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Effects of pretreatments on the electrochemical properties of $MlNi_{4.0}Co_{0.6}Al_{0.4}$ alloy electrode and the performance of a Ni/metal hydride battery

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Abstract

$MlNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy used as negative electrode material was pretreated in 6 M KOH or 6 M KOH+0.02 M KBH_4 solution. It was found that the pretreatment improved greatly the electrochemical properties of the metal hydride (MH) electrode. The cycle life at 1C of the Ni/MH battery after employing the treated alloy as negative electrode material increased from 40 cycles to above 300 cycles. The results of the electron probe microanalysis and inductively coupled plasma spectrometry analysis showed that a Ni-rich surface layer with high electrocatalytic activity was produced by the preferential dissolution of aluminium and the oxides on the alloy surface. It believed to be the main cause of the improved properties of the MH electrode and longer cycle life of the Ni/MH battery.
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Keywords: Metal hydride electrode; Hydrogen storage alloy; Cycle life; Ni/MH battery

1. Introduction

The characteristics such as hydrogen storage capacity and enthalpy of reaction are typical bulk properties, which depend mainly on the bulk compositions and crystal structure of the alloy. However, other properties such as activation, passivation, corrosion and oxidation in electrolyte, electrocatalytic activity, high-rate dischargeability and cycle life are mostly surface properties, depending chiefly on the surface characteristics of the alloy. Various surface treatments [1,2] and different additives [3,4] applied to the alloy powders and metal hydride (MH) electrodes have been introduced to improve the surface properties and hence the electrochemical performances of electrodes.

In the present paper, $MlNi_{4.0}Co_{0.6}Al_{0.4}$ hydrogen storage alloy was pretreated by immersion in different alkaline solutions. The effects of the pretreatments on the electrochemical properties of the alloy electrode and the cycle life of Ni/MH batteries made of differently treated alloys at 1C were investigated in detail.

2. Experimental

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

The hydrogen storage alloy $MlNi_{4.0}Co_{0.6}Al_{0.4}$ (Ml=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 purities of the constituent metals are: Ni 99.9%, Co 99.5% and Al 99.6%. The cast alloy ingots were crushed to below 200 mesh by hydrogen absorption/desorption cycling a few times. The alloy powder was pretreated in 6 M KOH or 6 M KOH+0.02 M KBH_4 solution at 80°C for 6 h. MH electrode was prepared by cold pressing mixtures of 0.100 g of the untreated or pretreated alloy powders with 0.200 g copper powders (about 360 mesh) at 20 MPa to form 10 mm diameter pellets.

The alloy powders (100 g) and 1% acetylene black powder of high specific surface area were mixed well with a small amount of 3% polyvinyl alcohol and 1% carboxymethyl cellulose solution, to form a paste which was scrubbed into a porous foamed nickel substrate, which was

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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 $Ni(OH)_2$ (doped with 4.8% Zn), 7% $Co(OH)_2$ and 4% carbon black as conductive agents. Negative electrode, ployamide separator and positive electrode were stacked together and wound spirally to form a cylindrical cell (AA size). Electrolyte (2.7 g) of a 6 M KOH–1 M NaOH–1 M LiOH solution was added.

2.2. Electrochemical measurements for MH electrodes

Electrochemical measurements were carried out in an open glass cell at the room temperature, employing a sintered nickel hydroxide electrode with a capacity much larger than that of the MH electrode as the counter electrode, Hg/HgO (6 M KOH) as the reference electrode, 6 M KOH solution as the electrolyte. MH electrodes were charged for 4 h and after a rest of 5 min discharged to −0.6 V vs. Hg/HgO at a constant current density of 100 $mA\cdot g^{-1}$. For high-rate dischargeability tests, MH electrodes were discharged at different current densities after charging at 100 $mA\cdot g^{-1}$ for 4 h. The high-rate dischargeability was described by the ratio of the discharge capacity measured at a high current density to the capacity at 100 $mA\cdot g^{-1}$.

The polarization resistance (R_p) and exchange current density (i_0) were measured by the linear sweep voltametry (Solartron 1287 electrochemical interface analyzer) at a scan rate of 1 $mV\cdot s^{-1}$ near the equilibrium potential ($\varphi_e \pm 10$ mV). Before every measurement, the MH electrode was firstly discharged to 50% depth of discharge. The polarization resistance (R_p) and exchange current density (i_0) were calculated by Eq. (1). The apparent activation energy (E_a) of the MH electrode reaction was calculated from the slope of $i_0 \sim 1/T$ curves at different temperatures using Eq. (2).

$$R_p = \frac{i}{\eta} = \frac{nFi_0}{RT} \qquad (1)$$

$$i_0 = A \exp \frac{-E_a}{RT} \qquad (2)$$

where R_p is polarization resistance, i is polarization current, η is polarization overpotential, $n=1$, F is Faraday constant, R is gas constant, T is absolute temperature, i_0 is exchange current density, A is a constant and E_a is apparent activation energy.

The electrochemical impedance spectroscopy (EIS) of MH electrodes was measured under open-circuit condition at about 50% DOD (depth of discharge) by using a Solartron 1250 frequency response analyser and a Solartron 1287 electrochemical interface analyzer. EIS was analysed with the nonlinear least squares fitting program EQUIVCRT [5].

2.3. Charge/discharge cycle of Ni/MH battery

The Ni/MH battery for testing was activated with the program of three cycles of charging/discharging at a constant current of 200 mA (charging for 7.5 h and discharging to 0.9 V). To measure its cycle life, Ni/MH battery was charged at 1C to cut-off $-\Delta V = 10$ mV and then discharged at 1C to 1.0 V after a rest of 10 min. The impedance of the battery was measured from 1000 Hz to 0.02 Hz at 50% DOD using a 1250 Solartron frequency response analyser and a 1287 Solartron electrochemical interface analyzer. The ohmic resistance and electrochemical reaction resistance of Ni/MH battery were calculated form its EIS.

3. Results

3.1. Effects of the pretreatment on the electrochemical properties of MH electrodes

The discharge capacities of the untreated and treated alloys electrodes as a function of cycling numbers are shown in Fig. 1. From this, it can be seen that the pretreatments increase the discharge capacity (C_0) at the first cycle, i.e., 225 $mAh\cdot g^{-1}$ for the untreated alloy, 250 $mAh\cdot g^{-1}$ for the alloy pretreated in 6 M KOH and 265 $mAh\cdot g^{-1}$ for the alloy pretreated in 0.02 M KBH_4 + 6 M KOH. The maximum discharge capacities for different treatments are also slightly increased. After three to four cycles of charging/discharging, both untreated and treated electrodes reach or approach their maximum capacities. If only the discharge capacity is considered, the activation cycle numbers of the untreated and treated alloys electrodes are almost same. But as shown in Fig. 2, the polarization resistance of the untreated alloy electrode

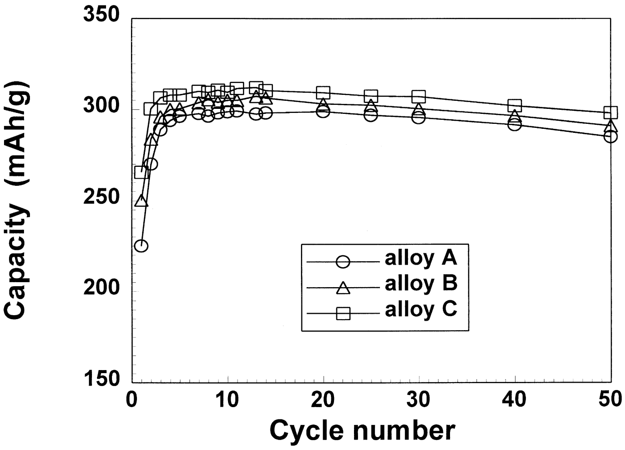

Fig. 1. Discharge capacity of the untreated and pretreated alloy electrodes as a function of cycling numbers, (alloy A, untreated; alloy B, pretreated in 6 M KOH at 80°C for 6 h; alloy C, pretreated in 6 M KOH + 0.02 M KBH_4 at 80°C for 6 h).

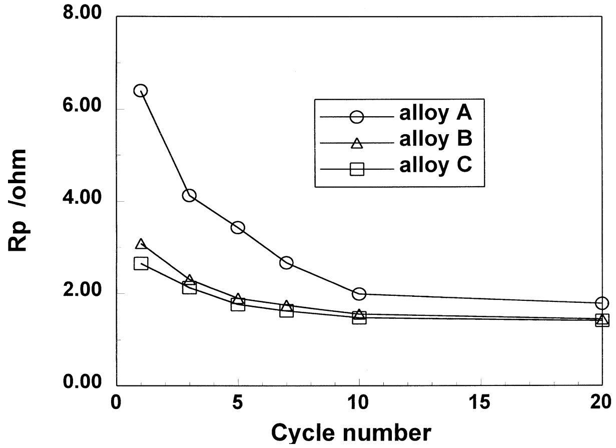

Fig. 2. Effect of the pretreatments on the polarization resistance of the alloy electrodes, (alloy A, untreated; alloy B, pretreated in 6 M KOH at 80°C for 6 h; alloy C, pretreated in 6 M KOH+0.02 M KBH_4 at 80°C for 6 h).

during its cycling is larger than that of the treated, especially in the first to tenth cycle. This fact means that the treated alloy electrode exhibits a lower polarization resistance and a better activation property compared with the untreated alloy electrode.

High-rate dischargeability is one of the important properties of MH electrodes. As shown in Fig. 3, the high-rate dischargeability of MH electrodes is greatly improved by pretreatments. For example, at a discharge current density of 900 mA·g^{-1}, the high-rate dischargeability is separately 56.1% (untreated), 71.5% (treated in 6 M KOH) and 78.3% (treated in 0.02 M KBH_4+6 M KOH). The EIS of the alloys electrodes are shown in Fig. 4. The cole–cole plots consist of two semicircles. The semicircle in the high-frequency region is attributed to the charge-transfer on the electrode surface, the semicircle in the low frequency region is caused by the adsorption of hydrogen atom on the surface. The equivalent circuit for EIS of the MH electrode is expressed in Fig. 5. The parameters are evaluated by the program EQUIVCRT. The results are summarized in Table 1. Table 1 shows that the surface pretreatment decreases the charge-transfer resistance and enhances the adsorption ability of hydrogen on the alloy surface.

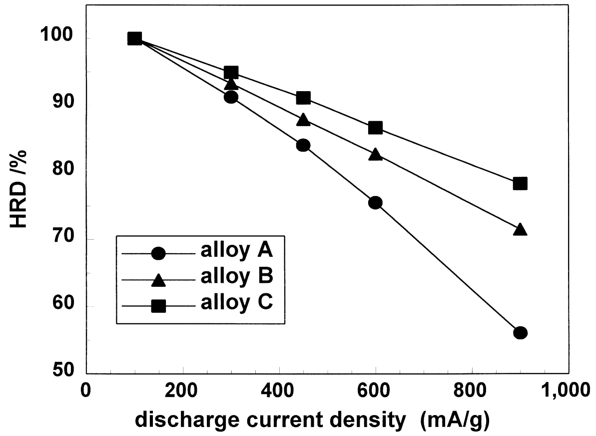

Fig. 3. Effect of the pretreatments on the high-rate dischargeability (HRD) of the alloy electrodes, (alloy A, untreated; alloy B, pretreated in 6 M KOH at 80°C for 6 h; alloy C, pretreated in 6 M KOH+0.02 M KBH_4 at 80°C for 6 h).

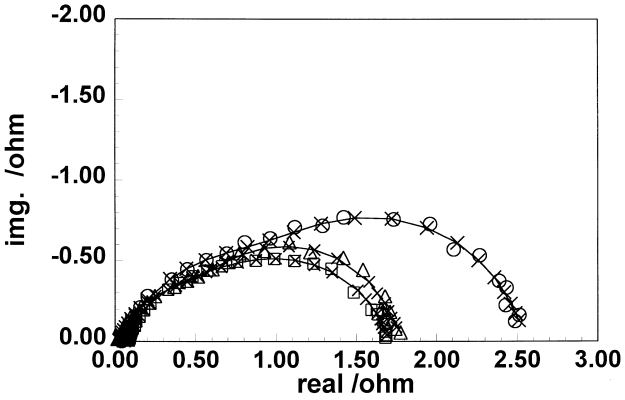

Fig. 4. EIS of the alloy electrodes, (○, untreated alloy; △, pretreated in 6 M KOH at 80°C for 6 h; □, pretreated in 6 M KOH+0.02 M KBH_4 at 80°C for 6 h; ×, stimulated).

The electrocatalytic activity is usually described by the exchange current density and activation energy of the electrode reaction. The influence of the pretreatments on their exchange current densities is shown in Fig. 6. It can be seen from Fig. 6 that the exchange current density of the treated alloy electrode is higher than that of the untreated electrode at same temperature. The apparent activation energy is calculated from the slope of the $\ln(i_0)\sim 1000/T$ line to be 21.3 kJ·mol^{-1} for untreated alloy electrode, 18.6 kJ·mol^{-1} for the alloy treated in 6 M KOH and 17.8 kJ·mol^{-1} for the alloy treated in 0.02 M KBH_4+6 M KOH. These results confirm that the pretreatments improve considerably the electrocatalytic activity of the MH electrode.

3.2. Ni/MH battery

Fast activation of the sealed Ni/MH battery is one of the key techniques for its industrialization. Many institutes and

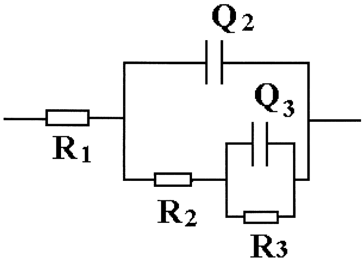

Fig. 5. The equivalent circuit for EIS of MH electrode, ($R_{1,}$ resistance of electrolyte; $R_{2,}$ charge-transfer resistance; $R_{3,}$ resistance of adsorption of hydrogen on the surface; Q_i, constant phase element, $Q_i(\omega)=\{Y_{i0}(j\omega)^n\}^{-1}$, $0<n\leq 1$).

Table 1
The parameters of the equivalent circuit for EIS of MH electrodes

Alloy sample[a]	R_1 (Ω)	R_2 (Ω)	Y_{20} (s)	n	R_3 (Ω)	Y_{30} (s)	n
Alloy A	0.0511	1.408	0.0428	0.794	1.088	0.183	0.931
Alloy B	0.0169	0.900	0.0589	0.796	0.855	0.166	0.969
Alloy C	0.0834	0.843	0.0138	0.858	0.773	0.0707	0.808

[a] Alloy A, untreated; alloy B, pretreated in 6 M KOH at 80°C for 6 h; and alloy C, pretreated in 0.02 M KBH_4 + 6 M KOH at 80°C for 6 h. R_1, R_2, R_3, Y_{20}, Y_{30} are defined in Fig. 5.

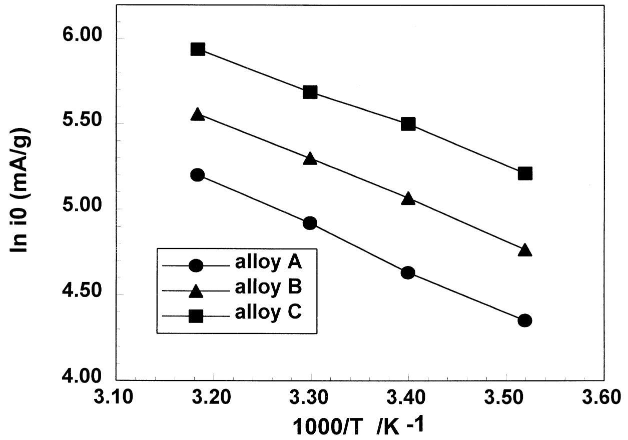

Fig. 6. Effect of the pretreatments on the exchange current density of the alloy electrodes, (alloy A, untreated; alloy B, pretreated in 6 M KOH at 80°C for 6 h; alloy C, pretreated in 6 M KOH + 0.02 M KBH_4 at 80°C for 6 h).

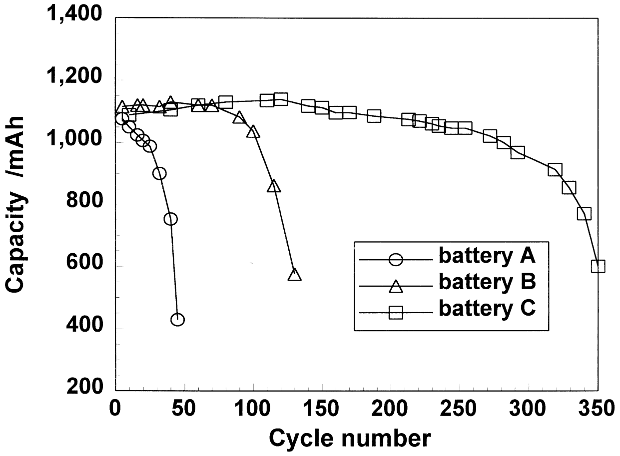

Fig. 7. Effect of the pretreatments on the cycle life of AA-size Ni/MH battery at 1C rate, (charge to $-\Delta V = 10$ mV cut-off, discharge to 1.0 V; battery A, untreated alloy; battery B, alloy pretreated in 6 M KOH at 80°C for 6 h; battery C, alloy pretreated in 6 M KOH + 0.02 M KBH_4 at 80°C for 6 h).

factories in China have been researching this technique. In our previous work [6], we have reported that the surface modification of MH electrode has noticeably good effect on the activation of sealed batteries. The second task of this study is to improve the cycle life of Ni/MH battery at 1C rate.

The results of EIS measurements are summarized in Table 2. It shows that the ohmic resistance (R_o) and charge-transfer resistance (R_{ct}) of the battery A are larger than these of the batteries B and C. We believe this to be caused by the oxide layer on the untreated alloy which not only increases the contact resistance between the current collector and alloy particles but also decreases its electrocatalytic activity. The discharge capacities at 1C of AA-size batteries as a function of number of cyclings are shown in Fig. 7. The cycle life of battery A is only about 40 cycles, that of battery B is about 110 cycles, while that of battery C goes up to above 300 cycles. These results indicate that the pretreatment improves significantly the cycle life of Ni/MH battery at 1C.

Table 2
Effect of the treatment on performances of Ni/MH batteries

Ni/MH battery[a]	R_o (Ω)	R_{ct} (Ω)	Cycle life
Battery A	0.0466	0.0389	~40
Battery B	0.0296	0.0268	~110
Battery C	0.0312	0.0212	~300

[a] Battery A, the untreated alloy; battery B, the alloy treated in 6 M KOH at 80°C for 6 h; battery C, the alloy treated in 0.02 M KBH_4 + 6 M KOH at 80°C for 6 h.

3.3. Surface compositions of the alloys

The content of the metal ions dissolved from the alloy surface during treatment were analysed by inductively coupled plasma spectroscopy (ICP) and the results are summarized in Table 3. It is found that the content of aluminium is much higher than other elements and nickel is hardly dissolved in comparison. Therefore, a Ni-rich surface layer is formed on the alloy surface because of the preferential dissolution of aluminium. In order to confirm this fact, the surface composition of the untreated or pretreated alloy was analysed by electron probe microanalysis (EPMA). The results are summarized in Table 4, which shows that the content of aluminium on the treated alloy surface is much lower than that on the untreated alloy surface, while the content of nickel on the treated alloy

Table 3
Content of metal ions in treating solution ($mg \cdot l^{-1}$)

Solution[a]	La	Ni	Co	Al
1	0.0312	0.412	25.9	56.2
2	0.0345	0.350	0.195	125

[a] (1) 6 M KOH; (2) 0.02 M KBH_4 + 6 M KOH.

Table 4
Atomic ratio on the surface of the untreated or pretreated alloy (at%)

Sample[a]	La	Ce	Pr	Nd	Ni	Co	Al
Alloy A	11.69	0.80	1.78	0.71	54.77	7.69	22.55
Alloy B	15.67	1.35	2.11	1.27	65.23	9.41	4.95
Alloy C	15.45	1.34	1.56	0.64	66.56	10.21	4.24

[a] Alloy A, untreated; alloy B, pretreated in 6 M KOH at 80°C for 6 h; and alloy C, pretreated in 0.02 M KBH_4+6 M KOH at 80°C for 6 h.

surface is higher than that on the untreated alloy surface due to the preferential dissolution of aluminium. It can be seen from Table 3 that the content of cobalt ion in 6 M KOH is larger than that in 0.02 M KBH_4+6 M KOH solution. It can be explained by the fact that the cobalt oxide or hydroxide can dissolve in alkaline solution according to equation: $Co(OH)_2+2OH^-=Co(OH)_4^{2-}$, but in alkaline solution containing reductant KBH_4, cobalt ion can be reduced to metallic cobalt by the reductant.

4. Discussion

The surface composition and morphology of the hydrogen storage alloy have an important influence on the electrochemical performance of the MH electrode, because the electrode reaction always takes place on the alloy surface. Moreover, the alloy surface has also a big influence on the oxygen–hydrogen recombination ability in the Ni/MH battery. On the untreated alloy surface, there is an oxide layer which is a film barrier to the dissociation of water and the diffusion of hydrogen. Therefore, the untreated alloy electrode exhibits a larger reaction resistance and lower high-rate dischargeability. In the pretreatment, the oxide layer is removed or eliminated. The results of ICP and EPMA analyses show that a Ni-rich layer is formed on the alloy surface because of the preferential dissolution of aluminum. Moreover, in our previous research [6], it was confirmed that the nickel oxide on the surface was reduced by KBH_4 and that the specific surface area was enlarged during the pretreatment of the alloy in alkaline. The higher nickel content on the alloy surface lead to faster activation and better electrocatalytic activity of the electrode.

It is well accepted that the MH electrode reactions include the following steps: (1) the electron transfer step on the electrode surface

$$\left(H_2O+M+e \underset{\text{discharge}}{\overset{\text{charge}}{\Leftrightarrow}} M-H_{ad}+OH^-\right);$$

(2) the adsorption of the hydrogen on the surface and (3) the hydrogen diffusion step

$$\left(M-H_{ad} \overset{\text{diffusion}}{\Leftrightarrow} M-H_{ab}\right).$$

The adsorption of hydrogen on the surface is the middle step of the overall electrode reaction. Therefore, the adsorption strength of hydrogen on the surface has an important influence on the speed of the electrode reaction. It is usually believed that too low or too high adsorption strength of hydrogen on the surface would lower its electrocatalytic activity. When the adsorption bond strength of $M–H_{ad}$ reaches a suitable value, the electrode has its maximum electrocatalytic activity. The relationship between the electrocatalytic activity of the electrode and the adsorption bond energy of hydrogen on its surface is usually described as the ‘‘volcano effect’’. As the oxide layer on the alloy surface obstructs the adsorption of hydrogen on the surface, the untreated alloy electrode exhibits only low electrocatalytic activity. After alloy pretreatment, the oxide layer on the surface is reduced or eliminated, and a Ni-rich surface layer in the form of Ni-cluster or Raney-Ni is formed by preferential dissolution of Al. The Ni-rich layer enhances the adsorbability of hydrogen on the surface and improve electrochemical activity. Moreover, the augmented specific surface area of the treated alloy increases the adsorption of hydrogen on the surface further. Therefore, the pretreated alloy electrode exhibits a higher exchange current density and a lower apparent activation energy.

The Ni-rich layer on the negative electrode surface also improves the catalytic ability of oxygen–hydrogen recombination on its surface. A good oxygen–hydrogen recombination ability not only lowers the internal pressure of the battery but also prevents the hydrogen storage alloy from being oxidized by the oxygen produced from the positive electrode during charge, which gives the Ni/MH battery employing the pretreated alloy as the negative electrode material a longer cycle life.

5. Conclusions

The activation property, high-rate dischargeability and electrocatalytic activity of the $Ml(NiCoAl)_5$ alloy electrodes are all significantly improved by surface pretreatment. Results of EPMA and ICP analyses demonstrate that a Ni-rich surface layer is formed on the alloy surface due to the preferential dissolution of aluminium. The Ni-rich layer which exits in the form of Ni-cluster or Raney-Ni enhances the adsorbability of hydrogen on the surface and improves the electrocatalytic activity of the MH electrode reaction.

The Ni/MH batteries adopting pretreated alloy electrodes can be activated readily after being sealed. The cycle life of an AA-size battery at 1C reaches to above 300 cycles as a result of the enhanced electrocatalytic activity and improved catalytic ability of oxygen–hydrogen recombination on the surface.

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