

Investigation into the deterioration in storage characteristics of nickel-metal hydride batteries during cycling

Katsuhiko Shinyama*, Yoshifumi Magari, Hiroyuki Akita, Kiyoshi Kumagae, Hiroshi Nakamura, Shigeki Matsuta, Toshiyuki Nohma, Masao Takee, Koji Ishiwa

Mobile Energy Company, Sanyo Electric Co. Ltd., 7-3-2 Ibukidai-higashimachi, Nishi-ku, Kobe, Hyogo 651-2242, Japan

Received 29 September 2004; received in revised form 10 November 2004; accepted 16 November 2004

Available online 21 January 2005

Abstract

The deterioration mechanism of the storage characteristics of nickel-metal hydride batteries for hybrid electric vehicles (HEVs) has been investigated. The deterioration in the storage characteristics during charge–discharge cycling is caused by the microscopic short circuit in the separator which is influenced by the deposits from the positive and negative electrode elements such as zinc, cobalt and manganese. Based on the elucidated deterioration mechanism, the deterioration in the storage characteristics of nickel-metal hydride batteries was suppressed by employing a hydrogen-absorbing alloy with higher oxidation resistance for the negative electrode.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Nickel-metal hydride battery; Self-discharge; Storage characteristics; Hybrid electric vehicle; Deterioration mechanism

1. Introduction

Recently, various types of clean cars have been and continue to be developed because of environmental issues. Since hybrid electric vehicles (HEVs) with rechargeable batteries are most promising among them, they have been receiving much attention [1]. For attractive HEVs, high-performance rechargeable batteries are strongly required. Nickel-metal hydride batteries are employed by almost all the commercialized HEVs because they have a better combination of output power, capacity, life, reliability and cost [2–6]. For the nickel-metal hydride batteries for HEVs, low self-discharge is strongly required as they influence the start-up of HEVs under various circumstances, especially when HEVs are driven after a long rest.

From the investigation into the self-discharge mechanisms of alkaline storage batteries such as nickel-metal hydride batteries [7–9], the self-discharge is known to be caused by:

(1) self-decomposition of the charged positive active material (NiOOH); (2) hydrogen gas evolution at the negative electrode; and (3) redox shuttle reaction by nitrate ions, metal ions and/or organic impurities. It has been reported that the self-discharge caused by redox shuttle reaction can be suppressed by using sulfonated and grafted separators [10–12]. However, these improvements were only examined at the initial stage and few reports have been made on the improvement of the self-discharge after a long period of cycling.

In this study, we report the self-discharge behavior during cycling that assumes an HEV usage and the improvement based on the elucidated mechanism.

2. Experimental

Cylindrical sealed-type D-size cells (32.3 mm in diameter and 58.5 mm in height) with a nominal capacity of 6.5 Ah were prepared. A sintered nickel positive electrode comprising nickel hydroxide coprecipitated with cobalt

* Corresponding author. Tel.: +81 78 993 1129; fax: +81 78 993 1094.
E-mail address: sinyama@sm.energy.sanyo.co.jp (K. Shinyama).

and zinc and a pasted negative electrode comprising $\text{MmNi}_{3.6}\text{Co}_{0.4}\text{Al}_{0.3}\text{Mn}_{0.5}$ (Mm: misch metal) hydrogen-absorbing alloys were wound with a hydrophilic-treated polyolefin separator. The electrolyte was composed of potassium hydroxide, sodium hydroxide and lithium hydroxide and the total concentration was 7 N.

Life tests were conducted under a condition accelerated by temperature of 50 A pulse charge–discharge and state of charge (SOC) 40–60% at 45 °C.

The storage characteristics were measured as follows. First, after being charged to SOC 80% at 0.5 C, a test cell was discharged up to 1.0 V at 0.5 C and this discharge capacity was regarded as the capacity before storage. Next, after being charged to SOC 80% at 0.5 C, the test cell was stored at 45 °C or 0 °C for 7 days. After the storage, the test cell was discharged up to 1.0 V at 0.5 C to measure the capacity after storage. A residual capacity ratio was calculated as the ratio of the capacities before and after the storage. The separator was analyzed using ICP, EPMA and XRD.

In order to investigate the influence of the degradation of the positive electrode on the self-discharge characteristics, the following experiment was conducted. The D-size test cells before and after cycling were disassembled and the positive electrodes were taken out. A two-electrode test cell with the positive electrode before or after cycling and a negative electrode of cadmium was used in order to measure

the storage characteristics. The electrolyte was composed of potassium hydroxide, sodium hydroxide and lithium hydroxide and the total concentration was 7 N. The test condition was the same as the D-size cells except that the storage condition of 60 °C was for 3 days.

In order to identify the deterioration mechanisms of the storage characteristics caused by the microscopic short circuit, two-electrode test cells with a positive electrode of nickel hydroxide and a negative electrode of cadmium were used. The test procedure is shown in Fig. 1. Two sheets of the separator were sandwiched between the positive and negative electrodes and a $\text{MmNi}_{3.6}\text{Co}_{0.4}\text{Al}_{0.3}\text{Mn}_{0.5}$ electrode was inserted into the electrolyte (Cell A). In this test cell, the alloy electrode was not electrically connected to the positive and negative electrodes. Another two-electrode test cell without an alloy electrode was also assembled for comparison (Cell B). The first storage test was conducted under the same condition as the D-size cells.

Using the electrodes and separators taken from the test cell A after the first storage test, two sets of test cells were prepared as also shown in Fig. 1. In the cell C, only the alloy electrodes were removed as compared to the first test. In the cell D, the alloy electrodes were removed and the separators on the negative electrode side were replaced with the unused separators. The second storage test of these two test cells and the test cell without an alloy were conducted under the same condition as the first test.

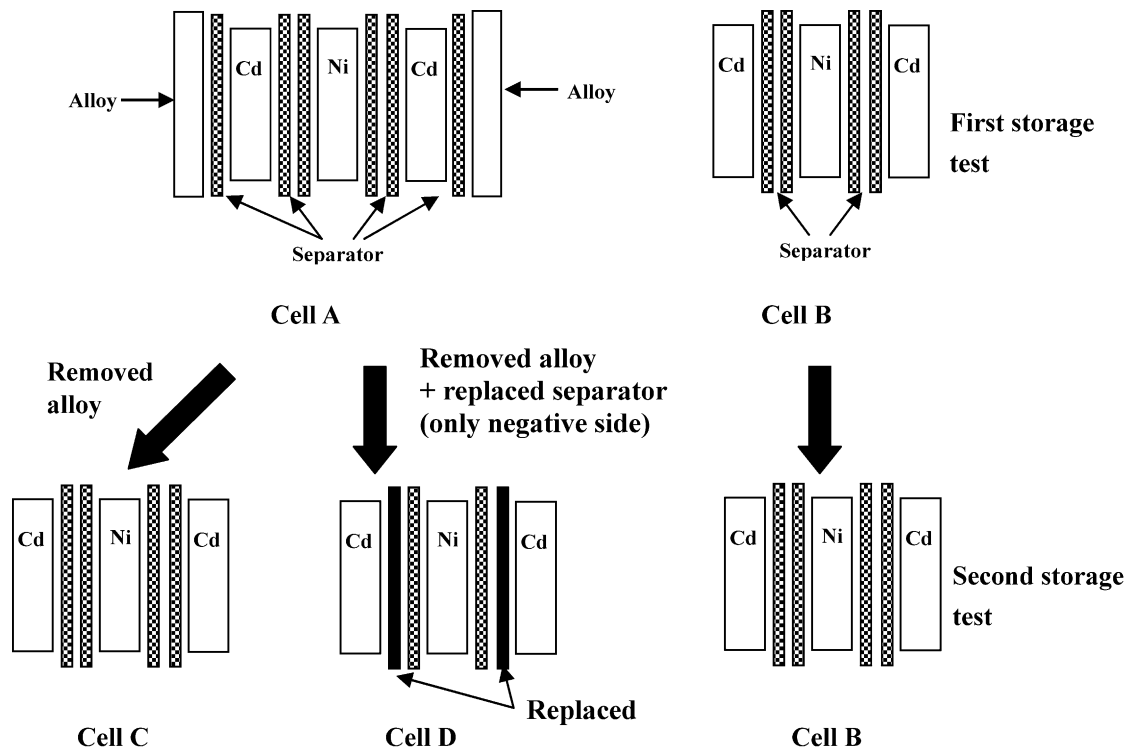


Fig. 1. Test procedure to examine the effect of a hydrogen-absorbing alloy on storage characteristics.

Table 1
Residual capacity ratio after storage for 7 days before and after cycling

Number of cycles	Storage temperature	
	45 °C	0 °C
0	80%	96%
22,000	44%	87%

Table 2
Chemical analysis of the separator using ICP before and after cycling (unit: wt.%)

Number of cycles	Ni	Zn	Co	Mn	Al	La
0	3.1	0.35	0.66	3.47	0.09	0.66
22,000	3.0	1.17	1.00	6.93	0.06	0.69
Ratio	0.97	3.34	1.51	2.00	0.67	1.05

3. Results and discussion

3.1. Change in the storage characteristics during cycling

The storage characteristics before and after cycling are shown in terms of the residual capacity ratio in Table 1. From 0 to 22,000 cycles, the residual capacity ratio was decreased from 80 to 44% at 45 °C, and from 96 to 87% at 0 °C, indicating the deterioration of the storage characteristics during cycling.

Table 2 shows the composition changes in the separator before and after cycling measured by ICP. The ICP results indicate the existence of nickel, zinc, cobalt, manganese, aluminium and lanthanum in the separators before and after cycling. Nickel and cobalt were originally contained in both the positive and negative electrodes. Zinc was originally contained in the positive electrode. Manganese, aluminium and lanthanum were originally contained in the negative electrode. In particular, the amount of zinc increased by more than three times compared to the initial value after cycling. The amount of manganese and cobalt also nearly doubled compared to the initial value.

The cross-sectional EPMA images of the separator after cycling are shown in Fig. 2. Zinc is observed near the negative electrode side although it was originally contained in the positive electrode. Manganese, cobalt and oxygen are distributed almost completely throughout the separator. XRD profiles of the separators before and after cycling are shown in Fig. 3. Several peaks are observed and they have been assigned to ZnMn₂O₄. Since no peaks assigned to cobalt compounds are observed, cobalt is considered to exist as amorphous oxides and/or hydroxides. Although generally neither ZnMn₂O₄ nor amorphous oxides and/or hydroxides of cobalt are regarded as electric conductors, it may be possible that they conduct a small amount of electricity.

3.2. Investigation into the deterioration mechanisms of the storage characteristics during cycling

For the deterioration in the storage characteristics during cycling, there are other possible causes mentioned before such as the decline in the oxygen evolution potential of the positive electrode and the increase in the redox shuttle reactive substances in the electrolyte. Firstly, the influence of the degradation of the positive electrode on the self-discharge

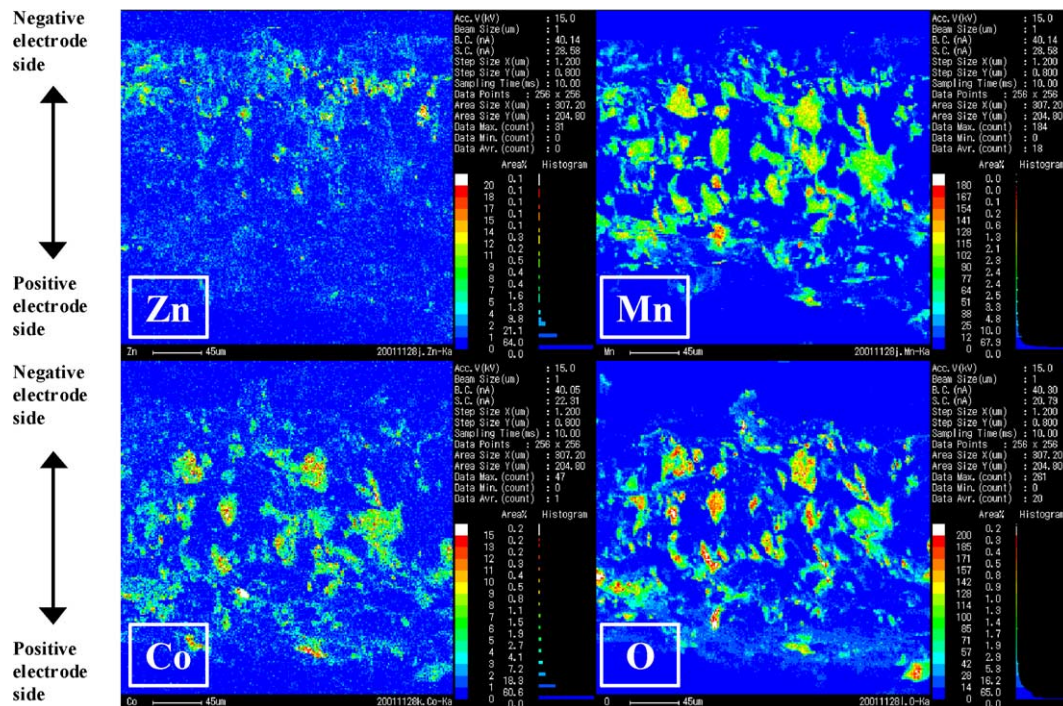


Fig. 2. Cross-sectional EPMA images of the separator after cycling.

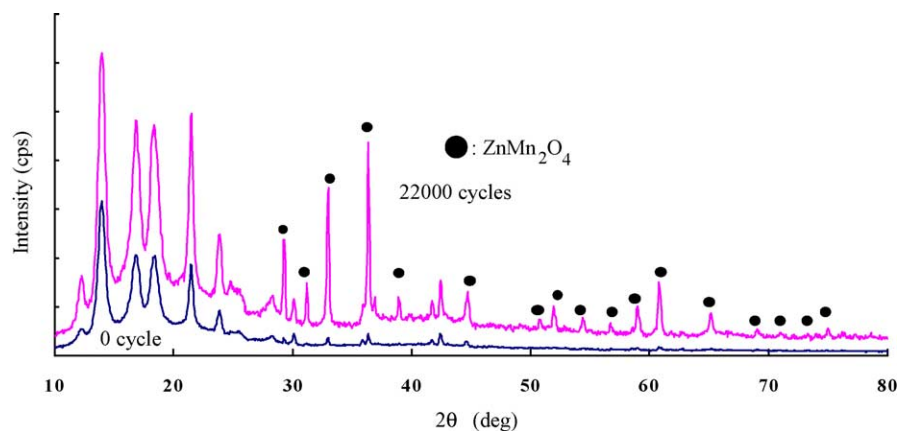


Fig. 3. XRD profiles of the separators before and after cycling.

characteristics was examined using the positive electrode of the D-size test cells before and after cycling. The residual capacity ratio of the cell using the positive electrode after cycling was comparable to that of the cell using the positive electrode before cycling, showing that change in the positive electrode brings a little influence to the deterioration in the storage characteristics (Table 3).

Secondly, the deterioration mechanisms of the storage characteristics caused by the microscopic short circuit were examined using two-electrode test cells shown in Fig. 1. Table 4 shows the first storage characteristics. The residual capacity ratio of the test cell A with the electrically disconnected alloy electrode was 64% which was 18 points smaller than that of the test cell B without the alloy electrode. The result indicates that the dissolved elements from the alloy electrode brought the deterioration in the storage characteristics.

Following the first storage test, the second storage test of the test cells was conducted. Table 5 shows the second storage characteristics. No residual capacity remained for the cell C. On the contrary, the residual capacity ratio of the cell D was the same as the cell B. In addition, in the second storage test for the test cell D, the positive and negative electrodes and the separators on the positive electrode side were not replaced. These parts contained about 25% of the electrolyte in the cell

Table 3
Storage characteristics using the positive electrode before and after cycling

Positive electrode	Residual capacity ratio (%)
Before cycling	82
After cycling	86

The cells were stored for 3 days at 60 °C.

Table 4
Effect of the addition of a hydrogen-absorbing alloy to the nickel–cadmium test cells on the storage characteristics; first storage test

Test cell	Residual capacity ratio (%)
Cell A	64
Cell B	82

in the first storage test judging from the weight change of the parts before and after drying. The residual capacity ratio, however, recovered to the same level of the cell B without the alloy electrode. This means that increase in the redox shuttle reactive substances in the electrolyte is unlikely to cause the deterioration in the storage characteristics.

From the results described in this section, it is considered that the deterioration in the storage characteristics is caused by the microscopic short circuit due to the deposits from the positive and negative electrode elements.

3.3.Suppressions of deterioration in storage characteristics during cycling based on the elucidated mechanism

Based on the results discussed above, it is found that suppressing the dissolution of the elements from the positive and negative electrodes is one of the effective methods in order to reduce the deposits in the separator and to prevent the microscopic short circuit. The improvement of the corrosion resistance of the negative electrode alloy is important in this sense. In addition, the hydrogen-absorbing alloy with higher oxidation resistance may suppress the dissolution of zinc from the positive electrode because zinc exists as a compound with manganese as $ZnMn_2O_4$ as indicated in the XRD profile.

In practice, the corrosion resistance of the negative electrode alloy has been improved by optimizing the alloy composition and the alloy production conditions such as annealing condition. More specifically on the alloy composition, the amount of cobalt and aluminium, both of which are known

Table 5
Effect of the addition of a hydrogen-absorbing alloy to the nickel–cadmium test cells on the storage characteristics; second storage test

Test cell	Residual capacity ratio (%)
Cell C	0
Cell D	85
Cell B	85

Table 6

Improvement of storage characteristics for cycling using a hydrogen-absorbing alloy with higher oxidation resistance and other new constituent parts

Number of cycles	Storage temperature	
	45 °C	0 °C
0	84%	99%
26,000	77%	98%

Residual capacity ratio after storage for 7 days before and after cycling.

to suppress the pulverization and oxidation of the alloy particles and the stoichiometry of the alloy, have been increased. Storage characteristics of a cell using the improved negative electrode alloy are shown in Table 6. The test was a 50 A pulse charge–discharge life test. The deterioration in the storage characteristics was suppressed by using the improved alloy; the residual capacity rate at 26,000 cycles maintained 77% for 7 days storage at 45 °C, and 98% for 7 days storage at 0 °C.

4. Conclusions

The deterioration mechanism of the storage characteristics of nickel-metal hydride batteries for HEVs was investigated. The storage characteristics deteriorate during cycling. The deterioration in the storage characteristics of the batteries is caused by the microscopic short circuit in the separator which is influenced by the deposits from the positive and negative

electrode elements such as zinc, cobalt and manganese. The decline in the oxygen evolution potential of the positive electrode and the increase in the redox shuttle reactive substances in the electrolyte have little influences on the deterioration in the storage characteristics. Based on the elucidated deterioration mechanism, the deterioration in the storage characteristics of nickel-metal hydride batteries was suppressed by employing a hydrogen-absorbing alloy with higher oxidation resistance for the negative electrode.

References

- [1] O. Bitsche, G. Gutmann, *J. Power Sources* 127 (2004) 8.
- [2] I. Yonezu, Proceedings of the Second International Advanced Automotive Battery Conference, 2002, p. 26.
- [3] M. Verbrugge, E. Tate, *J. Power Sources* 126 (2004) 236.
- [4] Yi-Fu Yang, *J. Power Sources* 75 (1998) 19.
- [5] A. Taniguchi, N. Fujioka, M. Ikoma, A. Ohta, *J. Power Sources* 100 (2001) 117.
- [6] P. Gifford, J. Adams, D. Corrigan, S. Venkatesan, *J. Power Sources* 80 (1999) 157.
- [7] Y.J. Kim, A. Visintin, S. Srinivasan, A.J. Appleby, *J. Electrochem. Soc.* 139 (1992) 351.
- [8] P.H.L. Notten, W.S. Kruijt, H.J. Bergveld, *J. Electrochem. Soc.* 145 (1998) 3774.
- [9] P.H.L. Notten, J.R.G.V. Beek, *Chem. Ind.* 54 (2000) 102.
- [10] M. Ikoma, Y. Hoshina, I. Matsumoto, C. Iwakura, *J. Electrochem. Soc.* 143 (1996) 1904.
- [11] P. Leblanc, P. Blanchard, S. Senyarch, *J. Electrochem. Soc.* 145 (1998) 844.
- [12] J.A. Cook, I.M. Lancaster, *Electrochem. Soc. Proc.* 98–15 (1998) 55.