

Role of Bismuth and Sulfide Additives on the Performance of Iron Electrodes in Rechargeable Alkaline Batteries

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Rechargeable iron-air and nickel-iron batteries are attractive for large scale energy storage applications because of the low cost and the robustness of the iron electrode [1]. In spite of its advantages, the iron electrode in these batteries is characterized by low charging efficiency and poor discharge rate capability [2].

When an iron electrode is charged, in addition to the reduction of iron (II) hydroxide (Eq. 1), hydrogen evolution (Eq. 2) also takes place on the iron electrode resulting in a very low charging efficiency.



In commercial iron electrodes, the rate of hydrogen evolution is very high and the efficiency of charging is only about 70%. We recently demonstrated an iron electrode prepared from carbonyl iron powder that operated at a charging efficiency of 96%. The high efficiency was achieved by using bismuth sulfide as an additive to the iron electrode. During charging, the bismuth sulfide was reduced to elemental bismuth on the iron electrode. Bismuth has a high hydrogen overpotential and reduces the amount of hydrogen evolved on the iron electrode during charging.

During discharge of the iron electrode, the iron active material is oxidized to iron (II) hydroxide (Eq. 1). The discharge product is electrically insulating and results in electrode passivation. Passivation of the electrode leads to an incomplete utilization of the active material and very poor high-rate performance during discharge. Sulfide additives are known to act as depassivating agents that prevent the complete passivation of the iron electrode [3, 4]. The carbonyl iron electrode with bismuth sulfide additive had a discharge capacity of 0.2 Ah/g at the 1C rate.

The goal of the present study is (i) to explore the possibility of using other bismuth additives to improve the charging efficiency of the iron electrode and (ii) to decouple the role of bismuth and sulfide in improving the charging efficiency and rate capability respectively.

Iron electrodes prepared by hot pressing a mixture of carbonyl iron powder and polyethylene binder on degreased nickel mesh were used in this study. The iron electrodes were tested in a three-electrode set up with a sintered nickel oxide counter electrode and a Hg/HgO reference electrode. The charging efficiency and rate capability measurements were performed on fully formed iron electrodes.

Iron electrodes were prepared with different proportions of bismuth oxide and sodium bismuth oxide

and the effect of these additives on the rate of hydrogen evolution and charging efficiency was studied.

The discharge rate capability of the iron electrodes was tested with soluble sodium sulfide added to the electrolyte and also with bismuth sulfide added to the iron electrode. It was observed that in the presence of sulfide additives the electrode did not passivate and high discharge capacities can be obtained even at high rates of discharge (Figure 1). The sulfide ions combine with the iron (II) hydroxide to form conductive iron sulfides that prevent the electrode from complete passivation during discharge.

The effectiveness of various bismuth additives on suppressing hydrogen evolution and the mechanism of sulfide additives in depassivating the iron electrodes will be presented.

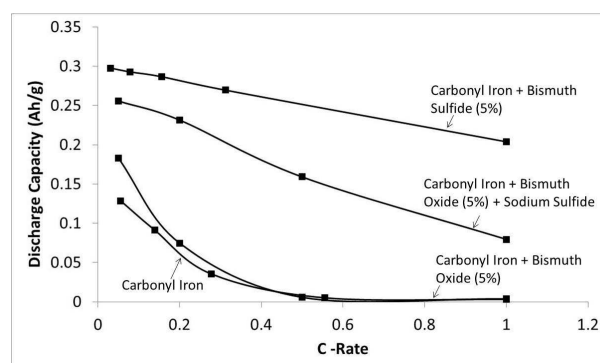


Figure 1: Discharge capacity of iron electrodes as a function of the normalized discharge rate

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