Effects of nickel- and copper-coating of hydride alloys on the electrode reactions of metal-hydride electrodes

H.S. Lim *, G.R. Zelter

Hughes Space and Communications Company, Torrance, CA 90509, USA

Abstract

We have studied effects of Ni- and Cu-coating of hydride-forming metal alloys on their performance as the cathode material of an Ni/MH_x cell. Ni or Cu (5–9 wt.%) was coated on alloy particles by an electroless coating technique prior to test electrode preparation. Mechanical stability of the alloy particles and the cycle life did not appear to be improved by such coatings. However, such coatings greatly improved the electrode rate capability and alloy activation time. The coating technique appears to be extremely useful for alloys which have other desirable properties, such as high specific capacity and long cycle life, but have low rate capability and long activation time.

1. Introduction

A nickel–metal-hydride (Ni/MH_x) cell is rapidly being commercialized, in recent years, for power sources for many applications, especially for consumer electronics. The Ni/MH_x system has received special attention from many battery developers and manufacturers especially due to environmental safety concerns regarding the Ni/Cd cell. Concerns about toxicity of Cd have led to stricter governmental environmental regulations, both in production processes and disposal of the cells. Such regulations made it more difficult to manufacture Ni/Cd cells and dispose of them economically after use. The Ni/MH_x cell has also the advantage of being able to replace an Ni/Cd cell virtually without a change of the existing power systems for many electronic devices because these two are similar in physical structure as well as in charge and discharge voltage characteristics. In addition, the Ni/MH_x cell has higher gravimetric and volumetric energy densities than Ni/Cd cells, by approximately 30%.

Despite its rapid commercialization, further improvement of the cell is desired for long cycle life, higher rate capability, and other properties. For some applications, high power is critically important. Performance of the cell in general, including rate capability, depends strongly on the alloy composition. Some alloys show high specific capacity and chemical stability but lack rate capability. Other alloys are

tediously slow in activation taking many cycles to reach full capacity. It has been reported that coating alloy particles with Cu and Ni can improve rate capability, utilization, and cycle life performance [1–3] of the alloy in an Ni/MH_x cell. In this study, we have investigated the alloy rate capability and cycle life of selected AB_5-type alloys before and after coating with Ni or Cu in an effort to develop an advanced Ni/MH_x cell [4].

2. Experimental

2.1. Alloys and coating

Alloy compositions studied in this paper are shown in Table 1. Non-atomized alloy samples (D31 and D32) were made by mechanical pulverization of ingots prepared by melting in an induction furnace. Atomized alloy samples (D31a, D32a, R02a, and R06a) were prepared by an atomization

Table 1
Alloy compositions

Alloy identification	Compositions
D31 and D31a	$La_{0.8}Ce_{0.2}Ni_{4.75}Sn_{0.25}$
D32 and D32a	$La_{0.8}Ce_{0.2}Ni_{4.75}Sn_{0.25}$
R02a	$La_{0.8}Ce_{0.2}Ni_{1.55}Co_{0.75}Mn_{0.4}Al_{0.3}$
R06a	$La_{0.7}Ce_{0.3}Ni_{1.2}Co_{1.0}Mn_{0.6}Al_{0.2}$

* Corresponding author.

technique described in Ref. [5]. Particle size range of all alloy samples was 38–90 μm in diameter. The coating was carried out using an electroless coating technique. Ni-coating was carried out in an alkaline hypophosphite bath (Niklad™ 776A and 776H). Typical weight gain by the coating was 8–9% of the original alloy weight. Cu-coating was carried out in an acidic copper sulfate bath. Cu-coating was achieved by a displacement reaction by introducing alloy powder in a vigorously stirred solution of approximately 0.5 M $CuSO_4$ containing Cu in a quantity corresponding to approximately 5% of the alloy weight.

2.2. Test electrodes and cells

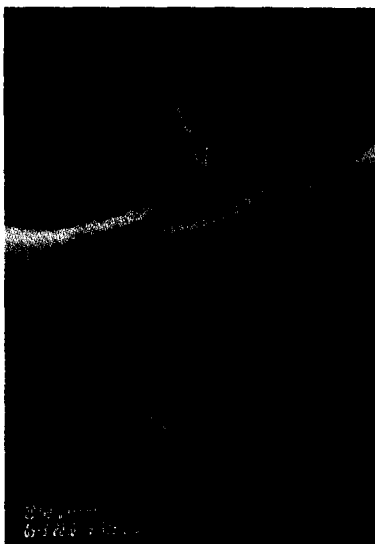The metal-hydride (MH_x) test electrodes were prepared by pasting a slurry of the alloy powder, Shawinigan acetylene

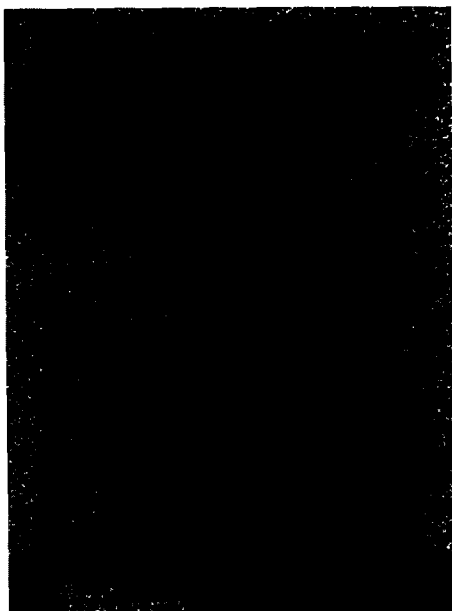Fig. 1. SEM photograph (×5000) of an electroless Ni-coated particle of a mechanical powder, D31.

Fig. 2. Phosphorous map of EDAX/SEM photograph (×5000) of the Ni-coated alloy particle of Fig. 1.

black (AB50), and polymer solution on a piece of nickel foam substrate of 80 to 100 pores per inch. Test electrodes were approximately 2.3 cm × 2.3 cm in size. Each electrode contained approximately 0.8 to 1 g of alloy. Performance tests of the MH_x electrodes are carried out in a flooded electrolyte Ni/MH_x cell containing 31 wt.% KOH electrolyte. After activation, the cells were immediately trickle charged at 10 to 20 mA for a minimum of several hours before measuring their initial capacities to prevent possible corrosive oxidation of the active alloy material

2.3. Test cycle regime

The cycling regime for the cycle life test was an aerospace low earth orbit (LEO) regime at approximately 50% depth-of-discharge with 110% recharge, i.e., 35 min discharge at 0.86C rate (285 mA) followed by recharge at 0.60C (198 mA) for 55 min. Interim capacity was measured by discharging the cells at 165 mA to 1.0 V after interrupting the cycle test at the end of charge followed by charging them at the same rate for 2.5 h. The discharge/charge cycle was repeated. These second cycle data are discussed below.

3. Results and discussions

3.1. Ni-coating

A scanning electron microscopy (SEM) picture (×5000) of the cross-sectional view of an Ni-coated D31 alloy is shown in Fig. 1. A partially peeled-off film (<1 μm thick) of the Ni-coating is shown in the middle of the picture (indicated by an arrow). To confirm that the film is made of Ni, P and Ni maps of energy dispersive analysis of X-rays

Fig. 3. Nickel map of EDAX/SEM photograph (5000×) of the Ni-coated alloy particle of Fig. 1.

(EDAX)/SEM were taken, see Figs. 2 and 3. High concentration of P in the film region of the map in Fig. 2 is indicating that the film is made of an Ni film, since an electroless coating of Ni from a hypophosphite bath generally contains P as much as 5–14 wt.% [6]. The Ni map as shown in Fig. 3 is also indicating that the film is Ni.

3.2. Electrode performance of Ni- and Cu-coated versus uncoated alloys

We have studied effects of the Ni- and Cu-coatings on the initial performance of alloys. Charge and discharge voltage curves of Ni/MH$_x$ cells containing alloys without and with Ni-coating are shown in Fig. 4 for a non-atomized alloy, D32, and in Figs. 5 and 6 for the atomized alloys, D32a and D31a, respectively. Charge voltages of uncoated alloys are noticeably higher and discharge voltages noticeably lower than those of the Ni-coated alloys for both the atomized and the non-atomized alloys. This observation indicates that the Ni-coating reduced substantially the electrode polarization, hence it greatly enhanced the electrode rate capability. This reduced polarization might be due to the possible catalytic activity of the Ni-coating for hydrogen oxidation and water reduction, while such a catalytic activity is not anticipated from the Ni atoms in the alloy. Charge and discharge voltage curves for an atomized alloy, R06a, without and with Cu-
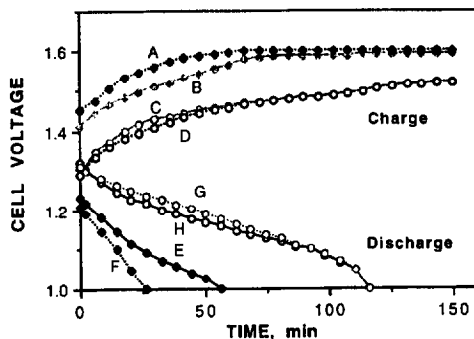
coating are shown in Fig. 7. Cu-coating also reduced the electrode polarization rather drastically thus improving substantially the electrode rate capability and the electrochemical utilization of the alloy. The effect of Ni-coating on the cycle life performance of the alloy D32a is shown in Fig. 8. The Ni-coated alloy was fully activated in 100 cycles giving approximately 200 mAh/g while the corresponding uncoated alloy was not fully activated giving less than 100 mAh/g. This alloy appears to be activated to approximately 160 mAh/g

Fig. 6. Charge (at 80 mA) and discharge (at 70 mA) voltage curves of Ni/MH$_x$ cells made of hydride electrodes containing uncoated and Ni-coated atomized D31a alloys. (A) Charge curve and (B) discharge curve are for the uncoated alloy. (C, D) Charge curves and (E. F) discharge curves are for Ni-coated alloys.

Fig. 4. Charge and discharge voltage of curves D32 alloy electrodes at 100 mA in an Ni/MH$_x$ cell. (A, B) Charge curves and (E, F) discharge curves are for the uncoated alloy. (C, D) Charge curves and (G, H) discharge curves are for Ni-coated alloys.
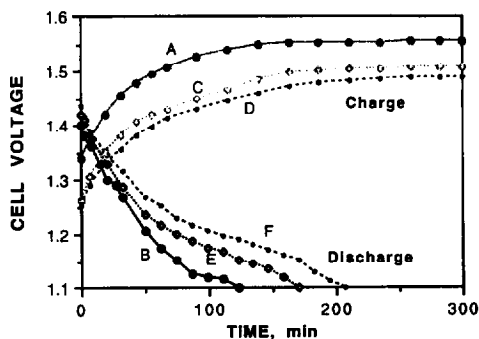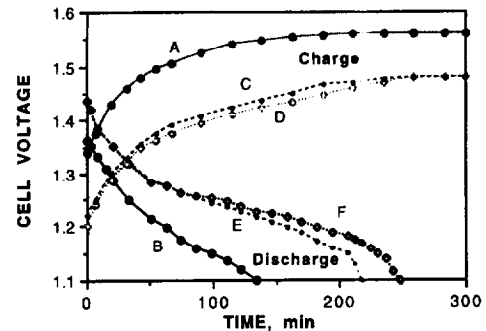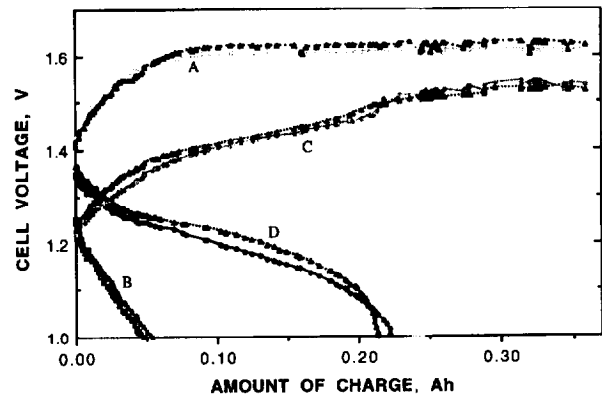

Fig. 7. Charge (at 70 mA) and discharge (at 75 mA) voltage curves of Ni/MH$_x$ cells made of hydride electrodes containing uncoated and Cu-coated atomized R06a alloys: (A) Charge curves of duplicate cells for the uncoated alloy (0.868 and 0.965 g, respectively); (B) discharge curves of these cells; (C) charge curves of duplicate cells for Cu-coated alloy (0.858 and 0.915 g, respectively), and (D) discharge curves of these cells.

Fig. 5. Charge (at 80 mA) and discharge (at 70 mA) voltage curves of Ni/MH$_x$ cells made of bare and Ni-coated atomized D32a alloy electrodes. (A) Charge curve and (B) discharge curve are for the uncoated alloy. (C, D) Charge curves and (E, F) discharge curves are for Ni-coated alloys.
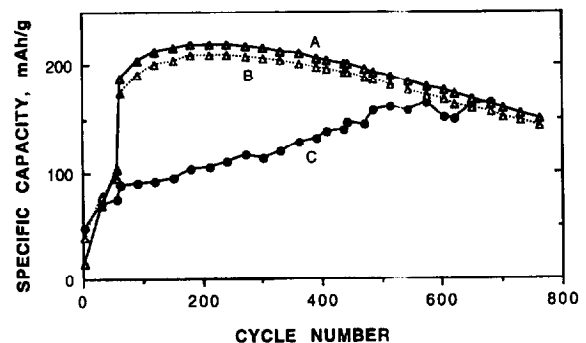

Fig. 8. Effects of Ni-coating on capacity of electrodes made of atomized D32a alloy powders: (A) and (B) Ni-coated, and (C) uncoated.
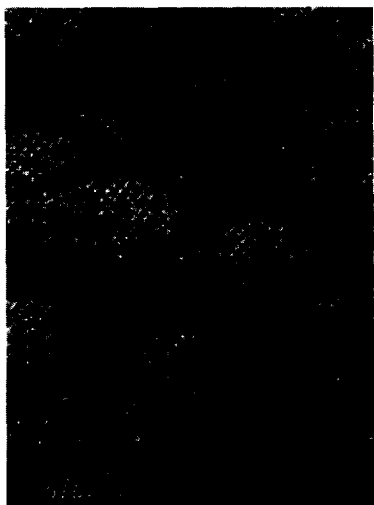
Fig. 9. SEM photograph (×500) of an Ni-coated atomized particles of R02a alloy.

Fig. 10. SEM picture of Ni-coated R02a alloy after 742 cycles.

after 700 cycles during which the Cu-coated alloy was partially degraded to give similar capacity value. This and other results showed that the Ni- and Cu-coatings provide faster activation than the corresponding uncoated alloys, but after long cycling their performances appear to converge to a similar specific capacity value as indicated in Fig. 8.

Physical degradation of Ni-coated alloy particles was studied by SEM. SEM pictures of Ni-coated atomized particles of R02a alloy before and after the cycling test are shown in Figs. 9 and 10, respectively. The degradation of Ni-coated R02a alloy particles after 742 cycles was rather pronounced as shown in Fig. 10. We have also previously discussed the mechanical degradation of atomized particles of other uncoated alloys [5]. Although Ni-coating gives the great benefit of reducing activation time of the alloy and reducing electrode polarization, it appears that the mechanical stability

of the alloy was not improved. Additional cycle test results on alloys with and without Ni-coating appears to show that cycle life of the alloy is not improved by the coating as illustrated in Fig. 8. This result is in contrast with an earlier report [3] that the cycle life of $LaNi_{4.7}Al_{0.3}$ alloy was improved by a factor of four by Cu-coating. The difference of the two observations appears to be due to the following reasons. The main degradation reaction of $LaNi_{4.7}Al_{0.3}$ alloy might be oxidation of the alloy by oxygen gas evolved from the Ni electrode of the Ni/MH_x cell. Hence, this cycle life improvement was due to the function of the Cu-coating as an oxygen barrier to protect $LaNi_{4.7}Al_{0.3}$ alloy from oxidation [3]. In contrast, the main degradation of the present alloys could be due to mechanical disintegration which is not protected by the present Ni-coating.

4. Summary

Ni and Cu, respectively, were coated on alloy particles by an electroless coating technique with a minor weight gain (5–9 wt.%) prior to the preparation of the test electrodes. Mechanical stability of the alloy particles and the cycle life did not appear to be improved by such coatings. However, the coating greatly improved the electrode rate capability and alloy activation time. The coating technique appears to be extremely useful for alloys which have other desirable properties, such as high specific capacity and long cycle life, but have low rate capability and long activation time.

Acknowledgements

References

[1] C. Iwakura, M. Matsuoka, K. Asai and T. Kohno, J. Power Sources, 38 (1992) 335–343.

[2] T. Sakai, A. Yuasa, H. Ishikawa, H. Miyamura and N. Kuriyama, J. Less-Common Met., 172–174 (1991) 1194–1204.

[3] T. Sakai, H. Ishikawa, K. Oguro, C. Iwakura and H. Yoneyamo, J. Electrochem. Soc., 134 (1987) 558.

[4] H.S. Lim, D.F. Pickett, J.F. Stockel and J.J. Smithrick, Advanced nickel–metal hydride cell development at Hughes — A joint work with US Government, Conf. NASA Centers for Commercialization and Development of Space, Albuquerque, NM, USA, 8–12 Jan. 1995; Proc. 10th Annual Battery Conf. Applications and Advances, 10–13 Jan. 1995, Long Beach, CA, USA, p. 65.

[5] H.S. Lim, G.R. Zelter, D.U. Allison and R E. Haun, J. Power Sources, 66 (1997) 101.

[6] W. Riedel (ed.), Electroless Nickel Plating, co-published by ASM International, Metals Park, Ohio, USA, and Finishing Publications, Stevenage, Hertfordshire, UK, 1991, p. 20.