

Short Communication

Open-circuit Potential-Recovery Transients of Alkaline Porous Iron Electrodes

K. VIJAYAMOHANAN, A. K. SHUKLA and S. SATHYANARAYANA*

Solid State and Structural Chemistry Unit and Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012 (India)

(Received November 5, 1986)

Open-circuit, potential-time transients during the discharge of alkaline porous iron electrodes at various states-of-charge have been studied. It has been possible to arrive at a correlation between the parameters of the self-discharge kinetics and the observed potential-recovery time constants. The study also provides a method of estimating state-of-charge of the rechargeable alkaline iron electrode.

The iron electrode reaction in alkaline media, *viz.*,



is of practical importance in the well known nickel/iron rechargeable battery as well as in the iron/air secondary battery under development [1, 2]. Major problems associated with the state-of-the-art of the alkaline porous iron electrode are: the high rate of self-discharge (especially at high ambient temperatures), and the low efficiency of utilisation of active iron (especially at low temperatures). In recent years, fundamental studies have been carried out into the effects of various additives or impurities on the kinetics of the iron electrode [3 - 5]. In this study, we have analysed the open-circuit, potential-time transients of alkaline porous iron electrodes at different states of charge and have arrived at a correlation between the parameters of the self-discharge kinetics and the observed potential-recovery time constants. The study also provides a means of estimating the state-of-charge (SOC) of the rechargeable alkaline iron electrode.

Statistically optimized, pressed-plate, iron electrodes were prepared as reported elsewhere [6]. In brief, a mixture of iron and magnetite powder obtained by thermal decomposition of ferrous oxalate blended with powdered graphite, polyethylene, and iron sulphide was hot-pressed on to a nickel grid. These electrodes were assembled with excess-capacity, sintered-nickel, positive electrodes to form nickel/iron cells. The electrolyte solution comprised 6 M KOH with 1 wt.% LiOH. The cells were subjected to charge/

*Author to whom all correspondence should be addressed.

discharge treatment at the $C/10$ rate for 25 cycles to stabilise the capacity prior to recording the open-circuit recovery transients at different SOC's.

The cells were given the same amount of overcharge, kept at open-circuit for 30 min, and then discharged with a constant current at the $C/10$ rate until the iron electrodes attained the required SOC. At this point, the discharge circuit was opened and the open-circuit potential of the iron electrode was measured against an Hg/HgO, 6 M KOH reference electrode provided with a Luggin capillary adjacent to the centre of the test electrode; all potentials are reported with regard to this reference electrode. The measured electrode potentials were accurate to ± 0.01 mV and were recorded using a Keithley-179 TRMS digital multimeter after backing-off a part of the potential difference with a Knick-S16 precision voltage source. An electrometric amplifier with unity gain and $10^{15} \Omega$ input impedance was interfaced between the digital multimeter and the test cell in order to minimise loading errors. All measurements were conducted with the cell placed in a thermostatically controlled bath held at $30 \pm 1^\circ \text{C}$.

The experiments were repeated at each SOC using at least three identically prepared, pressed-plate iron electrodes and fresh electrolyte solution. The SOC was calculated from the theoretical capacity for the first step of the iron electrode reaction (1).

The data for the open-circuit potential change with time at various SOC's reached during discharge of the porous iron electrode are shown in Fig. 1. It can be seen that the approach to equilibrium becomes increasingly sluggish as the SOC of the electrode is decreased. Indeed, at the lowest SOC

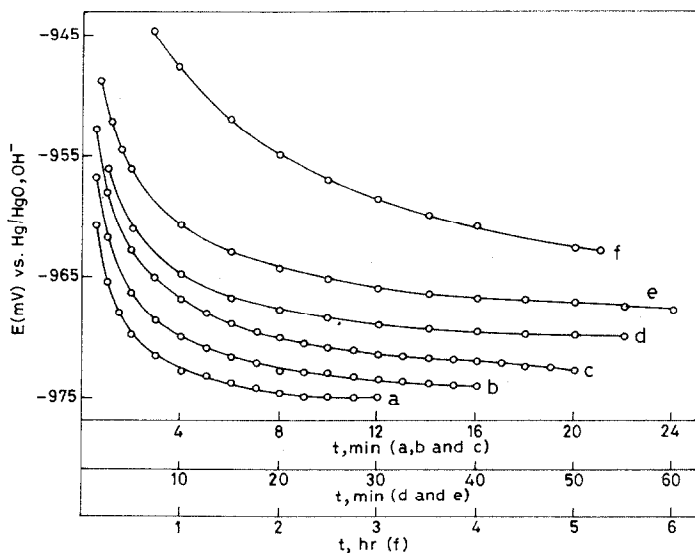
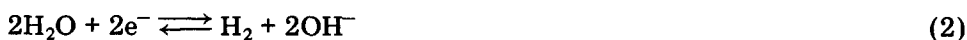


Fig. 1. Open-circuit, potential-time transients for an alkaline iron electrode at various SOC's: (a) 0.96, (b) 0.92, (c) 0.87, (d) 0.79, (e) 0.75, and (f) 0.67.

(curve (f)), equilibrium is not attained even after several hours at open circuit. This is probably because of the fact that at low SOCs, the surface of the grains of electrode material is enriched with the discharge products ($\text{Fe}(\text{OH})_2$, etc.), while active iron, if any, remains in the interior of the porous electrode. The diffusion and the redistribution of the active material from the interior of the grains are slower with increase in the depth of discharge and, hence, the equilibrium potential will be approached more slowly.

A theoretical analysis of the open-circuit, potential-recovery transient of the alkaline porous iron electrode may be developed as follows. The electrode reactions which could take place during open-circuit conditions on an active iron electrode are those of the reversible iron electrode, eqn.(1), the hydrogen electrode, eqn. (2), and the oxygen electrode, eqn. (3).



The reversible potentials (E^r) of the electrode reactions (1) - (3) in 6 M KOH solution are -0.975 V, -0.926 V and $+0.303$ V, respectively. On comparing these values with the experimental $E-t$ transients (Fig. 1), which span a region of about -0.95 V to -0.98 V, it follows that at potentials sufficiently positive to the E^r of reaction (1), the possible modes of charge consumption at the iron electrode on open-circuit are: (i) double-layer charging (or discharging); (ii) the anodic reaction of the iron electrode eqn. (1); (iii) the cathodic reaction of the hydrogen electrode, eqn. (2); (iv) the cathodic reaction of the oxygen electrode, eqn. (3). The latter may be ignored, as the supply of oxygen molecules to the electrode surface by diffusion is relatively slow. Thus, the iron electrode develops a mixed potential governed by the modes of charge consumption (i) - (iii).

From the above, it follows that the open-circuit transient in the absence of significant mass-transfer control (a justifiable assumption given the high KOH concentration and the fact that the SOCs are not too small compared with unity) may be written as:

$$-C \frac{dE}{dt} + I_{\text{cor}} [\exp -\alpha_c f(E - E_{\text{cor}}) - \exp \beta_m f(E - E_{\text{cor}})] = 0 \quad (4)$$

where: C is the double layer capacity; I_{cor} is the corrosion current at the iron electrode; E_{cor} is the corrosion potential (which is close to the final or equilibrium potential of the electrode); α_c is the apparent cathodic energy coefficient of reaction (2) on iron; β_m is the apparent anodic energy transfer coefficient of reaction (1); f is RT/F , when R , T and F have their usual meanings.

Linearisation of the exponential terms in eqn. (4) is not acceptable, since the data from Fig. 1 exhibit a strong non-linearity of dE/dt with E , as shown for a typical case in Fig. 2. On the other hand, integration of eqn. (4)

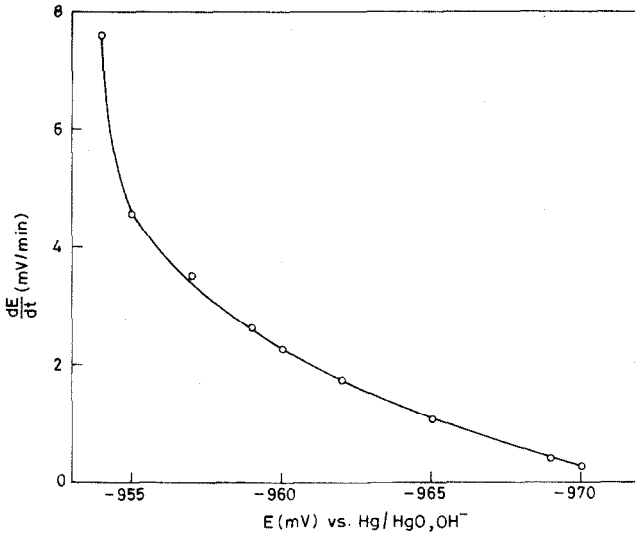


Fig. 2. Plot of dE/dt vs. E for curve (c) of Fig. 1.

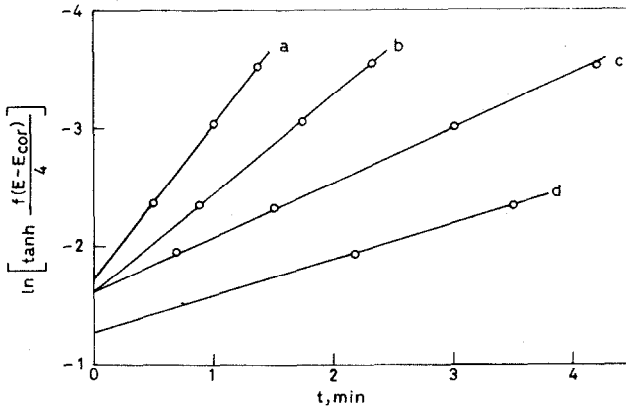


Fig. 3. Plot of $\ln \left[\tanh \frac{f(E - E_{cor})}{4} \right]$ vs. t at different SOCs: (a) 0.96, (b) 0.92, (c) 0.875, and (d) 0.79. Plots calculated from data in Fig. 1.

is possible since it has been established [7 - 9] that $\alpha_c \approx \beta_m \approx 0.5$. Hence, eqn. (4) becomes:

$$-C \frac{d(E - E_{cor})}{dt} + 2I_{cor} \sinh [0.5f(E - E_{cor})] = 0 \quad (5)$$

Assuming C to be constant over the narrow span of potential being considered here, the solution for eqn. (5) is:

$$\ln \left[\tanh \frac{f(E - E_{cor})}{4} \right] = \frac{I_{cor}f}{C} t + K \quad (6)$$

where K is an integration constant.

A comparison of eqn. (6) with experimental data is given in Fig. 3. The excellent linearity of the plots confirms the model and the theory developed above.

The sharp change in slope of the lines in Fig. 3 with change in the SOC of the iron electrode suggests that the latter may be predicted from the data obtained during open-circuit potential decay. Further, the slope of the lines in Fig. 3, i.e., $-(I_{\text{cor}}/C)$, could be used to determine the instantaneous value of the specific corrosion rate of the iron electrode, especially since the ratio (I_{cor}/C) is independent of the true area of the electrode. Thus, fast screening of promising additives to suppress the self-discharge of alkaline porous iron electrodes appears possible by conducting an analysis of the open-circuit potential decay curves and taking as reference any convenient value of the SOC.

Acknowledgement

Financial support from the Department of Non-Conventional Energy Sources, Government of India, New Delhi, is gratefully acknowledged.

References

- 1 S. Sathyanarayana, *The Nickel-Iron Storage Battery — A Status Report and Techno-economic Survey for India*. A report submitted to NRDC, Government of India, New Delhi, 1983.
- 2 L. Ojefors, *Studies on the Alkaline Iron Electrode*, Royal Institute of Technology, Sweden, 1975.
- 3 N. A. Hampson, R. J. Latham, A. N. Oliver, R. D. Giles and P. C. Jones, *J. Appl. Electrochem.*, 3 (1973) 61.
- 4 S. Yu. Volosova, Z. A. Iofa and T. G. Stepina, *Elektrokhimiya*, 13 (1973) 393.
- 5 L. Ojefors, *Electrochim. Acta*, 21 (1976) 263.
- 6 K. Vijayamohan, A. K. Shukla and S. Sathyanarayana, *Ind. J. Technol.*, 24 (1986) 430.
- 7 S. A. Rozentsveig and V. I. Levina, *Proc. 4th Conf. on Electrochemistry*, Vol. 3, Academy of Sciences of U.S.S.R., Moscow, 1959.
- 8 D. M. Drazic and C. Chen Hao, *Electrochim. Acta*, 27 (1982) 1409.
- 9 V. V. Lossev and B. N. Kabanov, *Zh. Fiz. Khim.*, 28 (1954) 824.