Mechanism of Formation of Carbonyl Iron Electrodes in Alkaline Batteries

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Iron based alkaline battery systems such as iron – air and nickel – iron batteries have the promise to meet the performance and cost requirements for grid scale energy storage applications. Iron, which is the primary raw material for these systems is globally abundant and is very inexpensive. In addition, the iron electrode is extremely stable and robust providing a battery system with long cycle life. However, the iron electrode suffers from low charging efficiency and poor discharge rate capability preventing its widespread use [1, 2].

As in the case of most rechargeable battery electrodes, the iron electrode in iron – air and nickel – iron batteries undergoes a "formation" process. During this process, the iron electrode is charged and discharged at specific rates several times until it achieves a stable discharge capacity. Although this is process is well known [3, 4], the factors affecting the rate of formation and the final capacity of iron electrodes are not well understood. This presentation focuses on our investigations of the formation process.

Vijayamohanan *et al* have investigated the formation of iron electrodes using galvanostatic polarization measurements performed at various stages during the formation process [4]. The authors have attributed the increase in capacity during formation to changes in the morphology and conductivity of the electrode.

In the present study, we investigate the effect of pore former, sulfide additives and wetting agents on the formation process. In our study, iron electrodes prepared from carbonyl iron powder were investigated. Carbonyl iron powder, mixed with polyethylene binder was spread on a degreased nickel mesh and hot pressed at 140°C. The electrode was tested in a three electrode arrangement with a nickel oxide counter electrode and a Hg/HgO reference electrode (MMO). A 30% solution of potassium hydroxide was used as the electrolyte. During formation, the electrodes were charged and discharged between -1.3V and -0.7V (vs MMO) till a stable discharge capacity could be obtained.

The potential – time curves measured during charging at various stages of the formation process is shown in Fig 1. It was observed that a plateau corresponding to the iron electrode reaction (Eq. 1) developed during formation. During the first few cycles, most of the charge current was consumed by the hydrogen evolution reaction (Eq. 2).

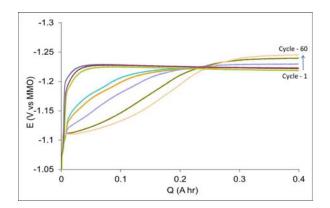
$Fe (OH)_2 + 2e^- \leftrightarrows Fe + 2OH^-$	$E^{o} = -0.877V$ (Eq. 1)
$2 \text{ H}_2\text{O} + 2\text{e-} \leftrightarrows \text{H}_2 + 2\text{OH}^-$	$E^{o} = -0.828V$ (Eq. 2)

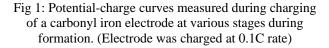
As formation proceeded, the charge corresponding to the reduction of iron hydroxide increased at the expense of the charge diverted to hydrogen evolution reaction.

The potential at which hydrogen evolution takes place was observed to become more negative during formation. This increase in potential indicates that the overvoltage for hydrogen evolution on the iron electrode progressively increases during the formation process.

The rate of formation and the discharge capacity of a fully - formed iron electrode were found to be dependent on the purity of the active material and the active area of the electrode.

Various electrode and electrolyte additives that act to increase the active area of the electrode and modify the electrode kinetics during charge and discharge have been studied. A mechanistic description of the formation process and the role of different additives on formation will be presented.





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