

Letter

Electrode characterisation of MmNi₅-based alloys for nickel–metal hydride batteries

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Abstract

Negative electrodes of the nickel–metal hydride battery were made from the hydrogen storage alloy Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3} and modified by coating with nickel and mixing with cobalt powder. When the alloy was mixed with 10 wt.% cobalt powder, the discharge capacity increased from 259 mAh g⁻¹ to 303 mAh g⁻¹ at 300 K. When the alloy was coated with 11 wt.% nickel and mixed with 10 wt.% cobalt powder, the discharge capacity decay for a scaled cell (AA size, 1 Ah) was only about 4% after 200 cycles.

1. Introduction

The nickel–metal hydride (Ni–MH) system is attractive as a secondary battery because of its high energy density and the low level of pollutants. Although several basic studies were carried out on LaNi₅-based alloys [1], the capacity decay of LaNi₅-based alloys was ascribed to oxidized decomposition of the alloys to La(OH)₃ compound. Willems and Buschow [2] found that the cycle lifetime of the alloys was improved by increasing the substituting content of nickel with cobalt, though the substitution caused a decrease in storage capacity. Now, the use of an unrefined mischmetal (Mm) is very effective in lowering the cost of the hydrogen storage alloys. It was found that the MmNi₅-based alloy, MmNi_{3.5}Co_{0.7}Al_{0.8}, had a very long cycle lifetime under special casting conditions [3, 4]. The modification of the LaNi₅-based alloy electrodes by electroless Cu, Ni–P and Ni–B coatings and reducing agent on electrocatalytic activity for the hydrogen electrode reaction and high-rate dischargeability was investigated [5–8]. The discharge capacity decay of the alloy electrode was also improved by mixing with cobalt powder [9, 10].

In this work, the characterisation of the structure and electrode of Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3} alloy was studied. The effect of Co powder on the discharge

capacity of this alloy electrode was studied in detail. A sealed Ni–MH cell (AA size, 1 Ah) using above alloy was constructed and researched.

2. Experimental details

The hydrogen storage alloy Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3} (where Mm denotes mischmetal, which is comprised of 43.1 wt.% La, 3.5 wt.% Ce, 13.3 wt.% Pr and 38.9 wt.% Nd) was prepared by induction melting and rapid cooling. The cast alloy was pulverized mechanically to particle size 50–100 μm. Some of the alloy powder was coated with 11 wt.% nickel in chemical plating solution. The alloy powder was filled in a porous nickel substrate together with a small amount of polyvinyl alcohol (PVA) solution as a binder and then pressed at a pressure of 150 kgcm⁻² after vacuum drying at 150 °C. The resulting electrode plate was used for the discharge capacity measurement. As counter and reference electrodes, a sintered nickel hydroxide plate and Hg/HgO 6M KOH electrodes were employed, respectively. The charge current was 150 mA g⁻¹ and discharge current was 100 mA g⁻¹. The end of discharge was set to -0.6 V vs. Hg/HgO. The alloy powder was mixed with 3 wt.% polytetrafluoroethylene (PTFE) dispersion, which contained 0.3 wt.% carboxyl methylcellulose (CMC) and 0.5 wt.% PVA aqueous solution, and a small amount of carbon, nickel or cobalt powder to ensure a good electric conductivity and the same amount of MH alloy. The mixture was filled in a porous nickel substrate and roller pressed in order to get a sheet, which was used to construct a small cylinder sealed cell. The sealed cell (AA size, 1 Ah) was also constructed by rolling the MH electrode (40×85 mm², ≥1.6 Ah), the separator and the sintered nickel electrode (40×75 mm², ≥0.9 Ah). A cycle test was conducted in the MH electrode of a sealed cell by repeated charging at 0.4 C rate up to 120% capacity and discharging at 0.4 C rate to 1 V.

The crystal structure of the alloy was identified by X-ray diffraction experiments with Co Kα radiation.

3. Results and discussion

The crystal structure of Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3} alloy was identified by X-ray diffraction. It was shown that the main phase of the alloy was hexagonal CaCu₅-type structure (space group *P6/mmm*). The lattice con-

stants a and c are equal to 0.5008 nm and 0.4043 nm respectively. A small amount of Ni_3Al phase in the alloys was observed by the X-ray diffraction patterns. The Ni_3Al phase do not change with the charge and discharge cycles (shown in Figs. 1(a) and (b)).

The discharge capacity of this alloy electrode modified with cobalt powder is shown in Fig. 2. After repeating charge and discharge cycles 20 times, the saturated value of the discharge capacity experimentally deter-

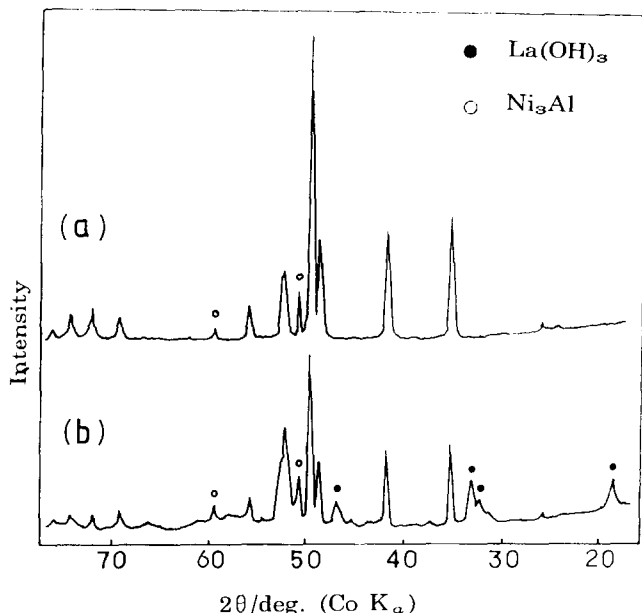


Fig. 1. X-ray diffraction diagrams of (a) $\text{Mm}_{0.9}\text{Ti}_{0.1}\text{Ni}_{3.9}\text{Mn}_{0.4}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy and (b) the alloy electrode after 100 cycles.

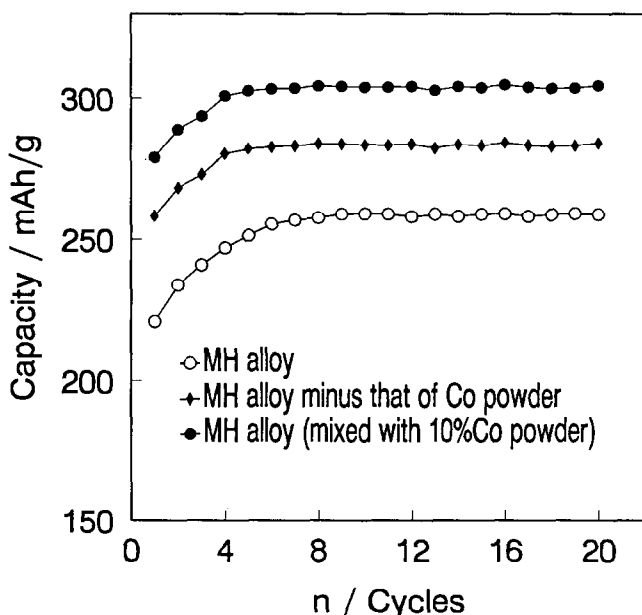
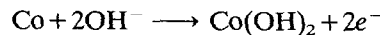


Fig. 2. Discharge capacity of $\text{Mm}_{0.9}\text{Ti}_{0.1}\text{Ni}_{3.9}\text{Mn}_{0.4}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy electrode mixed with cobalt powder as a function of cycle number.

mined for the alloy was found to be 259 mAh g^{-1} . When 10 wt.% cobalt powder was mixed with the alloy, the discharge capacity increased significantly up to 303 mAh g^{-1} . The cobalt powder showed additional discharge curve as in the following reaction:

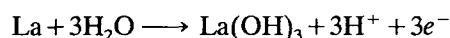


at $-830 \text{ mV vs. Hg/HgO}$ [11]

From our experiments the Co powder contributes to the capacity from 203 to 207 mAh g^{-1} (theoretically 910 mAh g^{-1}) with cycles. When the capacity of Co powder was subtracted by the capacity of the alloy (mixed with 10 wt.% Co powder) at every cycle, the discharge capacity of the alloy electrode reached to 282 mAh g^{-1} . The high-rate dischargeability was found to increase with the addition of Co powder into the alloy electrode. This fact indicated that the utilization efficiency of the discharge capacity for the hydrogen storage alloy increased.

The discharge capacity of the MH electrode in a sealed cell (AA size) as a function of the cycle number (shown in Fig. 3). The capacity decay for $\text{Mm}_{0.9}\text{Ti}_{0.1}\text{Ni}_{3.9}\text{Mn}_{0.4}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy coated with 11 wt.% nickel was about 8% after 200 cycles. But the discharge capacity of the alloy electrode unmodified with nickel at the alloy surface decreased by 35% after 200 cycles. So the cycle lifetime of the alloy electrode increased remarkably with surface modification by microencapsulation of Ni element. It is also shown in Fig. 3 that the cycle lifetime of the MH alloy electrode can be increased by mixing with cobalt powder. When the 10 wt.% cobalt powder was mixed with the alloy which was also coated with 11 wt.% nickel, the capacity decay was only about 4% after 200 cycles. The cycle life of the MH electrode of $\text{Mm}_{0.9}\text{Ti}_{0.1}\text{Ni}_{3.9}\text{Mn}_{0.4}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy can be improved by coating with nickel or mixing with cobalt powder. Sakai and co-workers [10] also indicated that the capacity decrease of $\text{MmNi}_{3.5}\text{Co}_{0.7}\text{Al}_{0.8}$ alloys was almost prevented by mixing with 10 wt.% Co powder after 40 cycles. Because the cobalt was coated on the alloy surface through dissolution and precipitation processes during charge and discharge cycles.

X-ray diffraction analysis of $\text{Mm}_{0.9}\text{Ti}_{0.1}\text{Ni}_{3.9}\text{Mn}_{0.4}\text{Co}_{0.4}\text{Al}_{0.3}$ alloy after 100 charge and discharge cycles was carried out (Fig. 1(b)). It is shown that the diffraction peaks with CaCu_5 -type hexagonal structure diminished and $\text{La}(\text{OH})_3$ peaks grew after 100 cycles. In the charge and discharge process, the La element was easily segregated on the alloy surface and mixed up with OH^- ion to form stable $\text{La}(\text{OH})_3$ compound. The reaction can be expressed as follows:



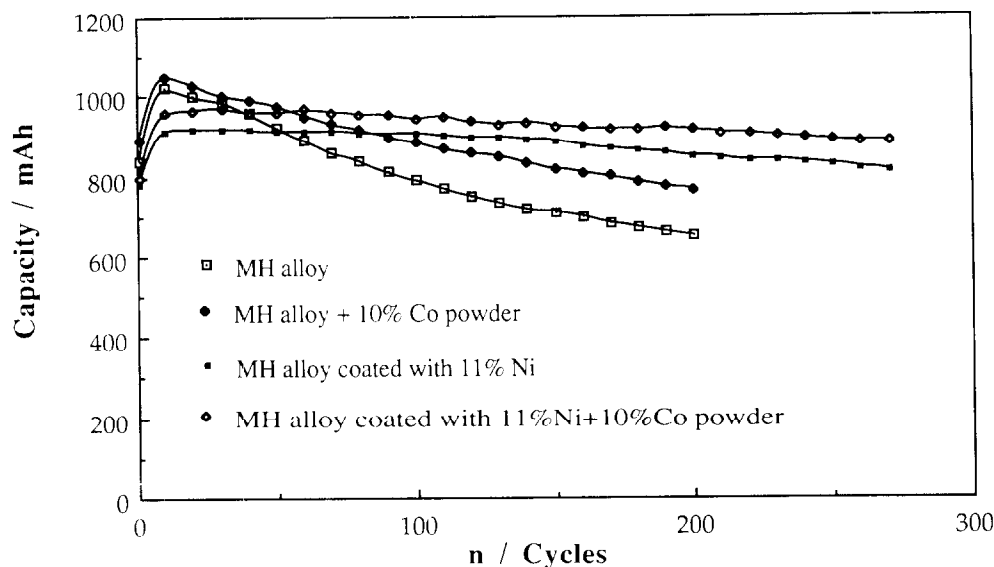


Fig. 3. Discharge capacity of MH electrode (nickel-coated and cobalt-mixed $Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3}$ alloy) as a function of cycle number for a sealed cell (AA size).

In this equation, the discharge capacity gradually decreased with the increase of $La(OH)_3$ compound and also decreased with the loss of electrolytes. The manganese hydroxides had not been observed from X-ray diffraction analysis (Fig. 1(b)). But the manganese was easily dissolved out from the alloy and deposited as manganese hydroxides on the cell components such as the separator, which resulted in a shorter cycle lifetime of the alloy electrode [10].

4. Conclusions

The main phase of the $Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3}$ alloy was $CaCu_5$ -type hexagonal structure. The maximum discharge capacity of this alloy electrode was 259 mAh g^{-1} at 300 K. When the cobalt powder (10 wt.%) was mixed with the alloy, the discharge capacity increased up to 303 mAh g^{-1} . The MH electrode using nickel-coated $Mm_{0.9}Ti_{0.1}Ni_{3.9}Mn_{0.4}Co_{0.4}Al_{0.3}$ alloy exhibited 8% capacity decay after 200 cycles. When the nickel-coated alloy was mixed with 10 wt.% cobalt powder, the capacity decay with the charge and discharge cycles was almost prevented.

Acknowledgments

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References

- 1 H.F. Bittner and C.C. Badcock, *J. Electrochem. Soc.*, **130** (1983) 193C.
- 2 J.J.G. Willems and K.H.J. Buschow, *J. Less-Common Met.*, **129** (1987) 13–30.
- 3 T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa, *J. Less-Common Met.*, **172–174** (1991) 1175–1184.
- 4 T. Sakai, A. Takagi, K. Kinoshita, N. Kuriyama, H. Miyamura and H. Ishikawa, *J. Less-Common Met.*, **172–174** (1991) 1185–1193.
- 5 T. Sakai, H. Ishikawa, K. Oguro, C. Iwakura and H. Yoneyama, *J. Electrochem. Soc.*, **134** (1987) 558–562.
- 6 T. Sakai, A. Yuasa, H. Ishikawa, H. Miyamura and N. Kuriyama, *J. Less-Common Met.*, **172–174** (1991) 1194–1204.
- 7 C. Iwakura, M. Matsuoka, K. Asai and T. Kohno, *J. Power Sources*, **38** (1992) 335–343.
- 8 M. Matsuoka, K. Asai, Y. Fukumoto and C. Iwakura, *J. Alloys Comp.*, **192** (1993) 149–151.
- 9 T. Sakai, H. Sugahara, H. Miyamura, N. Kuriyama, H. Ishikawa and T. Toide, *Rare Earths*, **19** (1991) 184.
- 10 T. Sakai, H. Miyamura, N. Kuriyama, I. Uehama, M. Muta, A. Takagi, U. Kajiyama, K. Kinoshita and F. Isogai, *J. Alloys Comp.*, **192** (1993) 158–160.
- 11 F. Meli, private communication, August 31, 1993.