Short communication

Self-discharge of Fe–Ni alkaline batteries

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Abstract

The effect of FeS and PbS on capacity and self-discharge of an iron porous electrode used in a Fe–Ni battery was investigated. Addition of 1 wt.% FeS or 1 wt.% PbS promotes a significant increase in capacity and inhibits the self-discharge of the iron electrode. This effect is most significant in the presence of PbS.
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1. Introduction

Alkaline Ni–Fe batteries present several advantages in relation to other types: longer service life, low cost and non-toxic materials, also tolerance to overcharge and deep discharge. However, the porous iron electrode has a low hydrogen overpotential, which limits its application in commercial batteries [1–4]. The hydrogen evolution occurring at open circuit causes the corrosion of the iron electrode and consequently a high self-discharge rate. Furthermore, this electrode has a low charge efficiency since the hydrogen evolution reaction competes with the discharge reaction [5,6].

Sulfide salts, as FeS and Na_2S are used to improve the iron electrode. Studies show that the addition of both FeS to the electrodes active material [7,8] and Na_2S to the KOH electrolytic solution [2,9] increases significantly the iron electrode capacity. In relation to the effect of sulfide salt on the hydrogen evolution rate on the iron electrode, Balasubramanian and Shukla [10] measured directly the rate of hydrogen evolution under open circuit conditions in the presence and absence of FeS and PbS and observed the reduction of the hydrogen evolution when these additives were present. These results show that this reduction is highest for PbS, in accord with the Pb hydrogen evolution potential being more cathodic than Fe. However, the effect of FeS and PbS on self-discharge of the iron electrode and the effect of PbS on the electrode capacity has not been clarified yet. The aim of the present research is to investigate the effect of FeS and PbS on the Fe electrode galvanostatic discharge.

2. Experimental

The iron electrodes used in this work were obtained by hot-pressing a nickel plated steel grid between two equal amounts of a mixture of electrolytic iron powder, produced in our laboratory [11], with 6% polyethylene and other additives. The compacting pressure of $240 \, kg \, cm^{-2}$ was applied for 3 min maintaining the temperature at $112 \, ^\circ C$.

The electrochemical measurements were carried out using a three-electrode cell. The counter electrode was a nickel plate. The electrolyte was a $6 \, M \, KOH + 0.33 \, M \, LiOH$ solution. Potentials were referred to a $Hg/HgO/6 \, M \, KOH$ reference electrode. A $123 \, mA \, g^{-1}$ charge current, for 5 h, and a $12.9 \, mA \, g^{-1}$ discharge current, until the potential reached $-700 \, mV$ versus $Hg/HgO/6 \, M \, KOH$, were applied in each charge/discharge cycle.

The iron electrode self-discharge was investigated by obtaining the electrode capacity after a time corresponding to the period in which the electrode was at rest. These measurements were carried out after the electrode have been submitted to stabilization cycles of charge and discharge, which are necessary for the stabilization of capacity.

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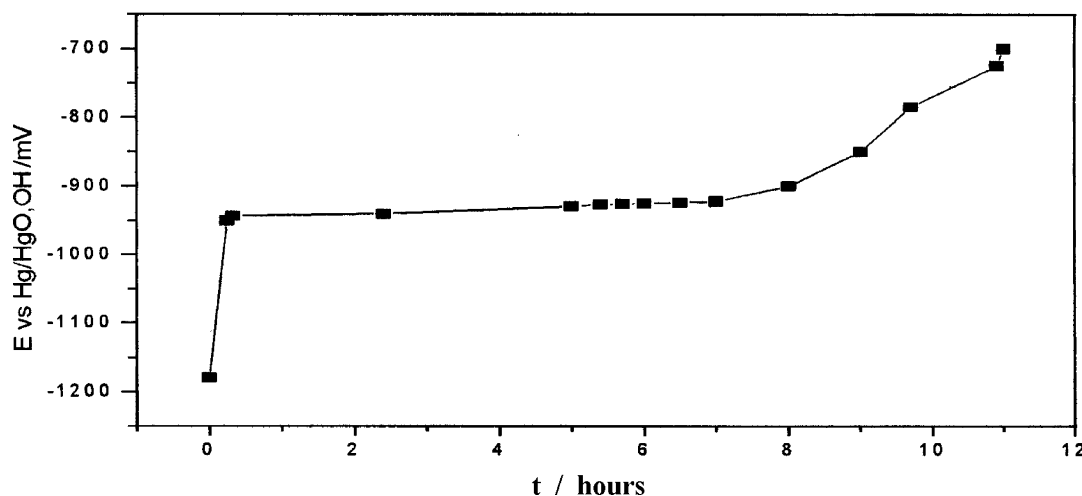*E-mail address:* ivani@dq.ufscar.br (I.A. Carlos).

Fig. 1. Typical discharge curve of an Fe electrode.

3. Results and discussion

Fig. 1 shows a typical discharge curve for the Fe electrode. It can be seen, in this Fig. 1, a plateau, which is associated with the characteristic oxidation reaction: Fe to $Fe(OH)_2$ [12]. Also, this plateau is lengthened and shifted to a more cathodic potential due to the addition of metallic sulfide. This result corroborates the hypothesis of sulfide ion incorporation in the discharge products, as previously discussed [8].

Fig. 2 shows the capacity evolution during the first 30 cycles. After some stabilization cycles, which are necessary for the distribution of the sulfate ions in the Fe electrode surface, the electrodes with 1 wt.% FeS and PbS show a marked increase in capacity with respect to the additive-free electrode. The effect of sulfide presence on the increase of the Fe electrode capacity is known [7] and is attributed [8] to sulfide ions incorporated in the $Fe(OH)_2$ film, which causes a distortion in film structure leading to an increase in ionic conductivity. This retards the passivation process and a thicker film is produced and consequently the discharge time is raised. Also, the results in Fig. 2 show that the capacity of the electrode containing 1 wt.% PbS is higher than that electrode with 1 wt.% FeS, which indicates that in addition to the sulfite ion, the metal present in the additive also affects the electrode capacity. Moreover, there exists an optimum content of PbS ($\sim$1 wt.% for the values analyzed), above this value the capacity falls abruptly. This behavior is probably due to increasing Pb^{2+} concentration, since this fall in capacity is not observed for electrodes containing 2 wt.% FeS in relation to an electrode containing 1 wt.% FeS [12]. Probably, the fall in capacity is due to the formation of PbO or $Pb(OH)_2$.
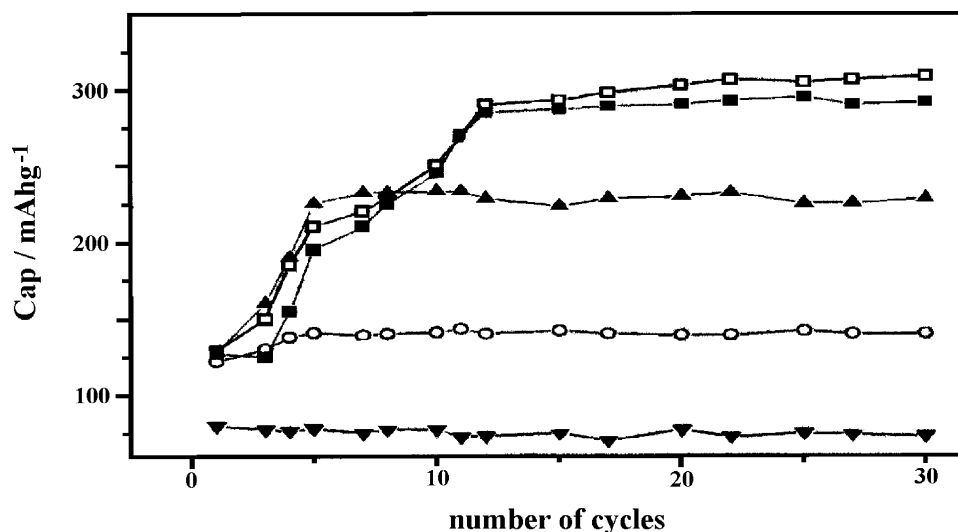

Fig. 2. Capacity values of iron electrodes in the absence and presence of the studied additives as a function of charge/discharge cycle. The values were obtained in 6 M KOH + 0.33 M LiOH solution at $I_d = 12.9\,\mathrm{mA\,g^{-1}}$; where (□) 1 wt.% PbS, (■) 1 wt.% FeS, (▲) 0.5 wt.% PbS, (○) in absence of additive, and (▼) 2% PbS.
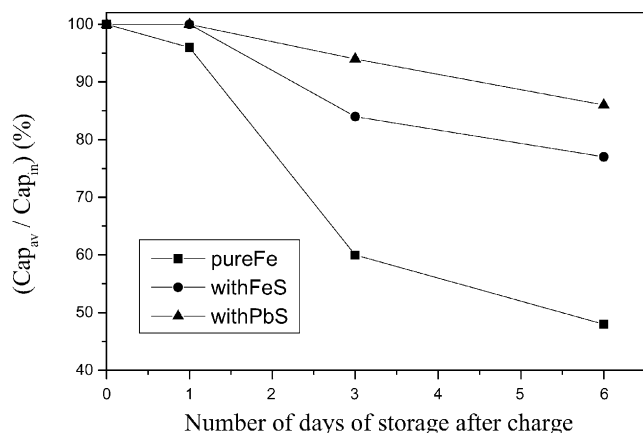
Fig. 3. Available capacity (Cap_{av}/Cap_{in}) of iron electrodes, in the absence and presence of additives 1 wt.% PbS and 1 wt.% FeS, at the end of different periods of storage at 30 °C. The values were obtained in 6 M KOH + 0.33 M LiOH solution at $I_d = 12.9\,\mathrm{mA\,g^{-1}}$; where (■) in absence of additive, (●) 1 wt.% FeS, and (▲) 1 wt.% PbS.

The effect of additives in self-discharge is seen in Fig. 3. In this figure are represented the available capacity percent of initial capacity (Cap_{av}/Cap_{in}) of electrodes at the end of different periods of storage. Clearly, both FeS and PbS are retarding the fall of capacity of electrodes with self-discharge, and this effect is most significant in the presence of PbS. It is possible that these results are related to the hydrogen evolution reaction inhibition caused by metal sulfite presence, which inhibits the self-discharge. The most significant inhibition in the presence of PbS, can be attributed to the higher hydrogen evolution overpotential on Pb in comparison to the Fe overpotential [13], which is consistent with the measurement rate of hydrogen evolution reported by Balasubramanian and Shukla [10].

Unfortunately, the voltammetric peak corresponding to this process is very large, especially for porous electrodes, complicating the investigation of the hydrogen evolution reaction kinetics using electrochemical methods. A more detailed investigation to account for the electrochemical action mechanism, of both PbS and FeS additives, is needed.

4. Conclusions

Addition of 1 wt.% FeS and 1 wt.% PbS promotes a significant increase in capacity and there exists an optimum content of PbS ∼1 wt.% above which the capacity falls abruptly.

The fall of capacity of iron porous electrodes due to the self-discharge is very high. The presence of both FeS and PbS retard the self-discharge, and this effect is most significant in the presence of PbS. These results have attributed inhibition of the hydrogen evolution reaction caused by metal sulfite, which inhibits the self-discharge and by the presence of Pb which is most significant. Nevertheless, the capacity decay during a period of 6 days remains as large as 30%, requiring further development of additives.

References

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