



Performance of metal hydride electrodes with organosilicon as a binder

Jeon Choi, Choong-Nyeon Park*

Department of Metallurgical Engineering, Chonnam National University, Kwangju 500-757, South Korea

Received 8 April 1994

Abstract

(LM)Ni_{4.49}Co_{0.1}Mn_{0.205}Al_{0.205} (LM, lanthanum-rich mischmetal) hydrogen storage alloy powder was coated by 25 wt.% electroless copper plating in an acidic bath, mixed with organosilicon and compacted into disk-type electrodes at room temperature. The characteristics of the metal hydride electrodes were examined through electrochemical measurements in a half-cell. As the amount of organosilicon increased, the initial discharge capacity of the electrode became lower and the activation rate at high current density was slower. For extended cycling, however, the electrodes with organosilicon were superior in terms of high rate discharge capacity, useful range of temperature and cycle life to the silicon-free electrode, though the charge retention was not improved. It is suggested from the results that organosilicon can be usefully applied as a binder in the preparation of metal hydride electrodes.

Keywords: Metal hydride electrodes; Organosilicon; Binders

1. Introduction

The metal hydride electrode using hydrogen storage alloys has been studied very extensively over recent years because of several advantages such as a high energy density, a fast charge–discharge rate and a very low toxicity. This electrode can suitably substitute for the cadmium electrode in the Ni–Cd battery [1–10].

However, in practical applications of the metal hydride electrode, one of the problems, especially when an alloy with a high hydrogen storage capacity is used, is a large decay of the discharge capacity upon repeated charge–discharge cycling.

Many studies [3–13] related to the cycle life of hydride electrodes have been reported. Willems [8] found that LaNi₅-type alloys with components such as Co, Al and Si had a much longer cycle life. In order to obtain good electrical conductivity, compactness and mechanical endurance, Ishikawa et al. [11] and Park and Kirchheim [12] coated the alloy powder with copper by employing an electroless plating method. Also, Sakai et al. [13] used polytetrafluoroethylene (PTFE) as a binding material. The adhesive material was found to bind the alloy powder easily to form a network, providing

good flexibility and close contact between powder particles. In this study we have examined the properties of electrodes prepared using organosilicon as a binding material. Organosilicon has been widely used as a sealant for windows, etc. and is very inexpensive compared with PTFE powder or a PTFE dispersion.

2. Experimental details

The hydrogen storage alloy with the composition (LM)Ni_{4.49}Co_{0.1}Mn_{0.205}Al_{0.205} (LM, lanthanum-rich mischmetal) was provided by JMC (Japan) as a powder with particle size below 100 μm. The hydrogen desorption plateau pressure of this alloy is 0.6 atm at 25 °C and the effective hydrogen storage capacity is about 0.9 H/M.

The alloy powder was coated with 25 wt.% copper by electroless plating in an acidic bath. Details of the method have been described in a previous paper [12]. The copper-coated alloy powder was mixed with 3–10 wt.% adhesive silicon sealant (organosilicon 780RTV, Lucky-DC Silicon Co. Ltd., South Korea) and cold compacted at 6 ton cm⁻² into disks of 10 mm diameter. The electrochemical measurements were conducted in a Pyrex test cell consisting of the metal hydride electrode,

*Corresponding author.

a platinum counterelectrode, a mercury oxide (Hg/HgO) reference electrode and 6 M KOH electrolyte. Charge–discharge cycles were carried out automatically up to 200 cycles.

The charge and discharge currents were of equal magnitude for all samples and changed from 10 mA for the first 10 cycles to 15, 30 and 60 mA for subsequent cycles. The charge times were 200 min at 10 mA, 130 min at 15 mA, 65 min at 30 mA and 33 min at 60 mA. Discharging was interrupted at -650 mV(Hg/HgO) in order to avoid oxidation of the copper. A rest time of 20 s was allowed for every change in the current direction.

3. Results

The influence of the amount of organosilicon on the activation of the electrodes is shown in Fig. 1. As the amount of organosilicon increased, the initial discharge capacity decreased, indicating that the organosilicon suppressed the electrode activation. This can be attributed to the fact that the organosilicon covered the surface of the alloy powder, resulting in a decrease in contact area between electrode and electrolyte. The maximum discharge capacities, however, were achieved at about the fifth cycle, since the volume change of the alloy upon charging and discharging caused many cracks in the alloy, producing new clean surfaces needed to activate the alloy.

Fig. 2 shows the discharge capacity as a function of the discharge current and the amount of organosilicon in the activated electrodes at 25 °C. As the amount of organosilicon increased, the discharge capacity at high discharge current became higher. When the electrode bound by 10 wt.% organosilicon was discharged at 60 mA, the discharge capacity was about 96% of the maximum capacity.

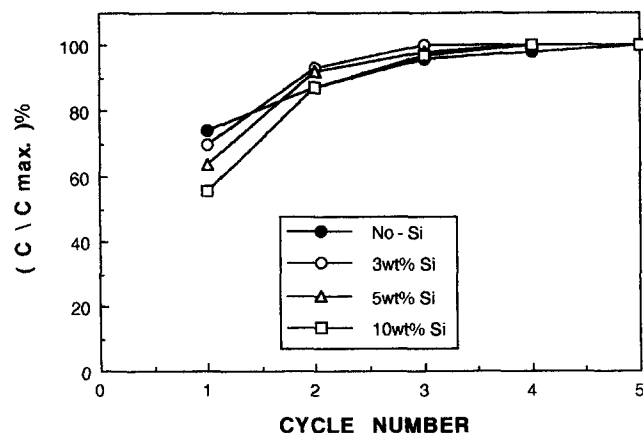


Fig. 1. Changes in discharge capacity of electrodes prepared with various amounts of organosilicon during initial charge–discharge cycling (charge 10 mA, 200 min; discharge 10 mA at 25 °C).

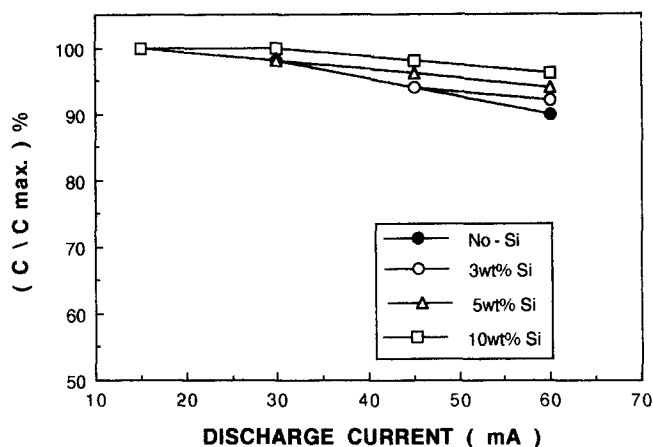


Fig. 2. Discharge capacity as a function of discharge current and amount of organosilicon in activated alloy electrodes (charge 15 mA, 130 min at 25 °C).

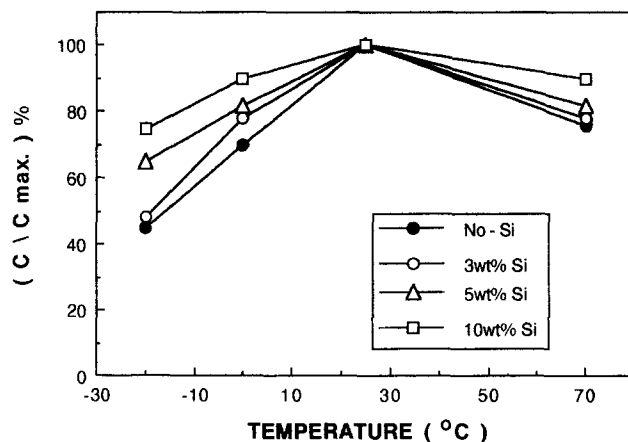


Fig. 3. Discharge capacity as a function of temperature and amount of organosilicon (charge 15 mA, 130 min; discharge 15 mA).

The temperature dependences of the discharge capacity of the organosilicon-bound electrodes are shown in Fig. 3. The maximum discharge capacity appeared at 25 °C for all electrodes. With any increase or decrease in temperature the discharge capacities decreased. The addition of organosilicon improved the useful range of temperature compared with the silicon-free electrode and the effect was more significant at low temperature.

The potential gaps between charging and discharging at various temperatures are illustrated in Fig. 4. It can be seen that the potential gap decreased with increasing temperature for all electrodes. Since the potential gap is a dynamic hysteresis and represents the rate of electrode reaction, the results in Fig. 4 reveal that the rate of electrode reaction decreases with decreasing temperature. This would appear to be reasonable because the electrode reaction is a thermally activated process. Thus the decrease in discharge capacities at low temperature in Fig. 3 was due to the slow rate of the electrode reaction. On the other hand, the decrease in capacities at high temperatures where the electrode

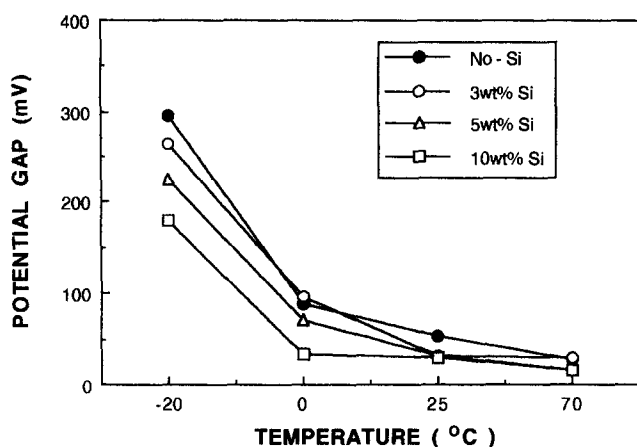


Fig. 4. Potential gap between charge and discharge as a function of temperature and amount of organosilicon.

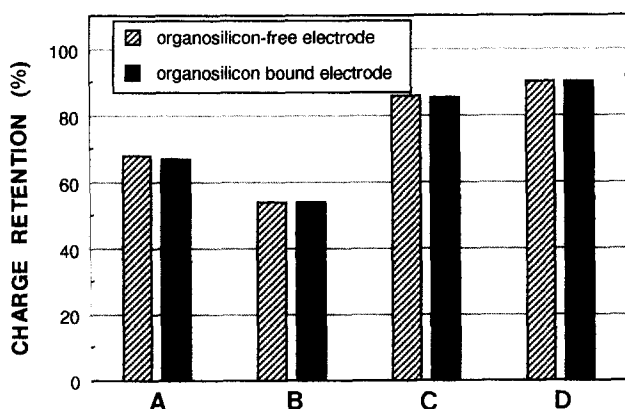


Fig. 5. Changes in discharge capacity ratio after various retention times at 25 °C: A, 1 day, discharge 15 mA; B, 5 days, discharge 15 mA; C, 5 days, discharge 3 mA; D, second cycle of A, discharge 15 mA.

reaction rate was faster could be attributed to the decrease in charging efficiency because of a higher plateau pressure for hydride formation than atmospheric pressure.

Fig. 5 shows the changes in discharge capacity in the organosilicon-free and 20 wt.% organosilicon-bound electrodes after various retention times at 25 °C. The results for the two electrodes were almost the same, indicating no effect of organosilicon addition on charge retention. When the electrode had been stored for 24 h after full charging and discharged at 15 mA, the discharge capacity decreased to about 68% (176 mA h g⁻¹) of the normal capacity. After storing for 5 days, it was about 54%. The reasons for the decrease in discharge capacity with retention time can be classified into two kinds: a self-discharge due to the desorption of hydrogen gas from the electrode and a self-deactivation of the electrode. The latter could come from a decay of the catalytic effect at the electrode surfaces. In order to clarify the actual reason, we attempted to discharge the electrode stored for 5 days at a very low current (3 mA). The discharge capacity increased sig-

nificantly to about 86% of the normal capacity. Another experiment, cycling of the electrode stored for 24 h, was conducted at the normal discharge current of 15 mA. The discharge capacity recovered from 68% at the first cycle to 90% at the second and gradually approached close to the normal value with increasing cycles. From the fact that the discharge capacity was strongly dependent on the discharge current, we could conclude that the decrease in discharge capacity with retention time was caused by the self-deactivation of the electrode.

The changes in discharge capacity with charge–discharge cycling of various organosilicon-bound electrodes are presented in Fig. 6. Similar to other metal hydride electrodes, these electrodes also showed considerable degradations in discharge capacity with increasing number of cycles. The maximum discharge capacities, appearing after about 4–5 cycles, were nearly the same, 250 mA h g⁻¹ (including the weights of coated copper and organosilicon), for all electrodes. The discharge capacities of the electrodes after 200 cycles were 66%, 68%, 71% and 76% for the silicon-free and 3, 5, and 10 wt.% organosilicon-added electrodes respectively as compared with their maximum capacities, i.e. increasing with the amount of organosilicon. This improvement in cycle life by the addition of organosilicon can be explained by a shielding effect of the organosilicon. Shielding of the alloy surface by the organosilicon can protect the alloy from oxidation and falling off from the electrode. However, it was very difficult to completely prevent the alloy powder from falling off during cycling in the open half-cell, because the volume expansion of the alloy with hydriding, confirmed by X-ray diffraction analysis, was about 25%.

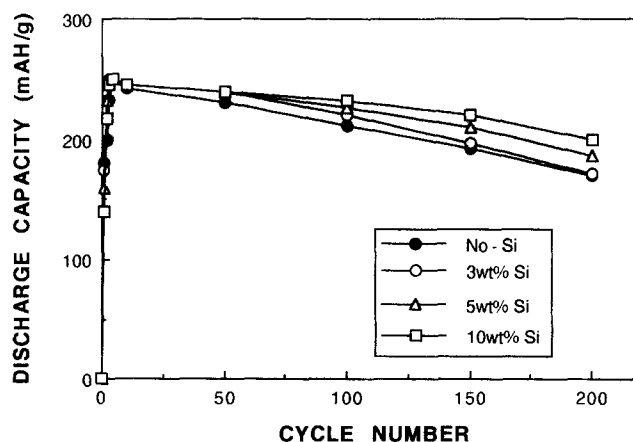


Fig. 6. Variation in discharge capacity of organosilicon-bound electrodes with cycles at 25 °C (charge 15 mA, 130 min; discharge 15 mA).

4. Conclusions

For the preparation of metal hydride electrodes, we have added silicon sealant as a binding material after 25 wt.% copper plating. From electrochemical measurements on the electrodes, we can draw the following conclusions.

(1) As the amount of organosilicon increases, the initial discharge capacity becomes lower, but the maximum discharge capacity can be achieved within 5 cycles.

(2) The electrodes with organosilicon are superior in terms of high rate discharge, useful range of temperature and cycle life to the silicon-free electrode, although there is no difference in the charge retention.

(3) Silicon sealant can be promisingly utilized as a binding material in the preparation of metal hydride electrodes.

Acknowledgments

We wish to thank the Korea Ministry of Trade, Industry and Energy (MOTIE) for support of this research.

References

- [1] H. Ewe, E.W. Justi and K. Stephan, *Energy Convers.*, **13** (1973) 109.
- [2] H.F. Bittner and C.C. Badcock, *J. Electrochem. Soc.*, **130** (1983) 193C.
- [3] H. Tamura, C. Iwakura and T. Kitamura, *J. Less-Common Met.*, **89** (1983) 567.
- [4] D.E. Hall, J.M. Saver and D.O. Gothard, *Int. J. Hydrogen Energy*, **13** (1988) 547.
- [5] A.H. Boonstra and T.N.M. Bernards, *J. Less-Common Met.*, **161** (1990) 355.
- [6] A.H. Boonstra, T.N.M. Bernards and G.J.M. Lippits, *J. Less-Common Met.*, **159** (1990) 327.
- [7] T. Sakai, K. Oguro, H. Miyamura, N. Kuriyama, A. Kato, H. Ishikawa and C. Iwakura, *J. Less-Common Met.*, **161** (1990) 193.
- [8] J.J.G. Willems, *Philips J. Res.*, **39** (1984) 1.
- [9] J.J.G. Willems and K.H.J. Buschow, *J. Less-Common Met.*, **129** (1987) 13.
- [10] T. Sakai, H. Ishikawa, K. Oguro, C. Iwakura and H. Yoneyama, *J. Electrochem. Soc.*, **134** (1987) 558.
- [11] H. Ishikawa, K. Oguro, A. Kato, H. Suzuki and E. Ishii, *J. Less-Common Met.*, **120** (1986) 123.
- [12] C.-N. Park and R. Kirchheim, *J. Alloys Comp.*, **182** (1992) 321–330.
- [13] T. Sakai, A. Yuasa, H. Ishikawa, H. Miyamura and N. Kuriyama, *J. Less-Common Met.*, **172–174** (1991) 1194.