AN IRON–AIR VEHICLE BATTERY

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Summary

A 30 kWh iron–air battery system for traction applications, having an energy density of 80 Wh/kg at the 5 h rate has been developed and tested. A description is given of the system and its components. The special problems associated with metal–air batteries are discussed and results from full scale test are given.

Introduction

Secondary metal–air batteries are very attractive from the point of view of energy density because the positive electrochemical reactant, oxygen, is supplied from outside the battery. Work on this kind of power source started in the middle 1960s both in the U.S.A., Japan and Europe and in several cases experience as well as know-how from fuel cell development work were used. Most of these projects have, however, not resulted in full scale batteries although metal–air battery systems still are considered to have the potential for use in hybrid vehicles and perhaps in electric vehicles [1].

For primary and mechanically rechargeable metal–air batteries zinc dominates the field as negative active electrode material. For secondary applications Japan Storage Batteries, Sanyo, Japan [2] and Laboratoires de Marcoussis [3] have been and are working on systems with this negative material. In the first of these projects with fixed electrolyte and conventional zinc electrodes 123 Wh/kg has been reported in a single 1.25 kWh module. The Sanyo battery uses, apart from a sintered Zn electrode and air electrode, a third auxiliary electrode to be used during charge. During discharge the electrolyte is circulated within the battery, while during charge it has to be connected to and circulated through an external tank. A full battery (124 V, 540 Ah) is reported to give 109 Wh/kg during 200 - 300 cycles. The French project is using a technique where the negative zinc material is suspended in the electrolyte which is pumped through tubular air cells during discharge. For this concept an energy density of 100 Wh/kg and a power density of

80 W/kg for a minimum of 500 cycles are expected. This performance is projected from results of 1 kWh modules. One advantage with the slurry systems is that the active material can be reduced externally, which means that a vehicle can be instantly charged by exchanging the slurry. Later reports [3] have shown that it may be better from logistic reasons to recharge the active material within the vehicle. This makes a special charging unit in the vehicle necessary which will increase the complexity and cost for the system.

Sony Corp. in Japan has also developed a zinc–air battery in which the active material is circulated. After demonstration in a vehicle (3 kW) in 1974 the project was shut down [4]. Low energy density on a volume basis and a need to pump the active material are considered to be the most apparent disadvantages with the slurry technique.

Matsushita in Japan has reported 88 Wh/kg from a 1.56 kWh iron–air module at the 7 h rate. The goal is to achieve 70 Wh/kg for 200 - 300 cycles in 1977 in a complete system [2]. This battery has a sintered iron electrode, a thin carbon based air electrode and an auxiliary pole for charging. Owing to the low power characteristics it is combined with a high power lead–acid battery when used in a test vehicle. During stops the lead–acid battery is charged from the iron–air power source [5].

Westinghouse are also active in this field [6, 7] and have developed bifunctional air electrodes giving promising results. No results from batteries have, however, been reported. Siemens [8] have published results from single cells and electrodes for an iron–air battery.

The iron–air battery project of the Swedish National Development Company (SNDC) seems to be the only one to have resulted in full scale batteries tested in vehicles. In 1974 a second generation prototype was tested in a 15 kWh battery in a mine vehicle [9]. Based on experience obtained during these tests a third generation was designed and a 30 kWh battery built and tested during 1974 and 1975. In this paper the design and performance of this battery as well as the future for iron–air batteries are discussed.

The iron electrode

Pocket negative iron electrodes have been in commercial use since the beginning of this century and sintered ones since the beginning of the 1950s although low utilization of active material, high self-discharge and poor charge efficiency have limited their use. As a result of this the use of the nickel–iron battery has decreased during the last decade in spite of its cheap and non-toxic negative active material [10]. Because of ruggedness, long life and a potential for energy densities in the range of 60 Wh/kg the nickel–iron concept is considered as a near term battery for electric vehicles.

In metal–air batteries the negative electrode will limit the total energy of the system. Consequently the aim has been to develop thick (2 - 5 mm) iron electrodes with a high Ah/volume ratio, working at elevated ($\sim 40\ ^\circ$C) temperatures. Since the active material will expand during discharge a highly

porous and homogeneous structure with good current conducting properties is necessary. Also the chemical composition of the active material is of great importance since the hydrogen overvoltage on pure iron is low which means high self-discharge and poor charge efficiency due to hydrogen evolution competing with the charge process. In parallel with the development work of this battery, investigations have been performed in order to get a better understanding of iron as an active material and its electrochemical reactions [11 - 14]. These efforts have resulted in sintered electrodes giving capacities as shown in Fig. 1. Although only the first potential step is considered, the capacities obtained are about 2 - 3 times higher both on volume and weight basis in comparison with cadmium and iron negative electrodes commercially available today. These electrodes can also be made comparatively thick (up to 5 mm) thus giving very high Ah/electrode area ratios. Figure 2 shows the half-cell curve for an electrode. In comparison with other iron electrodes the charge curve has a very marked potential step when going from reduction of $Fe(OH)_2$ to hydrogen evolution. This increase of the hydrogen overvoltage, which is similar to that of the cadmium electrode, leads to a low self-discharge and good charge efficiency. The capacities shown are maintained with 10 - 15% overcharge on an Ah basis [15]. These sintered electrodes are made from very cheap iron material by a process developed by SNDC.

This electrode, in thinner versions, has also been shown to be very attractive as negative counterpart in advanced nickel—iron batteries, which give about 60 Wh/kg at the 5 h rate.
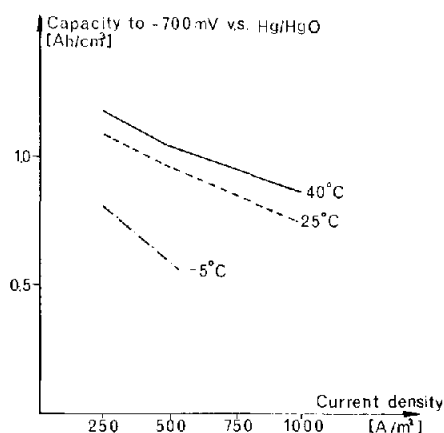

Fig. 1. Capacities for an iron electrode, 2.1 mm thick, at different temperature levels, after about 100 cycles.

The air electrode

The application of an air electrode in this battery differs somewhat from its use in fuel cells for which purpose most development work has until now been performed. This is because it is used as a counter electrode during the
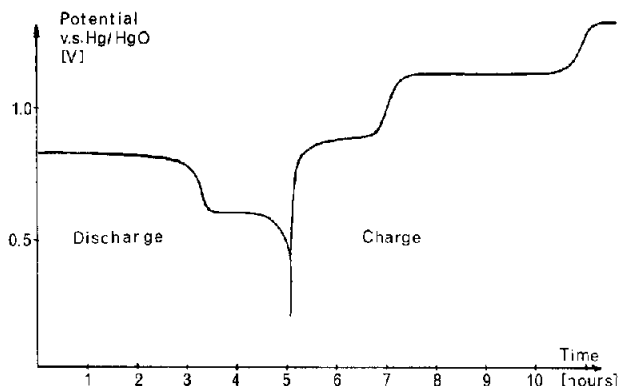
Fig. 2. Discharge – charge curves at 40 °C for an iron electrode, 3.2 mm thick, 250 A/m². The electrode is tested in a half-cell against a nickel plate.

charge process. It was decided early in the development work to use rechargeable air electrodes because an extra auxiliary electrode for evolving oxygen during charge will increase the volume and complexity of the stacks. This twofold duty puts a very high demand on the electrode, especially the structure and catalysts. The air electrodes used in this prototype are of a double layer type 0.6 mm thick with nickel as the supporting material. Attention has been focused on the following parameters during the development work.

Thickness

In a metal–air battery construction the number of air electrodes is normally twice that of the negatives. This fact together with the volume of the battery stack being more critical than the weight makes it necessary to use very thin air electrodes.

In combination with other requirements such as mechanical and chemical stability it is important to develop an optimized and fully controlled structure. The dual function also requires two layers — a hydrophilic with good current conducting properties on the electrolyte side and a hydrophobic coarse layer containing the catalyst on the air side. The air electrode used in this battery is a two layer sintered nickel plaque, 0.6 mm thick, and with the catalyst in the coarse layer.

Differential pressure

A low differential pressure will decrease the power required to pump the air through the system and also the demand on strength and stability of the stack construction and electrodes. The air electrodes of the SNDC iron–air battery are optimized to work with $\Delta P = 0.02$ bar, a pressure which also will decrease the risk of leakage.

Working temperature

Owing to the heat evolved in a secondary metal–air battery system it must always be kept at elevated temperature in order to obtain sufficient

cooling. It is, however, advisable to keep this temperature below 50 °C in order to achieve a long life for both electrodes and cell stack. The electrodes are designed to work at 40 °C but are stable to higher temperatures (up to 60 °C) which will appear at peak power.

Catalyst contents

In the prototype described here the classical nickel–silver system has been used as catalyst. This system which is in a position to give a very good performance has, however, the disadvantage that the oxygen evolution occurs in the corrosion region of Ag [16]. This means that silver has a tendency to leave its original site in the electrode and go out into the electrolyte causing a decrease in activity and sometimes even to short circuiting. By placing the silver in the active zone of the electrode and reducing the possibilities for dissolving into the electrolyte, the level can be kept as low as 2.5 mg/cm^2 without negative effects on life and performance.

Figures 3 and 4 give the potential of the air electrode as a function of current density and number of cycles. The apparent improvement in activity of the electrode during the first 40 cycles, which also has been observed by Cnobloch *et al.* [17], is probably due to an increase in the electrochemically active surface of the electrode.
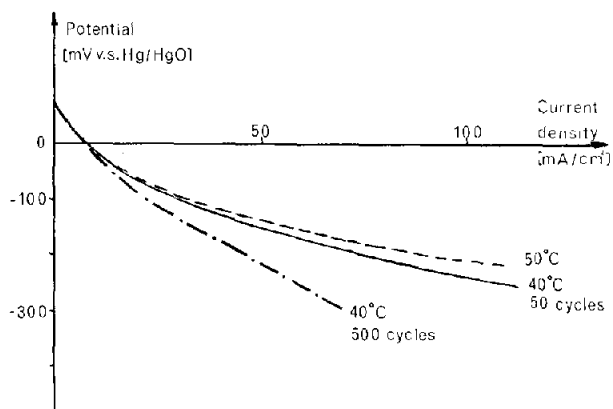

Fig. 3. Polarization curves for air electrodes. ΔP = 0.02 bar.

Stack build-up

Volume is an important factor for vehicle metal–air batteries. In the work to develop a stable easily produced and compact cell stack, know-how from the ASEA fuel cell project [9, 18] has been used by welding the air electrodes to polymer frames. By putting these frames two and two together an air element is formed. These elements are welded together with iron electrodes in between forming a very stable and compact pile (Fig. 5). This construction which is based on the experience from the two earlier prototypes has proved valuable in fulfilling the requirements set up for this battery.
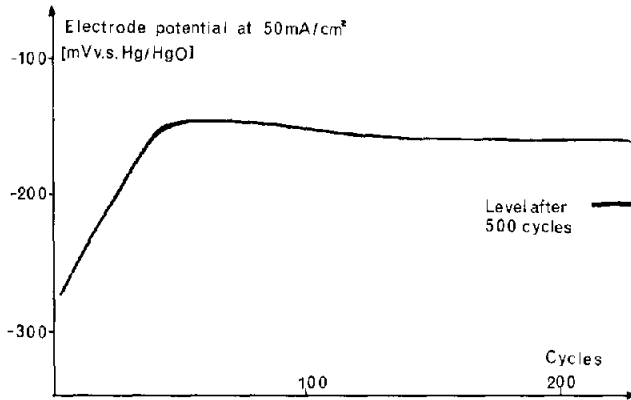
Fig. 4. Performance of air electrodes during cycling at 40 °C. Each cycle 2 h charge and 1 h discharge.
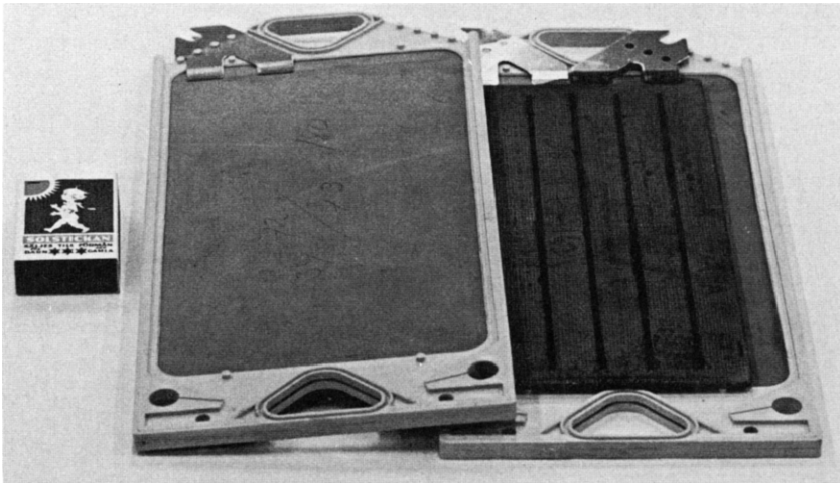

Fig. 5. Assembly of air pockets and iron electrode.

The prototype battery here described contains 8 piles each consisting of 190 air and 95 iron electrodes. The electrodes of each pile have been divided into 19 cells connected in series (Fig. 6). The size of the electrodes is approximately 10 × 20 cm.

Figure 7 gives a cross-section of a cell in the pile with air and electrolyte flow. By a very good distribution of air within the air element 50% of the oxygen introduced to the system is consumed at the air electrode at the 5 h rate. This high utilization is of great importance since it reduces the power consumption and size of the auxiliary system. The circulation of electrolyte is necessary to keep the system at operating temperature. It also allows filtering of the electrolyte which minimizes the risk of short circuiting. Because of the
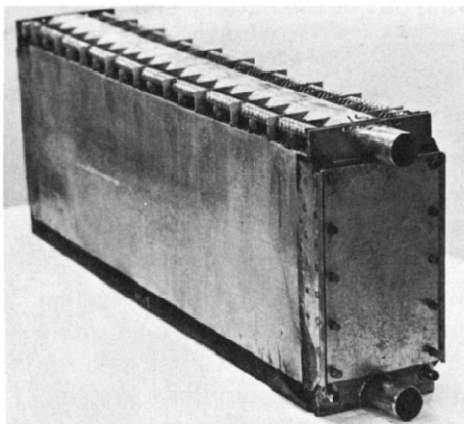
Fig. 6. Battery pile. The electrolyte leaves the stack by flowing over a free board along both sides of the pile.
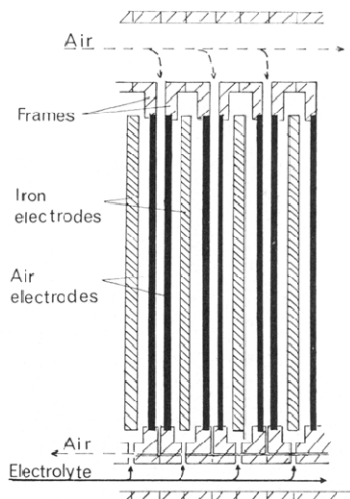
Fig. 7. Cross-section of SNDC iron–air battery pile.

very good stability of the electrodes, and in order to obtain good heat transfer, no separators are used except spacing ribs (0.8 mm) which are glued onto the iron electrodes.

Auxiliary system

When developing a complex battery system it is necessary to start with the basic components and stack before it can be connected to an auxiliary system. This means that up to now most of the effort has been used for developing electrode and pile design. The first prototype batteries had a comparatively simple system in comparison with what will be required for commercial batteries.

The auxiliaries of a rechargeable metal–air battery must take care of several functions of which the following are most important.

Circulation of electrolyte and air

These basic functions are supplied by a fan and rotating pump. The flow of electrolyte and air has to be regulated with the current taken out of the battery.

Cooling

Heat is evolved in the system mostly because of the polarization of the air electrode during charge and discharge. A heat exchanger directly or indirectly connected to the electrolyte system has to be used.

Moisture exchanger

Moisture must be exchanged between the incoming and outgoing air. Otherwise there will be a substantial drying out of the battery and a tank with compensating water has to be added.

Carbon dioxide remover

In order to avoid clogging of the air electrodes and carbonization of the electrolyte, carbon dioxide has to be removed from the air before introducing it into the piles. On the prototype described here this function was served by a Sodasorb powder bed at the air inlet. Further development aims to incorporate this function into the moisture exchanger.

Figure 8 shows a schematic figure of the battery and auxilary system. In the 30 kWh battery the 8 piles are in two decks with four piles on each deck. Figure 9 shows the whole battery system including auxilaries but without the external heat exchanger. The weight and volume of this auxiliary system, which is about 20% of the whole battery, can probably be decreased to about the half of this figure. The total energy consumption is estimated to be about 5% of the battery energy.
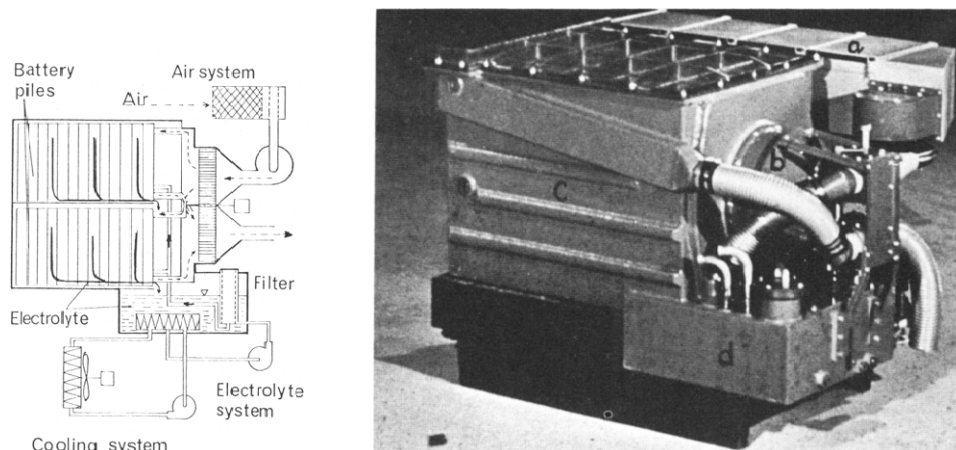

Fig. 8. Auxiliary system.

Fig. 9. 30 kWh battery system. (a) Carbon dioxide remover; (b) moisture exchanger; (c) box for battery piles; (d) box for internal heat exchanger and electrolyte storage. The external cooling system is not shown.

Performance

This battery has been tested both in the laboratory and in a vehicle. Power and energy density data for the whole battery including auxiliary system in comparison with results obtained from earlier generations are given in Fig. 10. An estimation on what can be achieved by further development of
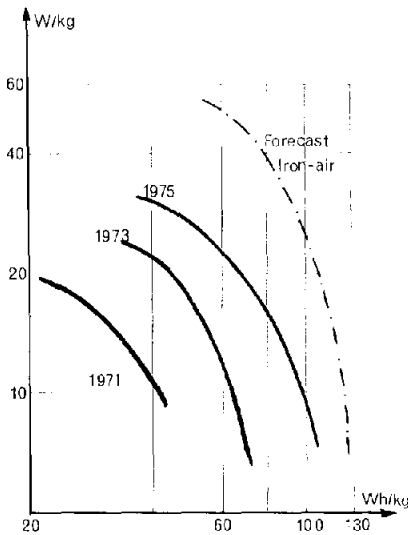
Fig. 10. Performance of SNDC iron–air batteries, including auxiliary system.

this concept is also shown. The piles have given more than 200 full cycles. The whole battery system including auxiliaries has been tested in a van in order to get experience of the problems associated with full scale battery systems working in vehicles. Figure 11 gives normal charge and discharge curves for a cell in the battery. The apparent difference in voltage on charge and discharge depends to about 70% on polarization losses in the air electrode.
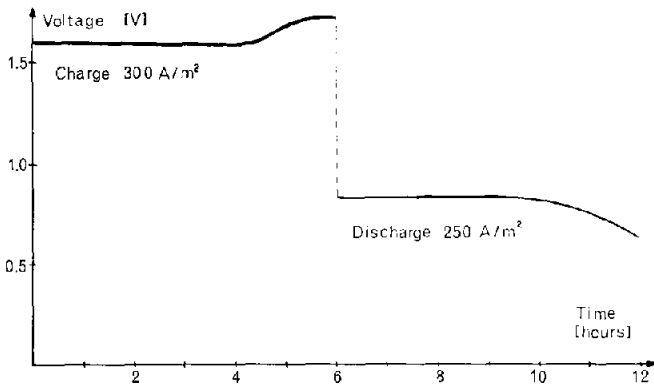

Fig. 11. Charge – discharge voltages for an average cell in a SNDC iron–air battery including auxiliary system.

Discussion

Testing of this full scale battery system has proved the feasibility of using an advanced metal–air battery in vehicles even for rough underground

applications. The iron electrode and stack design have fulfilled all requirements and will be used in future generations. The present life limiting factor is the air electrode where for this application better catalysts for both oxygen evolution and reduction still have to be developed. The advantages of rechargeable air electrodes are so obvious regarding both design and energy density that efforts must be directed towards finding catalysts which can sustain this dual function over more than 1000 cycles without decrease in capacity.

The circulating electrolyte system is necessary for the thermal balance of the system but gives also the possibility to filter and control the electrolyte. Since only distance ribs are placed between the electrodes the circulation and heat transfer processes are very efficient.

The auxiliary system is presently a weak link mainly due to lack of experience. In comparison with the present prototype system the weight and volume of the auxiliaries have to be decreased to less than 10% of the total system. The decarbonization process must be improved. The testing has shown no fundamental problems which means that this goal can probably be reached by only improving and optimizing the present technique.

A metal–air battery will always, due to polarization in the air electrodes, be a low power energy source. For this reason it will be practical to use it in hybrid systems where the property of high energy density of the metal–air battery can be optimized.

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