is, itself, partially covered by
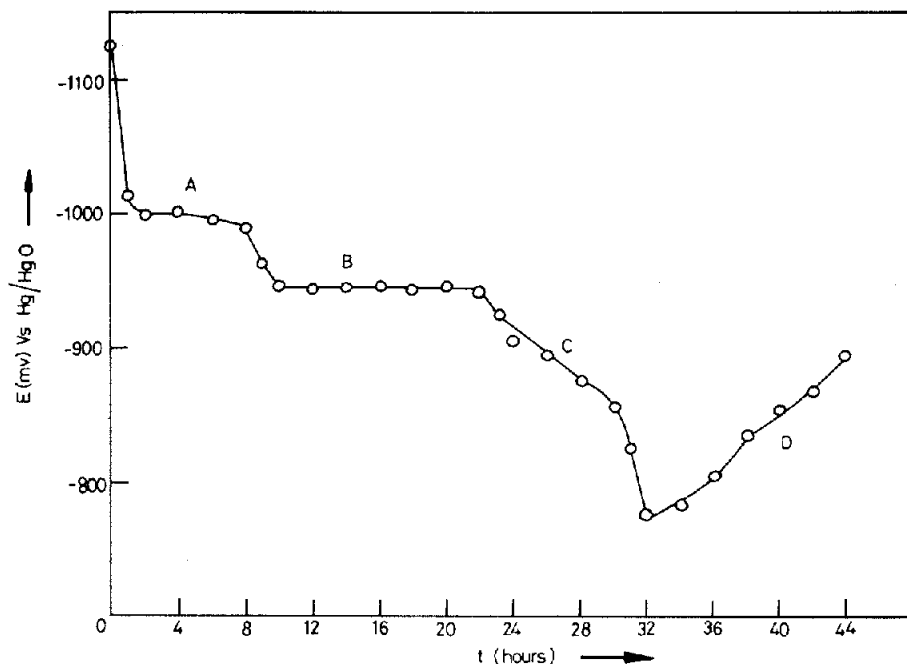
Fig. 4. Potential of the iron electrode vs. time for activated iron electrode discharged at $C/25$ rate.

divalent oxide. For a deeply discharged nickel electrode, it has been shown [12, 13] that the phase composition $0.125 \, NiO \cdot 0.875 \, Ni(OH)_2 \cdot 0.67 \, H_2O$ with a nickel valency of 2.25. The nickel surface is now completely dehydrated and protonated. This results in considerable reduction in both conductivity and capacity. Further discharge (> 12.8 A h) promotes the oxidation of nickel while the iron electrode undergoes the following reduction:

$$Fe_2O_3 + 2H^+ + 2e^- \rightleftharpoons FeO + Fe(OH)_2 \qquad (3)$$

This reaction causes the negative shift in the electrode potential.

Conclusions

Activation of iron electrodes by electrochemical impregnation of both mercury and sulfur marginally influences the capacity. On the other hand, ageing of activated electrodes is detrimental to performance.

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