

PIC-BAT 209/11

SECONDARY IRON-AIR BATTERIES

Otto C. Wagner

Power Sources Division, Electronic Components Laboratory
USAECOM, Fort Monmouth, N. J.

N 09-10286

In order to attain a maximum energy density from the iron air system, non-supported active iron-electrodes must be developed. The theoretical energy density of the iron anode for the iron-to-ferrous state is 556 watt-hours per pound; for the iron-to-ferric state the total theoretical energy density is 837 watt-hours per pound. To utilize the three electron change the system will discharge on two voltage plateaus; namely, 0.8-0.9 volts for the Fe/Fe^{++} reaction and 0.7-0.6 volts for the $\text{Fe}^{++}/\text{Fe}^{+++}$ reaction. The two voltage plateaus are disadvantageous for most portable power applications, although the energy realized from the total reaction is very attractive.

Another major advantage of the alkaline iron system is that iron is cheap and very abundant as a raw material. This factor is of greatest importance in addition to its high theoretical energy density. The long cycle life of the alkaline iron anode (more than 20 years of service in Edison Ni/Fe batteries, for example) provides another attractive feature for this system.

An important limitation of the iron-air system, employing the conventional iron anodes, is that its shelf life is very poor. This is due to the low hydrogen overpotential of the electrode. In addition, the conventional iron electrode requires 50-60 percent overcharge to attain maximum electrochemical utilization of the active material. This results in an appreciable loss of water, which means that a conventional alkaline iron-system would require considerable maintenance.

Approaches to overcome the limitations of the alkaline iron system have been reported by many investigators, and it appears that an iron-air and/or other alkaline iron systems can be developed to meet the needs of present day portable power requirements.

The major failure modes reported in the literature for the iron-air system are: (a) self-discharge, (b) oxidation of the anode, (c) loss of active material utilization on deep discharge and reverse discharge and (d) water loss.

The first topic is Self Discharge - The self discharge of the iron electrode is mainly caused by the couple action between the low hydrogen overpotential impurities on the electrode and the active iron powder. (1) Burshtein reports that this self-discharge can be reduced to minimal rate by partially passivating the electrode by treating it with benzene or other volatile organic liquids (2). It is also reported that the electrode can be beneficially treated by the addition of 1% water glass or sodium phosphate inhibitors to the electrolyte.

The self-discharge of the alkaline iron electrode is accelerated by the employment of nickel powder conductor material or other low hydrogen overpotential materials. Therefore, to provide the electrode with a conductive matrix which does not induce self discharge it is necessary to employ materials (in addition to the conductive Fe of the electrode itself) with hydrogen overpotentials higher than that of alkaline iron. In addition, the conductor must not form resistive oxide layers, or dissolve in the electrolyte. Mercury and copper have been beneficially employed in the conventional iron electrodes of the pocket or tubular types. Since these metals possess hydrogen overpotentials in alkaline electrolytes higher than that of iron it is possible that they provide the desired conductive matrix. Other effects such as extender or expander action are also possible.

The second topic is Oxidation of the Anode - Oxidation of the anode by air is a problem common with all metal-air systems. Methods to overcome this problem are: cladding the anode with semipermeable membranes and constructing the unit cell so that air can have access to the system only through the pores of the air cathode; that is, the unit cells must be designed as sealed structures.

The third topic is Loss of Active Material Utilization - It is known that pure alkaline iron systems, where the iron electrode is limiting on discharge, lose capacity by irreversible electrochemical reactions. It is reported in the literature that the active material utilization of iron powder is stabilized and increased by the use of graphite (3), molybdenum (4), tungsten (4), and sulfur additives. These additives may be beneficial by reducing the self-discharge reaction of the iron anode and/or providing expander and/or extender action.

Water Loss - The problem of water loss is common for all metal-air systems. For iron-air it is serious because of the self-discharge reaction and the need for extensive overcharge. Methods to minimize this problem are: (a) reducing the self-discharge reaction of alkaline iron (as previously discussed), (b) improving the active material utilization of the iron anode so that it is highly reversible and (c) providing the unit iron-air cell with a reserve of excess electrolyte in a reservoir.

Performance Characteristics of the Iron-Air System - General Telephone and Electronics has been pioneering the development of a practical iron-air system during the past several years. They report that they have developed iron-air cells of 5 to 20 ampere-hour capacities with a cycle life greater than 200 cycles at energy densities of 60-70 watt hour/pound. The regime was at 65 percent depth of discharge at the C/2 rate (5). As with the ECOM cadmium-air system the air cathode of the GT&E system was a bifunctional platinum electrode.

Up to the present time, R&D efforts at ECOM with the iron-air system have been very limited. Exploratory work has been done with iron electrodes supplied by GT&E and air cathodes by Leeson Moos. Data have been erratic and nonconclusive. Work will be carried out in the near future utilizing the knowledge of the present state-of-the-art of the electrodes as well as novel approaches derived from internal work.

Conclusion - If the self-discharge, capacity maintenance, oxidation and water loss problems of the iron-air couple are resolved, this system should become very attractive as a low cost, high energy density power source for communication and transportation applications.

References

1. Electrode Processes In New Electrochemical Sources of Current; V. S. Bagotski; Conference Moskau 1956; Pgs. 737-43.
2. The Iron-Carbon Cell; N. A. Shurmorskaia and R. K. Burshtein; Conference Moskau 1956; Pgs. 768-72.
3. Cathodic Reduction Of Iron; V. P. Galushko, E. F. Zavgorodnaya and L. I. Tishchenko; Zhur. Priklad Khim; 1959, 32, 1551-1555.
4. Hydrogen Overpotential at porous Iron Electrodes Containing Certain Alloying Metals (Cu, Ni, W, Co, and Mo); N. N. Voronin, I. B. Barmashenko, and D. S. Nadeszhdin; Ukrain Khim. Zhur. 1954, 20, 182-193.
5. Survey And Analysis on Metal-Air Cells; A. Fleischer; Tech Report AFAPL-TR-68-6; March 1968; Pgs. 27-28.