

Jeng-Kuei Chang · Dyi-Nan Simon Shong
Wen-Ta Tsai

Effects of alloying elements and binder on the electrochemical behavior of metal hydride electrodes in potassium hydroxide electrolyte

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Abstract This investigation examines the effect of alloying elements on the charge–discharge performance of $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes in 7 M KOH electrolyte. The activation behavior and the effect of binder content were also examined. Both half-cell and full-cell systems were employed to evaluate the electrochemical performance. Experimental results indicated that a few cycles of charge–discharge at a rate of 150 mA/g in 7 M KOH electrolyte were sufficient to activate the freshly prepared $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes. The amount of binder affected the activation behavior, the overvoltage for hydrogen ions reduction and the discharge capacity of the $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ electrode. In the alloy of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes, a high Co content helped to promote both the capacity at a relatively low discharging rate and the cyclic life. An increase of the Al content raised the discharge voltage and improved the high rate discharge capacity, but reduced the cyclic stability. The alloy with a high Mn content required the least cathodic polarization during charging but had the lowest discharge capacity at a rather high discharging rate.

Keywords Activation · Binder · Chemical composition · Cyclic stability · Metal hydrides

Introduction

Hydrogen storage alloys have been successfully used to replace the cadmium used in rechargeable nickel-cadmium batteries. Besides the merits of low toxicity and small memory effects, the metal hydride electrode has a higher energy density and a longer service life than the cadmium electrode [1]. Linden [2] pointed out that the important properties of metal hydride alloys include: good hydrogen storage to achieve a high energy density and battery capacity, thermodynamic properties suitable for reversible adsorption/desorption, low hydrogen equilibrium pressure, high electrochemical reactivity, favorable kinetic properties for high-rate performance, high oxidation resistance, and stability during repeated charge–discharge cycles in an alkaline electrolyte. Several important factors, including material processing, chemical composition, and the electrode manufacturing technique, among others, must be adequately controlled to meet the criteria stated above. Any of these factors may significantly affect the ultimate properties of hydrogen storage alloys.

The effects of the alloying element on the performance of a metal hydride electrode have received considerable attention. Adding Co to AB_5 (LaNi_5)-type hydrogen storage alloys has been found to be beneficial in many respects. For instance, the capacity and the cyclic stability could be improved by Co addition [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. Although the elements Al and Mn are known to be commonly present in AB_5 -type alloys, their relationship to the electrochemical properties of metal hydride electrodes has not been amply discussed. Furthermore, Co, Mn, and Al may co-exist in the alloys, and the change in these alloys' performance due to the adjustment of the relative proportion of each constituent is of interest. This work systematically explores the effects of Co, Mn, and Al contents in $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ alloy on the electrochemical behavior of metal hydride electrodes in KOH electrolyte. The activation behavior and the effect

J.-K. Chang · W.-T. Tsai (✉)
Department of Materials Science and Engineering,
National Cheng Kung University, Tainan, Taiwan
E-mail: wttsai@mail.ncku.edu.tw
Tel.: +886-6-2757575 ext. 62927
Fax: +886-6-2754395

D.-N. S. Shong
Hydrogen Development Center,
Gloria Material Technology Corporation,
Tainan, Taiwan

of binder on the charge–discharge performance of a $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ metal hydride electrode were also studied.

Experimental

The hydrogen storage alloys prepared for this study had a chemical composition of $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$. The relative amounts of Co, Mn, and Al were varied to form $\text{LaNi}_{3.6}\text{Co}_{0.84}\text{Mn}_{0.28}\text{Al}_{0.28}$ (alloy A), $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.42}\text{Al}_{0.28}$ (alloy B), and $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ (alloy C). These alloys were prepared by arc melting on a water-cooled copper hearth in an argon atmosphere. The samples were inverted and remelted four times to ensure good homogeneity. They were then crushed and ground mechanically into powders. The crystal structures of these alloys were examined by X-ray diffraction using Cu-K α radiation.

Commercial hydrogen storage alloy powder, with the chemical composition $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ (Mm: misch metal), was also used to examine the effect of binder content on the electrochemical performance of the metal hydride electrodes. The powder was first mixed with fine nickel powder in a weight ratio of about 10:1 with a certain amount (2 wt% and 5 wt%) of methylcellulose as a binder. The paste was then poured into the nickel foam to a thickness of 1.8 mm to make an electrode. Finally, the resulting electrode was dried and pressed to a thickness of about 0.8 mm. Before electrochemical testing, each electrode was immersed in 7 M KOH electrolyte for at least one day to ensure that it was fully wet.

An EG&G model 273 potentiostat incorporated in a three-electrode system was employed for the electrochemical testing. A platinum sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Each electrode was activated by charging at 150 mA/g for 2.5 h and discharging at the same rate to a cut-off potential of -0.8 V vs. SCE in 7 M KOH, until the electrochemical behavior of the electrode became stable. Consequently, the charge–discharge characteristics of the electrodes were evaluated.

Full-cell electrochemical performance tests were also performed to evaluate the effects of alloying elements on the charge–discharge behavior of $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ alloys. A large capacity $\text{Ni}(\text{OH})_2$ electrode was used as the positive electrode in each test. Before the test, the cell was also immersed in 7 M KOH electrolyte for at least one day. In all the tests, each cell was charged at 150 mA/g for 2.5 h. Each cell was discharged at a rate of 150 mA/g to a cut-off cell potential of 1 V in 7 M KOH to evaluate its capacity. The effect of discharging rate on the discharge capacity of the cells with various anode materials was examined with the discharging current density from 75 to 600 mA/g. Furthermore, the cyclic charge–discharge performance of the cells was also tested at a current density of 150 mA/g to examine the durability of various metal hydride electrodes in 7 M KOH electrolyte. A Kikusui battery performance tester was used in the charging and discharging tests.

Results and discussion

Figure 1 shows the powder diffraction patterns of the three $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ alloys with different chemical compositions. The XRD results indicated that these alloys were all homogenous and had a single phase with a hexagonal CaCu_5 -type structure.

Activation behavior

The absorption and the release of hydrogen from the newly prepared, negative electrode were slow. This

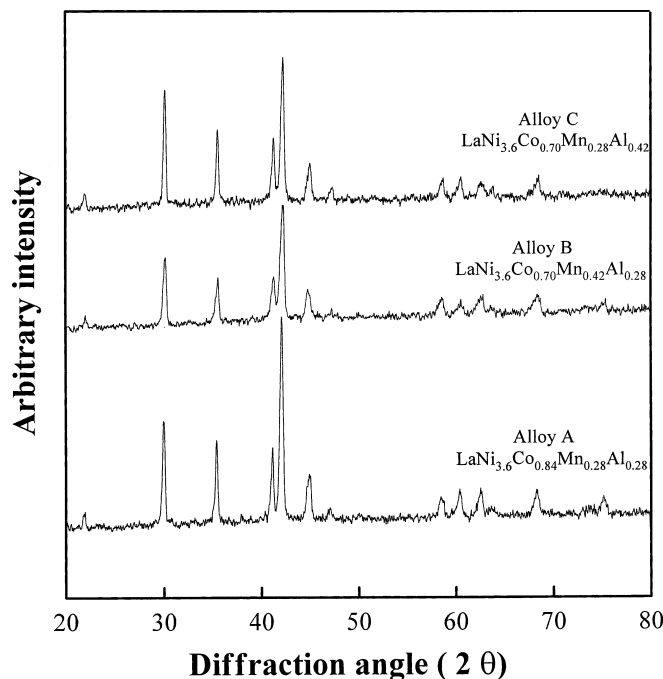


Fig. 1 X-ray diffraction patterns of the three different alloys prepared

electrode must be activated before a fast charge–discharge performance can be obtained. One method of activating the negative electrode is to charge and discharge it in the electrolyte for a few cycles [1]. The activation behavior can be examined by conducting galvanostatic polarization using a three-electrode system. Under galvanostatic (or charging at constant current density) conditions, the absorption of hydrogen resulting from the cathodic reduction of hydrogen ions in the electrolyte requires the electrode to be polarized to a negative potential. A lower charging potential indicates that the reduction of hydrogen ions is more difficult. Figure 2 plots the charging curves for a $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ electrode in 7 M KOH electrolyte for up to 2.5 h at a charging rate (or current density) of 150 mA/g. The cathodic charging extent in Fig. 2 manifests the time of charging. As soon as the cathodic current of the first cycle was applied, the electrode potential (vs. SCE) decreased drastically to (-1200 mV) 1200 mV and then gradually to (-1230 mV) 1230 mV, at which it remained almost steady. As can be seen in Fig. 2, the charging potential became less negative as the number of charging cycles was increased. The results indicate that the overvoltage required for hydrogen ion reduction was reduced as the electrode was charged for more cycles. It means that the new electrode becomes activated with easy processes of hydrogen ion reduction and hydrogen atom transport within the electrode. The small difference between curves 4 and 5 in Fig. 2 shows that the $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ electrode in 7 M KOH electrolyte was almost fully activated after five cycles of charge–discharge.

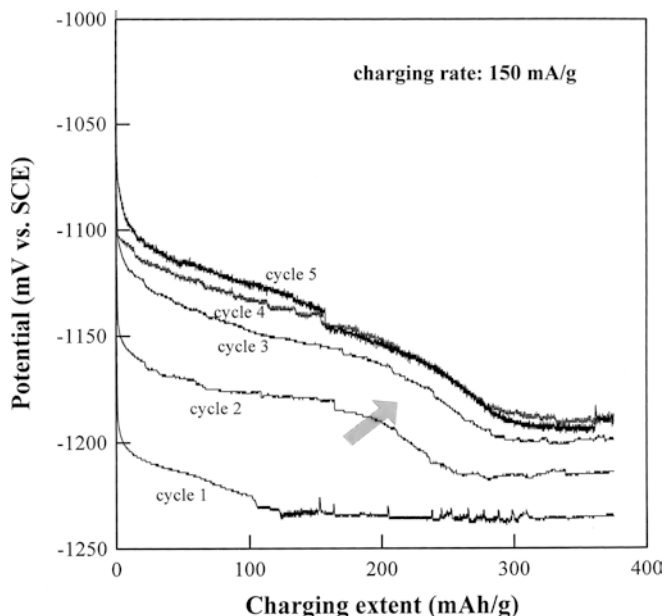


Fig. 2 Charge curves of the $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ metal hydride electrode during activation

Immediately after being charged at 150 mA/g for 2.5 h, the electrode was discharged at the same rate until a cut-off potential of (-800mV) 800 mV (vs. SCE) was reached. Figure 3 plots the discharge curve. During the discharge at the first cycle, the potential dropped quickly to the cut-off potential. The short period required for the potential to drop to the cut-off potential indicated that a small amount of hydrogen was stored in the electrode. However, as the number of charge–discharge cycles was increased, the extent of discharging also increased, indicating that the electrode was activated and more hydrogen could be absorbed. The results in Fig. 3 also indicate that the electrode was almost fully activated after five charge–discharge cycles. Similar results were obtained for the other $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes.

Effect of binder content on the electrochemical performance

The type and amount of binder used in preparing an electrode significantly affects the electrochemical behavior [16]. In this investigation, methylcellulose was used as the binder. The charge curves of the $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ (commercial powder) electrodes with 2 wt% and 5 wt% methylcellulose after full activation are shown in Fig. 4. The results clearly indicate that the higher binder content in the electrode led to a lower charge potential of the metal hydride electrode. An excess amount of binder increased the overvoltage for hydrogen ion reduction and lowered the surface reaction activity during charging. Similarly, excess binder impaired the discharging performance. As shown in Fig. 5,

the electrode that contained 5 wt% binder had a higher discharging potential, indicating a higher resistance to discharge. The results presented in Figs. 4 and 5 show that a high amount of binder adversely affects the charging and discharging performance of the $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ electrode. Similar results were obtained for the other $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes.

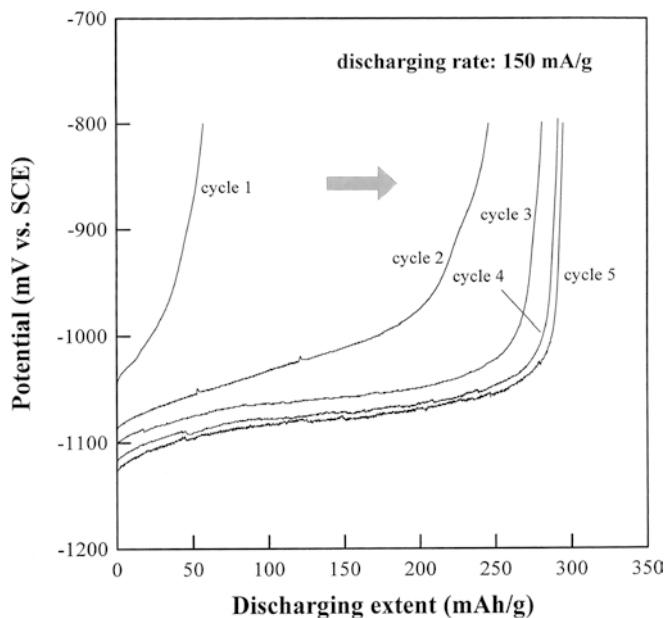


Fig. 3 Discharge curves of the $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ metal hydride electrode during activation

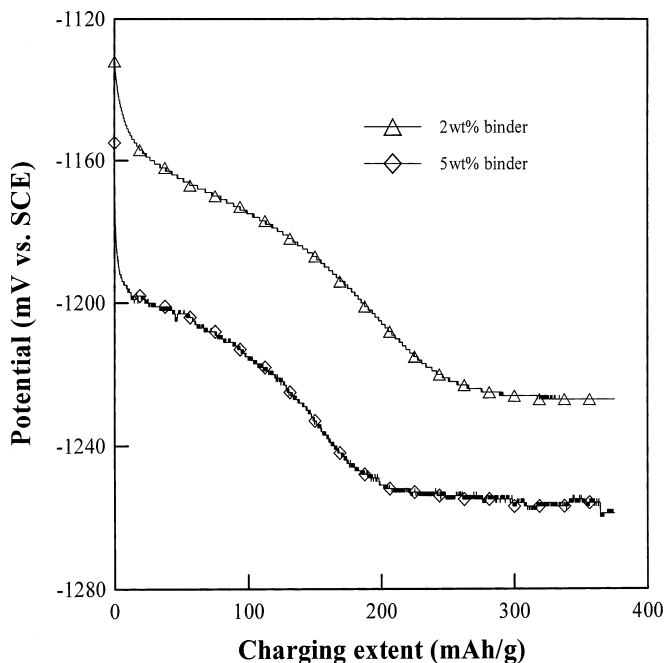


Fig. 4 Charge curves of the $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ metal hydride electrodes with different amounts of binder content

The effect of binder content on the discharge capacity during the activation process was also investigated. Figure 6 shows the variation of discharge capacities during the first few charge–discharge cycles for electrodes with different binder contents. The results in Fig. 6 show that the electrode with less binder has a higher discharge capacity. Figure 6 also reveals that the

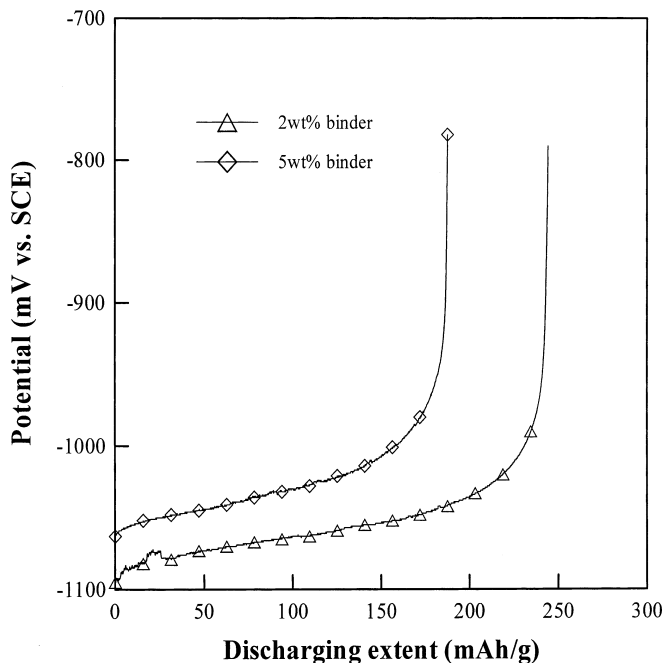


Fig. 5 Discharge curves of the $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ metal hydride electrodes with different amounts of binder content

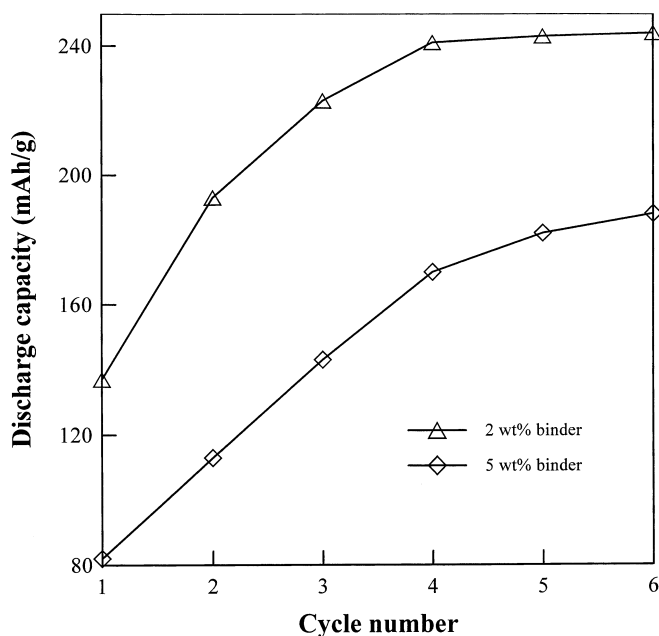


Fig. 6 Discharge capacity of the $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ metal hydride electrodes with different amounts of binder content during activation

discharge capacity of the electrode with a 2 wt% binder reached a stable value of about 240 mAh/g after four charge–discharge cycles. In contrast, the discharge capacity of the electrode with 5 wt% binder content, measured after the same number of charge–discharge cycles, had not yet reached the saturation value. The results also indicated that the electrode with a higher binder content is harder to be activated. Accordingly, the binder content used for electrode preparation was 2 wt% in the rest of this work.

Effect of electrode composition on the charge/discharge characteristics

Figures 7 and 8 show the effect of alloy composition on the charge and discharge characteristics of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes after they are fully activated. The half-cell electrochemical behavior of these electrodes was evaluated by charging at a rate of 150 mA/g for 2.5 h and discharging at the same rate to a cut-off potential of $(-0.8 \text{ V}) 0.8 \text{ V}$ vs. SCE in 7 M KOH. Figure 7 shows the variations of charging potential with extent of charging for different metal hydride electrodes. As shown in this figure, the $\text{LaNi}_{3.6}\text{Co}_{0.84}\text{Mn}_{0.28}\text{Al}_{0.28}$ electrode required the highest cathodic polarization during charging at a constant current as compared with the other two $\text{LaNi}_{3.6}\text{Co}_{0.70}(\text{Mn} + \text{Al})_{0.7}$ electrodes. Moreover, of the electrodes with a Co atomic ratio of 0.70, the alloy containing a higher Mn content, namely $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.42}\text{Al}_{0.28}$, had a higher charging potential than that with a higher Al content. This may be attributed to the lattice expansion of the metal hydride

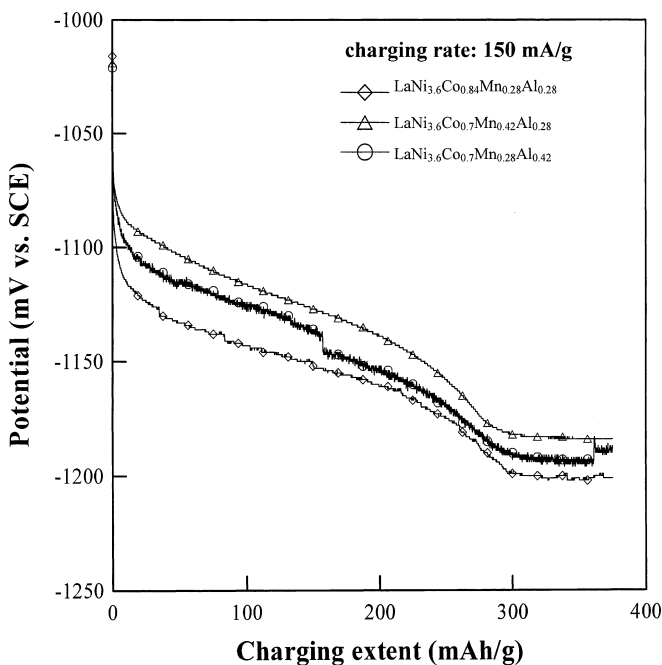


Fig. 7 Charge curves of the metal hydride electrodes with different alloy compositions in 7 M KOH electrolyte

alloy that favored the absorption/diffusion of hydrogen during charging [17].

Figure 8 shows the effect of alloying composition on the discharge behavior of $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes. The electrodes evaluated were all fully activated. They were charged at a rate of 150 mA/g for 2.5 h and discharged at the same rate to a cut-off potential of -800 mV (SCE) in 7 M KOH electrolyte. The results showed that the discharge potential of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrode with a high Al content (atomic ratio of 0.42) was the lowest. The discharge potentials of the electrodes with an Al atomic ratio of 0.28 were almost the same, regardless of Co and Mn contents. The results suggest that a high Al content improved the discharging potential of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes. Furthermore, the discharge capacities of the $\text{LaNi}_{3.6}\text{Co}_{0.84}\text{Mn}_{0.28}\text{Al}_{0.28}$, $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$, and $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.42}\text{Al}_{0.28}$ electrodes, determined at a cut-off potential of -800 mV (SCE), were 298, 296, and 291 mAh/g, respectively. The results (also shown in Fig. 8) indicate that Co was advantageous as far as discharge capacity was concerned, although not significantly. The beneficial effect of Co on electrochemical capacity may be related to the number of available sites in the crystal lattice which could be occupied by hydrogen atoms [18]. Tetrahedral and octahedral sites are known to be favored for hydrogen occupancy in LaNi_5 alloys. These sites may be distorted if Ni is replaced by other alloying elements. Compared with Mn and Al, the size of a Co atom is closer to Ni. Consequently, the lattice distortion of the crystal structure was less for the alloy that contained

more Co. The beneficial effect of Co on the capacity of the metal hydride alloys found in this study agrees closely with that identified in other investigations [3, 4, 5].

The effect of composition on the discharge performance of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes was also evaluated using a full cell (or two-electrode) system. The $\text{Ni}(\text{OH})_2$ electrode, with a high capacity, was used as the positive electrode. Figure 9 plots the discharge curves of three batteries with negative electrodes of different $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ compositions, after being fully activated and discharged at a rate of 150 mA/g. The results show that the electrode with a high Al content had a high discharge potential, while that with a high Co content had a high discharge capacity. These observations agree with those obtained from half-cell (or three-electrode system) measurements (Fig. 8).

The effect of composition on the discharging performance of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes at various discharging rates was also investigated. The results, shown in Fig. 10, demonstrate the dependences of the discharge capacities on the composition of the electrode and the discharging rate. Clearly, the discharge capacities decreased as the discharging rates were increased. A lower discharge capacity was found for the $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.42}\text{Al}_{0.28}$ electrode, particularly at a high discharging rate. Table 1 lists the discharge capacities of the three different electrodes at discharging rates of 75 and 600 mA/g. Unlike Co and Al, which have been reported to promote high rate discharging [4, 6, 9, 19, 20, 21], the deleterious effect of Mn was recognized (Fig. 10 and Table 1).

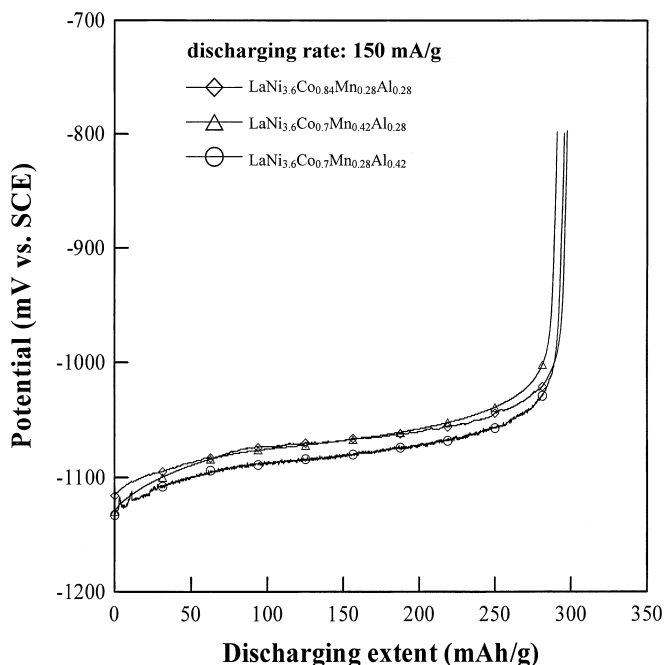


Fig. 8 Discharge curves of the metal hydride electrodes with different alloy compositions in 7 M KOH electrolyte

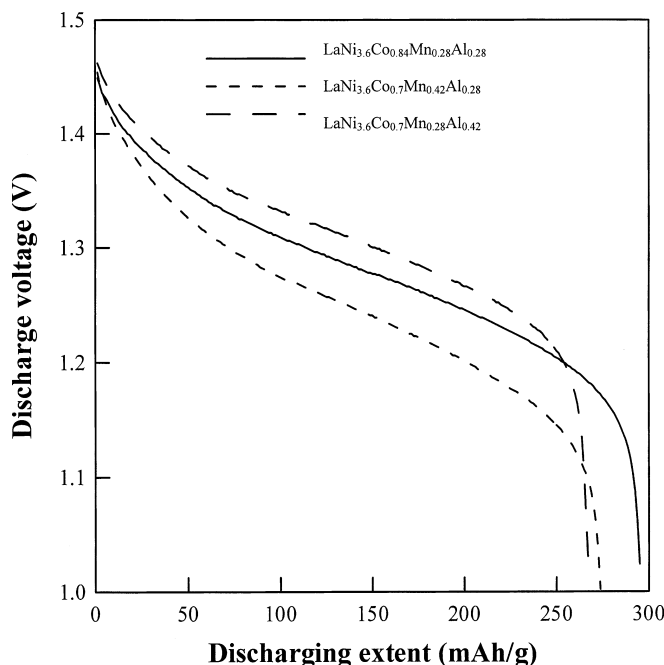


Fig. 9 Discharge curves of the three different alloys at a discharging rate of 150 mA/g

Cyclic stability of the electrodes with various alloying compositions

Capacity decay due to the corrosion, passivation, and pulverization of the hydrogen storage powder generally occurs for the metal hydride electrodes with repeated charging and discharging processes [6, 7, 22, 23, 24]. Figure 11 shows the relationships between discharge capacity and cycle number for the three alloys. These electrodes were repeatedly charged at a rate of 150 mA/g for 2.5 h and discharged at the same rate to a cell voltage of 1 V. The cyclic stability was evaluated from the percentage capacity decay (ΔC), defined by the following equation: $\Delta C = (C_{\max} - C_{150}) / C_{\max}$, where C_{\max} is the maximum detected capacity and C_{150} is the capacity obtained at 150 cycles. Table 1 presents the results.

The experimental results show that the alloy with a high Co content ($\text{LaNi}_{3.6}\text{Co}_{0.84}\text{Mn}_{0.28}\text{Al}_{0.28}$) had not only the highest capacity but also the greatest resistance to cyclic decay of the three alloys. After repeated charging and discharging for 150 cycles, the alloy retained 89% of its capacity. The beneficial effects of Co are three-fold. Firstly, Co reduces the hardness of the alloy to improve the cyclic durability [3, 10, 15]. Secondly, it decreases the volume expansion from metal to

hydride [6, 7, 8, 9, 10, 11, 12, 13]. Thirdly, it suppresses the dissolution of other elements from the alloy into KOH solution [11, 13, 14]. Therefore, Co is thought to be the most important component for obtaining a satisfactory cyclic stability of metal hydride electrodes.

As shown in Fig. 11, the cyclic stability of $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ alloy was even lower than that of $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.42}\text{Al}_{0.28}$. A capacity decay of 30% after 150 cycles was observed for the high Al content alloy. This result differs from other results in the literature [8, 15, 18, 25, 26]. Mn was found to reduce the electrochemical cyclic stability, while Al improved the cycle life. However, the beneficial effect of Al in improving the cyclic stability of the metal hydride electrode was not recognized in this investigation. Here, both Al and Mn were present in the alloys, with different contents. The detrimental effect of Al on cyclic stability is probably due to its relatively high reactivity in the KOH electrolyte. One of our earlier investigations showed that Al accounted for 95% of the dissolved metal of an AB_5 alloy (containing 1.71 wt% Al) in 7 M KOH electrolyte [27]. This fact may explain the low cyclic stability of an electrochemical cell with a metal hydride electrode with a high Al content.

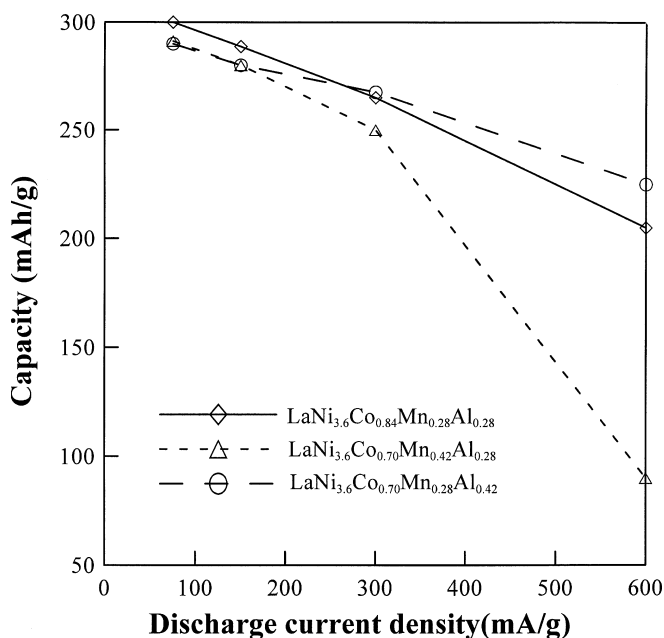


Fig. 10 Effects of discharging rate on the discharge capacity of the three different alloys

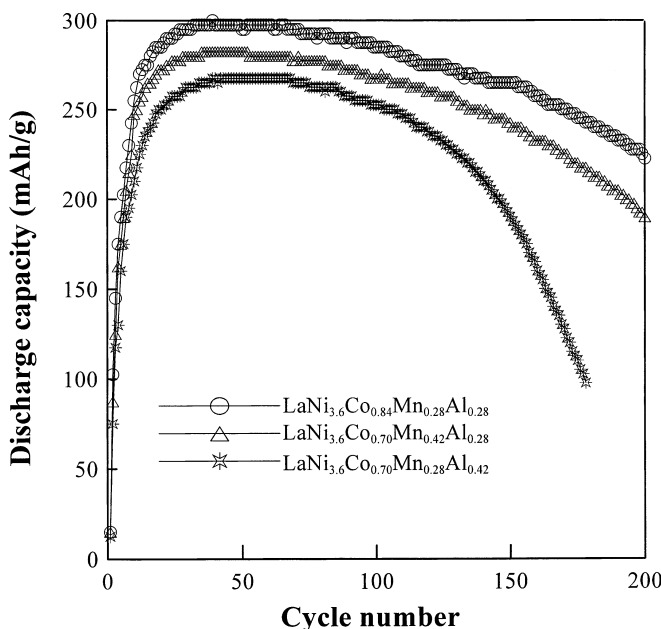


Fig. 11 Discharge capacity vs. cycle number for the three different alloys. Charge at a rate of 150 mA/g for 2.5 h; discharge at the same rate until a cell potential of 1 V

Table 1 Electrochemical characteristics of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ hydrogen storage alloys

Chemical composition	Capacity at the discharge rate of 75 mA/g	Capacity at the discharge rate of 600 mA/g	Capacity decay $(C_{\max} - C_{150}) / C_{\max}$
$\text{LaNi}_{3.6}\text{Co}_{0.84}\text{Mn}_{0.28}\text{Al}_{0.28}$	300 mA h/g	205 mA h/g	10.9%
$\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.42}\text{Al}_{0.28}$	292 mA h/g	90 mA h/g	14.2%
$\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$	290 mA h/g	225 mA h/g	30.0%

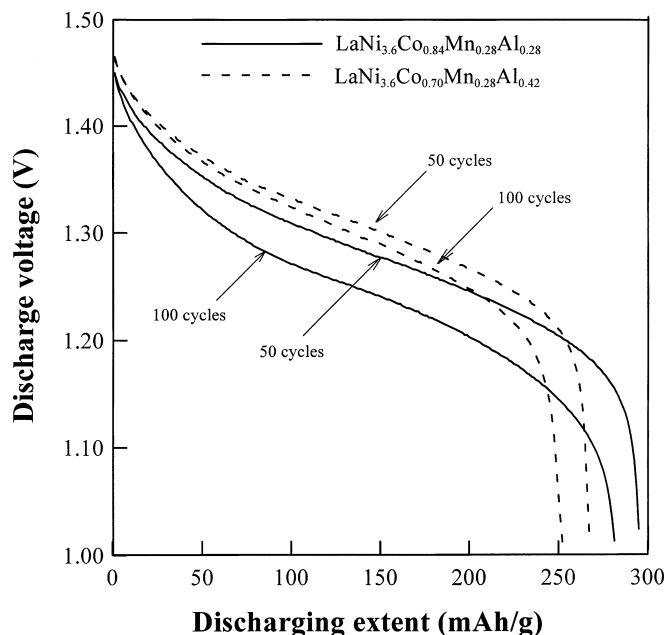


Fig. 12 Discharge curves of $\text{LaNi}_{3.6}\text{Co}_{0.84}\text{Mn}_{0.28}\text{Al}_{0.28}$ and $\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ alloys at 50 and 100 cycles; discharged at a rate of 150 mA/g

Although a high Al content in the alloy accelerated the capacity decay during cycling, it seemed to help to maintain the discharge voltage. Figure 12 shows the discharge curves for both $\text{LaNi}_{3.6}\text{Co}_{0.84}\text{Mn}_{0.28}\text{Al}_{0.28}$ and $0\text{LaNi}_{3.6}\text{Co}_{0.70}\text{Mn}_{0.28}\text{Al}_{0.42}$ alloys at 50 and 100 cycles. Clearly, the decay of the discharge voltage, between 50 and 100 cycles, was less for the electrode with a higher Al content.

Conclusions

1. Freshly prepared $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes could be activated by charging and discharging in 7 M KOH electrolyte for a few cycles. A decrease in the overvoltage required for hydrogen ion reduction and an increase in the discharge capacity were obtained after activation. An excess of binder, however, retarded the activation process, increased the overvoltage for hydrogen ions reduction, and decreased the discharge capacity of the $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ electrode.
2. The electrochemical performance and the cyclic stability of the $\text{LaNi}_{3.6}(\text{Co} + \text{Mn} + \text{Al})_{1.4}$ electrodes varied with the contents of the alloying elements. A high Co content in the alloy helped to promote the capacity at a relative low discharging rate and also the cyclic life. An increase in the Al content raised the

discharge voltage and significantly improved the high rate discharge capacity, but reduced the cyclic stability. The high Mn content alloy required the least cathodic polarization during charging but had the lowest discharge capacity at a rather high discharging rate.

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