



ELSEVIER

Journal of Power Sources 92 (2001) 102–107

JOURNAL OF  
**POWER  
SOURCES**

www.elsevier.com/locate/jpowsour

# Effects of surface treatments of $MNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy on the activation, charge/discharge cycle and degradation of Ni/MH batteries

Weixiang Chen

*Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China*

Received 8 November 1999; received in revised form 26 April 2000; accepted 24 May 2000

## Abstract

The effects of the surface treatment of the hydrogen storage alloy on the activation property and cycle life of nickel/metal-hydride (Ni/MH) batteries were investigated by means of the electrochemical impedance spectra. It was found that the oxide layer on the alloy surface affected its electrochemical properties and catalysis for the oxygen combination. Therefore, Ni/MH battery employed the untreated alloy as negative electrode material exhibited bad activation property, short cycle life and high internal pressure. Because of the improvement in the metal hydride electrode electrochemical characteristics and catalysis for oxygen recombination by the surface treatment of the alloy in 0.02 M  $KBH_4$ +6 M KOH or 6 M KOH solution, the battery used the treated alloy as negative exhibited good activation, long cycle life and low internal pressure. The composition and dissolution of the alloy surface were analyzed by an electron probe microanalysis (EPMA) and induced coupled plasma spectroscopy (ICP). It was found that the Ni-rich surface layer was an important factor to improve the activation and cycle life of battery. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Nickel/metal-hydride battery; Electrochemical impedance spectra; Hydrogen storage alloy; Activation; Surface treatment

## 1. Introduction

Recently, nickel/metal-hydride (Ni/MH) batteries have been developed and commercialized because of their higher energy density, high rate dischargeability, long cycle life, no memory effect and environment cleanness compared with Ni/Cd batteries. Many kinds of the hydrogen storage alloys such as the rare earth or mischmetal-based  $AB_5$  type alloys [1–5], Zr-based Laves alloys [5–8], Mg-based alloys [9–12] have been extensively researched for the negative electrode of Ni/MH battery. Of above alloys, the  $AB_5$ -type alloy is most widely applied in commercialized Ni/MH battery [2,3,5]. The MH electrode properties could be significantly improved by multicomponent substitutions [1–3], optimization of the rare earth composition in mischmetal [13,14], surface treatments, and using non-stoichiometric  $AB_{5-x}$  alloy [15]. It was also confirmed that the electrode performance greatly depends on not only the alloy composition but also its surface state. The hydrogen storage capacity, the enthalpy of the metal hydride formation and equilibrium pressure of hydrogen are typical bulk properties and depend mainly on the alloy bulk composition. While the electro-

catalytic activity, activation, anti-corrosion in the electrolyte are typical surface properties, depend chiefly on the alloy surface composite and morphology, which is very important for its electrochemical application. Therefore, various surface treatments such as micro-encapsulation [16,17], addition of the other metal or metal oxide [17–19] and alkali-treatment [20–23] have been applied to improve the MH electrode electrochemical performances. The surface treatment by immersing in an alkaline solution is one of the very effective methods to improve the discharge capacity, high rate capability, cycle life, electrocatalytic activity, because of that the surface composition of the alloy was changed to a Ni-rich one, which has a high electrocatalytic activity. The alkaline treatment method was further developed by addition of a small amount of reductant  $H_3PO_2$  or  $KBH_4$ , first proposed by Iwakura and co-workers [24,25]. Recently, Ikoma and co-workers [26] have studied the effect of the alkali-treatment of hydrogen storage alloy on the degradation of Ni/MH battery. It is considered as the main factors to improve the cycle life of Ni/MH battery that Al dissolves from alloy surface, rare earth metal hydroxides form on the alloy surface, and Ni and Co exist as metals near the surface.

Electrochemical impedance spectra (EIS) is an effective technique for analyzing the reaction mechanisms of MH

*E-mail address:* weixiangchen@css.zju.edu.cn (W. Chen).

electrodes. Kuriyama and co-workers [27,28] applied EIS to study the electrochemical reaction and deterioration behavior of the metal hydride electrodes. In this work, the  $\text{MNi}_{4.0}\text{Co}_{0.6}\text{Al}_{0.4}$  alloy was treated by immersing in an alkaline solution or one containing reductant  $\text{KBH}_4$ . The effects of the surface treatments on the activation, charge/discharge cycle life and degradation of Ni/MH batteries were investigated by means of EIS. The influences of the surface treatment on the compositions of the alloy surface are evaluated by using induced coupled plasma spectroscopy (ICP) and electron probe micro-analyzer (EPMA).

## 2. Experimental details

### 2.1. Preparation of alloy powders, MH electrode and Ni/MH battery

The hydrogen storage alloy  $\text{MNi}_{4.0}\text{Co}_{0.6}\text{Al}_{0.4}$  (M=La-rich mischmetal, La: 64.6%; Ce: 5.9%; Pr: 26.6%; Nd: 2.2%) was prepared in an induction furnace under argon atmosphere. The cast alloy ingots were crushed to below 200 mesh by hydrogen absorption/desorption cycling a few times. The alloy powder was treated by immersing in 6 M KOH or 6 M KOH+0.02 M  $\text{KBH}_4$  solution at 80°C for 6 h. Alloy powders of 100 g and 1% acetylene black powder were mixed well with a small amount of 3% polyvinyl alcohol and 1% carboxymethyl cellulose solution, to form a paste which was casted into a porous foamed nickel substrate, which was then dried in vacuum and finally pressed to form the negative electrode of Ni/MH battery. Positive electrode was prepared by filling a nickel foam substrate with the active material consisting of  $\text{Ni}(\text{OH})_2$  codoped by 3 wt.% Zn, a small amount of cobalt compound and graphite as additive. A negative electrode, which contained about 7.4 g hydrogen storage alloy powders and its capacity was about 1700 mAh, ployamide separator and a positive electrode, which contained about 5.6 g  $\text{Ni}(\text{OH})_2$  and its capacity was about 1150 mAh, were spirally wound to form a cylindrical sealed cell (AA size). The electrolyte was a 6 M KOH–1 M NaOH–1 M LiOH solution. For conveniently reciting, the battery employed untreated alloy was defined as battery A, the battery employed alloy treated by 6 M KOH as battery B, and the battery employed alloy treated by 6 M KOH+0.02 M  $\text{KBH}_4$  as battery C.

### 2.2. Activation, charge/discharge cycle of Ni/MH batteries and the measurements of electrochemical impedance

The activations of the sealed Ni/MH batteries were carried out by three cycles of charging/discharging at a constant current of 200 mA (charging for 7.5 h and discharging to 0.9 V). The cycle life of Ni/MH battery was examined by a galvanostatic charging/discharging at 1 C (the charge/discharge current was 1000 mA). The battery was charged to cut-off  $\Delta V=-10$  mV, after a rest of 10 min, discharged to

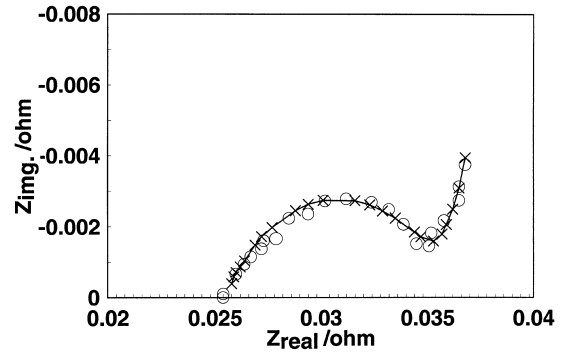


Fig. 1. A typical electrochemical impedance spectra of AA-size sealed Ni/MH battery; (O) experimental data and (x) stimulated data.

1.0 V. The activation and cycles were performed using a DK-2000. The electrochemical impedance of the battery was measured from 1000 to 0.02 Hz at 50% depth of discharge (DOD) using a 1250 Solartron frequency response analyzer and a 1287 Solartron electrochemical interface analyzer. A typical EIS of AA-size sealed Ni/MH battery is illustrated in Fig. 1. The impedance in high-frequency region is attributed to the charge-transfer resistance of the positive and negative electrode, and the slope in low frequency region is caused by the Warburg impedance of the negative and positive electrodes. The full equivalent circuit of EIS of Ni/MH battery may be represented by Fig. 2. But there are too much variables to simulate, so that the full equivalent circuit of Fig. 2 is simplified as Fig. 3. The parameters in Fig. 3 were calculated with the non-linear least squares fitting (NLLSF) program EQUIVCR[29]. The polarization resistances of the positive and negative electrodes for the opened battery were individually measured by the linear sweep voltammetry using a Solartron 1287 electrochemical interface analyzer at a scan rate of  $1 \text{ mV s}^{-1}$  near the equilibrium potential.

### 2.3. Analysis of compositions and dissolution of the alloy surface

The surface compositions of the alloys before and after treatment were examined by electron probe microanalysis.

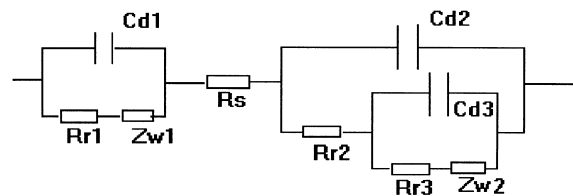


Fig. 2. A full equivalent circuit of electrochemical impedance spectra of Ni/MH battery.  $R_{r1}$ ,  $Z_{w1}$  and  $C_{d1}$  are the charge transfer resistance, Warburg impedance and double layer capacity of the positive, respectively.  $R_s$  is the ohmic resistance of the battery.  $R_{r2}$ ,  $C_{d2}$ , and  $Z_{w2}$  are the charge-transfer resistance, double layer capacity and Warburg impedance of MH electrode, respectively.  $R_{r3}$  and  $C_{d3}$  are the resistance and capacity due to absorbing of hydrogen on the hydrogen storage alloy.

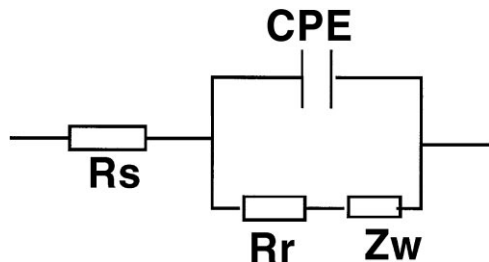


Fig. 3. The simplified equivalent circuit of electrochemical impedance spectra of Ni/MH battery.  $R_s$  is the ohmic resistance of the battery.  $R_r$  is the overall charge-transfer resistance of the battery, which includes the resistance of the absorbing of hydrogen on the surface of hydrogen storage alloy surface.  $Z_w$  is the total Warburg impedance of positive and negative electrodes. CPE is constant phase element for simulating by NLLSF,  $Z_{CPE}(\omega) = \{Y_0(j\omega)^n\}^{-1}$ ,  $0 < n \leq 1$ .

By means of induced coupled plasma spectroscopy (ICP), the dissolution of the alloy surface in the alkaline solution during treating was analyzed.

### 3. Results

#### 3.1. Electrochemical impedance of Ni/MH batteries activation

Fig. 4 shows the charge-transfer and ohmic resistance of Ni/MH batteries as function of the charge/discharge

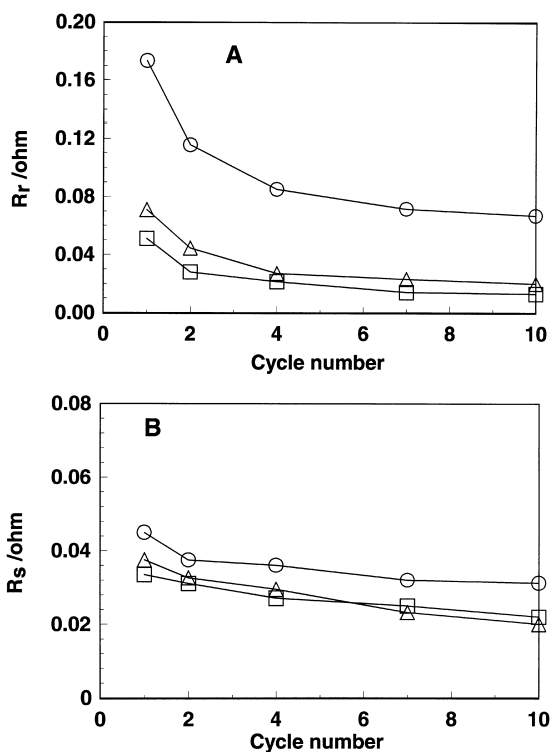


Fig. 4. Variety of charge-transfer resistance (A) and ohmic resistance (B) of AA-size sealed Ni/MH batteries during their activation. (○) Battery A; (△) battery B; and (□) battery C.

Table 1

The polarization resistances of the positive and negative electrodes of opened Ni/MH battery

Electrode	Polarization resistance ( $\Omega$ )		
	Battery A	Battery B	Battery C
Positive	0.051	0.052	0.051
Negative	0.046	0.032	0.029

activation cycle number. It can be seen from Fig. 4(A) that the charge-transfer resistance of Ni/MH batteries decrease with increasing charge/discharge cycle. It is worth notice that the charge-transfer resistances of battery B and C are apparently lower than that of battery A, at the same cycle. For example, at the first cycle, the charge-transfer resistance of battery A is  $0.17 \Omega$ , while that of battery B and C are  $0.071$  and  $0.051 \Omega$ , respectively. After 3–4 cycles, the charge-transfer resistances of battery B and C became smaller and do not apparently change, which indicates that the batteries are activated on the whole. But even after 7–10 cycles, the battery A exhibited still the higher charge-transfer resistance, which indicates that it is difficult for the activation of battery A. Assuming that the activation properties of the positive electrodes of the battery A, B and C are same on the whole, the good activation property is mainly caused by the improvement in electrochemical performances of MH electrode. In order to confirm the point, the battery A, B and C were disassembled after three cycles, then the polarization resistances of the positive and MH electrodes were individually measured. As shown in Table 1, the polarization resistances of the positive electrodes of battery A, B and C were almost same, but that of the negative electrode of battery A was apparently larger than that of negative electrode of battery B or C. The fact confirmed that the surface treatment improved the MH electrode activation property and hence the activation of Ni/MH battery. Fig. 4(B) also indicates the ohmic resistance of the battery A is slightly larger than that of battery B and C. It is likely due to that the surface treatment removed or eliminated the oxide film on the alloy surface, hence lowered the contact resistance of the alloy powder with each other and the foam nickel substrate.

#### 3.2. Electrochemical impedance of Ni/MH batteries during charge/discharge cycle

The charge/discharge cycle at 1 C rate of Ni/MH batteries are illustrated in Fig. 5. It can be seen that the surface treatments of the alloy have greatly improved the cycle life of the Ni/MH battery. Fig. 6 shows the charge-transfer and ohmic resistance of Ni/MH battery as a function of the charge/discharge cycle number. It can be seen that the charge-transfer and ohmic resistance of battery A rapidly increase after 20 cycles, which is coincident with a sharp decrease in the discharge capacity as shown in Fig. 5. The

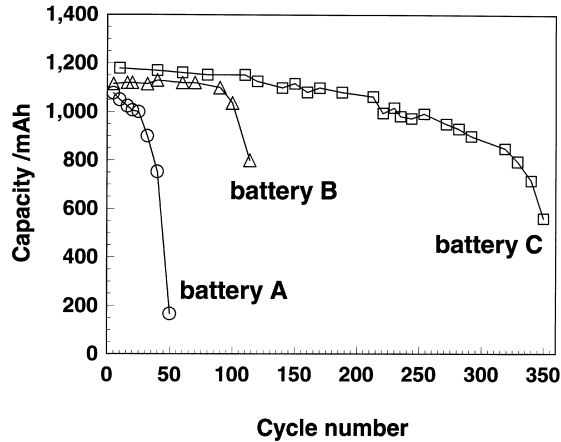


Fig. 5. Charge/discharge cycle life of Ni/MH batteries at 1 C rate.

charge-transfer and ohmic resistance of battery B begin to increase apparently after 90 and 60 cycles, respectively. The charge-transfer and ohmic resistance of battery C begin to increase apparently after 300 and 220 cycles, respectively. The facts confirm again that the surface treatment improved substantially the cycle durability of the Ni/MH battery.

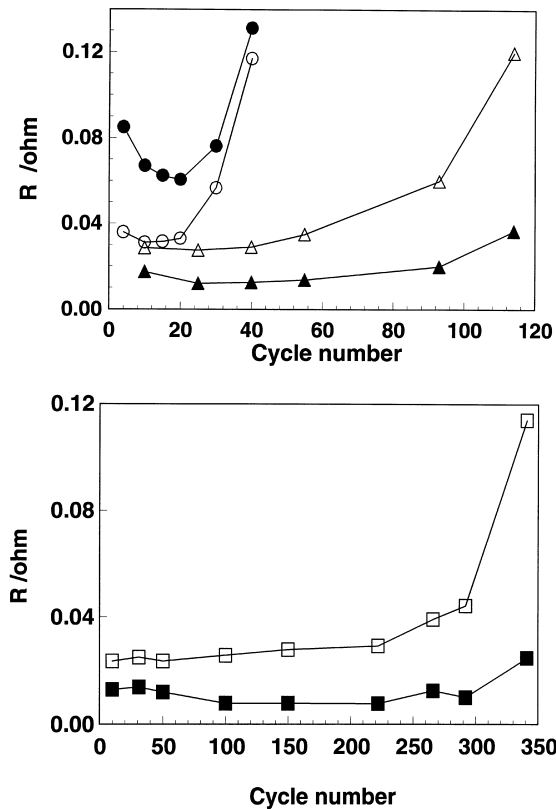


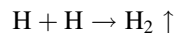
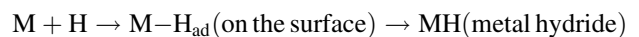
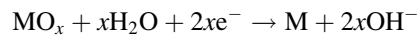
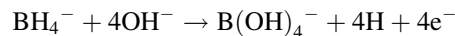
Fig. 6. Variety of electrochemical impedance of Ni/MH batteries during cycling. (○)  $R_s$  of battery A; (●)  $R_r$  of battery A; (△)  $R_s$  of battery B; (▲)  $R_r$  of battery B; (□)  $R_s$  of battery C; and (■)  $R_r$  of battery C.

#### 4. Discussion

Hydrogen storage alloy employed as the negative electrode of Ni/MH battery is required to be of good activation, electrocatalytic activity for electrode reaction, anti-corrosion in the electrolyte and cycle durability. The surface of the hydrogen storage alloy is very easily oxidized. The oxide layer on the alloy surface affects seriously the activation and electrocatalytic activity of the electrode. Therefore, it is difficult to activate for battery A employed untreated alloy as negative electrode and its charge-transfer resistance during activation is more larger than that of battery B or C at the same cycle.

The studies [24,25] revealed that the Ni-rich surface layer was produced and the specific surface area was augmented because of the preferential dissolution of Mn and Al and etching of heat alkaline solution. For these reasons, the electrocatalytic activity, high-rate dischargeability, activation property of MH electrode were markedly improved. Therefore, the battery B and C employed the treated alloy as negative electrode exhibited good activation property and low charge-transfer resistance. By the separate examination of polarization resistance of the positive and negative electrodes of disassembled batteries, it is confirmed that the improvement in activation of battery is mainly caused by the good electrochemical characteristics of the treated alloy electrode.

In addition, for the treatment in the alkaline containing  $\text{KBH}_4$ , both the electron and atomic hydrogen are released during treating. The oxide on the alloy surface would be reduced and eliminated. The previous works [30,31] confirmed that part of nickel oxide was reduced to metallic nickel by means of XPS analysis. The atomic hydrogen released during treating was adsorbed on the alloy surface and may penetrate into the alloy bulk or recombine to hydrogen gas to evolve. The above processes may be expressed as following equations:



The repeating hydrogenation/dehydrogenation during treatment gives rise to the surface micro-crack and pulverization of the alloy, which enhance the etching effect of the alkaline solution on the alloy and augment the specific surface area. Table 2 shows the results of ICP analysis for the dissolution of the alloy surface metal elements in the solutions during treating. The dissolution amount of aluminum is the largest. In addition, the content of aluminum in the alkaline containing  $\text{KBH}_4$  is two times higher than that in single alkaline solution. During treating of the hydrogen storage alloys in hot alkaline solution containing  $\text{KBH}_4$ , the reducing agent released a large amount of

Table 2

The content of metal ions in the solution dissolved from the alloy surface during treating ( $\text{mg l}^{-1}$ )

Solution	La	Ni	Co	Al
1 <sup>a</sup>	0.0312	0.412	25.9	56.2
2 <sup>b</sup>	0.0345	0.350	0.195	125

<sup>a</sup> 6 M KOH.

<sup>b</sup> 0.02 M  $\text{KBH}_4$ +6 M KOH.

hydrogen, the part of which was absorbed by the alloys, and another part was recombined to evolve hydrogen gas. The absorbing and evolution of hydrogen was dynamic equilibrium. The alloy powders were cracked and pulverized by the repeating absorbing/desorbing. Therefore, it may be believed that the etching effect was enhanced by  $\text{KBH}_4$ . While the content of Co in alkaline solution is 100 times higher than that in the alkaline solution containing  $\text{KBH}_4$ . It is due to that a small quantity of Co can dissolve in the strong base solution to form a complex-ion  $[\text{Co}(\text{OH})_4]^{2-}$ . As existing of the reducing agent  $\text{KBH}_4$ , the complex ion  $[\text{Co}(\text{OH})_4]^{2-}$  was reduced to metallic Co to deposit on the alloy surface. As shown in Table 3, the surface Co composite of the alloy treated by the alkaline containing  $\text{KBH}_4$  is slightly higher than that of the alloy treated by single alkaline solution. Matsuoka et al. [32] conclude that the electrochemical properties of  $\text{Mm}(\text{Ni}_{3.6}\text{Mn}_{0.4}\text{Co}_{0.7}\text{Al}_{0.3})_{0.92}$  hydrogen storage alloy were remarkably improved by coating Co or Pd. It might be believed that the increase in Co compositions on the alloy surface is also benefit to improve electrochemical property of MH electrode.

In sealed Ni/MH battery, MH electrode are required not only good electrochemical performances but also the catalysis for the oxygen recombination. If the oxygen evolved on the positive electrode during charging cannot be recombined on the negative surface in time, the internal pressure of Ni/MH battery would increase and the alloy surface be oxidized. The oxide layer on the untreated alloy surface interfered with the oxygen recombination in sealed battery, leading to high internal pressure, corrosion of the alloy and bad activation property of Ni/MH battery. After treatment, the Ni-rich layer on the alloy surface has a catalysis for oxygen recombination. Fig. 7 shows the internal pressure of batteries as function of the

Table 3

The composition on the surface of the hydrogen storage alloy before and after treatment (at.%)

Alloy	La	Ce	Pr	Nd	Ni	Co	Al
Untreated	11.69	0.80	1.78	0.71	54.77	7.69	22.55
Treated by 1 <sup>a</sup>	15.67	1.35	2.11	1.27	65.23	9.41	4.95
Treated by 2 <sup>b</sup>	15.45	1.34	1.56	0.64	66.56	10.21	4.24

<sup>a</sup> 6 M KOH.

<sup>b</sup> 0.02 M  $\text{KBH}_4$ +6 M KOH.

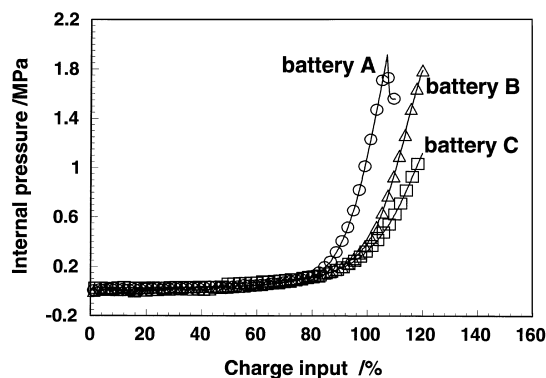


Fig. 7. The cell internal pressure as a function of charge input at 1 C.

charge input. At the same charge input, the internal pressure of batteries is in order of battery A>battery B>battery C. The oxygen recombination in time suppresses the oxidization corrosion of the alloy in the electrolyte, hence substantially improves the activation property and cycle life of Ni/MH battery.

During charge/discharge cycle, the electrolyte was redistributed among the positive and negative electrodes and separator due to an increase in surface area and pore volume and swelling of positive electrode. An extensive research on the electrolyte distribution during charge/discharge cycling of Ni/MH battery was carried out by Singh [33]. The electrolyte level of MH electrode did not apparently change during cycle on the whole, while that of positive electrode and separator had an apparent change. The electrolyte level of the positive electrode increased from initial 18 to 43% at the 150th cycle and that of separator decreased from original 45 to 19% at the 150th cycle and to 10% at 350th cycle. Therefore, it might be believed that the quick increase in ohmic resistance in the later stage of cycle would be caused by the drying out of the separator. After the degradation, the Ni/MH batteries were disassembled and it was found that the separator had already dried out. Leblanc et al. [34] suggested that the corrosion of the alloy in the electrolyte consumed a small amount of water, which accelerate the drying out of the separator. While the over high cell internal pressure made the gas in battery release out, leading to the electrolyte losing. Therefore, the ohmic resistance of battery A sharply increased after 20 cycles. In the case of the treated hydrogen storage alloys, the metallic Ni and Co on the surface can prevent the alloy from further corrosion, while that Al dissolves from the alloy surface could suppress the consumption of electrolyte in sealed Ni/MH battery. Moreover, the charge efficiency and catalysis for oxygen recombination are improved by the surface modifications. Therefore, the battery C exhibited a low cell internal pressure and long cycle life. In the end of cycle, the ohmic resistances of battery B and C are much larger than their charge-transfer resistances, which indicated that the degradation is mainly contributed to the drying out of the separator.

## 5. Conclusions

The surface property is an important factor to affect the activation and cycle life of Ni/MH battery. The hydrogen storage alloy was pretreated by immersing in an alkaline solution or one containing reductant in order to improve the electrochemical performances of MH electrode. A nickel-rich surface layer was produced because of the preferential dissolution of Al and etching of the heat alkaline solution. In an alkaline containing reductant  $\text{KBH}_4$ , the Co dissolved by alkaline solution was again reduced to a metallic Co on the alloy surface. In addition, the surface treatment augmented the specific surface area of the alloy. The above facts can be considered as the main factors for improving the electrochemical characteristics of MH electrode, anti-corrosion in a strong base solution and catalysis for oxygen recombination of the alloy, resulting in a good activation, long cycle life and low internal pressure of Ni/MH battery. In this work, the degradation of battery was mainly caused by the drying out of the separator for the treated alloy. For the untreated alloy, the degradation of battery was caused by both the corrosion of the hydrogen storage alloy and the drying out of the separator.

## Acknowledgements

The project was supported by the National Advanced Materials Committee of China. The author expresses thanks to Dr. Y.J. Lang in Zhejiang University for his help in measurement of electrochemical impedance and Prof. Y.X. Chen and H. Hong in Tianjin University for their help in examination of the cell internal pressure.

## References

- [1] J.J.G. Willems, Philips J. Res. 39 (1984) 1.
- [2] C. Iwakura, M. Matsuoka, Prog. Batteries Battery Mater. 10 (1991) 81.
- [3] N. Furukawa, J. Power Sources 51 (1994) 45.
- [4] A. Anani, A. Visintin, K. Petrov, S. Srinivasan, J. Power Sources 47 (1994) 261.
- [5] Q.D. Wang, C.P. Chen, Y.Q. Lei, J. Alloys Comp. 253/254 (1997) 627.
- [6] X.G. Yang, Y.Q. Lei, W.K. Zhang, G.M. Zhu, Q.D. Wang, J. Alloys Comp. 243 (1996) 151.
- [7] A. Zuttle, F. Meli, D. Chartouni, L. Schlapbach, F. Lichtenberg, B. Friedrich, J. Alloys Comp. 239 (1996) 175.
- [8] J. Chen, S.X. Dou, H.K. Liu, J. Alloys Comp. 256 (1997) 40.
- [9] N.H. Goo, J.H. Woo, K.S. Lee, J. Alloys Comp. 288 (1999) 286.
- [10] S. Nohara, K. Hamasaki, S.G. Zhang, H. Inoue, C. Iwakura, J. Alloys Comp. 280 (1998) 104.
- [11] N. Cui, B. Luan, H.J. Zhao, H.K. Liu, S.X. Dou, J. Alloys Comp. 233 (1996) 236.
- [12] C.Y. Yang, P. Yao, D.H. Bradhurst, H.K. Liu, S.X. Dou, J. Alloys Comp. 285 (1999) 267.
- [13] G.D. Adzic, J.R. Johnson, J.J. Reilly, J. McBreen, S. Mukerjee, J. Electrochem. Soc. 142 (1995) 3429.
- [14] Y.Q. Lei, J.J. Jiang, D.L. Sun, J. Wu, Q.D. Wang, J. Alloys Comp. 231 (1995) 553.
- [15] M. Nogami, M. Tadokoro, M. Kimoto, Y. Chikano, T. Ise, N. Furukawa, Denki Kagaku. 61 (1993) 1088.
- [16] K. Naito, T. Matsunami, K. Okuno, M. Matsuoka, C. Iwakura, J. Appl. Electrochem. 24 (1994) 808.
- [17] M. Matsuoka, K. Asai, Y. Fukumoto, C. Iwakura, J. Alloys Comp. 192 (1993) 149.
- [18] C. Iwakura, Y. Fukumoto, M. Matsuoka, T. Kohno, K. Shinmo, J. Alloys Comp. 192 (1993) 152.
- [19] C. Iwakura, M. Matsuoka, T. Kohno, J. Electrochem. Soc. 141 (1994) 2306.
- [20] H. Ogawa, M. Ikoma, H. Kawano, I. Matsumoto, J. Power Sources 12 (1988) 393.
- [21] M. Ikoma, K. Komori, S. Kaida, C. Iwakura, J. Alloys Comp. 284 (1999) 92.
- [22] W.K. Choi, S.G. Zhang, J.I. Murayama, R. Shin-ya, H. Inoue, C. Iwakura, J. Alloys Comp. 280 (1998) 99.
- [23] C. Iwakura, W.K. Choi, S.G. Zhang, H. Inoue, Electrochim. Acta 44 (1999) 1677.
- [24] C. Iwakura, M. Matsuoka, K. Asai, T. Kohno, J. Power Sources 38 (1992) 335.
- [25] M. Matsuoka, K. Asai, Y. Fukumoto, C. Iwakura, Electrochim. Acta 38 (1993) 659.
- [26] M. Ikoma, K. Komori, S. Kaida, C. Iwakura, J. Alloys Comp. 284 (1999) 92.
- [27] N. Kuriyama, T. Saki, H. Miyamura, I. Uehara, H. Ishikawa, J. Alloys Comp. 192 (1993) 161.
- [28] N. Kuriyama, T. Saki, H. Miyamura, I. Uehara, H. Ishikawa, J. Alloys Comp. 202 (1993) 183.
- [29] B.A. Boukamp, Solide State Ionics 20 (1986) 31.
- [30] W.X. Chen, Z.Y. Tang, H.T. Guo, Z.L. Liu, C.P. Chen, Q.D. Wang, J. Power Sources 74 (1997) 38.
- [31] W.X. Chen, Z.Y. Tang, C.P. Chen, Acta Chimica Sinica (in Chinese) 56 (1998) 564.
- [32] M. Matsuoka, M. Terashima, C. Iwakura, Electrochim. Acta 38 (1993) 1087.
- [33] D. Singh, J. Electrochem. Soc. 145 (1998) 116.
- [34] P. Leblanc, C. Jordy, B. Knosp, P.H. Blanchard, J. Electrochem. Soc. 145 (1998) 3.