Short communication

Lab-size rechargeable metal hydride–air cells

Wei-Kang Hu*, Dag Noréus

Department of Materials and Enviromental Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

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ABSTRACT

Lab-size rechargeable metal hydride–air (MH–air) cells with a gas management device were designed in order to minimize the loss of electrolyte. An AB_5-type hydrogen storage alloy was used as anode materials of the MH–air. The thickness of the metal hydride electrodes was in the range of 3.0–3.4 mm. Porous carbon-based air electrodes with Ag_2O catalysts were used as bi-functional electrodes for oxygen reduction and generation. The electrodes were first examined in half-cells to evaluate their performance and then assembled into one MH–air cell. The results showed the good cycling stability of the rechargeable MH–air cell with a capacity of 1990 mAh. The discharge voltage was 0.69 V at 0.05–0.1 C. The charge efficiency was about 90%. The specific and volumetric energy densities were about 95 Wh kg^{-1} and 140 Wh L^{-1}, respectively.

1. Introduction

Rechargeable Li-ion or Li-polymer cells have occupied the main share in small size rechargeable battery market because of their higher energy densities, especially per unit weight. This has made them dominate the portable applications such as mobile telephones and laptop computers. Rechargeable nickel/metal hydride (NiMH) cells, on the other hand, have left this battery market segment since commercialisation in 1990, but they have become the main battery for hybrid electric vehicles (HEV) where safety and long lifetime are important. If the nickel hydroxide electrode in the rechargeable NiMH cell is replaced by a light-weight bi-functional air electrode, the increase in energy densities could reach that of a Li battery by developing a rechargeable MH–air cell. Several MH–air cell systems have been studied during the past years [1–7], showing a possibility to reach a satisfactory cycle life. However, some critical issues still need to be addressed in order to give the MH–air cell acceptable performance for practical application. Firstly, the cycling stability of porous carbon-based bi-functional electrodes needs to be significantly improved upon, especially under the condition of a longer charge period. Secondly, since air instead of pure oxygen gas is used at the cathode for practical operation, we need to evaluate any detrimental influence on performance from the CO_2 content in air. Different conclusions concerning the alleged CO_2 poisoning have been discussed in the literatures. Third, an active gas/electrolyte management should be implemented in order to

reduce electrode polarization and keep good ion conductivity, especially during charging. In addition, anode fabrication and electrode thickness are also important to optimize when a rechargeable MH–air cell with good cycling stability is to build. In this paper, we discuss these issues and investigated a Lab-size rechargeable MH–air cell with a capacity of 1800–2000 mAh. Cycling stability and rate capability were also evaluated.

2. Experimental details

2.1. Preparation of metal hydride electrode

AB_5-type metal hydrogen storage alloys with the composition $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ (CaCu5 hexagonal structure and unit cell dimension of 5.012 Å and 4.057 Å, respectively) were used as active materials in the MH anode. The hydride powder with a particle size of <75 μm was mixed well with graphite powder in a weight ratio of 95:5. A 2% PTFE suspension was added to obtain a slurry. The slurry was pasted onto a nickel mesh substrate with a thickness of 0.15 mm. After drying at 60 °C for 1 h, the MH electrodes were pressed under the pressure of 20–30 bar. Each electrode contained about 4.0 g MH powder. The finial physical metal hydride electrode dimension was 51 mm in length, 27 mm in width and 1.5–1.7 mm in thickness. The MH electrodes were immersed in a 9N KOH solution for several hours, and then activation by performing three charge–discharge cycles was carried out in a half-cell at room temperature. A nickel hydroxide electrode with a larger capacity was used as a counter-electrode and a HgO/Hg electrode was used as the reference electrode. After this activation, the MH electrode was made into the anode of the MH–air cell.

* Corresponding author. Tel.: +46 8161253; fax: +46 8 152187.
  E-mail address: wkhu@struc.su.se (W.-K. Hu).

2.2. Preparation of bi-functional air electrode

The bi-functional air electrodes in this work were composed of two layers, a catalytic layer and a gas-diffusion layer. In order to give the air electrodes bi-functional properties, hydrophobic and hydrophilic sites in the catalytic layers were optimized by adjusting the ratio of hydrophobic to hydrophilic parts. Thus, a stable three-phase reaction interface/zone between the electrolytes, gas and catalytic sites was attained. Polytetrafluoroethylene (PTFE) is very stable and effective hydrophobic agent. The PTFE materials used in this work are in the form of a colloidal suspension, produced by Aldrich. High surface ($300 \, m^2 \, g^{-1}$) Vulcan-72 carbon powder having the less wet-proofed characterization was used as conductive materials, while the catalyst used was Ag_2O powder. The catalyst load was 4.7–5.7 mg cm^{-2}. The ratio of hydrophobic to hydrophilic materials is in the range of 18–25:82–75 in weight.

The gas-diffusion layer was more hydrophobic than the catalytic layer. The hydrophobic properties in the gas-diffusion layer ensure a stable gas supply for the reactant gas that can easily diffuse through the pores towards the catalytic layer, where the electrochemical reaction of oxygen reduction and generation takes place. In addition, this layer also acts as a barrier to prevent penetration of the electrolyte. The gas-diffusion layer contained 45% PTFE and 55% Vulcan-72 carbon.

A rolling technique prepared the both layers with an initial thickness of 0.7–0.9 mm. Then, both layers were pressed together with a nickel mesh at 60–80 bar for 10 min at a temperature of 80 °C, and dried at 60–80 °C for one night. After then, the air electrode was heat-treated at 280–300 °C to burn off the remained organic additives in order to produce a porous structure. The finial thickness of air electrode was 1.0–1.15 mm.

In order to ensure good performance of the MH–air cells, the air electrode was also examined first in a half-cell with the same concentration electrolyte. Air was supplied on the back of air electrodes. No carbon dioxide filter was used. Oxygen reduction and generation cycles were recorded by Electrochemical Test Stations.

2.3. Design and assembly of MH–air cells and electrochemical evaluation

A laboratory scale MH–air cell case was designed, as shown in Fig. 1. The part A having many small holes with a diameter of 0.15–0.20 mm is the air electrode. Air flows naturally through the holes and enters the catalytic layers via the diffusion layers. The
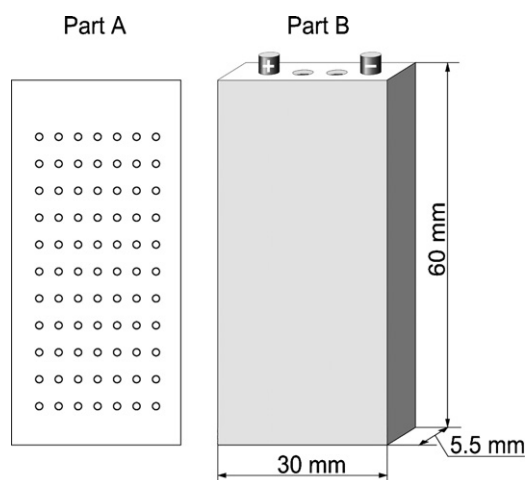
Fig. 1. Schematic drawing of rechargeable MH–air case where part A with many holes is for the air-diffusion electrode, and part B with two terminals of anode and cathode and two holes is the house of MH electrode and electrolyte.
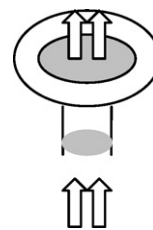
Fig. 2. The gas management device where two circle hydrophobic cements are contained to manage the gas.

total surface area exposed to the electrolyte of the air electrode was about 17 cm^2. The metal hydride electrode was assembled on part B by resistance welding. There are two terminals for anode and cathode, and two open holes for electrolyte and gas managements, respectively. A special device for gas management was designed, as shown in Fig. 2, where a hydrophobic cement material was used to separate water and gas before they go out of the cell system. The separation between water ($H_3O_2^-$) and gas (O_2) is critical for all kinds of rechargeable metal–air cells. The other hole is for electrolyte management. A gradual reduction of the electrolyte amount would be observed as the cell operates with repeated charge–discharge. The reduction of electrolyte was attributed to the following factors: (a) the humidity difference between inside and outside of the cell. The higher humidity insider the cell facilitates the loss of water molecules via the air electrode or the gas management unit; (b) during charging, water is consumed to produce humid oxygen gas. By filtering the gas management unit, most of the water can be recovered. But an occasional injection of fresh electrolyte through the rubber lid in the other hole was needed to keep the electrolyte amount. The charging rate also influences the efficiency of gas management device. For higher rate drain, gas management becomes very important because a lot of O_2 is produced. In this work, the gas management device worked well at a relatively low charge rate of 200 mA.

After assembly, the MH–air cell was charging with a current of 200 mA at room temperature for 11 h, followed by a discharge of 100 mA to an end voltage of 0.6 V. Air was naturally vented through the holes on the part A of the battery case. No extra air pump and no CO$_2$ scrubber were used, respectively. The charge–discharge processes were controlled by Electrochemical Test Stations.

3. Results and discussion

3.1. Electrochemical behaviour of MH electrodes and air electrodes

Fig. 3 shows the charge and discharge curves of two pieces of MH electrodes assembled in parallel. The total thickness of MH electrodes was within 3.0–3.4 mm. As seen, the charge or discharge curves of the MH electrodes had a steep slop. As discussed in a previous paper [8], the electrochemical behaviour of thick MH electrodes was much different from thin MH electrodes. The former exhibits a steep charge/discharge curves while the latter has a flat charge/discharge curves with little potential and capacity drops. The significant dependence of thickness on the electrochemical properties is supposed to be related to mass transport (H_2O/OH^-) during charge–discharge. Mass transport dominates the electrochemical performance of the thick MH electrodes, particularly at higher current densities [8]. In this work, the MH electrode with the thickness of 3.0–3.4 mm showed a specific capacity of 240 mAh g^{-1} at the discharge rate of 200 mA, much lower compared with thin MH electrodes having a specific capacity of 300 mAh g^{-1} which is close to the theoretical possibility.
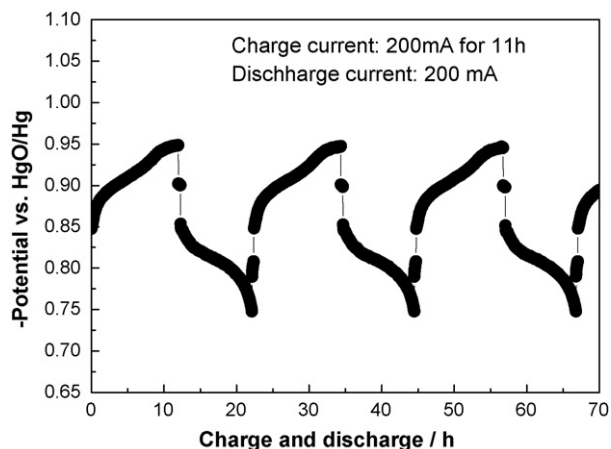
Fig. 3. The charge–discharge curves of MH electrodes with the thickness of 3.0–3.4 mm in a half-cell having 9N KOH at room temperature.

The air electrode showed lower activities during the initial cycles due to the hydrophobic nature and poor electrolyte-wetting in the three-phase reaction zone. However, significant improvement was obtained after a number of cycles. Fig. 4 presents the charge (oxygen generation) and discharge (oxygen reduction) behaviour of the air electrode after activation. Charge and discharge time lasted 12 and 10 h, respectively, at a current density of 16 mA cm^{-2}. As seen in Fig. 4, the air electrode showed very stable bi-functional properties. Moreover, no CO_2 scrubber was used and the air electrode was not shown to be sensitive to CO_2. Other researchers have also found that a CO_2 content less than 500 ppm in the air did not significantly influence the electrochemical performance of anode or cathode in alkaline fuel cells (AFC) [9]. However, an increase of carbonate concentration in the electrolyte was observed. Carbon oxidation of the support material in the air electrode during a charge period also adds to the carbonate content in the electrolyte.

3.2. Performance of MH–air cells

Fig. 5a shows the charge–discharge curves of the MH–air cells. The average charge voltage was about 1.56 V at a charge current of 200 mA (corresponding 11.7 mA cm^{-2} in the air electrode). The discharge voltage was about 0.69 V at a discharge current
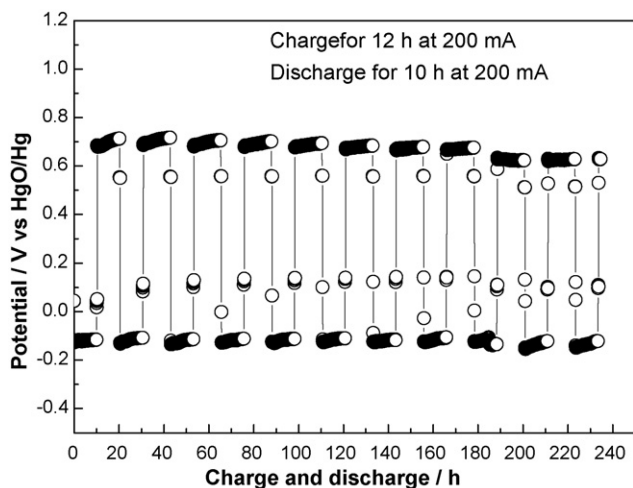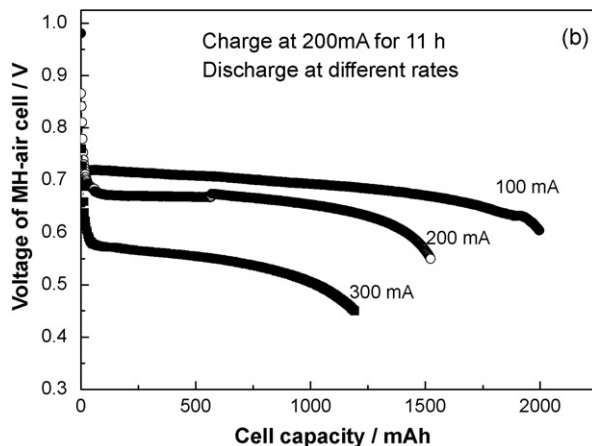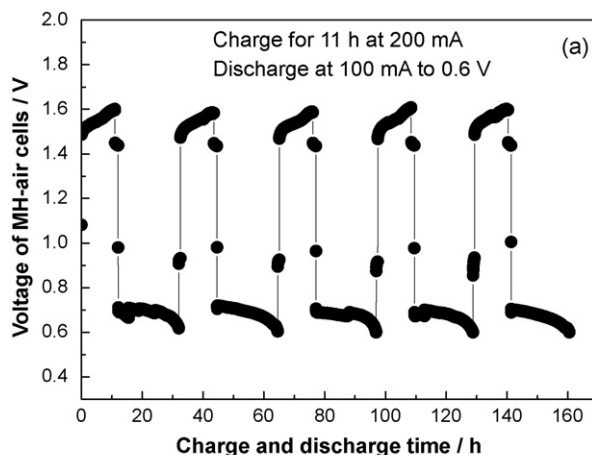

Fig. 5. (a) Charge–discharge performance of MH–air cells in 9 N KOH at room temperature. (b) Discharge curves of MH–air cells at different current densities.

of 100 mA. The charge efficiency calculated on charge capacity against discharge capacity was about 90%. The specific and volumetric energy densities of the laboratory scale MH–air cells were about 95 Wh kg^{-1} and 140 Wh L^{-1}, respectively. However, the cell capacity and discharge voltage declined as the discharge current increased to 300 mA, as shown in Fig. 5b. This is because the capacity utilization of a thick MH electrode is reduced, leading to a voltage drop between the anode and cathode as the discharge rate
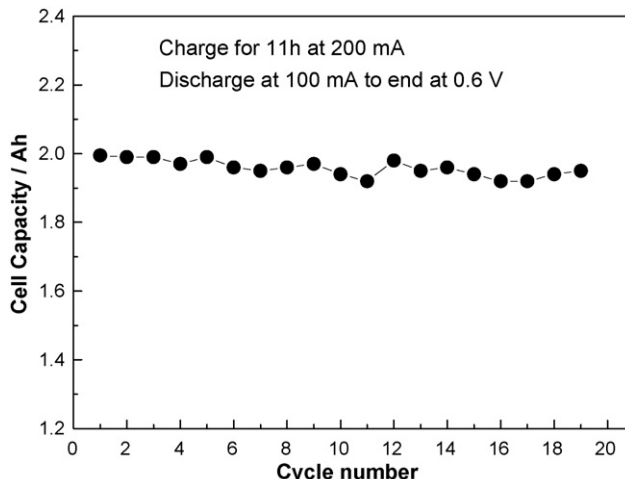

Fig. 4. Charge–discharge behaviour of air-diffusion electrodes in a half-cell having 9 N KOH at room temperature.

Fig. 6. The cycling performance of MH–air cells in 9N KOH at room temperature.

increased. Although the performance at higher rate drain needs to be improved, the laboratory size MH–air cells exhibited very good cycling stability with a discharge capacity of 1940–1990 mAh, as shown in Fig. 6.

The capacity of the MH electrode determines the total capacity of MH–air cells. Therefore the MH electrode capacity should be as high as possible. However, thick MH electrodes have negative effect on the utilization of active materials and rate capability. Thus, how to optimize electrode thickness is an important parameter. For different applications, the design and thickness of MH electrodes could be flexible to meet different requirements. For low charge–discharge drains, thicker MH electrodes are preferred, whereas thin MH electrodes are used for high power densities in applications such as bicycles and electric vehicles.

4. Conclusions

AB_5-type hydrogen storage alloys can easily be adapted as anode materials in MH–air batteries. Due to mass transport problem of H_2O/OH^-, MH electrodes should not excess a thickness of 3.0–3.4 mm in order to keep utilization above 240 mAh g^{-1}. Our research also concludes that an air electrode based on a Ag_2O catalyst and PTFE binder supported by Vulcan-72 carbon can be used both for O_2 reduction and hydroxide (OH^-) oxidation with good cyclic stability. The charge efficiency of the MH–air cell was about 90% at discharge rates below 100 mA. However, the cell performance declined significantly at discharge rates of more that 300 mA. The rate limiting step in the thick MH electrode was attributed to a longer diffusion/migration path for mass transport from electrode/electrolyte interface to the interior of MH electrodes. This has a negative effect on the capacity, charge–discharge voltage and rate capability.

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