Effect of metal-sulfide additives on charge/discharge reactions of the alkaline iron electrode

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Abstract

The effect of FeS, PbS and Bi_2S_3 additives on the charge/discharge reactions of porous iron electrodes in alkaline media are examined by means of steady-state galvanostatic and potentiostatic polarization, as well as by gasometric methods. It is found that these additives do not affect the reaction kinetics on fully-charged iron electrodes, but retard the rapid onset of passivation. By contrast, a distinct effect of these additives is observed on the kinetics of the hydrogen-evolution reaction during electrode charging.

Introduction

One of the major problems in the area of electrochemical reaction kinetics concerns the electrocatalysis of the iron electrode in alkaline media:

$$Fe(OH)_2 + 2e^- \rightleftharpoons Fe + 2OH^- \tag{1}$$

This reaction is of importance for the practical realization of Ni/Fe and Fe/air rechargeable batteries. The factors that adversely affect the performance of the iron-electrode reaction are: (i) the thermodynamic instability of iron in alkali, and (ii) the low hydrogen overvoltage.

Although various metal sulfides have been employed as additives with iron electrodes for circumventing the above problems [1–10], the studies conducted to examine their synergistic role have not evinced any conclusive information. This is because most of the studies [11–13] have employed fast-sweep techniques that exhibit nonequilibrium behaviour. In a recently reported [4] steady-state galvanostatic and potentiostatic polarization investigation on iron electrodes containing iron sulfide, the state-of-charge** (SOC) of the electrodes could not be controlled and was found to vary substantially from the initial value (SOC ≈ 1) during the course of experiment. Consequently, it was found futile to derive meaningful electrode-kinetic parameters for the iron-electrode reactions from such data in the Tafel regime.

In the present study, we have tackled this problem by limiting the total variation in the SOC of the iron electrodes—both undoped and doped with various metal sulfides, namely FeS, PbS and Bi_2S_3—during galvanostatic polarization from an initial SOC value of ≈ 1. Gasometric studies on the fully-discharged (SOC ≈ 0) iron electrodes have been conducted to examine the effect of the sulfide additives on the hydrogen-

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**State-of-charge (SOC) is the ratio of available capacity to the maximum attainable capacity.

evolution reaction (HER) during charging. It is found that while the metal-sulfide additives do not affect the kinetics of the iron-electrode reaction of the fully-charged electrodes (SOC ≈ 1), these additives do retard the rapid onset of passivation. Nevertheless, there is a distinct effect of these additives on the kinetics of the HER that occurs concomitantly [14–17] with the iron-reduction reaction during charging of the electrodes.

Experimental

Preparation of porous iron electrodes

Iron electrodes were prepared as described previously [7]. In brief, iron oxalate was vacuum decomposed at 500 °C and the resulting iron and magnetite powder (80 wt.%) was mixed mechanically with appropriate amounts of graphite (10 wt.%), polyethylene powder (9 wt.%) and sulfide additives (1 wt.%). This mixture was hot pressed (118 °C, 125 kg cm^{-2}) on to a degreased nickel grid to obtain porous iron electrodes of geometrical area 2.8 cm × 2.4 cm and of thickness ≈ 1 mm. The electrodes were subjected to continuous charge/discharge cycling against nickel-oxide counter electrodes placed on either side in 6 M KOH electrolyte containing 1 wt.% LiOH, until the electrode formation was complete. The temperature of the cell was maintained at 27 ± 1 °C and changes in the iron-electrode potentials were monitored using a precalibrated Hg/HgO,OH$^-$ (6 M KOH) reference electrode. All studies were conducted on completely formed electrodes.

Polarization studies

Galvanostatic and potentiostatic polarization studies were conducted on iron electrodes that were both with and without metal sulfides. During the galvanostatic studies, the electrodes were subjected to polarization at various values of the currents for defined periods. The resulting changes in potential with time were monitored on a Philips PM-3305 storage oscilloscope. The potential-time data at various currents were then recorded on a Philips PM-8043 x-t recorder that was interfaced to the oscilloscope. For currents above 100 mA, the steady-state value was attained within 10 s. This was not the case, however, for currents lower than 100 mA; the polarization time was therefore extended to 20 s for these currents. As a consequence, the total change in SOC of the electrodes was kept within 7% of the initial value. During potentiostatic polarization, the electrodes were first subjected to anodic polarization in 20 mV steps by means of a Wenking Model LB-81 potentiostat up to the passivation region, and to cathodic polarization up to −1200 mV versus Hg/HgO,OH$^-$ (6 M KOH), where vigorous evolution of hydrogen gas occurred. As reversal in the direction of the polarization up to the rest potential was then carried out to complete the full scan.

Gasometric studies

Gasometric studies on the fully discharged (SOC ≈ 0) iron electrodes, both with and without metal-sulfide additives, were conducted employing the setup shown in Fig. 1. The electrolyte (6 M KOH containing 1 wt.% LiOH) was purged with hydrogen gas with the reservoir open to the air; excess-capacity iron electrodes were employed as counter electrodes. The volumes of hydrogen evolved at the test electrodes during charging at a fixed current (30 mA) over a period of ≈ 4 h were measured. The concomitant changes in potential with time during this process were also monitored for various electrodes.
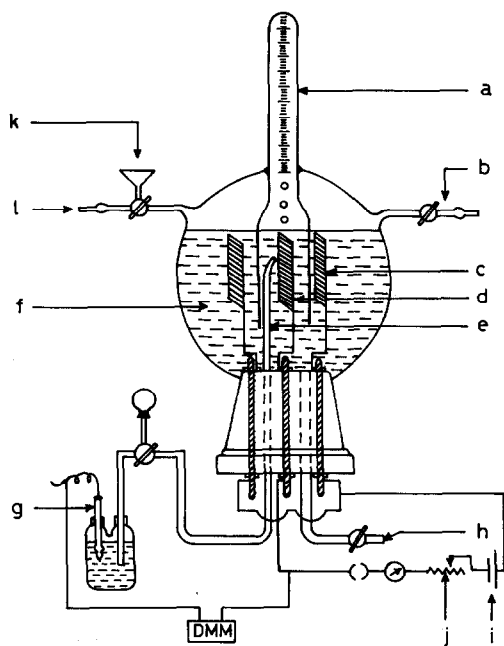
Fig. 1. Schematic representation of experimental setup for gasometric studies: (a) graduated glass-tubing; (b) opening to air; (c) counter electrodes; (d) working electrode; (e) luggin capillary; (f) electrolyte; (g) reference electrode; (h) drain tube; (i) d.c. power supply; (j) rheostat; (k) funnel, and (l) hydrogen gas inlet.

Results and discussion

From the potential-time curves obtained during anodic polarization of fully-charged iron electrodes (SOC $\simeq 1$), both with and without sulfide additives, the electrode overpotentials (η) at various current loads have been derived and plotted against the square root of time ($\sqrt{t}$) (Fig. 2). The linearity of the data subsequent to a particular time interval ($\simeq 5$ s) indicates that the polarization of all the electrodes in this region is governed by a mass-transfer process. The mass-transfer component of the polarization was eliminated by extrapolating the η versus $\sqrt{t}$ plot to $t = 0$ [18, 19]; the polarization data thus obtained are shown in Fig. 3. Ohmic drops for the various electrodes at different SOC values were also measured and were found to be nearly similar ($\simeq 0.03$ Ω). In any case, owing to the high conductivity of the electrolyte solution, the ohmic-polarization values of the electrodes at different SOC values are unlikely to differ appreciably.

The kinetic parameters obtained from galvanostatic polarization data in the anodic direction of the fully-charged iron electrodes containing sulfide additives are given in Table 1. Although well-defined Tafel slopes could be obtained for the iron electrodes containing sulfides of Fe, Pb and Bi, the Tafel region for the undoped iron electrode is not distinctly defined. As the Tafel slopes for all three doped iron electrodes are virtually the same, it is hard to ascribe any catalytic role to these metal sulfides during the discharge of the iron electrodes. Nevertheless, since the magnitude of the polarization
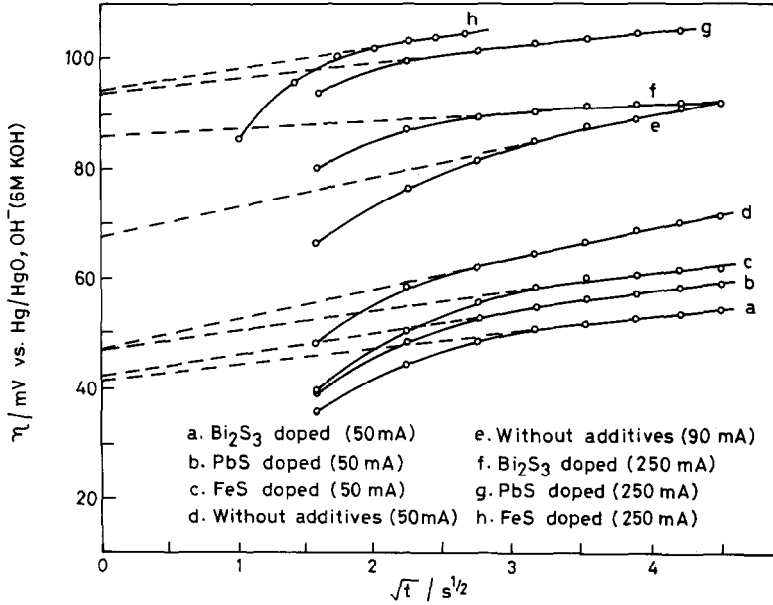
Fig. 2. Typical plots of overpotential (η) vs. square root of time ($\sqrt{t}$) for undoped and sulfide-doped iron electrodes at different load currents.
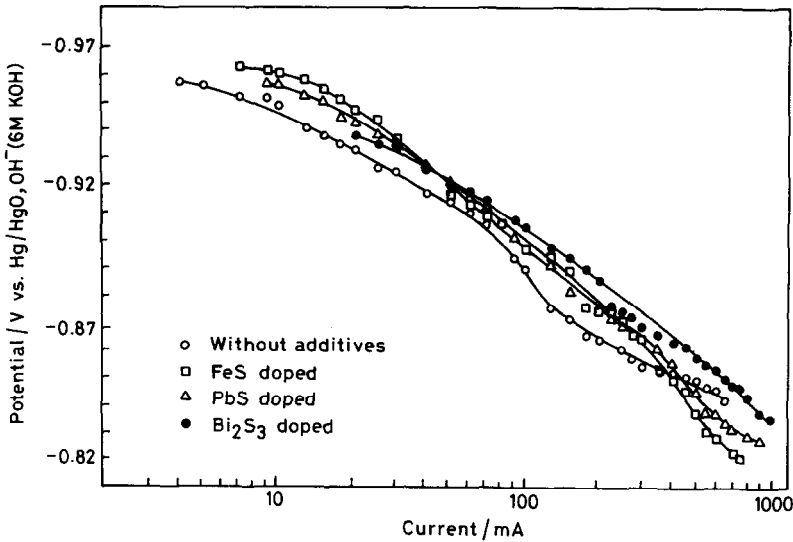

Fig. 3. Galvanostatic polarization data obtained after subtracting the mass-transfer polarization component for various iron electrodes.

for the iron electrodes with sulfide additives is smaller than the value for the undoped electrode, it is concluded that sulfide additives retard the passivation rate. This effect is at a maximum for the electrode containing Bi_2S_3.

TABLE 1

Kinetic parameters for fully-charged iron electrodes containing various sulfide additives

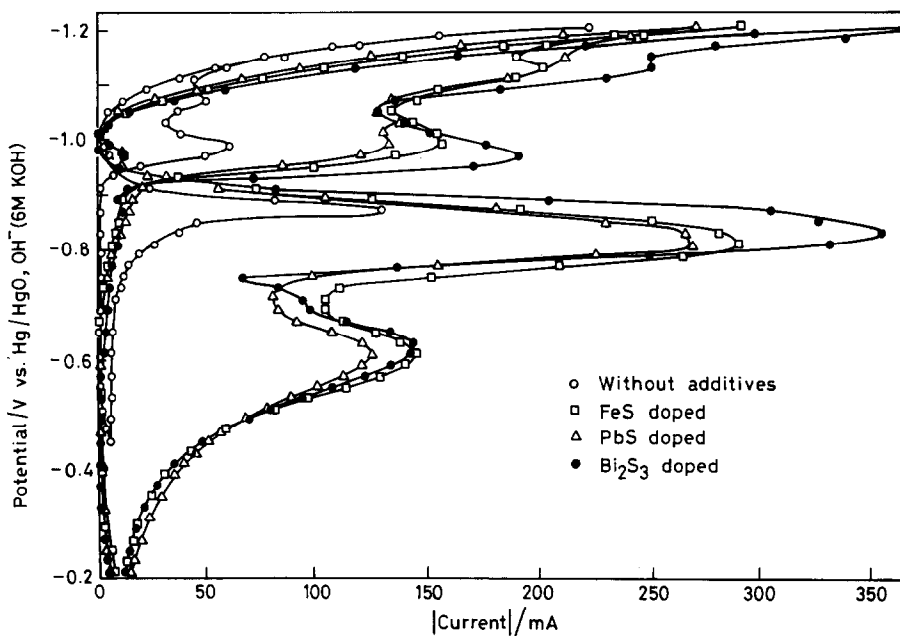| Electrode type	Tafel slope (mV/decade)	Exchange current (mA)
FeS-doped	72	9.8
PbS-doped	70	9.8
Bi_2S_3-doped	63	7.8

Fig. 4. Potentiostatic polarization data for undoped and sulfide-doped iron electrodes.

Figure 4 shows the steady-state potentiostatic polarization data for fully-charged iron electrodes (SOC $\simeq$ 1), both with and without metal-sulfide additives. The critical current value for the electrode without the metal-sulfide additive is found to be 128 mA, while the corresponding values for electrodes with FeS, PbS and Bi_2S_3, are 290, 268 and 355 mA, respectively. In addition, there is an anodic shift in the passivation potential for the doped electrodes compared with the undoped electrode. The passivation region is also smaller for the doped iron electrodes. These signatures are reflected in the capacity data of the respective iron electrodes (Fig. 5), and are in accordance with the galvanostatic polarization data.

Figures 6(a) and (b) show, respectively, the variation in potential and volume of hydrogen $V(H_2)$, evolved at normal temperature and pressure (NTP) with time during charging (current 30 mA) of fully-discharged (SOC $\simeq$ 0) iron electrodes. Both sets of data vary appreciably. Among the various electrodes studied, the volume of hydrogen evolved is largest for the undoped electrode, and least for the Bi_2S_3-doped iron electrode.
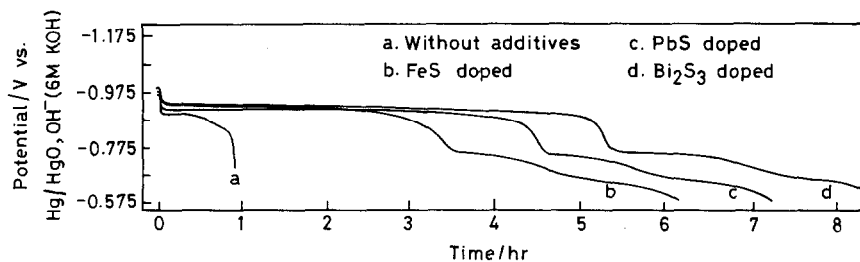
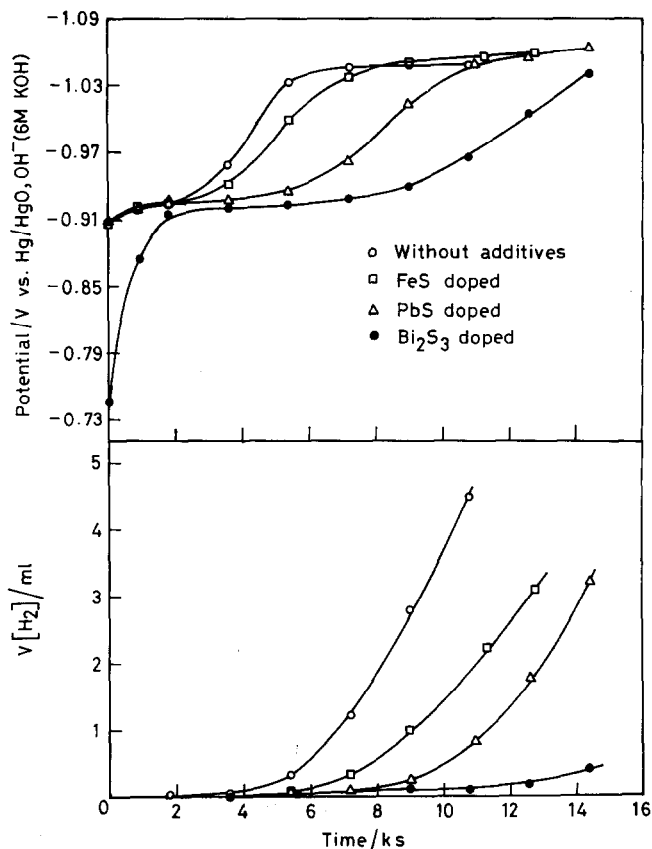Fig. 5. Galvanostatic discharge (current = 40 mA) curves for undoped and doped iron electrodes.

Fig. 6. (a) Potential vs. time, and (b) volume of H_2 evolved at normal temperature and pressure, $V(H_2)$, vs. time; undoped and sulfide-doped iron electrodes during charging (current = 30 mA).

Conclusions

It is concluded that the various sulfide additives employed in this study retard passivation of the iron electrode during discharge and suppress the rate of the HER during charging. The electrode doped with Bi_2S_3 shows minimum passivation and

maximum suppression of the HER. Accordingly, the electrode doped with Bi_2S_3 exhibits the maximum efficiency among the various electrodes investigated.

Acknowledgements

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