

Self-discharge behavior of LaNi₅-based hydrogen storage electrodes in different electrolytes

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Received: 5 July 2007 / Revised: 19 December 2007 / Accepted: 7 January 2008 / Published online: 4 March 2008
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Abstract Nickel–metal hydride (Ni–MH) batteries using hydrogen storage alloys as negative electrode materials have been developed and commercialized because of their high energy density, high rate capability and long cycle life, without causing environmental pollution (Song et al. *J Alloys Comp* 298:254, 2000; Jang et al. *J Alloys Comp* 268:290, 1998). However, the self-discharge rate is relatively higher than that of the Ni–Cd batteries, which would certainly be disadvantageous in practical applications. The capacity loss of a battery during storage is often related to self-discharge in the cells. Self-discharge takes place from a highly charged state of a cell to a lower state of charge (SOC) and is typically caused by the highly oxidizing or reducing characteristic of one or both of the electrodes in the cell. This self-discharge behavior may be affected by various factors such as gases, impurities, temperature, type of alloy electrode, electrolytes, or charge/discharge methods. The loss of capacity can be permanent or recoverable, depending on the nature of the mechanism (chemical or electrochemical) and aging condition.

Contribution to ICMAT 2007, Symposium K: Nanostructured and bulk materials for electrochemical power sources, July 1–6, 2007, Singapore.

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In this paper, the effects of electrolyte composition and temperature on self-discharge behavior of LaNi₅-based hydrogen storage alloy electrodes for Ni–MH batteries have been investigated. It was found that both reversible and irreversible capacity loss of MH electrode tested at 333 K were higher than that at 298 K. When tested at 298 K and 333 K, reversible capacity loss was mainly affected by the electrolyte, while the irreversible capacity loss was not affected. The dissolution of Al from the electrode can be reduced more effectively in an electrolyte with Al addition, compared with that in normal electrolyte. This resulted in a lower reversible capacity loss for the electrode exposed in the Al³⁺-rich electrolyte. SEM analysis has shown that some needle shape and hexagonal corrosion products were formed on the surface of the alloy electrodes, especially after storage at high temperature.

Keywords Self-discharge · Hydrogen storage · Capacity retention · Metal-hydride electrode · Electrolyte

Introduction

Understanding the self-discharge behavior and charge retention characteristics of Ni–MH battery is important to its application and the prediction of battery performance. Several researchers have investigated the self-discharge mechanism of Ni–H batteries. Iwakura et al. [3] have investigated the self-discharge behavior of the LaNi₅ system and identified capacity loss as reversible and irreversible. The reversible capacity loss is attributed to the chemical desorption of hydrogen from the MH anode, while the irreversible capacity loss is attributed to the degradation of the MH anode itself. Mao et al. [4] have suggested that the self-discharge loss of a fully charged nickel oxide cathode is caused by the direct

chemical oxidation of hydrogen through the nickel oxide cathode or by the electrochemical oxidation of hydrogen. Several possible mechanisms which have been considered in the past [5–7] are:

- 1) Self-decomposition in the positive Ni electrode, due to inherent thermodynamic instability of the NiOOH composition;
- 2) Reduction of the positive Ni electrode by hydrogen gas generated from the MH electrode, causing the positive Ni electrode to lose capacity;
- 3) A redox shuttle mechanism between nitrite ions and ammonia;
- 4) Surface degradation of the negative MH electrode resulting from the oxidation of the active material during aging. This process results in capacity loss in the negative MH electrode.

Recently, the self-discharge behavior of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloy affected by state-of-charge, temperature, storage time and antioxidizing Cu over-layer was reported [7]. It was found that the self-discharge rate decreased with decreasing temperature and storage time, and was significantly decreased when the alloy is encapsulated with a thin Cu layer. Wang et al. [8] investigated the effect of ZnO addition to $\text{LaNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ electrode and found there was no obvious effect on self-discharge; however, the addition prevented the corrosion of the MH alloy. Indeed, little work has been done on the effects caused by the factors from surrounding environment (such as electrolyte, temperature, component of alloy).

In this paper, simulated battery tests have been used to investigate the self-discharge behavior of a LaNi_5 -based AB_5 hydrogen storage alloy. La rich alloy $\text{La}_{0.58}\text{Ce}_{0.25}\text{Pr}_{0.06}\text{Nd}_{0.11}\text{Ni}_{3.66}\text{Co}_{0.74}\text{Mn}_{0.41}\text{Al}_{0.18}$ was used to prepare the negative electrodes. Two different electrolytes: original electrolyte (6 M KOH + 1 wt% LiOH) and Al^{3+} -rich electrolyte (6 M KOH + 1 wt% LiOH, but with Al addition). The self-discharge properties were studied through cross-examination between different combinations of MH electrode–electrolyte systems.

Experimental details

Synthesis, characterization, and fabrication of testing battery

LaNi_5 -based alloys were synthesized in an arc-melting furnace under argon atmosphere, and turned over and remelted several times to assure homogeneity. Then, the alloys were mechanically crushed and grounded to powders below 250 mesh under a protective argon atmosphere. The negative electrodes [metal-hydride (MH) electrode] were

fabricated by the following procedures: Firstly, the alloy powder (0.6 g) were mixed with nickel powder (1.2 g) and binded with a small amount of polytetrafluoroethylene (PTFE). Secondly, the mixture was pasted onto both sides of the nickel foam sheet ($2.5 \times 2.5 \text{ cm}^2$). Finally, the nickel foam pasted with alloy powder were cold pressed to a pellet at a compacting pressure of 155–175 MPa. The commercial nickel hydroxide ($\text{Ni}(\text{OH})_2$) were used as the counter electrode (positive). The negative electrode was separated from the counter electrodes by a porous frit in aqueous electrolyte. Two electrolytes were prepared: original electrolyte (6 M KOH + 1 wt% LiOH) and Al^{3+} -rich electrolyte (6 M KOH + 1 wt% LiOH, but with Al addition). EO corresponds to the alloy in original electrolyte, and EA corresponds to the alloy in Al^{3+} -rich electrolyte.

The pressure–composition isotherms (PCI) were measured using a gas reaction controller. The specimen surface was characterized by scanning electron microscopy (LEO 1530 FEG-SEM). X-ray diffraction (XRD) analysis was carried out with a Philips PW 1710 diffractometer and $\text{Cu-K}\alpha$ radiation.

Electrochemical measurement

Charge and discharge tests were carried out on a Kikusui PFX40W-08 battery testing instrument controlled by computer. The charge/discharge tests aimed to characterize the electrochemical capacity and stability of the negative electrode, thus the capacity of the positive electrode plates was designed to be in excess of the negative electrode. Two methods of self-discharge were used: (1) step-mode self-discharge and (2) continuous mode self-discharge.

- 1) Step mode self-discharge: In this test, two identical test batteries were prepared and activated to ensure that the MH electrodes stay in an active state. The first battery was overcharged to 120% S.O.C (state of charge) at 0.2 C, after being stored for 2 days at a predetermined temperature; it was then discharged at the same rate to 1.0 V cutoff voltage, Q_2 denotes the value of this discharge capacity. The temperature was set at 298 K or 333 K. The second battery was also overcharged to 120% S.O.C, but it was discharged immediately at 0.2 C, in which Q_3 denotes the value of this discharge capacity. Q_1 denotes the maximum value of discharge capacity of test battery (after being activated). The difference between Q_3 and Q_2 represents the reversible self-discharge capacity loss; and the difference between Q_3 and Q_1 represents the irreversible self-discharge capacity loss.
- 2) Continuous mode self-discharge: As described above, test batteries were fully activated before test. They were then overcharged to 120% S.O.C at 0.2 C and discharged

at the same rate to 1.0 V of cutoff voltage after being stored for a period of time at a given temperature. Capacity retention can be calculated by this equation: Capacity retention (%) = $(Q_2/Q_1) \times 100\%$; where Q_1 denotes the maximum value of discharge capacity of test battery after being activated, and Q_2 denotes the value of discharge capacity obtained after storage.

Results and discussion

XRD results and PCI curve

The XRD pattern of LaNi₅-based alloy is shown in Fig. 1. It can be seen that the alloy has the same phase as that of CaCu₅ hexagonal structure, with sharp (111), (101), (110), and (200) peaks of LaNi₅. The calculated values of lattice constant a and c were 4.988 and 4.08 Å, respectively. From the PCI curve of the alloy in Fig. 2, good hydrogen-absorption behaviors have been observed, where the value of H/M and plateau pressure in hydrogen absorbing process were found to be 1.7 and ~0.3 atm, respectively.

Self-discharge behavior

As observed from Fig. 3, the reversible self-discharge of the alloy in Al³⁺electrolyte (EA) was lower than that in the original electrolyte (EO), regardless of the storing temperature. At room temperature (298 K), the reversible capacity losses were 20~30 mAh/g for EA system, and 40~45 mAh/g for EO system. At high temperature (333 K), the reversible capacity losses were 50~60 and 70~120 mAh/g for EA and EO systems, respectively. Thus, it is evident that the reversible capacity was halved when Al³⁺-rich electrolyte was used. The small fluctuations in the reversible capacity loss at 298 K is very reasonable, suggesting that the capacity loss is not affected by the number of cycles. Hence, Al³⁺-rich

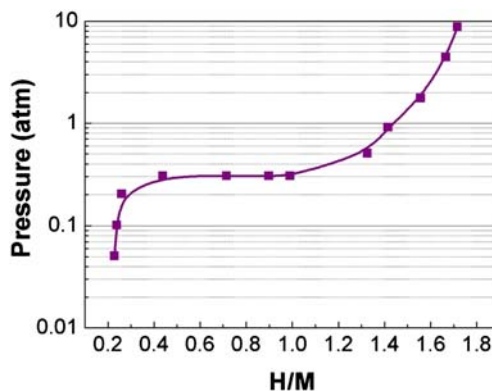


Fig. 2 PCI curve for alloy powder at room temperature (298 K)

electrolyte would lower and stabilize the reversible capacity loss at the temperatures we studied. The reduction of reversible capacity in Al³⁺-rich electrolyte was more significant especially at high temperature. On the other hand, for irreversible capacity loss, as observed from Fig. 4, the irreversible capacity was similar whether the system was exposed in Al³⁺-rich electrolyte or original electrolyte, although the irreversible capacity loss was higher at high temperature (5–25 mAh/g at 333 K and 5–10 mAh/g at 298 K).

It is well-known that the change in electrode potential is due to desorption of hydrogen from MH electrode triggered by the difference between the partial pressure of hydrogen in the cell and the equilibrium hydrogen pressure at the MH electrode [9]. This results in reversible capacity loss. When a battery is fully charged, as calculated, the open potential of MH electrode in KOH electrolyte is about -0.94 V vs Hg/HgO at room temperature, and hydrogen pressure inside MH electrode will reach 1.82 atm. A low open potential of MH electrode corresponds to a high hydrogen pressure within MH electrode [10]. When the same hydrogen storage alloy is used, the open potential of MH electrode is mainly determined by the type of electrolyte. Our previous work [10] have proven that in comparison to that

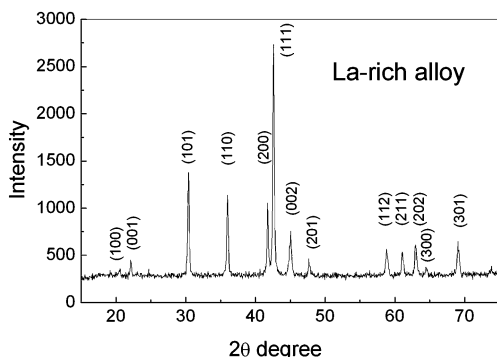


Fig. 1 X-ray diffraction pattern of the LaNi₅-based alloy studied in this work

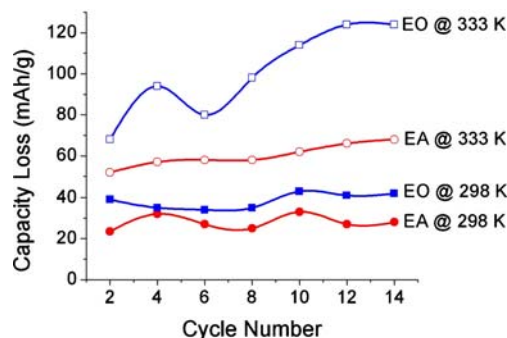


Fig. 3 Reversible self discharge in EO and EA in different electrolytes at 298 K and 333 K

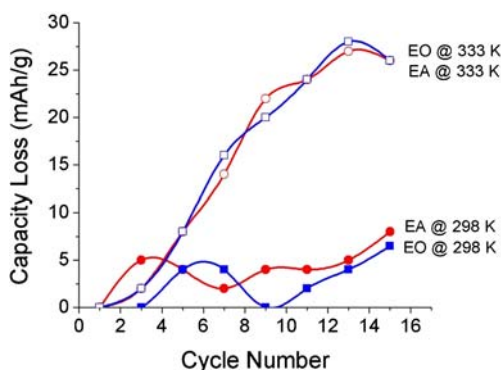


Fig. 4 Irreversible self discharge in EO and EA in different electrolytes at 298 K and 333 K

in OE system, MH electrode showed a higher open potential in Al^{3+} -rich electrolyte and a lower hydrogen pressure inside MH electrode; hence, less reversible capacity loss have been observed for the alloy in EA system.

Capacity retention at 298 K

Figure 5 shows the capacity retention for the EO and EA systems after 4 and 16 days of storage at 298 K. It can be clearly seen that the alloy electrodes in Al^{3+} -rich electrolyte have a higher capacity retention than those in original electrolyte. After 16 days, about 78% of capacity was retained in the EA system, compared to 70% in the EO system. In general, MH electrode degradation contributes to irreversible capacity loss because of the loss of active components inside the alloy and the corrosion on the surface. The surface morphology of the alloy electrode immersed in EA and EO after 4 and 16 days are given in Fig. 6. Comparing to the as-pasted sample, there were a few needle-shaped corrosion products formed on the alloy

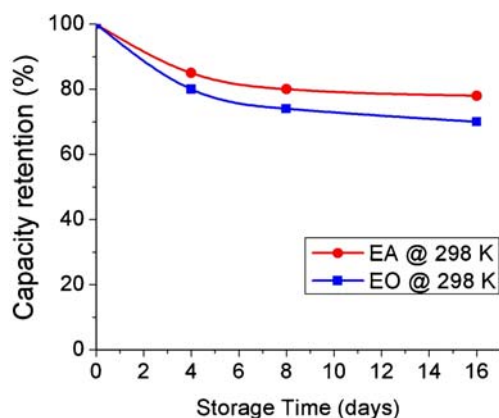


Fig. 5 Capacity retention of LaNi_5 -based alloy in different electrolytes at 298 K

surface after 4-day immersion in the electrolyte; the amount of corrosion products were similar in both EO and EA systems. As the immersion time was increased to 16 days in the EO system, the amount of needle-shaped corrosion products increased significantly and agglomerated into blocks. In contrast, the amount of needle-shaped corrosion products remained fairly similar in the EA system. Maurel et al. [11] also reported this phenomenon on the study of $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ alloy, in which the needle-shaped corrosion products mainly consisted of metal oxides and hydroxides, and some rare earth oxides existed as hexagonal corrosion products. Our EDX analysis also confirmed their finding. A detailed discussion on this topic, with respect to different types of negative electrodes and electrolytes, will appear in a forthcoming paper.

In addition, our EDX surface analysis also suggested that a protective oxide layer can be formed on alloy surface more easily in electrolyte EA than in electrolyte EO. Such a layer can effectively reduce the diffusion rate of hydrogen and Al inside the alloy into the electrolyte. This results in the reduction of the reversible capacity loss in electrolyte EA. This phenomenon will be more apparent at higher temperatures.

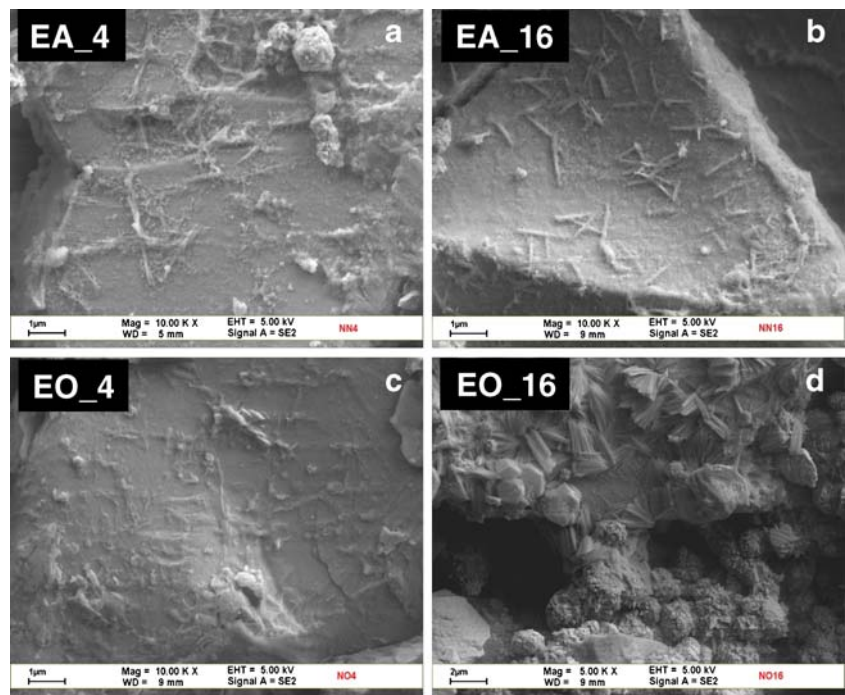
Capacity retention at 333 K

Figure 7 shows the capacity retention for the EO and EA systems after 2 days of storage at 333 K. The alloy electrodes in Al^{3+} -rich electrolyte EA have a higher capacity retention than that in original electrolyte EO. After 2 days, about 65% of capacity retained in the EA system but only 50% in the EO system. As expected, the capacity retentions of all systems obtained after storing 16 days at 298 K were still higher than that obtained after storing 2 days at 333 K. Such results indicate that the increasing temperature can result in more vigorous self-discharge behavior, owing to the higher diffusion rate and accelerated hydrogen absorption/desorption kinetics of AB_5 alloy at higher temperature.

At high temperature, the solubility of Al inside the alloy in original electrolyte can also increase, more Al dissolves from the bulk alloy into electrolyte EO, causing a slight increase in plateau pressure of hydrogen absorption/desorption process, thus higher reversible capacity loss. On the contrary, the solubility of Al inside the alloy can be effectively reduced in Al-rich electrolyte EA, a lower reversible capacity loss has been observed in the EA systems at 333 K.

In addition to the increased hydrogen diffusion and aluminum desolution, the rate of corrosion on the surface of alloy powder can also be accelerated under higher temperature condition. As a result, more corrosion products have been observed with increasing storage time. This is shown in the

Fig. 6 Surface morphology of LaNi₅-based alloy electrode immersed in EA and EO after 4 and 16 days at 298 K. The numbers on the left top corner of the micrographs denote the immersion time in days



surface morphology of the alloy after storing in electrolyte EA and EO for 2 days at 333 K (Fig. 8a and b, respectively). Both needle-shaped and hexagonal corrosion products can be clearly observed. Compared to the results of self-discharge test at 298 K (Fig. 6), an interesting phenomenon is that no obvious hexagonal corrosion product was observed on the alloy surface tested in Al³⁺-rich electrolyte (EA) at 298 K, but such products can be clearly identified in samples tested at 333 K. Moreover, the size of these hexagonal corrosion products obtained in original electrolyte EO was larger than that in EA, indicating that more rare earth metals were lost from the alloy in electrolyte EO. These needle-shaped and hexagonal corrosion products are composed of some metals, rare earth oxides, and hydrox-

ides, which belong to non-hydrogen storage materials; therefore, the amount of corrosion products have a corresponding relationship to the irreversible capacity loss of the alloy.

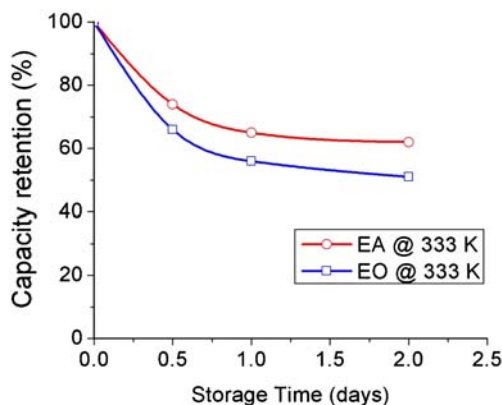


Fig. 7 Capacity retention for the alloy at 333 K

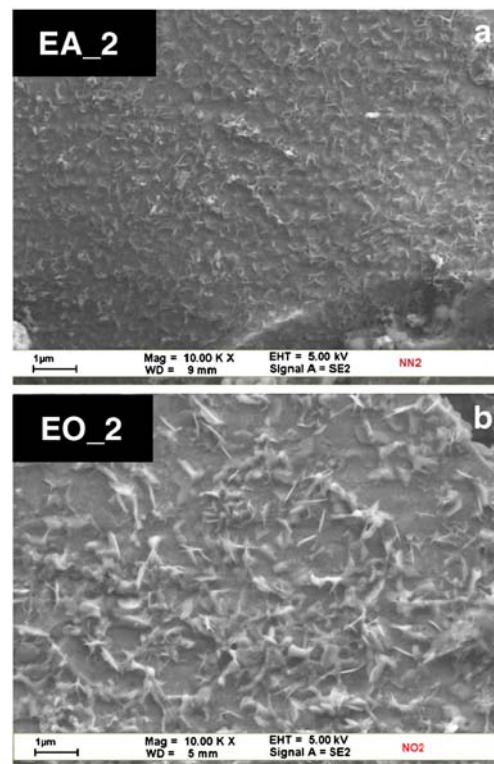


Fig. 8 Surface morphology of the alloy after storing in Al³⁺-rich electrolyte (a) and original electrolyte (b) for 2 days at 333 K

Conclusions

Self-discharge behavior of LaNi₅-based alloy has been studied through cross-examination of different MH electrode–electrolyte systems. Base on the above results, it can be concluded that:

- 1) With regard to electrolytes, the reversible capacity loss of the LaNi₅-based alloy at both 298 K and 333 K, is mainly affected by the chemical composition of the electrolytes. The dissolution of Al from the bulk alloy can be reduced effectively when excess Al is added to the commercial electrolyte. In this way, a lower reversible capacity loss can be obtained than that in the original electrolyte EO system. This addition, however, was found to have little effect to the irreversible capacity loss, and in this case, the self-discharge behavior was similar in different electrolytes studied.
- 2) With regard to temperature, both reversible and irreversible capacity losses in the EO and EA systems at 333 K were higher than that at 298 K. This result agrees with previous study of LaNi_{4.7}Al_{0.3} alloy, which found that the higher the temperature, the higher was the rate of self-discharge [7]. The above observations illustrate the importance of self-discharge control if Ni–MH batteries are to be used at high temperature.

- 3) Al³⁺-rich electrolyte lowers the reversible capacity loss regardless of the temperature, it is especially effective when tested in higher temperature, thus resulting in a higher capacity retention. Hence, electrolyte with excess Al addition is beneficial to the resistance to self-discharge of the negative electrodes.

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