

# Effects of Co, Mn contents on the electrochemical characteristics of the $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$ electrodes in potassium hydroxide electrolyte

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## Abstract

The effects of Co and Mn contents on the electrochemical characteristics of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes were examined systematically. The lattice cell parameters, discharge characteristics, high-rate charging or discharging performance and cyclic stability of the series of alloys were all evaluated. The experimental results show that Co would play the role of improving the electrochemical capacity and discharge cell voltage. In addition, the cyclic stability of the metal hydride electrodes could be enhanced with increasing the Co content in the alloys. On the other hand, replacing the Co by Mn in the alloys could cause a expansion of the lattice cell volume and assist hydrogen diffusion in the metal hydride electrodes, which subsequently promoted the high-rate charging performance. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrogen storage alloy; Chemical composition; Electrochemical characteristics; Metal hydride electrodes; Cyclic stability

## 1. Introduction

Hydrogen storage alloys have been successfully used to replace the cadmium used in the rechargeable nickel–cadmium battery. Besides the merits of less toxic and small memory effects, the metal hydride electrode also exhibits a higher energy density and longer service life than the cadmium electrode. It has been pointed out by Linden [1] that the important properties of the 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, stability with repeated charge/discharge cycles in alkaline electrolyte, etc. To reach the above-mentioned criteria, there are several important factors such as material processing, chemical composition, etc., must be controlled adequately. Any of these factors may affect significantly the ultimate properties of hydrogen storage alloys in all aspects.

The effect of alloying element on the performance of metal hydride electrode has been of interest to many

researchers [2–9]. As for the  $\text{LaNi}_5$  type hydrogen storage alloys, the Co and Mn are commonly present and has been found to be beneficial in many respects [10–14]. But the performance change of this type of alloys due to the relative adjustment of Co and Mn contents is not well discussed. Furthermore, the price of Co is very expensive and fluctuates constantly. Looking for the suitable manner to diminish the use of Co in the metal hydride electrodes is one of the main efforts many researchers aim to [3–5,9,15–20]. Therefore, in this investigation, the effects of Co and Mn relative contents in the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  alloys on the electrochemical characteristics are explored. The Co and Mn content ratio is adjusted from 3:1 to 1:3. The relationship between the alloy composition and electrochemical characteristics of electrode is investigated systematically.

## 2. Experimental details

### 2.1. Alloy preparation and X-ray diffraction (XRD)

The hydrogen storage alloys prepared had a chemical composition of  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$ . The relative amounts of Co and Mn were varied, and the chemical compositions of the specimens used were  $\text{LaNi}_{3.8}\text{Co}_{0.72}\text{Mn}_{0.24}\text{Al}_{0.24}$ ,  $\text{LaNi}_{3.8}\text{Co}_{0.60}\text{Mn}_{0.36}\text{Al}_{0.24}$ ,  $\text{LaNi}_{3.8}\text{Co}_{0.48}$

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$\text{Mn}_{0.48}\text{Al}_{0.24}$ ,  $\text{LaNi}_{3.8}\text{Co}_{0.36}\text{Mn}_{0.60}\text{Al}_{0.24}$ , and  $\text{LaNi}_{3.8}\text{Co}_{0.24}\text{Mn}_{0.72}\text{Al}_{0.24}$ , respectively. These alloys were prepared by arc-melting on a water-cooled copper hearth under an argon atmosphere. The samples were inverted and remelted four times to ensure good homogeneity. Thereafter, they were crushed and ground mechanically into powders below 325 mesh. The crystal structures of these alloys were examined by XRD using  $\text{Cu K}\alpha$  radiation.

## 2.2. Electrochemical measurements

To fabricate the metal hydride electrodes, the hydrogen storage alloy powders were mixed with fine nickel powder in a weight ratio of about 1:1 and cold pressed to pellets of 10 mm diameter and 3 mm in thickness. For constructing an anodic limitation electrochemical cell, large capacity  $\text{Ni}(\text{OH})_2$  electrodes were used as the positive electrodes. A sheet of appropriate separator was placed between the positive and the negative electrodes. Before the electrochemical tests, the electrodes were immersed in 7 M KOH electrolyte at least 1 day in order to wet completely. Each electrode in this investigation was examined for its electrochemical characteristics and cyclic stability at ambient pressure and temperature. The hydride electrodes were continuously charged at 100 mA/g for 4 h and discharged at the same rate to a cut-off cell voltage of 1 V in 7 M KOH to activate the hydrogen storage alloys. When the electrodes became activated, the individual discharge characteristic curve and maximum electrochemical capacity were obtained. The charging current density was kept constant at 100 mA/g until 120% of maximum discharge capacity for each cell when the discharging capability at different rate was discussed. On the other hand, when the high-rate charging performance was considered, the discharging current density was held at 100 mA/g. In addition, the cyclic stability was determined by repeating charging and discharging at the rate of 300 mA/g and measured the capacity retention after 150 cycles. Charging and discharging conditions in our investigation were controlled by KIKUSUI battery performance tester.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1 shows the XRD patterns of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  alloys with different chemical compositions. The XRD results indicated that these alloys examined were all homogenous with a single phase corresponding to a hexagonal  $\text{CaCu}_5$  type structure.

Careful examination of diffraction angle revealed that peak shift as a function of composition occurred. By increasing the Mn content, the diffraction peaks of the (1 1 0) and (2 0 0) planes were found to shift to lower angles. According the following equation:

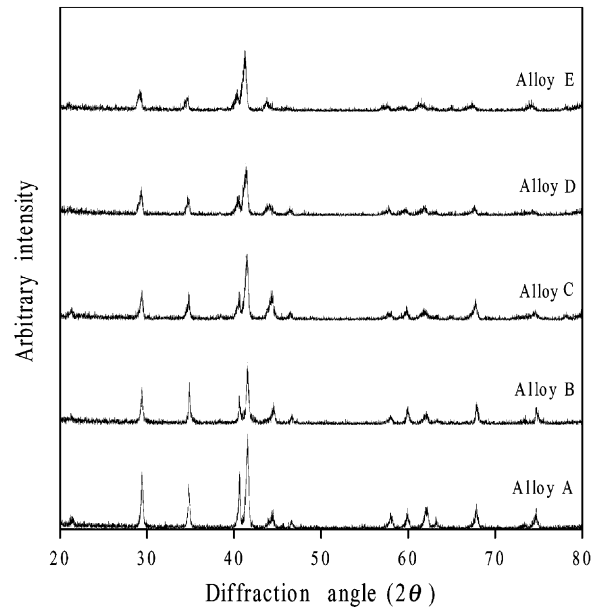


Fig. 1. XRD patterns of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  alloys with different chemical compositions.

$$4 \sin^2 \left( \frac{\theta}{\lambda^2} \right) = \frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2 + l^2/c^2},$$

the axis  $a$  of the hexagonal lattice expanded as the Mn content in the alloy was increased. On the other hand, the peaks of the (0 0 1) and (0 0 2) planes were also shifted to lower angles when the Co was gradually replaced by Mn in these hydrogen storage alloys. Raising the Mn content would also cause an expansion of the axis  $c$  of the hexagonal cell. The lattice parameters of  $a$ - and  $c$ -axes determined are listed in Table 1.

### 3.2. Electrochemical capacity, discharge curves and charging efficiency

The effects of Co and Mn contents on the electrochemical capacities of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes were evaluated by charging at a rate of 100 mA/g for 4 h and discharging at the same rate to a cut-off cell voltage of 1 V in 7 M KOH electrolyte. The results showed that the discharge capacities of  $\text{LaNi}_{3.8}\text{Co}_{0.72}\text{Mn}_{0.24}\text{Al}_{0.24}$ ,  $\text{LaNi}_{3.8}\text{Co}_{0.60}\text{Mn}_{0.36}\text{Al}_{0.24}$ ,  $\text{LaNi}_{3.8}\text{Co}_{0.48}\text{Mn}_{0.48}\text{Al}_{0.24}$ ,  $\text{LaNi}_{3.8}\text{Co}_{0.36}\text{Mn}_{0.60}\text{Al}_{0.24}$ , and  $\text{LaNi}_{3.8}\text{Co}_{0.24}\text{Mn}_{0.72}\text{Al}_{0.24}$  alloys were 327, 326, 325, 318, and 300 mAh/g, respectively. Clearly,

Table 1

The lattice parameters of  $a$ - and  $c$ -axes of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  alloys

Alloy composition	$a$ -axis (Å)	$c$ -axis (Å)
$\text{LaNi}_{3.8}\text{Co}_{0.72}\text{Mn}_{0.24}\text{Al}_{0.24}$	5.1279	4.0639
$\text{LaNi}_{3.8}\text{Co}_{0.60}\text{Mn}_{0.36}\text{Al}_{0.24}$	5.1293	4.0680
$\text{LaNi}_{3.8}\text{Co}_{0.48}\text{Mn}_{0.48}\text{Al}_{0.24}$	5.1349	4.0835
$\text{LaNi}_{3.8}\text{Co}_{0.36}\text{Mn}_{0.60}\text{Al}_{0.24}$	5.1443	4.1151
$\text{LaNi}_{3.8}\text{Co}_{0.24}\text{Mn}_{0.72}\text{Al}_{0.24}$	5.1556	4.1375

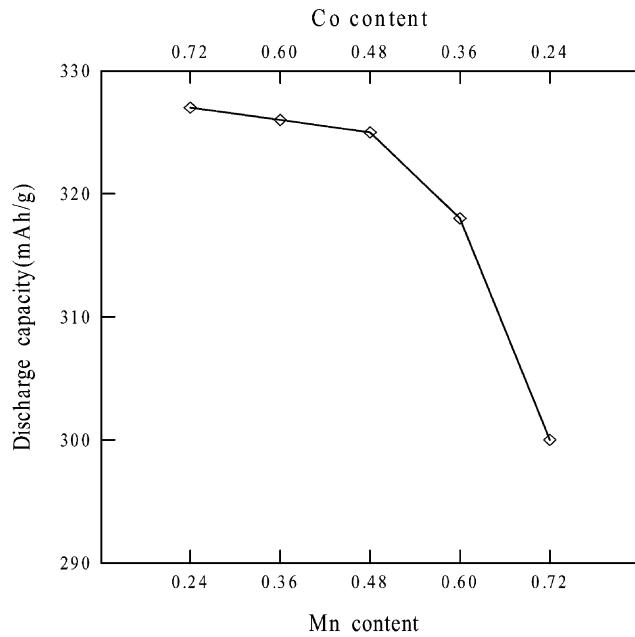


Fig. 2. The effects of Mn and Co contents on the electrochemical capacities of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes at the discharging rate of 100 mA/g.

Co had a positive influence while Mn had an adverse effect when the electrochemical capacity was concerned. With the Co/Mn atom ratio in the range of 3/1 to 1/1, the discharge capacities were almost the same. But a substantial reduction in discharge capacities were found when the Mn content was higher than Co, as can be seen in Fig. 2. The change of capacity, as indicated in [21], is related to the number of effective sites in the crystal lattice for hydrogen atoms to occupy and to release. The beneficial effect of Co on the capacities of the metal hydride alloys found in this study is in good agreement with other investigations [3,18,22,23]. Furthermore, the results shown in Fig. 2 indicated that as long as the Co content was higher than Mn in the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  alloys, the capacity as high as 325 mAh/g could be obtained. Most importantly, however, the results indicated that a Co/Mn ratio of 1 might be used in order to produce less expensive metal hydride electrode without sacrificing the discharge capacity.

Fig. 3 shows the discharge curve of these alloys at the discharge rate of 100 mA/g after being fully activated. The discharge voltage did not remain constant, similar to most metal hydride electrodes, but decreased as the discharging time increased. When, the discharge voltage reached approximately 1.15 V, it dropped with an even higher rate. As can be seen in this figure, the discharge voltage of the  $\text{LaNi}_{3.8}\text{Co}_{0.72}\text{Mn}_{0.24}\text{Al}_{0.24}$  alloy was the highest among all the alloys tested. More specifically, the higher was the Co content in the metal hydride electrode, the greater the discharge voltage of the full cell could be raised. With Co was gradually replaced by Mn, not only the discharge cell voltage was suppressed but also the capacity was lost progressively.

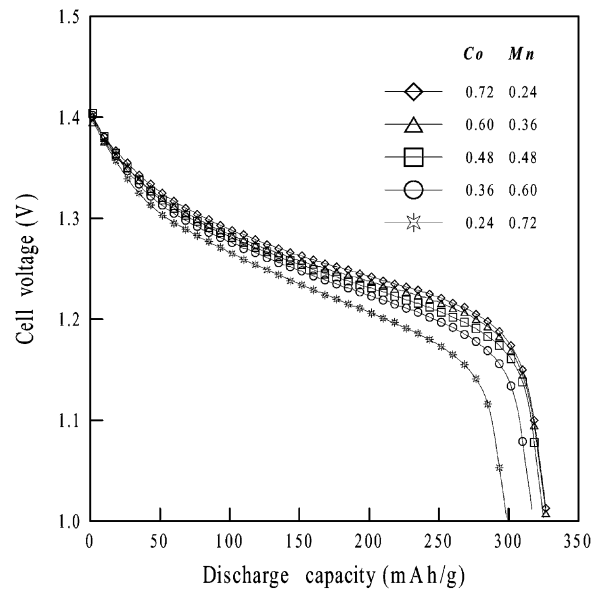


Fig. 3. Discharge curves of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes of various compositions at the discharging rate of 100 mA/g.

After the electrodes were fully activated, the charging efficiency of each alloy was also estimated. The discharge capacities of the each electrode charged to 80–140% of its maximum electrochemical capacity were measured. The charging efficiency defined as the ratio of discharge capacity to charge capacity was thus determined. The charging efficiency as a function of the degree of charging for the  $\text{LaNi}_{3.8}\text{Co}_{0.72}\text{Mn}_{0.24}\text{Al}_{0.24}$  electrode with a discharging rate of 100 mA/g is shown in Fig. 4. As seen in this figure, the charging efficiency decreased with increasing extent of charging. Clearly, the charging efficiencies were all less

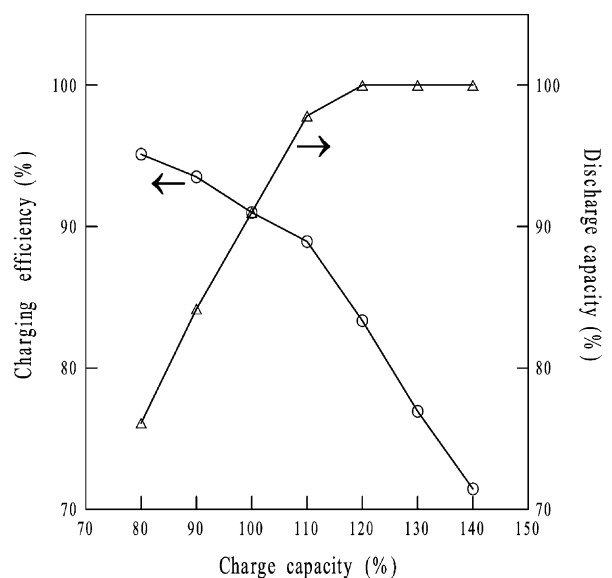


Fig. 4. The variations of charging efficiency and discharge capacity of the  $\text{LaNi}_{3.8}\text{Co}_{0.72}\text{Mn}_{0.24}\text{Al}_{0.24}$  electrode with charge capacity in the range of 80–140% maximum capacity; all charging and discharging at 100 mA/g.

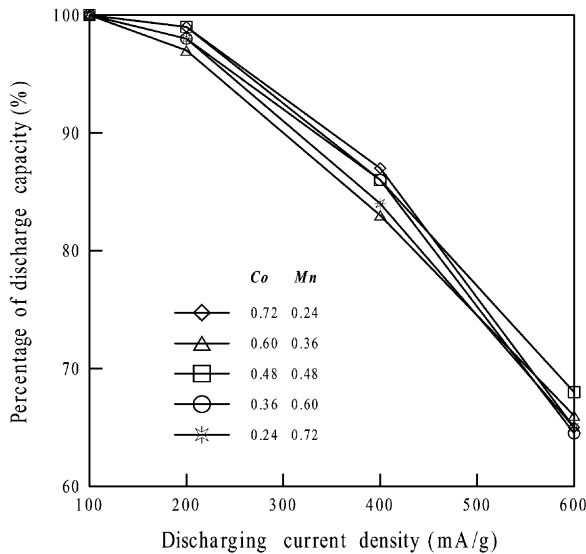


Fig. 5. The dependence of discharge capacity on the different discharging rate for the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes (charging rate: 100 mA/g).

than unity, indicating the irreversible characteristics of the charging/discharging cycles. A substantial drop in charging efficiency was observed as the electrode was charged over 110% of the maximum capacity. Nevertheless, with overcharging less than 10%, a charging efficiency in the range of 0.9–0.95 could be obtained. Similar results were also found in other alloys with different composition.

### 3.3. Discharging capacity at different discharge rate

Taking the discharge capacity at a discharging rate of 100 mA/g as unity and making the comparison of the capacity at each different discharging current density with it, the dependence of discharge capacity on discharging rate for each electrode is shown in Fig. 5. The results clearly showed that the discharge capacity decreased with increasing discharging rate. However, the effect of Co and Mn compositional adjustment in the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes on the high-rate discharge capacity was not discernable as demonstrated in Fig. 5. At a discharge rate less than 200 mA/g, all the alloys exhibited satisfactory discharge kinetics with a capacity above 98%. At a very high discharging rate (600 mA/g), only about 65% of the capacity (compared with that at a discharging rate of 100 mA/g) was retained for each metal hydride electrode tested.

It is generally reported that Co is an effective element in improving the high-rate discharging performance [3,18,22,23]. This may be attributed to a good electronic conductivity of cobalt hydroxide precipitated on the alloy surface as compared with other alloying elements [24,25]. But in this investigation, no significant adverse effect on the high-rate discharging performance was observed by replacing Co with Mn. It might suggest that Mn has the similar

beneficial effect, or at least not deleterious, to enhance the high-rate discharging capability of the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes.

### 3.4. Effect of charging rate on discharging performance

The variation of charging rate may affect the discharge capacity of the hydride electrodes, which may eventually influence the discharging characteristics. There may be two important factors that influence the high-rate charging performance of the metal hydride electrodes [4,13–15,23,26–28]. The first is associated with the reactive activity of the electrode surface where adsorption and charge transfer process of hydrogen atom takes place. It has been reported that the presence of nickel on the electrode surface may improve the surface reaction kinetics [4,15,26,27]. Secondly, the diffusion process of hydrogen atom in the bulk of the hydrogen storage alloy can also affect the high-rate charging capability.

The dependence of the discharge capacity on the charging rate (from 100 to 600 mA/g) for the series of the alloys studied is demonstrated in Fig. 6. As expected, the discharge capacity at a rate of 100 mA/g decayed with increasing charging current density. Nevertheless, all these alloys still exhibited excellent discharge capacity even at a high charging rate. At the charging rate of 600 mA/g,  $\text{LaNi}_{3.8}\text{Co}_{0.72}\text{Mn}_{0.24}\text{Al}_{0.24}$  alloy had a capacity of about 87.5% of that charged at a rate of 100 mA/g. The high-rate charging performance could be even improved as the Co/Mn ratio decreased. At the same charging rate, the decrease in discharge capacity was reduced as the Co/Mn ratio decreased for the respective alloy. The promotion on high-rate charging capability implied that the hydrogen atoms were absorbed more easily during charging. The discharge capacities measured at a discharging rate of 100 mA/g for various

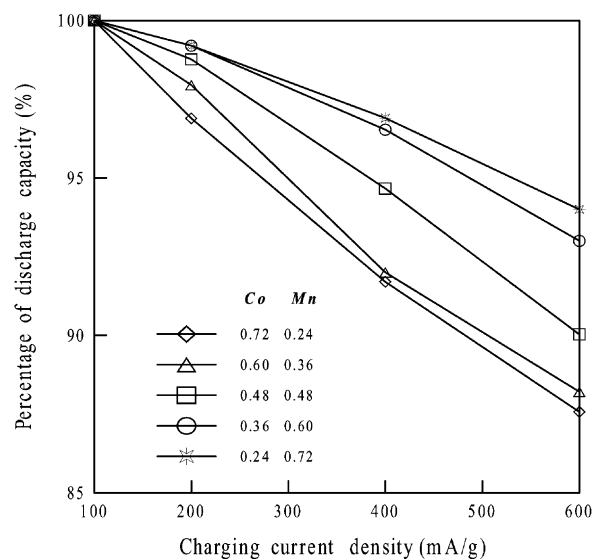


Fig. 6. Effect of charging rate on the discharge capacity for the  $\text{LaNi}_{3.8}(\text{Co} + \text{Mn})_{0.96}\text{Al}_{0.24}$  electrodes (discharging rate: 100 mA/g).

Table 2

The discharge capacity ratio measured at a discharging rate of 100 mA/g for various hydride electrodes and at different charging rates<sup>a</sup>

Composition	Charging rate (mA/g)			
	100	200	400	600
LaNi <sub>3.8</sub> Co <sub>0.72</sub> Mn <sub>0.24</sub> Al <sub>0.24</sub> (%)	100	96.9	91.7	87.6
LaNi <sub>3.8</sub> Co <sub>0.60</sub> Mn <sub>0.36</sub> Al <sub>0.24</sub> (%)	100	98.0	92.0	88.2
LaNi <sub>3.8</sub> Co <sub>0.48</sub> Mn <sub>0.48</sub> Al <sub>0.24</sub> (%)	100	98.8	94.7	90.0
LaNi <sub>3.8</sub> Co <sub>0.36</sub> Mn <sub>0.60</sub> Al <sub>0.24</sub> (%)	100	99.2	96.5	93.0
LaNi <sub>3.8</sub> Co <sub>0.24</sub> Mn <sub>0.72</sub> Al <sub>0.24</sub> (%)	100	99.2	96.9	94.0

<sup>a</sup> Taking the discharge capacity at a charging rate of 100 mA/g as unity.

hydride electrodes and at different charging rates are given in Table 2. The results showed that a high Mn content in the LaNi<sub>3.8</sub>(Co + Mn)<sub>0.96</sub>Al<sub>0.24</sub> alloys favored the absorption/diffusion of hydrogen at the high-rate charging. One of the beneficial effects of Mn on high-rate charging might be attributed to the expanded lattices that subsequently caused an expansion of the interstitial site in favor of hydrogen diffusion. The increase in chargeability with increasing Mn content is clearly associated with the increase in the lattice constants of *a*- and *c*-axes as revealed in Table 1.

### 3.5. Cyclic stability

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 process [7,14,27,29,30]. The discharge capacity retention after 150 sequent cycles for the alloys with different chemical composition is given in Fig. 7.

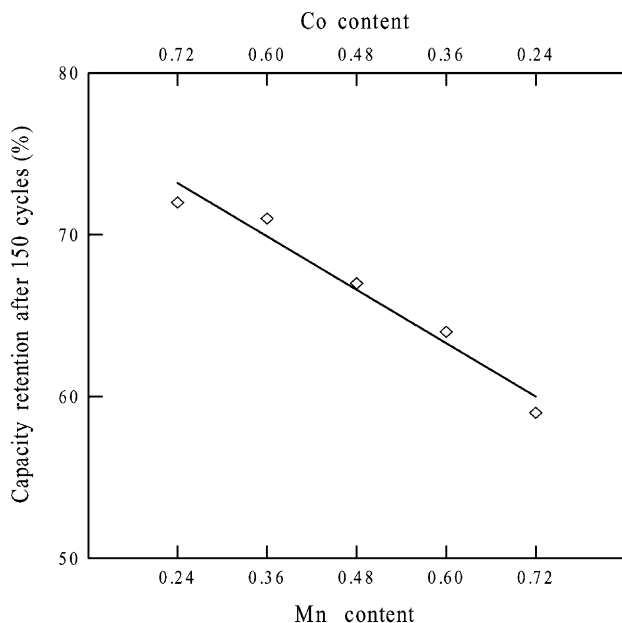


Fig. 7. Cyclic stability about the discharge capacity of the LaNi<sub>3.8</sub>(Co + Mn)<sub>0.96</sub>Al<sub>0.24</sub> electrodes after 150 charging and discharging cycles (charging/discharging rate: 300 mA/g).

The results showed that the more Co was contained in alloys, the greater resistance to cyclic decay they could obtain. After repeated charging and discharging for 150 cycles, only 59% of capacity still remained in the alloy of LaNi<sub>3.8</sub>Co<sub>0.24</sub>Mn<sub>0.72</sub>Al<sub>0.24</sub>, while about 70% capacity was retained for the high Co containing alloy, namely LaNi<sub>3.8</sub>Co<sub>0.72</sub>Mn<sub>0.24</sub>Al<sub>0.24</sub>.

The beneficial effects of Co in metal hydride electrodes are three-fold as can be found in the literature. First, it reduces the hardness of the alloy to improve the cyclic durability [31,32]. Secondly, it causes a decrease in the volume expansion ratio from metal to hydride [5,7,9,10,24,29,31,33]. And thirdly, the electrochemical dissolution of other elements from the alloy into KOH solution can be suppressed with the presence of Co [9,10,34]. Therefore, Co is thought to be one of the most important components for obtaining satisfactory cyclic stability of the metal hydride electrodes. The results obtained in this investigation were in good agreement with that reported in the literature. On the other hand, the deleterious effect of Mn, as far as cyclic stability was considered, was also revealed in Fig. 7. Clearly, cyclic stability increased as Co/Mn increased from 1/3 to 3/1.

From economical point of view, the replacement of expensive Co with a much cheaper element is always considered. From the results obtained in this investigation, Mn could be considered as a good substitute for Co. But an appropriate Co/Mn ratio should be maintained to achieve suitable performance (such as capacity, charging/discharging rate and cyclic stability, etc.) and cost-effectiveness.

## 4. Conclusions

The variation of Co/Mn atomic ratio in the LaNi<sub>3.8</sub>(Co + Mn)<sub>0.96</sub>Al<sub>0.24</sub> alloys greatly affected their crystal structures and charging/discharging characteristics. The results are summarized as follows.

1. The expansion of lattice parameter increased with increasing Mn substitution for Co in the LaNi<sub>3.8</sub>(Co + Mn)<sub>0.96</sub>Al<sub>0.24</sub> hydrogen storage alloys.
2. A higher discharge capacity and a higher discharge cell voltage could be obtained for higher Co containing LaNi<sub>3.8</sub>(Co + Mn)<sub>0.96</sub>Al<sub>0.24</sub> alloys. With the Co/Mn ratio kept above 1/1, a discharge capacity of 325 mA/g could be obtained. The replacement of Co with Mn with a Co/Mn ratio less than 1/1 would result in a substantial decrease in discharge capacity.
3. For all the LaNi<sub>3.8</sub>(Co + Mn)<sub>0.96</sub>Al<sub>0.24</sub> alloys tested, the extent of discharge capacity decreased as the charging rate increased from 100 to 600 mA/g. However, enhanced high-rate charging performance was found by increasing Mn content in the hydrogen storage alloys.
4. The cyclic stability of the LaNi<sub>3.8</sub>(Co + Mn)<sub>0.96</sub>Al<sub>0.24</sub> electrodes in 7 M KOH electrolyte increased as the Co/Mn ratio increased from 1/3 to 3/1.

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