

# Electrochemical behaviour of Teflon-bonded iron oxide electrodes in alkaline solutions

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## Abstract

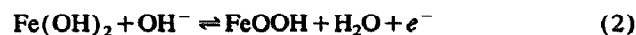
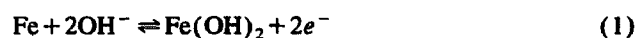
The electrochemical behaviour of Teflon-bonded iron oxide electrodes in 5.35 M KOH + 0.65 M LiOH solution that contains various additives (such as thiourea, ethylenediaminetetraacetic acid (EDTA), hexamine and sodium sulfide) is examined by cyclic voltammetry, chronopotentiometry, open-circuit potential (OCP) decay and charge/discharge studies. The incorporation of Na<sub>2</sub>S in the alkaline electrolyte improves the performance of iron oxide electrodes by increasing the value of the OCP and decreasing the transient time. Moreover, the addition of Na<sub>2</sub>S gives maximum capacity for the iron oxide electrode and a value of zero for  $dE/dt$ . The addition of thiourea lowers the performance of pressed iron electrodes. Thus, the incorporation of Na<sub>2</sub>S in the alkaline electrolyte is essential for improving the performance of these electrodes.

*Keywords:* Iron oxide electrodes; Cyclic voltammetry studies; Transient time; Open-circuit decay; Charge/discharge studies

## 1. Introduction

The iron electrode forms the negative electrode in both nickel/iron and iron/air rechargeable batteries. These batteries, which utilize virtually inexhaustible resources of iron, have been examined as practical electrochemical power sources [1,2].

The anodic oxidation of iron proceeds in two main steps [3–5]:



The net cell reaction in a secondary nickel/iron cell is



The performance of the battery can be improved by mixing additives with the iron and iron oxide powder [6–9]. Pressed electrodes containing Fe<sub>3</sub>O<sub>4</sub> and carbon black have 20% utilization of iron, which increases with the addition of copper or graphite [10]. The present study deals with the study of the electrochemical behaviour of Teflon-bonded electrodes in 5.35 M KOH + 0.65 M LiOH (base electrolyte) solution with different additives.

## 2. Experimental

### 2.1. Preparation of iron oxide electrodes

Statistically optimized, pressed iron oxide electrodes were made from a mixture of magnetite, copper, mercuric oxide and electrolytic iron powder. The mixture was prepared in a glass mortar using isopropyl alcohol that contained 10% polytetrafluoroethylene (PTFE) solution. The resulting paste was spread as a thin sheet over a smooth surface by rolling with a glass rod, and then wrapped between two nickel-plated, mild-steel substrates placed on each side of the iron oxide paste. Finally, the electrodes were pressed using a hydraulic press at 20 tonnes per 30 cm<sup>2</sup> for 30 min.

### 2.2. Preparation of electrolyte solution

The electrolyte was 5.35 M KOH + 0.65 M LiOH solution and contained various additives such as 0.05 M thiourea, 0.025 M EDTA, 0.01 M Na<sub>2</sub>S and 0.1 M hexamine. Double-distilled water and AR grade chemicals were used to prepare the electrolyte.

### 2.3. Cyclic voltammetric studies

Cyclic voltammetric studies were carried out with a three-electrode glass cell assembly that had the pressed iron oxide

as the working electrode,  $\text{Hg}/\text{HgO}/\text{OH}^-$  as a reference electrode, and a platinum foil of large surface area as the counter electrode. These experiments were performed at various sweep rates, viz., 1 to 20  $\text{mV s}^{-1}$  in 5.35 M KOH + 0.65 M LiOH solution, with and without addition of agents such as thiourea, EDTA, hexamine and  $\text{Na}_2\text{S}$  in the range of  $-1.3$  to  $-0.1$  V. Before polarization studies, each electrode was cathodically treated at  $-1.3$  V for 5 min. A bio-analytical system (BAS-100 A) was used for this study.

#### 2.4. Chronopotentiometric studies

The electrodes and experimental setup for chronopotentiometric investigations were similar to those described above for cyclic voltammetric studies. Iron oxide electrodes were cathodically polarized at constant currents that ranged from 100 to 700 mA. After 1 h, different anodic current steps in the range 10 to 70 mA were applied. The potential was then followed for 30 min via a printing voltmeter.

#### 2.5. Open-circuit potential decay studies

The electrodes and the experimental setup for open-circuit potential (OCP) decay studies were similar to those used for cyclic voltammetric studies. Iron oxide electrodes were cathodically polarized at different currents for 60 min. The current was then switched off and the OCP decay was followed until steady values of the potential were reached.

#### 2.6. Charge/discharge studies

Iron oxide electrodes were combined with excess-capacity, sintered nickel hydroxide positive electrodes to assemble 4 Ah nickel/iron cells for characterizing charge/discharge behaviour.

### 3. Results and discussion

#### 3.1. Cyclic voltammetric studies

A cyclic voltammogram for the pressed iron oxide electrodes in 5.35 M KOH + 0.65 M LiOH solution is given in Fig. 1. The forward scan reveals that the anodic peaks occur at  $-776$  mV (I),  $-520$  mV (II) and  $-324$  mV (III). On the reverse scan, a cathodic peak appears at  $-995$  mV (IV). With further cycling, the anodic peak potentials I and II are shifted towards more positive values, while the cathodic peak potential IV moves towards a more negative value. This suggests that the reaction is becoming irreversible.

In the presence of 0.025 M EDTA in the base electrolyte (BE) solution, the cyclic voltammogram for pressed iron oxide electrodes, on the forward scan displays anodic peaks at  $-792$  mV (I),  $-564$  mV (II) and  $-308$  mV (III), Fig. 2. On the reverse scan, a cathodic peak occurs at  $-990$  mV (IV). The zero-current crossing potential in the forward scan

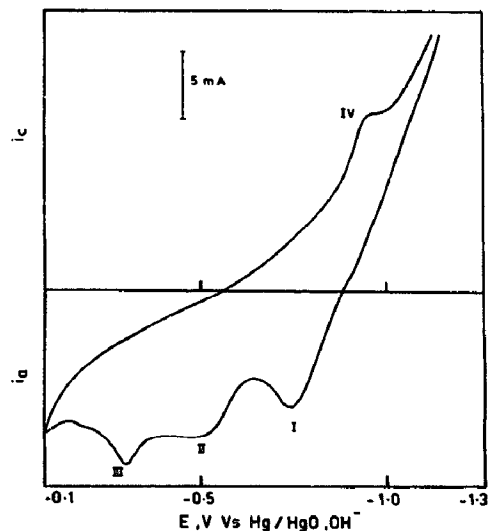


Fig. 1. Typical cyclic voltammogram for the pressed iron electrode in 5.35 M KOH + 0.65 M LiOH solution.

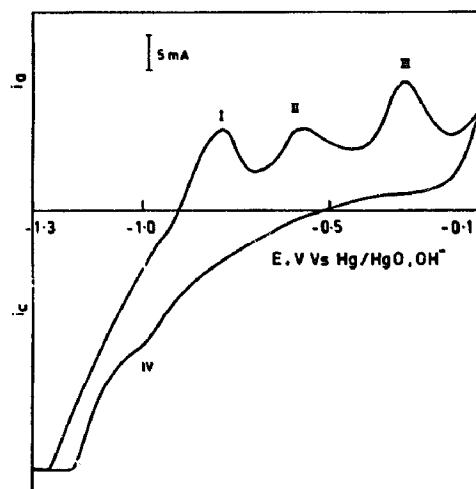


Fig. 2. Typical cyclic voltammogram for the pressed iron electrode in 5.35 M KOH + 0.65 M LiOH + 0.025 M EDTA solution.

occurs at  $-900$  mV, while in the reverse scan it occurs at  $-520$  mV. An increase in the scan number shifts the potentials of peaks I and II towards more positive values and the potential of the cathodic peak IV to more negative values. This suggests that the reactions are becoming irreversible with repetitive sweeping. In the forward scan, the appearance of peak I is due to the conversion of iron to  $\text{Fe}(\text{OH})_2$ , followed by further oxidation to  $\text{FeOOH}$  at  $-564$  mV. The appearance of peak IV is due to the reduction of  $\text{Fe}(\text{OH})_2$  to iron at  $-990$  mV.

With 0.01 M  $\text{Na}_2\text{S}$  in the BE solution, the cyclic voltammogram for the pressed iron oxide electrode (Fig. 3) gives anodic peaks at  $-825$  mV (I),  $-595$  mV (II),  $-360$  mV (III) on the forward scan and a cathodic peak at  $-960$  mV (IV) on the reverse scan. Further cycling reduces the charges under peaks I to IV. The zero-current crossing potential occurs at  $-945$  and  $-705$  mV in the forward and reverse

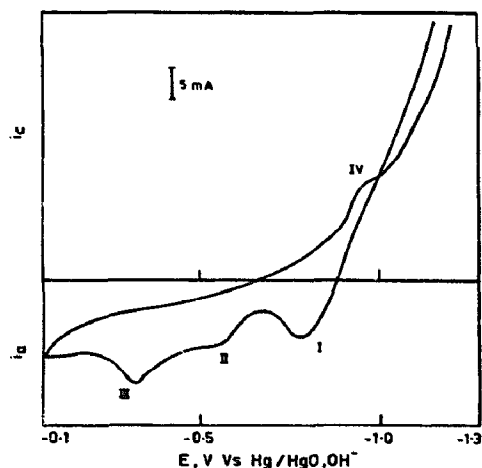


Fig. 3. Typical cyclic voltammogram for the pressed iron electrode in 5.35 M KOH + 0.65 M LiOH + 0.01 M Na<sub>2</sub>S solution.

scans, respectively. This is due to incomplete reduction of the oxide on the surface [11]. In the forward scan, the appearance of peak I is due to the conversion of iron to Fe(OH)<sub>2</sub>, followed by the appearance of peak IV which corresponds to the conversion of Fe(OH)<sub>2</sub> to iron, and finally hydrogen evolution takes place at -1090 mV.

The anodic peak appears at a potential that is more negative in the BE that contains 0.01 M Na<sub>2</sub>S solution than other electrolyte solutions, i.e. BE + 0.05 M thiourea, BE + 0.025 M EDTA, or BE + 0.01 M hexamine.

### 3.2. Chronopotentiometric studies

In chronopotentiometric studies, two basic assumptions have been made: (i) all the applied currents initiate the reaction between the electrodes and hydroxyl ions, and (ii) mass transfer is controlled by the diffusion of hydroxyl ions in solution.

Chronopotentiometric studies for the iron oxide electrode in 5.35 M KOH + 0.65 M LiOH with different additives have been conducted in order to examine the self-discharge characteristics of the electrode. It is possible to choose a suitable electrolyte that can improve the performance of the electrode. The chronopotentiograms for the oxide electrode at different currents (such as 20, 30, 40 and 50 mA) are given in Figs. 4–8. In Fig. 4, it is seen that there is a gradual fall in potential at lower currents. With increase in current, however, a steep fall in potential is observed. The addition of 0.05 M thiourea has no beneficial influence on the performance of the oxide electrode (Fig. 5); the fall in potential at different current densities is faster than in the absence of thiourea. By contrast, the addition of 0.025 M EDTA has a beneficial influence on the performance of the electrode (Fig. 6). Although there is a steep fall in potential, it is not so rapid as in the case of the electrolyte with thiourea. The addition of 0.01 M hexamine has a favourable influence on the performance of the electrode (Fig. 7). The time taken to reach the potential of the first plateau (-0.8 V versus Hg/HgO/OH<sup>-</sup>) is found to be

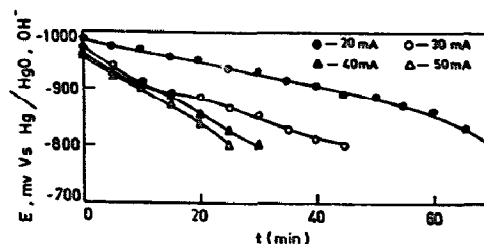


Fig. 4. Typical chronopotentiograms for the pressed iron electrode at different anodic currents in 5.35 M KOH + 0.65 M LiOH solution.

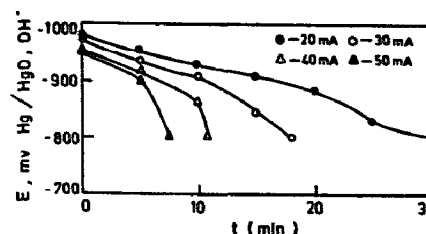


Fig. 5. Typical chronopotentiograms for the pressed iron electrode at different anodic currents in 5.35 M KOH + 0.65 M LiOH + 0.05 M thiourea solution.

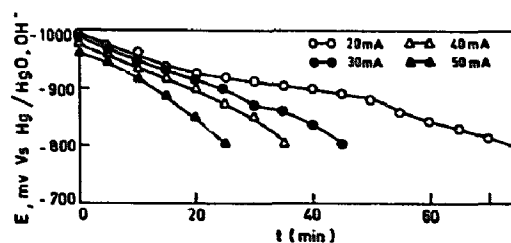


Fig. 6. Typical chronopotentiograms for the pressed iron electrode at different anodic currents in 5.35 M KOH + 0.65 M LiOH + 0.025 M EDTA solution.

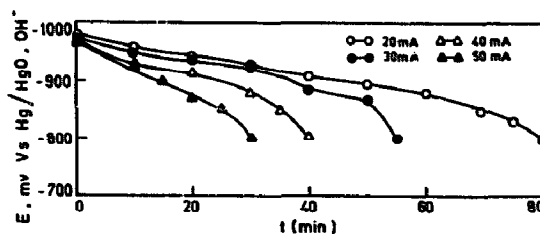


Fig. 7. Typical chronopotentiograms for the pressed iron electrode at different anodic currents in 5.35 M KOH + 0.65 M LiOH + 0.01 M hexamine solution.

greater than that in the case of thiourea and EDTA for all currents. It is seen from Fig. 8 that the addition of 0.01 M Na<sub>2</sub>S has a remarkable influence on the performance of the electrode. The fall in potential (Figs. 4–8) is sluggish in case of the oxide electrode. With the addition of thiourea, EDTA and hexamine to the BE solution, a constant potential or plateau is not observed, except at the lowest current (20 mA).

Values of the potential and the transient time ( $\tau$ ) for the oxide electrode in different electrolyte solutions are given in Table 1. At all currents, BE solution with 0.05 M thiourea, 0.025 M EDTA or 0.01 M hexamine do not cause a beneficial influence on the potential, but BE containing 0.01 M Na<sub>2</sub>S

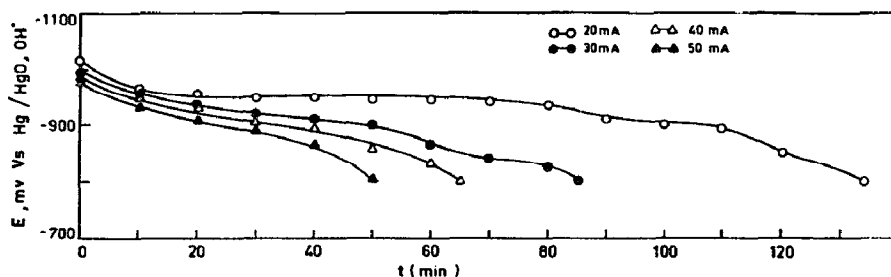


Fig. 8. Typical chronopotentiograms for the pressed iron electrode at different anodic currents in 5.35 M KOH + 0.65 M LiOH + 0.01 M Na<sub>2</sub>S solution.

Table 1

Parameters derived from the first plateau in chronopotentiograms of the iron oxide electrode in BE: the effect of additives

Electrolyte	20 mA		30 mA		40 mA		50 mA	
	<i>E</i> (mV)	<i>t</i> (min)	<i>E</i> (mV)	<i>t</i> (min)	<i>E</i> (mV)	<i>t</i> (min)	<i>E</i> (mV)	<i>t</i> (min)
BE	-800	70	-805	43	-800	30	-802	23
BE + thiourea	-805	28	-810	17	-825	11	-820	7
BE + EDTA	-815	78	-800	55	-800	40	-815	29
BE + hexamine	-810	71	-800	45	-810	34	-800	25
BE + Na <sub>2</sub> S	-820	130	-800	85	-820	63	-810	45

Table 2

Percentage utilization of active material of iron oxide electrode in BE: the effect of additives

Electrolyte	20 mA <i>Q</i> <sub>app</sub> = 60 mAh		30 mA <i>Q</i> <sub>app</sub> = 70 mAh		40 mA <i>Q</i> <sub>app</sub> = 80 mAh		50 mA <i>Q</i> <sub>app</sub> = 90 mAh	
	<i>Q</i> <sub>con</sub>	%	<i>Q</i> <sub>con</sub>	%	<i>Q</i> <sub>con</sub>	%	<i>Q</i> <sub>con</sub>	%
BE	23	39	22	30	20	25	19	21
BE + thiourea	9	16	8	12	7	9	6	7
BE + EDTA	26	43	26	39	26	33	24	27
BE + hexamine	24	39	22	32	22	28	21	23
BE + Na <sub>2</sub> S	43	72	42	61	42	53	37	40

enhances the potential of the first plateau reaction. The plateau potentials lie between the equilibrium potentials of Fe/Fe(OH)<sub>2</sub> and Fe(OH)<sub>2</sub>/FeOOH. with the addition of 0.01 M Na<sub>2</sub>S to the BE, the plateau potentials become more active. This suggests that the oxidation of Fe/Fe(OH)<sub>2</sub> is favoured by the addition of 0.01 M Na<sub>2</sub>S to the BE, while an increase in anodic current shifts the potential towards more noble values.

The data presented in Figs. 4–8 clearly demonstrate that the addition of Na<sub>2</sub>S improves the performance of the oxide electrode considerably and similarly the transient time has considerably decreased in the following order for different electrolytes BE + Na<sub>2</sub>S > BE + hexamine > BE + EDTA > BE > BE + thiourea.

The percentage utilization of active materials for the iron oxide electrode is given in Table 2. For all the electrolytes under study, the variation in the percentage utilization with current does not follow a definite trend. For all currents, the percentage utilization increases in the same order as observed for potential and transient time values.

### 3.3. Open-circuit potential decay studies

The variation of OCP with time for the pressed electrode in BE with additives is given in Fig. 9. There is a steep fall in the potential within 5 to 10 min. Steady-state values are reached after 15 min and lie within the reversible potentials of the Fe/Fe(OH)<sub>2</sub>, Fe/HFeO<sub>2</sub><sup>-</sup> and H<sub>2</sub>O/H<sub>2</sub> reactions. The equilibrium potentials [12] of the reactions at pH 14 at 30 °C are -995, -919 and -925 mV versus Hg/HgO/OH<sup>-</sup>, respectively. The steady-state values of the OCP decay curve are mixed potentials and may be due to the conversion of Fe to Fe(OH)<sub>2</sub> accompanied by hydrogen evolution. The cathodic currents that flow at negative potentials are due to the hydrogen evolution and to the conversion of Fe(OH)<sub>2</sub> to iron

$$i_c = C_{dl} \left( \frac{dE}{dt} \right) + i_{o,M} \exp(\alpha_c F \eta / RT) + i_{o,H} \exp(-\alpha_c' F \eta / RT) \quad (4)$$

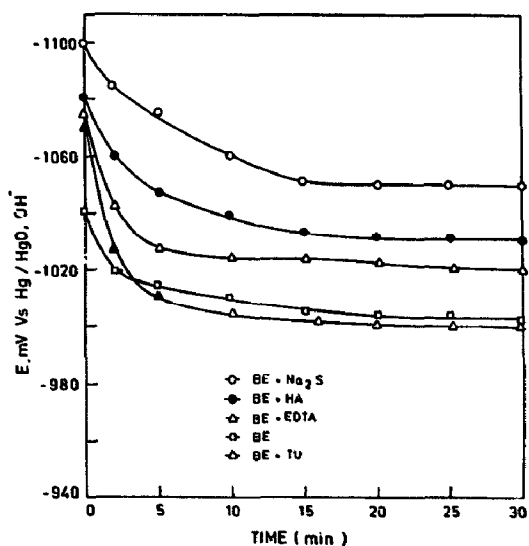


Fig. 9. Open-circuit potential decay curves for the pressed iron electrode in 5.35 M KOH + 0.65 M LiOH solution with different additives.

where  $i_{o,M}$  and  $i_{o,H}$  are the exchange-current densities for the Fe/Fe(OH)<sub>2</sub> and H<sub>2</sub>O/H<sub>2</sub> reactions;  $\alpha_c$  and  $\alpha_c'$  are the cathodic transfer coefficients for Fe(OH)<sub>2</sub> reduction and hydrogen evolution;  $C_{dl}$  is the double-layer capacitance;  $\eta$  is the overpotential. When the current is switched off, the equation becomes

$$-C_{dl} \left( \frac{dE}{dt} \right) = i_{o,M} \exp(-\alpha_c F \eta RT) + i_{o,H} \exp(-\alpha_c' F \eta RT) \quad (5)$$

As there is no Fe(OH)<sub>2</sub> or HFeO<sub>2</sub><sup>-</sup> in the solution, the iron deposition current is negligible and the equation becomes

$$-C_{dl} \left( \frac{dE}{dt} \right) = i_{o,H} \exp(-\alpha_c' F \eta RT) \quad (6)$$

It can be observed from the Fig. 9 that the addition of Na<sub>2</sub>S enhances the OCP more than other additives. The enhancement of the OCP follows the order: BE + Na<sub>2</sub>S > BE + hexamine > BE + EDTA > BE > BE + thiourea.

In all the electrolytes under study, there is a fall of potential up to a duration of 10 min and then it gradually becomes steady. Thus, it is clear from this study that the addition of Na<sub>2</sub>S to BE improves the performance of the pressed electrode.

A straight line with a slope of  $\alpha_c' F/RT$  and an intercept of  $\ln i_{o,H}/C_{dl}$  should be obtained when  $\log dE/dt$  is plotted against  $E$ . The intercept should be independent of the surface area of the electrode. The exchange-current densities for the hydrogen-evolution reaction can be obtained by extrapolating the linear segment of the thermodynamic reversible hydrogen-evolution potential of  $\log dE/dt$  versus  $E$  curve, with the assumption that  $C_{dl}$  does not vary with the potential.

A plot of  $dE/dt$  versus  $E$  (cathodic potential) for pressed iron electrode in different electrolytes is presented in Fig. 10.

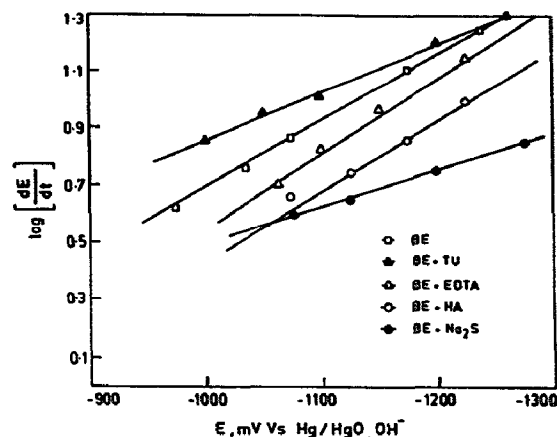


Fig. 10. Log  $dE/dt$  vs. cathodic potential  $E$  for the pressed iron electrode in 5.35 M KOH + 0.65 M LiOH with different additives.

Table 3

Values of  $dE/dt$  obtained from OCP decay curves for different alkaline electrolytes

Electrolyte	$dE/dt$ (mV/min)
BE	5
BE + thiourea	13
BE + EDTA	8.6
BE + hexamine	6.6
BE + Na <sub>2</sub> S	5

The values of  $dE/dt$  for the pressed electrode in the BE solution containing different additives is given in Table 3. The results show that all additives, except Na<sub>2</sub>S, enhance the value of  $dE/dt$ . In the case of Na<sub>2</sub>S, the value of  $dE/dt$  remains unaffected.

### 3.4. Formation process

The variation of capacity with formation cycles for pressed electrodes in five different electrolytes is displayed in Fig. 11. During charge/discharge cycles, the capacity of the oxide electrode slowly increases and attains the full capacity at 20 to 30 cycles. The addition of 0.01 M Na<sub>2</sub>S to the BE solution leads to a maximum capacity for the oxide electrode. It also gives a more stabilized capacity than other additives in the BE solution. For pressed electrodes during initial formation

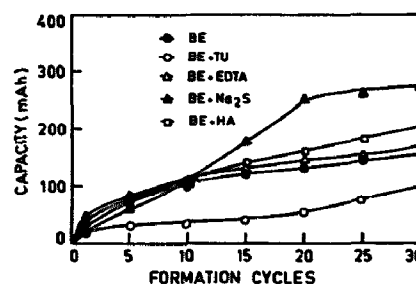


Fig. 11. Variation of capacity of the pressed electrode in 5.35 M KOH + 0.65 M LiOH with different additives.

cycles, most of the charging current is consumed by the hydrogen-evolution reaction and the first few cycles yield only a low capacity. As formation cycling continues, a maximum capacity is attained with respect to the first discharge of the iron electrode [13,14]. For pressed electrodes, more than 25 to 30 cycles are necessary to attain maximum capacity [15].

### 3.5. Performance of 4 Ah cell

The discharge characteristics of a 4 Ah cell with pressed iron electrode are shown in Fig. 12 in terms of the potential versus capacity delivered by pressed electrodes in five different electrolytes at the  $C/2$  rate. The voltage falls by about 300 to 350 mV during the delivery of 69% of the capacity when the cell is discharged up to a cutoff voltage of  $-1.2$  V in BE with  $\text{Na}_2\text{S}$ . For the rest of the capacity, the potential falls by 200 mV until the electrode is discharged to a cutoff voltage of  $-1.0$  V. Pressed electrodes show the delivery of lesser values of capacity when BE is incorporated with other additives such as hexamine, EDTA and thiourea. The first delivery capacity for the pressed iron electrode in the presence of different additives incorporated in the BE follows the order:  $\text{BE} + \text{Na}_2\text{S} > \text{BE} + \text{hexamine} > \text{BE} + \text{EDTA} > \text{BE} > \text{BE} + \text{thiourea}$ . This order clearly demonstrates that the addition of  $\text{Na}_2\text{S}$  improves the performance of pressed iron electrode, whereas the addition of thiourea has a deleterious effect, even though both contain sulfur. Thus, the incorporation of sulfide in the electrolyte is found to be essential for improving the performance of the pressed iron electrode.

Values of  $dE/dt$  obtained for a pressed iron electrode discharged at the  $C/2$  rate in BE alone and in BE with different additives are listed in Table 4. A value of almost zero is obtained for the pressed iron electrode in BE with  $\text{Na}_2\text{S}$ ,

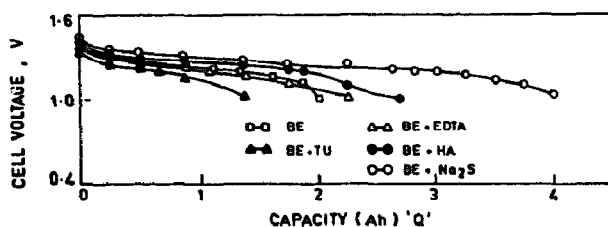


Fig. 12. Potential vs. different capacity curves for the pressed iron electrode in 5.35 M KOH + 0.65 M LiOH with different additives.

Table 4

Parameters derived from discharge studies at  $C/2$  rate for iron oxide electrode

Electrolyte	$(dV/dQ)_{Q=50\%} \times 10^{-3} (\text{V C}^{-1})$
BE	0.32
BE + thiourea	
BE + EDTA	0.12
BE + hexamine	0.10
BE + $\text{Na}_2\text{S}$	0.05

whereas BE with other additives record high values of  $dE/dt$ . This observation also supports the inclusion of sulfide in the base electrolyte to improve the performance of the iron electrode.

## 4. Conclusions

Investigations of the electrochemical behaviour of Teflon-bonded iron oxide electrodes in alkaline solutions in the presence of different additives leads to following conclusions:

1. Cyclic voltammetry shows that the anodic oxidation peak potential becomes more negative only in the electrolyte that contains  $\text{Na}_2\text{S}$ .
2. Self-discharge studies using chronopotentiometric measurements reveal that the incorporation of  $\text{Na}_2\text{S}$  improves the performance of the iron oxide electrode by shortening the transient time of the iron oxide electrode.
3. Addition of  $\text{Na}_2\text{S}$  enhances the OCP.
4. Incorporation of  $\text{Na}_2\text{S}$  does not affect the value of  $dE/dt$ .
5. The addition of  $\text{Na}_2\text{S}$  to the base electrolyte yields maximum capacity.
6. Incorporation of thiourea lowers the performance of the iron oxide electrode.

Thus, sulfide is beneficial in improving the performance of the iron oxide electrode.

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