Journal of Alloys and Compounds 330–332 (2002) 766–770

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Air–metal hydride secondary battery with long cycle life

D. Chartouni*, N. Kuriyama, T. Kiyobayashi, J. Chen

Osaka National Research Institute, AIST, MITI, 1-8-31 Midorigaoka, Ikeda, 563-8577 Osaka, Japan

Abstract

We report the evaluation of a novel air–metal hydride rechargeable battery. A copper plated $MmNi_{3.5}Co_{0.7}Al_{0.7}Mn_{0.1}$ alloy was used as the active material in the metal hydride electrode. The metal hydride electrode was charged and discharged via a gas diffusion electrode based on a $La_{0.6}Ca_{0.4}CoO_3$ perovskite (supported on carbon) as the catalyst for both oxygen reduction (discharge) and oxygen evolution (charge). In a laboratory cell, measurements on a 2.5×2.5 cm metal hydride electrode sandwiched between two air-electrodes of the same size were performed in a 6 M KOH electrolyte at 25°C with oxygen or air supply. A very long cycle life of 250 cycles at 1C charge and discharge (1 h charge and 1 h discharge) was achieved. After 250 cycles, the capacity of the metal hydride electrode had decreased by about 10%, from 268 mAh g^{-1} to 242 mAh g^{-1}. After more than 220 cycles, the discharge voltage of the cell was 0.64 V for oxygen and 0.55 V for air. At 10 mA cm^{-2} (approx. 2 h charge and 2 h discharge) the cell voltage was 1.57 V for charge and 0.77 V for discharge (using oxygen), measured after more than 100 cycles. Peak power was 51.0 mW cm^{-2} for oxygen and 34.8 mW cm^{-2} for air. These values were measured at currents of 150 mA cm^{-2} for oxygen and at 100 mA cm^{-2} for air. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rechargeable battery; Air–metal hydride system

1. Introduction

The demand for small size nickel–metal hydride rechargeable batteries is rapidly growing. The long charge discharge cycle life, the lack of memory effect and especially the low toxicity of the active material makes them an attractive substitute for nickel cadmium cells.

In recent years, the use of portable electronics has increased the demand for batteries having high capacities but medium or low power. Further increase of the energy density is required to make them suitable for such low power application. A significant increase of the energy density per unit weight of typically 15–20% can be achieved by replacing the heavy Ni-electrode by a light weight air-electrode [1,2].

In commercial Ni–MH batteries the Ni-electrode has approximately the same weight as the MH-electrode but only 2/3 of the capacity. Therefore, despite the lower cell voltage of the air–metal hydride system, the energy density per unit weight is higher in comparison to the Ni–MH system.

Using an air–electrode capable of both oxygen reduction and evolution, a rechargeable battery can be obtained.

Charge '→' and discharge '←' reactions of the Air–MH system proceed as follows:

$$\text{positive (air-electrode):}\quad 4\,OH^- \leftrightarrow 2\,H_2O + O_2 + 4\,e^-$$

$$\text{negative (MH-electrode):}\quad 4\,M + 4\,H_2O + 4\,e^- \leftrightarrow 4\,MH + 4\,OH^-$$

$$\text{Total reaction:}\quad 2\,H_2O + 4\,M \leftrightarrow 4\,MH + O_2$$

During discharge, oxygen gas must be supplied to the positive electrode. If the air-electrode is comprised of catalyst/carbon composite material, carbon can be oxidized during the charging process. In previous works [1,3], this problem has been overcome by using a third electrode (NiOH or Ni-mesh) for the charging process. However, the extra weight of a third electrode diminishes the advantage of a light weight air electrode. In contrast, by using a bifunctional air-electrode, the third electrode can be omitted, resulting in the desired system.

Several reports of experimental cells using this principle

---

*Corresponding author. Present address: ABB Corporate Research Ltd., CH-5405 Baden-Daettwil, Switzerland.

0925-8388/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0925-8388(01)01466-9

have been published [4,5]. As catalyst material in the air-electrodes, mixed nickel and cobalt oxides were used. However, — with one exception where 175 cycles have been reported [5] — the cycle life time of these systems were always less than 70 charge/discharge cycles due to the short life time of the air-electrodes. The use of bifunctional air-electrodes that are less sensitive to corrosion is therefore demanded for a necessary increase of the cycle life time. The material used as the bifunctional catalyst and the carbon support material greatly influence the life time of the air-electrode [6]. At the present stage, employing $La_{0.6}Ca_{0.4}CoO_3$ perovskite material as the catalyst and graphite like carbon material as the support show the most promising results [7].

We report the evaluation of a laboratory air–metal hydride rechargeable battery with a very long cycle life.

2. Experimental

2.1. Metal hydride electrode

Mischmetal based alloy, $MmNi_{3.5}Co_{0.7}Al_{0.7}Mn_{0.1}$ purchased from Santoku metal industry was crushed down to particles smaller than 150 μm. The powder was used without any heat treatment and handled in air. It was chemically coated with copper (20 wt% of alloy) and dried in air. It was then mixed with 5 wt% PTFE dispersion (Daikin Industry, POLYFLON TFE D-2). The wet mixture was shaped to form a 3×3 cm sheet of typically 0.9 mm thickness. This sheet was sandwiched between two fine nickel mesh and pressed at 300 $kgf\,cm^{-2}$ at 320°C for 5 min under vacuum. Unless otherwise stated, the final thickness prior to cycling was typically 0.8 mm.

2.2. Bifunctional air-electrodes

The air-electrodes are composed of two layers. A hydrophobic gas diffusion layer (on the gas side) containing carbon black and PTFE and an active layer (on the electrolyte side), containing the $La_{0.6}Ca_{0.4}CoO_3$ perovskite catalyst supported on graphite like carbon material and PTFE. The carbon material was Vulcan XC72 (Cabot) that had been graphitized at 2700°C [6]. Both layers, together with a nickel mesh current collector on top of the gas diffusion layer, were pressed together at 320°C at 40 $kgf\,cm^{-2}$ for 20 min. The thickness of the electrodes used in this experiments were typically 0.6 mm. For a first evaluation of the system, air-electrodes produced at the General Energy Research Laboratory of the Paul Scherrer Institute in Switzerland were used for these experiments (see [6,7] for a detailed description of the production of the air-electrodes). For air-electrodes produced in our laboratory, high surface area graphite (300 $m^2\,g^{-1}$) was used as the carbon support in the active layer (publication in preparation).

2.3. Electrochemical cell

A special cell was constructed (Fig. 1). The metal hydride electrode is sandwiched between two identical air-electrodes. The distance between the metal hydride electrode and each air-electrode was 5 mm and the geometrical surface area of the electrodes in contact with the electrolyte was 6.25 cm^2 (2.5×2.5 cm). For the metal hydride electrode, typically 1 g of active $MmNi_{3.5}Co_{0.7}Al_{0.7}Mn_{0.1}$ alloy was immersed in the electrolyte.

For the air-electrodes, air or oxygen was supplied through holes in the Plexiglas plates. When air was used, a constant flow of 50 $ml\,min^{-1}$ was pumped through the cell. This flow is approximately three times more than that required for a discharge current of 1A. No CO_2 filter was used. When pure oxygen was used, the flow was set to typically 20 $ml\,min^{-1}$.

The electrolyte was 6 M KOH and the temperature 25°C, except where stated otherwise. During charge and overcharge hydrogen evolved from the metal hydride electrode. In order to remove hydrogen gas, the electrolyte was slowly pumped through the cell (12 $ml\,min^{-1}$). Through a small hole in one of the central Plexiglas plates a capillary for the Hg/HgO/6 M KOH reference electrode was inserted.

The cell was controlled by a Solartron SI 1280B electrochemical measurement unit. The cell was connected

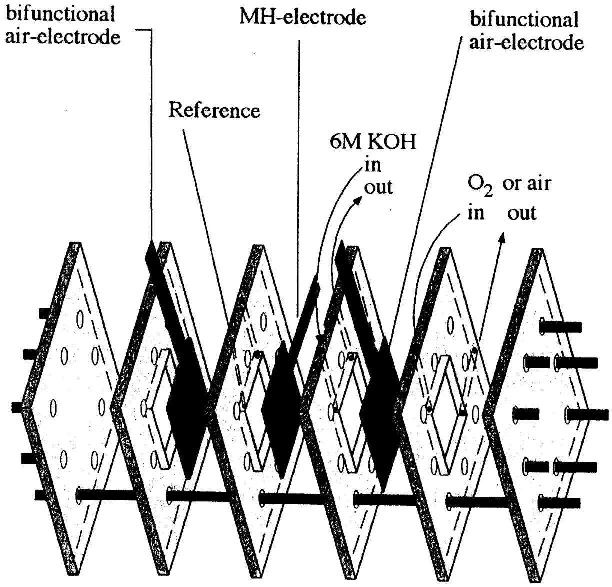

Fig. 1. Assembly of the air–metal hydride rechargeable battery. See main text for full description.

in the three electrode configuration with the measurement unit. The metal hydride electrode was the work-electrode and the air-electrodes the counter electrode. The potential of the air-electrodes was determined without iR-correction by measuring the total cell voltage.

2.4. Electrochemical measurements

Currents in mA g^{-1} are given as mA per gram of active metal hydride alloy material. Current densities in mA cm^{-2} are given in mA per cm^{2} of the geometrical air-electrode surface (the total geometrical surface area of the two air-electrodes is 12.5 cm^{2}).

In order to activate the metal hydride electrode, a low current of typically 50 or 100 mA g^{-1} was used for the first five cycles. The charge capacity was always 300 mAh g^{-1}. The battery was discharged until the metal hydride reached a potential of −600 mV vs. the reference electrode. The discharge capacity was calculated from the discharge current and the discharge time.

The cycle life performance was tested by using a current of ±300 mA g^{-1} (typically 20–25 mA cm^{-2}). After charge and after discharge a break of 5 min was imposed.

The discharge power was determined by performing discharges at different currents. The cell voltage was measured directly. The cell voltage at 50% depth of discharge and the current (in mA cm^{-2}) used for that particular discharge gave the power in mW cm^{-2}.

3. Results and discussion

3.1. Cell voltage

Typical cell voltage curves for a 1 h charge and 1 h discharge using oxygen or air are shown in Fig. 2. The discharge plateau cell voltage after more than 220 cycles was 0.64 V for oxygen and 0.55 V for air (Fig. 2). The highest discharge voltage and the lowest charge voltage was observed after about 70 cycles; using oxygen, values of 0.70 V for discharge and 1.62 V for charge were measured.

For 10 mA cm^{-2} (approx. 2 h charge and 2 h discharge) the cell voltage was 1.57 V for charge and 0.77 V for discharge (using oxygen), after more than 100 cycles. This corresponds to a voltaic efficiency of 49%.

3.1.1. Effect of the temperature on the cell voltage

With increasing temperature, the cell voltage decreases for charging and increases for discharging. Thus, the charging efficiency is improved. At currents of 300 mAh g^{-1} (20–25 mA cm^{-2}) the improvement is due mainly to the improved kinetics at the air-electrode.

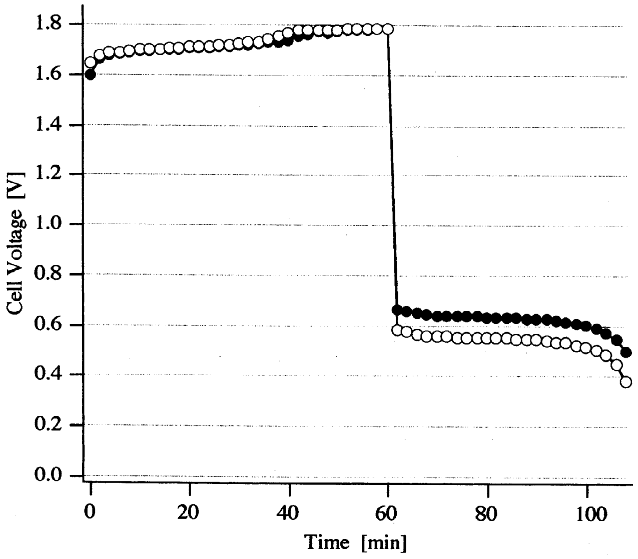

Fig. 2. Cell voltage of a full charge/discharge cycle using oxygen –●– and using air –○–. Current: 300 mA g^{-1} (=23.4 mA cm^{-2} for the air-electrode). Electrolyte: 6 M KOH at 25°C.

3.1.2. Effect of the electrolyte concentration on the cell voltage

With increasing electrolyte concentration, the cell voltage decreases for charging and increases slightly for discharging. The decrease in the charging voltage is due to the decrease of the air-electrode overpotential. For discharge however, OH^{-} ions are needed only at the metal hydride side, but not at the air-electrode side.

In summary, a higher voltaic efficiency is achieved by increasing both the temperature and the KOH concentration. However, such conditions would shorten the cycle life of the battery.

3.2. Capacity

The total capacity of the air–metal hydride battery is limited by the metal hydride electrode. The air-electrode itself is not charged or discharged, it only reduces or evolves oxygen (see introduction). The capacity decay upon cycling depends on the metal hydride alloy composition and on various experimental parameters, such as temperature, pretreatment of the active material and on the electrode structure [8]. The alloy used in these experiments is close to the standard composition used in commercial batteries. It has a good cycle life, loosing only 10% of its capacity after 250 cycles (Fig. 3).

3.3. Cycle life

The end of the battery life is determined by the cycle life of the air-electrode. The more the carbon material is oxidized during charging, the higher the risk that the catalyst particles loose contact or increase the contact resistance with the carbon support, i.e. the higher the

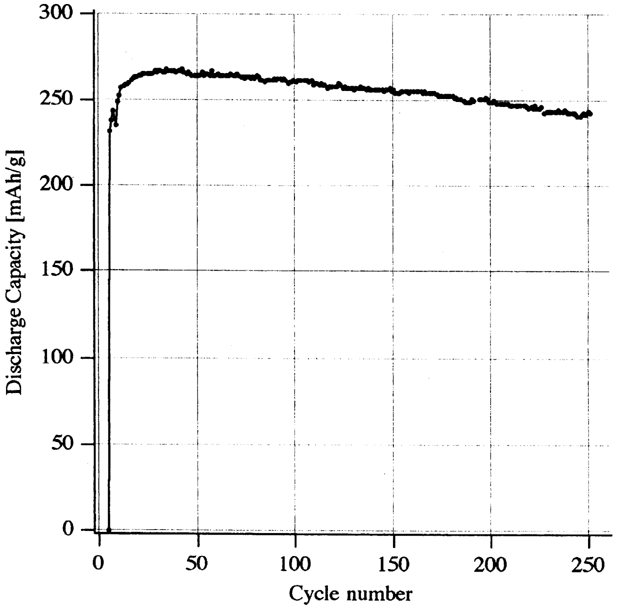

Fig. 3. Discharge capacity vs. the number of cycles (after five activation cycles). Cycled with 300 mA g^{-1} (1 h charge and 1 h discharge) using oxygen.

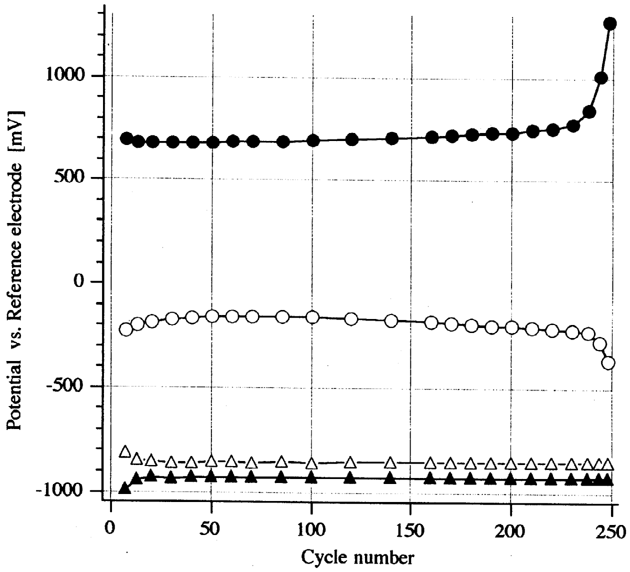

Fig. 4. Plateau potentials (after 50% charge or discharge) vs. the number of cycles. Potential of the air-electrode during charge –●– and discharge –○–, and metal hydride electrode during charge –full triangle– and during discharge –empty triangle– (same conditions as in Fig. 2).

overpotential. Reversibly, the higher the potential during charging the faster the oxidation of the carbon support material. This leads to a considerable weight loss of the air-electrode. Finally, the diffusion layer is wetted by the electrolyte and as a consequence the oxygen diffusion to the active layer is strongly hindered. At this point, the oxygen reduction is not possible and the battery can not be discharged anymore. In the example shown in Fig. 3, this happens after 250 cycles.

The plateau potentials of the metal hydride and of the air-electrode depend on the cycle number (Fig. 4). The metal hydride electrode needs about 15 to 20 cycles to be completely activated. Therefore, the overpotential is higher at the beginning of the cycle life. After activation, the overpotential of the metal hydride electrode does not change (assuming always the same current).

For the air-electrode the situation is different. First, it shows a fairly constant charge discharge potential behavior for the first 200 cycles. Then — due to the accelerated degradation (described above) — the overpotential starts to increase until the end of the cycle life of the air-electrode is reached.

3.4. Discharge power

The discharge power vs. current density using air or oxygen is shown in Fig. 5. The curves were measured for a cell containing two air-electrodes as shown in Fig. 2. Since the current density is given in mA per geometrical surface area of the air-electrodes, the absolute cell current through the cell is obtained by multiplying the current density in (mA cm^{-2}) with the total geometrical surface area of the air-electrodes (12.5 cm^2). In this measurement (Fig. 5) a metal hydride electrode with a thickness of 650 μm and with a loading of 980 mg of active metal hydride material was used. A further increase in the discharge power can be achieved by improving the metal hydride electrode (e.g. by reducing the thickness). In the experiments reported here, the metal hydride electrodes were not optimized from the viewpoint of the fast discharge behavior as the focus was the long cycle life of the cells.

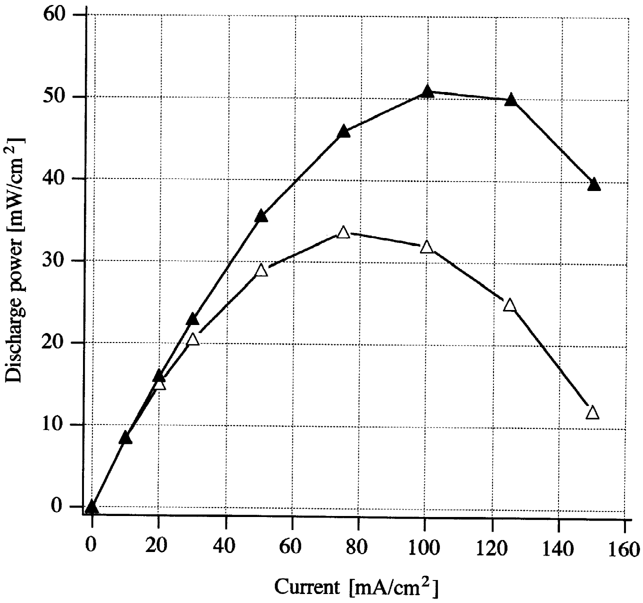

Fig. 5. Discharge power density for a cell composed of two air-electrodes (as described in Fig. 1) using oxygen (full triangles) and using air (empty triangles). Electrolyte: 45% KOH at 40°C.

4. Conclusion

A very high cycle stability of the air–metal hydride cell was achieved. 250 full charge discharge cycles could be performed at a rate comparable with that for nickel–metal hydride batteries (1 h for full charge and 1 h for full discharge). The metal hydride electrode lost only 10% of its initial capacity during this long cycling test. In addition, the bifunctional air-electrodes using a $La_{0.6}Ca_{0.4}CoO_3$ perovskite catalyst showed an excellent performance.

The system showed a maximum discharge power density of 34.8 $mW\,cm^{-2}$ for air and 51.0 $mW\,cm^{-2}$ for oxygen.

This laboratory cell was not optimized for delivering a high discharge power, because we focussed on the long cycle life of the battery.

Our results show that the metal hydride–air secondary battery is a promising alternative to the nickel metal hydride battery, especially for low power application demanding a high energy density.

Acknowledgements

We wish to thank Mr. Stefan Müller and Mrs. Gertraud Masanz from the General Energy Research Laboratory of the Paul Scherrer Institute (Switzerland) for providing the air-electrodes and helpful information on rechargeable air–metal battery systems. Further more, we wish to thank Dr. Hajime Arai from NTT Energy Laboratories (Japan) for helpful discussions.

References

[1] T. Sakai, T. Iwaki, Z. Ye, D. Noreus, J. Electrochem. Soc. 142 (12) (1995) 4040–4045.

[2] L. Jörissen, J. Garche, in: V. Barsukov, F. Beck (Eds.), New Promising Electrochemical Systems For Rechargeable Batteries, 1996, pp. 159–169.

[3] N. Vassal, E. Salmon, J.-F. Fauvarque, Electrochem. Soc. Proc. 97–18 (1997) 869–880.

[4] S. Gamburzev, W. Zhang, O.A. Velev, S. Srinivasan, A.J. Appleby, J. Appl. Electrochem. 28 (1998) 545–549.

[5] S. Gamburzev, A.J. Appleby, A. Visintin, in: B.J. Carlos, V.T. Nejat (Eds.), Volume 2 of the Proceedings of the 12th World Energy Conference on Hydrogen Energy Progress, 1998, pp. 1663–1668.

[6] S. Müller, F. Holzer, H. Arai, O. Haas, J. New Mater. Electrochem. Systems 2 (1999) 227–232.

[7] S. Müller, K. Striebel, O. Haas, Electrochim. Acta 39 (11/12) (1994) 1661–1668.

[8] T. Sakai, H. Miyamura, N. Kuriyama, H. Ishikawa, I. Uehara, Zeitschrift für Physikalische Chemie 183 (1994) 333–346.