Cyclic voltammetric studies of porous iron electrodes in alkaline solutions used for alkaline batteries

P. Periasamy, B. Ramesh Babu, S. Venkatakrishna Iyer

Central Electrochemical Research Institute, Karaikudi 630006, India

Abstract

Cyclic voltammetric studies have been conducted in order to develop a suitable method for characterizing the performance of sintered porous iron electrodes in 5.35 M KOH with 0.65 M LiOH solution. The separation of peak potential (ΔE_p) and the ratio of cathodic to anodic charges (Q_c/Q_a) of the Fe/Fe(II) and Fe(II)/Fe(III) couples at zero sweep rates are used to evaluate the reversibility of the porous iron and iron–sulfur electrodes. The influence of additives to the solution (i.e., 0.05 M thiourea, 0.025 M ethylenediaminetetraacetic acid (EDTA), 0.01 M hexamine and 0.01 M Na_2S) on the electrode reversibility is also examined.

1. Introduction

By virtue of its high theoretical capacity, acceptable density, low price, long life and good stability to both mechanical and electrochemical mistreatment, the porous iron electrode is attracting attention as a negative active material in nickel–iron and iron–air batteries. In recent years, increasing interest has been devoted to the development of rechargeable porous iron electrodes [1,2].

During the discharge of an iron electrode in 5 M KOH solution, most of the metallic iron is oxidized to $Fe(OH)_2$ at the first discharge plateau, and then to a mixture of FeOOH and Fe_3O_4 at the second plateau [3–6]. Mossbauer spectroscopy [7] has identified, in situ, the phases during which the cyclic galvanostatic oxidation and reduction of iron occur. The first anodic arrest is due to $Fe(OH)_2$ and the second to β-FeOOH and unreacted $Fe(OH)_2$ [8]. Scanning electron microscopic (SEM) studies revealed the formation of $Fe(OH)_2$ during the first discharge. On continuous discharge, the reaction product formed on the electrode becomes a sludge, probably of FeOOH [9]. Single and repetitive cyclic voltammetry studies have been undertaken [10–14] on solid and porous iron in high alkali concentrations and at elevated temperatures. In the present study the voltammetric behaviour of porous iron electrodes in alkaline solution, and of the corresponding effect of different additives to the solution on the reversibility of the electrodes processes.

2. Experimental

2.1. Preparation of solid iron electrodes

Solid iron electrodes were prepared from pure-iron sheets and made into discs of 1 cm^2 in surface area. These discs were embedded in Teflon gaskets with a provision for electrical connection.

2.2. Preparation of porous iron electrodes

Electrolytic iron powder (300 mesh) was spread uniformly over a nickel-plated, iron wire mesh substrate of (0.12 mm thickness) housed in a graphite die. The electrode was sintered in the temperature range from 1173 to 1223 K for 30 min under a hydrogen atmosphere [15]. A thin copper rod was welded to the sintered iron pellet to provide an electrical contact.

2.3. Electrochemical impregnation

Iron electrodes of 60–65% porosity were impregnated cathodically with 5.35 M KOH solution that contained 0.05 M sulfur. The impregnation was effected by applying a cathodic current of 15 mA for 10 min. The amount of substance deposited was calculated from the increase in electrode weight.

3. Results and discussion

Cyclic voltammograms were recorded using an electrochemical analyser BAS (100 A). A platinum foil was used as the counter electrode and an Hg/HgO, OH⁻ as the reference electrode. (Note, all potentials are reported with respect to this reference electrode.) The electrodes were subjected to sweep rates (1 to 60 mV) in 5.35 M KOH + 0.65 M LiOH solution in the absence or presence of addition agents such as 0.05 M thiourea, 0.025 M ethylenediaminetetraacetic acid (EDTA), 0.01 M hexamine and 0.01 M Na$_2$S. Before polarization, the electrodes were cathodically treated at − 1300 mV for 5 min. The electrolyte was de-aerated by the passage of purified electrolytic hydrogen gas for 30 min. Several experiments were performed in order to obtain reproducible $E − i$ curves at the different sweep rates.

3.1. Solid iron electrodes

A cyclic voltammogram for a solid iron electrode in 5.35 M KOH + 0.65 M LiOH solution is shown in Fig. 1. The anodic plateau appears at − 1020 mV (I), with anodic peaks at − 840 mV (II), − 650 mV (III) and cathodic peaks at − 1000 mV (IV) and − 1150 mV (V). On repetitive scanning at higher sweep rates, the current flowing under peaks (III) and (IV) increases with the scan number. This suggests that the peaks are conjugated.

An ideal reversible battery requires the positive and negative electrodes to be electrodes of the second kind [16,17], i.e., a metal in contact with its sparingly soluble salt and a solution saturated with the salt.

$$O + X + ne \rightleftharpoons R + Y \qquad (1)$$

where O and R are oxidant and reductant present in the solid phase, and the species X and Y are species from the electrolyte.

The process involves the dissolution from kink sites and deposition by nucleation of the above materials in the oxidized and reduced forms of the solid phase.

In the case of the iron electrode, dissolution can occur through the oxide layer (or the oxide itself dissolves) to yield soluble species such as HFeO$_2$⁻. The thickness of the oxide film increases with increase in the electrode potential. This explains the appearance of a plateau current in the cyclic voltammogram. The anodic peak (II) and the cathodic peak (V) corresponds to the Fe/Fe (II) redox couple and peak (III) and peak (IV) to the Fe(II)/Fe(III) redox couple. For solid electrodes, the $(\Delta E_p)_{\nu=0}$ values for the Fe/Fe(II) and Fe(II)/Fe(III) couples are 225 and 290 mV, respectively (Fig. 2).

For an ideally reversible case (Q_c/Q_a) is equal to 1. As (Q_c/Q_a) varies with the sweep rate, $(Q_c/Q_a)_{\nu=0}$ is taken as a measure of the reversibility. For a solid electrode, the values of $(Q_c/Q_a)_{\nu=0}$ for the Fe/Fe(II) and Fe(II)/Fe(III) couples are 0.63 and 0.80, respectively (Fig. 3).

Cyclic voltammograms have been obtained for the porous iron electrode and iron electrodes activated with sulfur in the base electrolyte with different additives. To obtain a clear idea of the influence of these additives on the performance of porous iron electrodes, however, only the influence of EDTA and Na$_2$S is reported in a detail. The parameters obtained from the voltammograms for all systems are compared in order to determine the best additives.
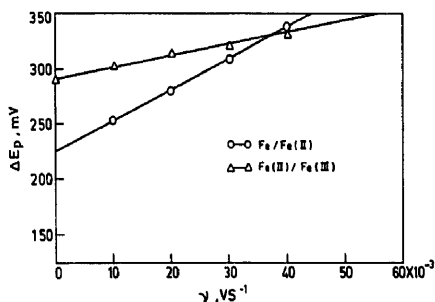

Fig. 2. Plot of ΔE_p vs. sweep rate for Fe/Fe(II) and Fe(II)/Fe(III) couples in 5.35 M KOH + 0.65 M LiOH solution.
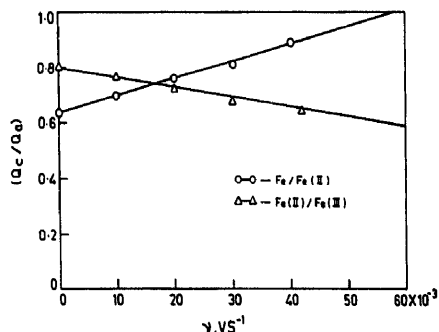

Fig. 3. Plot of Q_c/Q_a vs. sweep rate for Fe/Fe(II) and Fe (II)/Fe(III) couples in 5.35 M KOH + 0.65 M LiOH solution.

Fig. 1. Typical cyclic voltammogram for solid iron electrode in 5.35 M KOH + 0.65 M LiOH solution. Sweep rate = 20 mV sec⁻¹, $E_{\lambda,c}$ = − 1.3 V and $E_{\lambda,a}$ = − 0.3 V.

3.2. Porous iron electrodes

The cyclic voltammogram for the porous iron electrode in 5.35 M KOH + 0.65 M LiOH (base electrolyte) solution is presented in Fig. 4. The forward scan revealed a plateau around −990 mV (I), followed by two anodic peaks at −835 mV (II) and −635 mV (III), respectively. The reverse scan revealed two cathodic peaks at −990 mV (IV) and −1155 mV (V). On repetitive scanning, the current flowing under the peaks increased and this indicate, that the reactions are occurring in a sequence.

3.3. Addition of EDTA to base electrolyte solution

The cyclic voltammogram obtained for the electrolytic iron electrode in 5.35 M KOH + 0.65 M LiOH + 0.025 M EDTA solution (see Fig. 5). For the forward scan, anodic peaks appear at −984 mV (I), −764 mV (II) and −643 mV (III). On the reverse scan, cathodic peaks appear at −930 mV (IV) and −1186 mV (V). In the forward scan, iron is oxidized to $Fe(OH)_2$ and FeOOH. In the backward scan, FeOOH is reduced to $Fe(OH)_2$ and, finally, to iron. Increasing the scan number shifts the anodic peak potentials (II) and (III) to more negative values, while cathodic peak potentials (IV) and (V) are displaced to more positive values. This suggests that the reactions are becoming irreversible. In the case of a porous iron electrode in contact with the base electrolyte containing 0.025 M EDTA, conversion of iron to $Fe(OH)_2$ occurs with a potential shift from −850 mV to −764 mV, i.e., to more positive values. At the same time, conversion of $Fe(OH)_2$ to iron in the cathodic region shifts the potential from −1115 to −1186 mV, i.e., to more negative values.

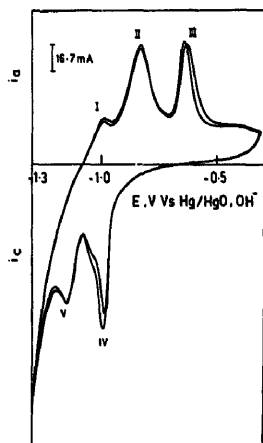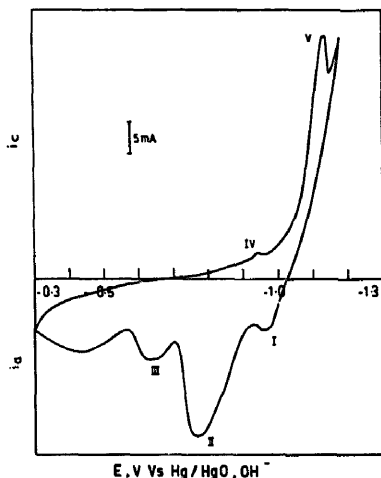Fig. 5. Typical cyclic voltammogram for porous iron electrode in 5.35 M KOH + 0.65 M LiOH + 0.025 M EDTA solution. Sweep rate = 2 mV sec^{-1}; $E_{\lambda,c}$ = −1.3 V and $E_{\lambda,a}$ = −0.3 V.

3.4. Addition of Na_2S to base electrolyte solution

The cyclic voltammogram obtained for the electrolytic iron electrode in 5.35 M KOH + 0.65 M LiOH + 0.01 M Na_2S (Fig. 6) reveals that, during the forward scan, the zero-current crossing potential occurs at −1070 mV, followed by a plateau around −1020 mV (I) and anodic peaks at −780 mV (II) and −580 mV (III). On the reverse scan, cathodic peaks appear at −1050 mV (IV). Subsequent sweeping reduces the charges under the peaks (II) and (IV). This suggests that peaks (II) and (IV) belong to a redox couple.
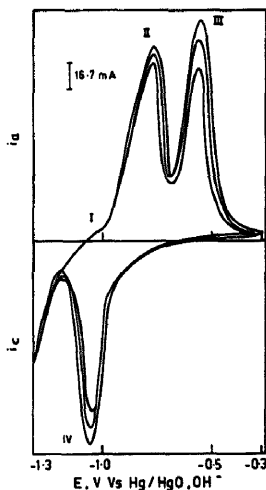
Fig. 4. Typical cyclic voltammogram for porous iron electrode in 5.35 M KOH + 0.65 M LiOH solution. Sweep rate = 2 mV sec^{-1}, $E_{\lambda,c}$ = −1.3 V and $E_{\lambda,a}$ = −0.3 V.

Fig. 6. Typical cyclic voltammogram for porous iron electrode in 5.35 M KOH + 0.65 M LiOH + 0.01 M Na_2S solution. Sweep rate = 2 mV sec^{-1}; $E_{\lambda,c}$ = −1.3 V and $E_{\lambda,a}$ = −0.3 V.

In the presence of 0.01 M Na_2S in the electrolyte solution, a mixture of $Fe(OH)_2$ and $FeOOH$ combine to give a single peak for iron. The addition of Na_2S increases the overpotential of the formation of ferrous and ferric oxides and decreases the reduction overpotential of the ferric iron [18].

The variations of ΔE_p and (Q_c/Q_a) versus sweep rates for the Fe/Fe(II) and Fe(II)/Fe(III) redox couples in base electrolyte with 0.05 M thiourea, 0.025 M EDTA, 0.01 M hexamine and 0.01 M Na_2S are shown in Fig. 7 and Fig. 8, respectively. Table 1 gives parameters derived from cyclic voltammograms for the porous iron electrode.

The cyclic voltammetric behaviour of an electrolytic iron with sulfur (2 wt.%) electrode in base electrolyte with 0.01 M Na_2S is presented in Fig. 9. The zero-current crossing potential occurs at -1100 mV followed by anodic peaks at
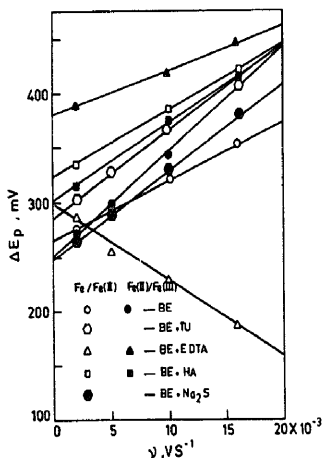
Fig. 9. Typical cyclic voltammogram for porous iron electrode with 2 wt.% sulfur in 5.35 M KOH + 0.65 M LiOH + 0.01 M Na_2S solution. Sweep rate = 2 mV sec^{-1}, $E_{\lambda,c} = -1.3$ V and $E_{\lambda,a} = -0.3$ V.

-830 mV (I) and -560 mV (II). On the reverse scan a cathodic peak appears at -1010 mV (III). Increasing the scan number shifts the peak potentials (I) and (II) to more negative values, while the peak potential (III) moves towards more noble values. There is no peak corresponding to the reduction of FeOOH to $Fe(OH)_2$. Adsorption of sulfur atoms alters the interfacial potential, as indicated [19] by the shifting of zero-current potentials to more noble values. Trivalent iron may be formed via $Fe(OH)_2$ or $HFeO_2$, formation of which is hindered by the adsorbed sulfur. In dilute alkaline sulfide solutions, the formation of sodium ferric sulfide has

Fig. 7. Plot of ΔE_p vs. sweep rate for Fe/Fe(II) and Fe(II)/Fe(III) couples in 5.35 M KOH + 0.65 M LiOH solution (BE) and BE + additives; (TU: thiourea, HA: hexamine).
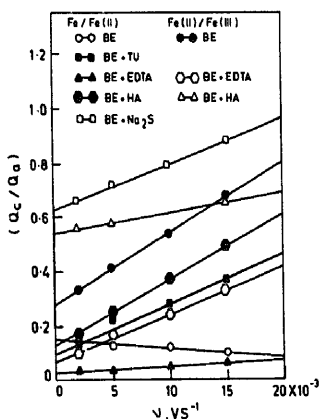
Fig. 8. Plot of Q_c/Q_a vs. sweep rate for Fe/Fe(II) and Fe(II)/Fe(III) couples in 5.35 M KOH + 0.65 M LiOH solution (BE) and BE + additives; (TU: thiourea, HA: hexamine).
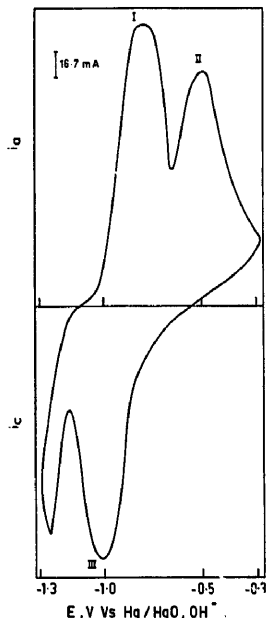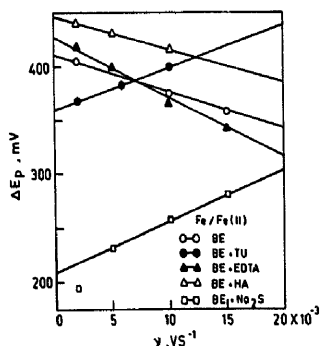
Fig. 10. Plot of ΔE_p vs. sweep rate for Fe/Fe(II) and Fe(II)/Fe(III) couples in 5.35 M KOH + 0.65 M LiOH solution (BE) and BE + additives: (TU: thiourea, HA: hexamine).

Table 1
Parameters derived from cyclic voltammograms for porous iron electrode: effect of additives in the solution

Sample no.	Solution	Fe/Fe(II) couple		Fe(II)/Fe(III) couple	
		$(\Delta E_p)_{\nu=0}$	$(Q_c/Q_a)_{\nu=0}$	$(\Delta E_p)_{\nu=0}$	$(Q_c/Q_a)_{\nu=0}$
1	BE [a]	265	0.15	250	0.28
2	BE + 0.05 M TU [b]	285	0.10		
3	BE + 0.025 M EDTA	300	0.03	330	0.08
4	BE + 0.01 M HA [c]	325	0.13	300	0.54
5	BE + 0.01 M Na$_2$S	249	0.63		

[a] BE: base electrolyte, 5.35 KOH + 0.65 M KOH.
[b] TU: thiourea.
[c] HA: hexamine.

Table 2
Parameters derived from cyclic voltammograms for iron–sulfur electrode: effect of additives in the solution

Sample no.	Solutions	Fe/Fe(II) couple		Fe(II)/Fe(III) couple	
		$(\Delta E_p)_{\nu=0}$	$(Q_c/Q_a)_{\nu=0}$	$(\Delta E_p)_{\nu=0}$	$(Q_c/Q_a)_{\nu=0}$
1	BE [a]	412	0.64		
2	BE + 0.05 M TU [b]	360	0.82		
3	BE + 0.025 M EDTA	425	1.05		
4	BE + 0.01 M HA [c]	447	0.31		
5	BE + 0.01 M Na$_2$S	210	0.69		

[a] BE: base electrolyte, 5.35 KOH + 0.65 M KOH.
[b] TU: thiourea.
[c] HA: hexamine.

been identified [20] and the oxidation of the sulfide ion leads to re-passivation of the electrode by elemental sulfur.

Fig. 10 and Fig. 11 present, respectively, the variations of ΔE_p and Q_c/Q_a with sweep rate for Fe/Fe(II) and Fe(II)/Fe(III) redox couples in base electrolyte containing 0.05 M thiourea, 0.025 M EDTA, 0.01 M hexamine and 0.01 M Na$_2$S. The parameters obtained from cyclic voltammograms for the porous iron electrode containing sulfur are listed in Table 2.
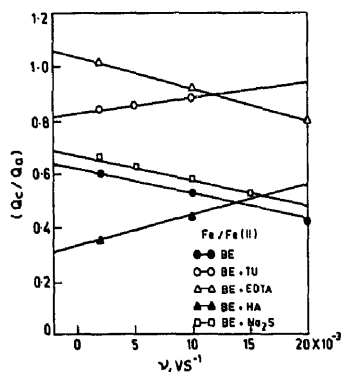

Fig. 11. Plot of Q_c/Q_a vs. sweep rate for Fe/Fe(II) and Fe(II)/Fe(III) couples in 5.35 M KOH + 0.65 M LiOH solution (BE) and BE + additives. (TU: thiourea, HA: hexamine).

It is a well known fact that, during the discharge, the iron electrode is first oxidized to Fe(OH)$_2$. At more positive potentials, Fe(OH)$_2$ is oxidized to hydrated FeOOH. In a battery, the first reaction is the only one of practical importance [21]. An electrode which gives $(\Delta E_p)_{\nu=0}$ and $(Q_c/Q_a)_{\nu=0}$ values close to the solid electrode is considered to be the best electrode. As can be seen from the data in Tables 1 and 2, the porous iron and iron–sulfur electrode values of $(\Delta E_p)_{\nu=0}$ and $(Q_c/Q_a)_{\nu=0}$ are close to the solid electrode only on the addition of Na$_2$S to the base electrolyte solution, but the discharge behaviour of the two electrodes are almost similar. The iron electrode in Na$_2$S has a lower capacity than the iron–sulfur electrode in Na$_2$S at different rates of discharge [22]. Thus, on the basis of the above characteristics, iron–sulfur electrodes are considered to be the best candidates in a base electrolyte that contains 0.01 M Na$_2$S solution.

4. Conclusions

A study of the voltammetric behaviour of porous iron electrodes in alkaline electrolyte with different additives has given rise to the following conclusions.

1. A porous iron electrode which gives $(\Delta E_p)_{\nu=0}$ and $(Q_c/Q_a)_{\nu=0}$ values close to a solid iron electrode can be considered to be an ideal electrode, suitable for use in alkaline solutions.

2. Incorporation of sulfur, both in the electrolyte and on the electrode surface, appears to be advantageous.

3. A sulfur-incorporated porous iron electrode in contact with the base electrolyte containing Na_2S is the best electrode.

Acknowledgements

References

[1] C. Chakkaravarthy, P. Periasamy, S. Jegannathan and K.I. Vasu, J. Power Sources, 35 (1991) 21.

[2] K. Vijayamohanan, T.S. Balasubramanian and A.K. Shukla, J. Power Sources, 34 (1991) 269.

[3] H.G. Silver and E. Leaks, J. Electrochem. Soc., 117 (1970) 5.

[4] J. Cerny, J. Jindra and K. Micka, J. Power Sources, 45 (1993) 267.

[5] T.K. Teplurskaya, N.N. Fedorova and S.A. Rozentsveig, Zh. Fiz. Khim., 38 (1964) 2167.

[6] A.J. Salkind, C.J. Venuto and S.U. Falk, J. Electrochem. Soc., 111 (1964) 493.

[7] Y. Geronov, I. Tomov and S. Georgiev, J. Appl. Electrochem., 5 (1975) 351.

[8] A.M. Pritchard and B.J. Mould, Corros. Sci., 11 (1971) 1.

[9] L. Ojefors, J. Electrochem Soc., 123 (1976) 1691.

[10] V.S. Muralidharan and M. Veera Shanmugamani, J. Appl. Electrochem., 15 (1985) 675.

[11] D.D. Macdonald and B. Roberts, Electrochim. Acta, 23 (1978) 781.

[12] A. Wieckowski and E. Ghali, Electrochim. Acta, 30 (1985) 1423.

[13] B.O. Andersson and L. Ojefors, J. Electrochem. Soc., 123 (1976) 824.

[14] B. Ramesh Babu, S. Venkatakrishna Iyer and T.K.G. Namboodhiri, J. Electrochem. Soc., 43 (1994) 141.

[15] P. Periasamy, B. Ramesh Babu, S. Jegannathan, S. Muralidharan, C. Chakkaravarthy and K.I. Vasu, Bull. Electrochem., 6 (1990) 263.

[16] S. Sathyanarayana, Trans. SAEST, 11 (1976) 19.

[17] M. Jayalakshmi, B. Nathira Begum, V.R. Chidambaram, R. Sabapathy and V.S. Muralidharan, J. Power Sources, 39 (1992) 113.

[18] G. Paruthimal Kalaignan, V.S. Muralidharan and K.I. Vasu, J. Appl. Electrochem., 17 (1987) 1083.

[19] H. Kaesche, Werkst. Korros., 21 (1970) 185.

[20] D.W. Shoesmith, P.Taylor, M.G. Bailey and B. Ikeda, Electrochim. Acta, 23 (1978) 903.

[21] J.O.M. Bockris, B.E. Conway, E. Yeager and R.E. White, Comprehensive Treatise of Electrochemistry, Vol. 3, Plenum, New York, 1981, p.325.

[22] P. Periasamy, submitted for publication.