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# Effect of advanced alkaline treatment on the electrochemical characteristics of hydrogen storage alloys

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## Abstract

An advanced technique is studied for the formation of a composite surface layer of the powder of hydrogen storage alloys, in which metallic Cu is distributed in the rare-earth hydroxide layer. An alkaline solution which contains a Cu salt ( $\text{CuSO}_4$ ), reductive agent and stabilizing agent for stabilizing  $\text{Cu}^{2+}$  was developed to implant metallic Cu in the surface layer. Through the surface analyses using EDS and AES and testing of the electrochemical properties, it has been found that it is possible to synthesize a composite surface layer in which Cu is implanted in the rare-earth hydroxide layer. This is effective for activity enhancement and for improving the high rate discharging capability of metal hydride electrodes. © 1999 Published by Elsevier Science S.A. All rights reserved.

*Keywords:* Hydrogen storage alloys; Alkaline treatment; Surface; Ni–MH battery

## 1. Introduction

Ni–MH batteries are the focal point of research and development in the field of chemical power source because of their great advantages, such as high capacity, long cycle life and no pollution. Ni–MH batteries are replacing the traditional Cd–Ni batteries' market share quickly and steadily. It is the aim to devise a hydrogen storage alloy with good overall performance in aspects of electrochemical capacity, activation, high rate discharge and cycle life, etc.

In order to improve the performance of hydrogen storage alloy electrode, a great number of surface treatments have been tried, of which alkaline etching and the copper coating are two common examples [1–4].

Alkaline etching is effective in enhancing the activation performance of alloys, but decreases their high rate discharging capacity. On the contrary, copper coating treatment improves the high rate discharging capacity, but delays the initial activation of alloys.

With the proper treatment solution and process, the alloy was treated compositely with alkaline etching and copper coating, in order to solve the disadvantages caused by single treatments.

## 2. Experimental

Four different treatment solutions (s1, s2, s3, s4) were tested on the alloy  $\text{MmCo}_{0.8}\text{Al}_{0.4}\text{Mn}_{0.3}\text{Ni}_{3.5}$  at  $80^\circ\text{C}$ . The four treatment solutions all contained KOH, a Cu salt ( $\text{CuSO}_4$ ), reductive agent ( $\text{H}_2\text{PO}_3$ ,  $\text{KBH}_4$ ) and stabilizing agent ( $\text{K}_3\text{Fe}(\text{CN})_6$ ), the type and quantity of the reductive agent and stabilizing agent being different in the four solutions.

A 10-g amount of the powder of the alloy was treated by 200 ml of the solution. Treated powder was heated at  $80^\circ\text{C}$  in a drier, after being washed with distilled water and alcohol each for three times. The stove powder was mixed with Ni powder in the proportion of 1:3, and pressed into a pellet as a negative electrode. The electrochemical performance of the treated alloy powder was tested at different charging and discharging currents (200 and 800 mA/g).

The features of the treated powders were inspected by SEM, the components of the treated powder were analyzed by EDS and the distribution of elements in the surface of the alloy powder was studied by AES.

## 3. Results and discussion

Table 1 shows the discharging capacity of the alloys treated by different process at different discharging cur-

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Table 1  
Discharging capacity of the alloy treated by different process

Solution	Current of discharge (mA/g)	Discharging capacity (mAh/g)				
		1 h	2 h	3 h	4 h	5 h
1	200	301	300	303	301	300
	800	256	252	248	241	231
2	200	299	297	301	300	299
	800	242	252	253	246	239
3	200	297	300	300	300	299
	800	238	258	252	243	239
4	200	301	300	305	302	302
	800	238	255	275	260	248

rent. Fig. 1 shows the relationship between time of treatment and  $C_{800}/C_{200}$ .  $C_{800}$  and  $C_{200}$  are the rates of the discharging capacity when the discharging current is, respectively, 800 and 200 mA/g.

The stabilizing agent used in solutions 1, 2 and 4 is the same, but the content increases from 1 to 4. Comparing the

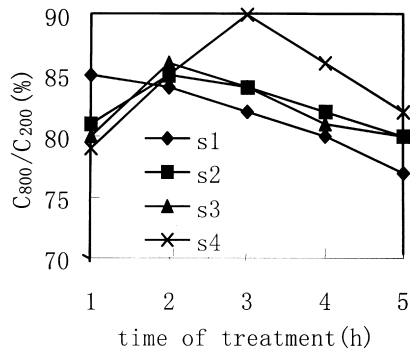


Fig. 1.  $C_{800}/C_{200}$  of four solutions at different times of treatment.

performance of the alloy treated by solutions 1, 2 and 4, the best results were achieved at 1, 2 and 3 h, respectively. With the increase of the content of stabilizing agent, these times increased. The increase in the content of stabilizing agent decreased the speed of the copper coating operation. The reasons for the reduction of the performance later could be that the quantity of rare-earth hydroxide increased with the increase of time, but the copper content remained stable.

The difference between s2 and s3 is that they contained a different reductive agent, but the high rate discharging capacity of the alloy after treatment by both methods was similar.

The distinction between s2 and s4 is that s4 had more reductive agent; the performance of the alloy treated by s4 is better than that by s2. This can be attributed to the increased reductive agent leading to an increase in the content of Cu in the surface layer, which improved the high rate discharging performance.

Fig. 2 compares the high rate discharging performance of the alloys which are not treated and those treated by the four solutions at the optimal time. Before treatment  $C_{800}/C_{200}$  of the alloy is 75%. The result shows that the high rate discharging performance of alloy has been improved compared with the untreated alloy and that solution 4 is the best.

All of the treated alloys activated no more than three cycles, so the discharging capacity of the first cycle express the activation performance of the alloys.

Fig. 3 shows the relationship between treatment time and discharging capacity of the first cycles. Fig. 4 shows the discharging capacity of the optimal treatment of the four solutions and the untreated one.

The activation performance of the alloys treated by s1 is

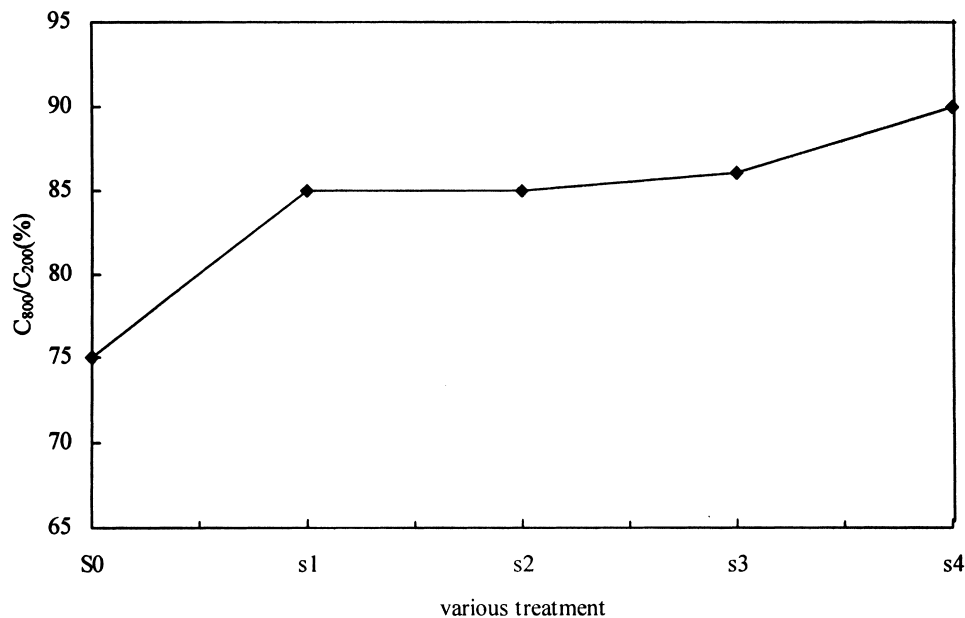


Fig. 2. High rate discharging performance of the alloys treated variously (S0: no treatment).

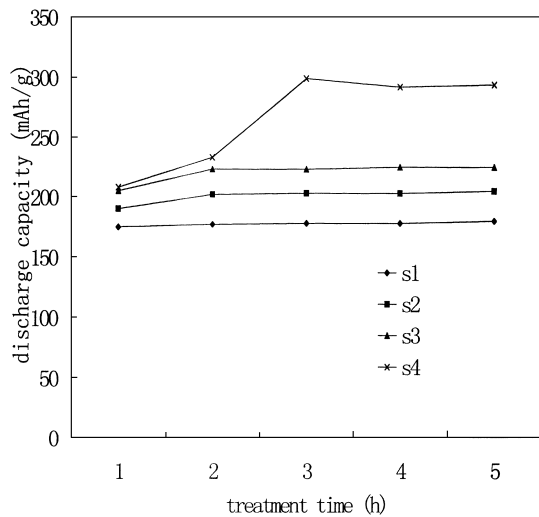


Fig. 3. Relationship between treatment time and discharging capacity of the first cycles.

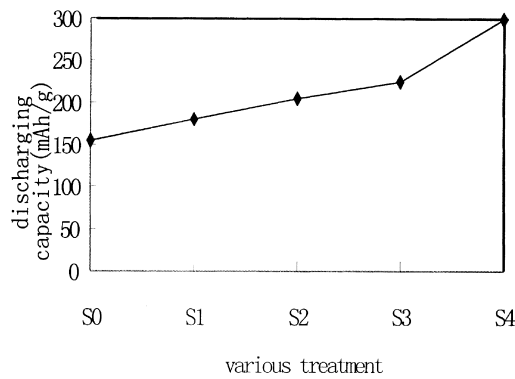


Fig. 4. Discharging capacity of the first cycle of the alloys treated variously (S0: no treatment).

poor, because the speed of coating copper is so fast that the process of alkaline etching is inhibited. S2 performs better than s1, because the increase of stabilizing agent in s2 decreases the speed of coating copper. The reductive agent that s3 contains is different from that of s2, the former activation performance is better than the latter one. S4 contains more stabilizing agent, it decreases the speed of coating copper, so the activation performance of the alloys treated by it improved.

To consider both the performance of activation and high rate discharging, the sample treated for 3 h by s4 showed good performances over the untreated alloy. To analyze the sample treated 3 h by s4, SEM and EDS were used. Fig. 5 shows the distribution of several elements such as Cu, Ni and La on the surface. Cu distributed homogeneously on the surface of the particles.

Fig. 6a and b show the AES depth profiling on bulk samples with and without treatment, respectively. The oxide layer becomes thicker after treatment and Ni enriches in the layer, proving that the alkaline etching treatment does work. The content of Cu turns less along the depth of the alloy particles, showing that the metallic Cu implants in the oxide on the surface. The composite layer made both the performances of activation and high rate discharging better.

#### 4. Conclusion

A composite surface layer of the hydrogen storage alloy powder with metallic Cu implanted in the rare-earth hydroxide layer was attained through the proper treatment. The layer is effective for improving activity of catalysis

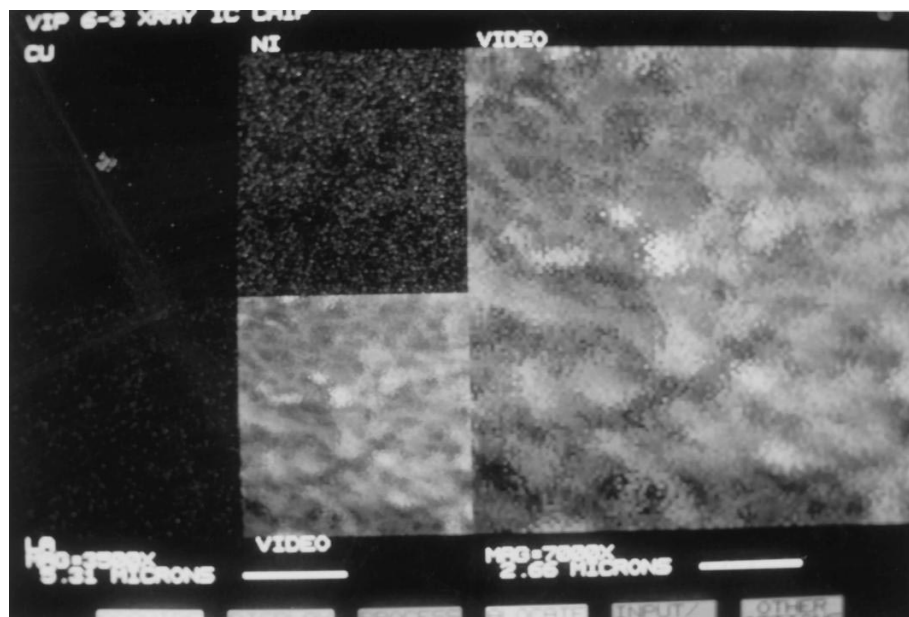


Fig. 5. Distribution of several element such as Cu, Ni and La on the surface of particles.

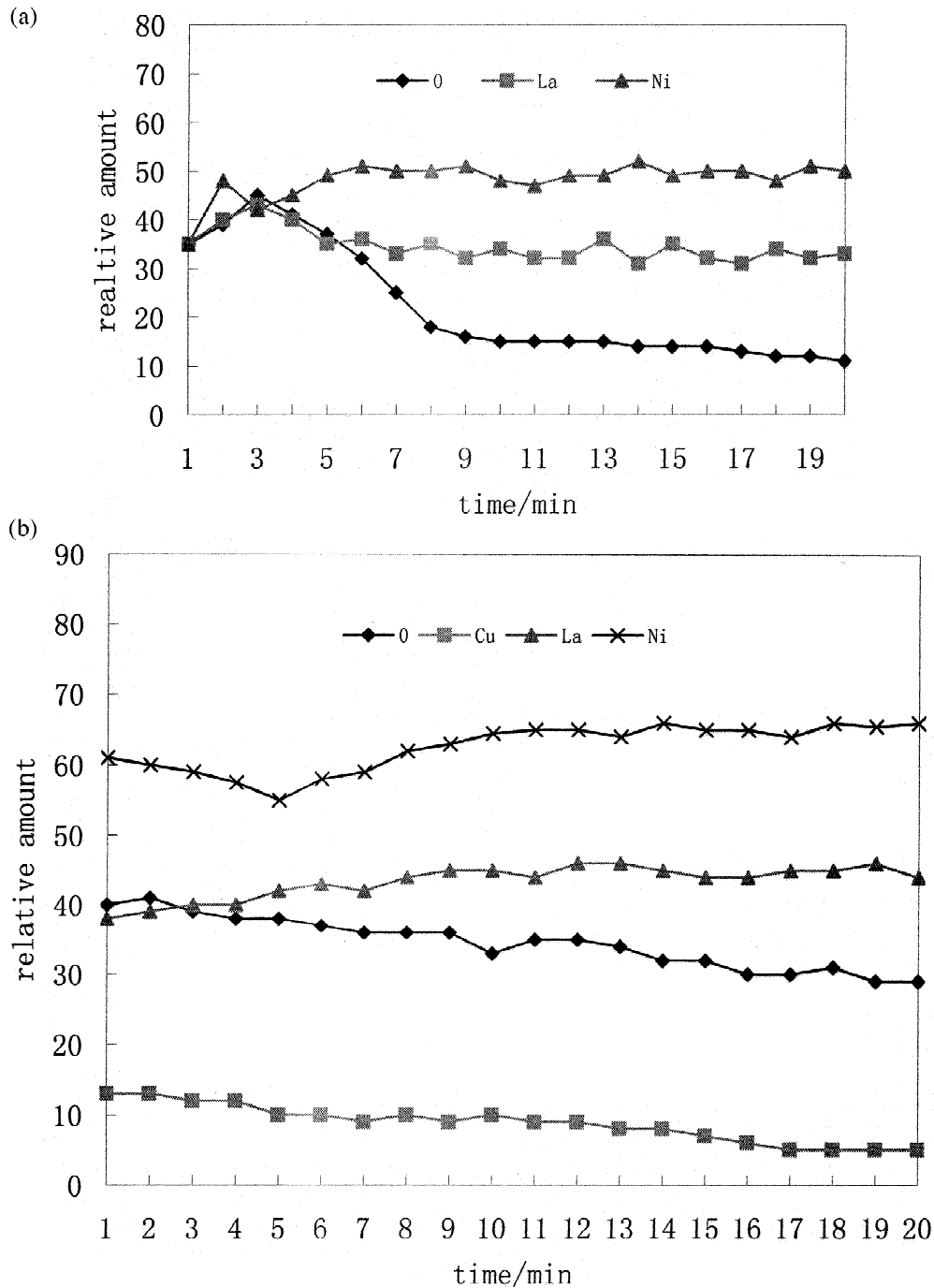


Fig. 6. AES depth profiling (a) without treatment (b) with treatment.

and conductivity. Both performances of activation and high rate discharging capacity was improved because of the formation of the new composite surface layer, and the disadvantage of the single treatment was solved.

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