

Short communication

Effect of long-term overcharge and operated temperature on performance of rechargeable NiMH cells

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Abstract

In this article, sub-C size cylindrical NiMH cells were constructed for the performance investigation under long-term overcharge and elevated temperatures. The influence of operated conditions on cell performance and electrode materials was examined. The experimental results revealed that the NiMH cells had good tolerance for 1-month overcharge at a 0.2C rate, remaining the capacity and capacity-rate performance and showing promise as a candidate for backup power sources. However, the sub-C size NiMH cells did not exhibit good performance at elevated temperatures, and the cycling stability with 100% DOD (depth of discharge) at temperature of >50 °C is necessary to be further improved. The deterioration of electrochemical capacity and cycling stability at elevated temperatures was analyzed and the reasons were discussed.
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1. Introduction

Due to having high energy densities, high power densities and environmental friendliness, small size rechargeable nickel-metal hydride (NiMH) batteries have been applied in a variety of portable electronic apparatus such as mobile phones, laptop computers, electric toys, small power tools and so on [1]. The NiMH batteries also show the promise for applications as power sources in electric and hybrid vehicles (EV and HEV) [2] (for instance, HEV Toyota Prius with NiMH batteries have been available on the market for a few years) and as backup power sources in bank, hospital, military and telecomm equipments etc. [3–7]. The requirements of the NiMH batteries in above applied areas are, however, different from those in the portable electronic devices. For example, the NiMH batteries are required to be capable of charging rapidly and working in a wide-temperature range 0–60 °C for EV and HEV applica-

tions. For the rechargeable NiMH cells used as backup power sources in the military, telecommunication, bank and hospital, the batteries must fulfill long-term overcharge requirements (floating charge) at a low charge rate. Therefore, it is significant to investigate the influence of various operation conditions on the performance of NiMH cells in order to wide their applications. In this work, sub-C size NiMH cells were made for the investigations and their performances were evaluated under different operation conditions. After cycling tests, positive and negative electrode materials were analysed. The reasons of cell degeneration were discussed and approaches to improve the cell performance were suggested.

2. Experimental details

2.1. Preparation of metal hydride (MH) and nickel electrodes

AB₅-type hydrogen storage alloys having a chemical composition of LnNi_{3.6}Co_{0.5}Mn_{0.6}Al_{0.3} and a theoretical capacity of 300–320 mAh g⁻¹ were used as active materials of nega-

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tive electrodes. The MH powder with an average size of $36\ \mu\text{m}$ was mixed well with carbon powder and a polytetrafluoroethylene (PTFE) solution in a weight ratio of 97.5:1:1.5 to obtain a paste. Punched stainless steel coated with nickel and a thickness of $0.06\ \text{mm}$ was used as the substrate and filled with the paste. After drying at room temperature for 24 h, the MH electrodes were mechanically pressed into the physical dimension of $320\ \text{mm}$ in length, $34\ \text{mm}$ in width and $0.3\ \text{mm}$ in thickness. The total weight of negative electrode was $18.0 \pm 0.5\ \text{g}$. For the positive electrodes, β -phase spherical nickel hydroxide powder with 0.8% cobalt and 4.5% Zinc and having a tap density of $2.0\text{--}2.2\ \text{g ml}^{-1}$ was used as active material. Pasted-type nickel electrodes were prepared as follows. The β -phase nickel hydroxide powder and cobalt oxide powder were mixed in a weight ratio of 94:6. A 1.0 wt.% carboxymethyl cellulose (CMC) was added to the mixture and stirred to obtain a past. Porous nickel foam was used as the nickel electrode substrate. The nickel substrate was then filled with the past, dried and mechanically pressed to obtain positive electrodes. The size of positive electrodes was $260\ \text{mm}$ in length, $34\ \text{mm}$ in width and $0.65\ \text{mm}$ in thickness. The mass amount of negative electrode was $16.0 \pm 0.5\ \text{g}$.

2.2. Cell assembly and electrochemical tests

Cylindrical sub-C size NiMH cells were assembled by spirally winding the nickel hydroxide positive electrode and the MH negative electrode along with a $0.01\ \text{mm}$ thick polyamide separator. The capacity ratio of positive to negative electrodes was 1.48:1.55. The amount of electrolyte used was in the range $4.95\text{--}5.10\ \text{g}$ with the composition of $6.0\ \text{M KOH} + 1.0\ \text{M LiOH}$. Before electrochemical evaluation, the NiMH cells were activated at temperature of $35\text{--}40\ ^\circ\text{C}$ with a charge rate of 0.1C for 15 h and the same rate of discharge to $1.0\ \text{V}$ for 2–3 cycles. Then, a 0.2C rate charging for 6 h and discharging at the same rate at room temperature ($22\ ^\circ\text{C}$) were used to measure the cell capacity until stable values were obtained. Afterwards, different operation conditions were fulfilled to evaluate cell performance.

3. Results and discussion

3.1. Influence of long-term overcharge on performance and electrode materials

Performance of sub-C size NiMH cells after 1–2 month overcharge at a 0.2C rate was examined in this section. Fig. 1 shows the electrochemical discharge curves before long-term overcharge and after 30, 60-day overcharge at a 0.2C rate. The cell weight is 56.38 and $56.37\ \text{g}$ before and after 60-day overcharge, respectively. The unchanged weight implies that the electrolyte inside the cell did not leak (we also did not observe any track of carbonate on the cell cap even after 60-day overcharge). The sub-C size NiMH cells have an electrochemical capacity of $3000\ \text{mAh}$ at a 0.2C rate and exhibit good discharge capability at room temperatures, as shown in Fig. 1a. After 30-day overcharge, the NiMH cell retained the discharge capacity at the 0.2C rate. But, its rate performance declined slightly. The discharge capacity remained 97% and 91% at the 0.5C and 1.0C rates,

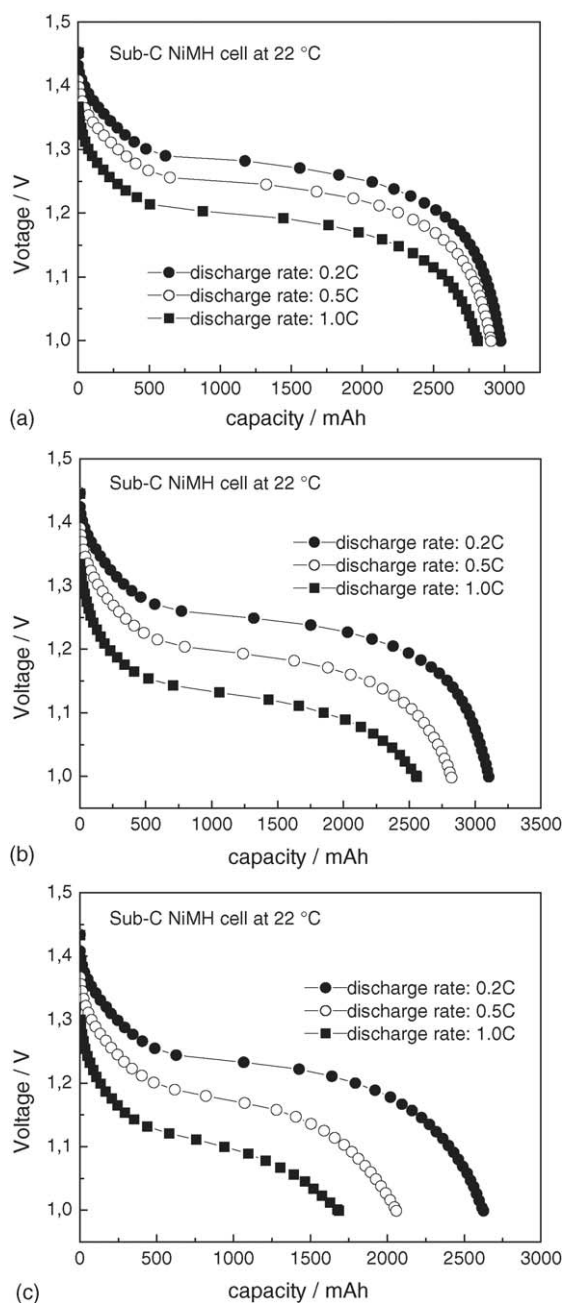


Fig. 1. Discharge curves of sub-C NiMH cells at 0.2C to 1.0C rates and $22\ ^\circ\text{C}$. (a) before long-term overcharge. (b) after 30 days overcharge at a 0.2C rate and $22\ ^\circ\text{C}$. (c) after 60 days overcharge at a 0.2C rate and $22\ ^\circ\text{C}$.

respectively, compared with before overcharge (see Fig. 1b). The results show that the NiMH cells are able to sustain the relatively longer overcharge even though the capacity-rate performance is faded slightly. After 60-day overcharge, however, the performance reduced obviously (see Fig. 1c). The discharge capacity decreased to 88%, 70% and 60% at the 0.2C , 0.5C and 1.0C rates, respectively. The average discharge potential was also depressed. A larger polarization during charge processes was also observed, as shown in Fig. 2, especially in the case of 60-day overcharge. In order to find the reasons why the performance was deteriorated after 60-day overcharge, the tested NiMH cells were opened in the 50% charged state. The negative and positive

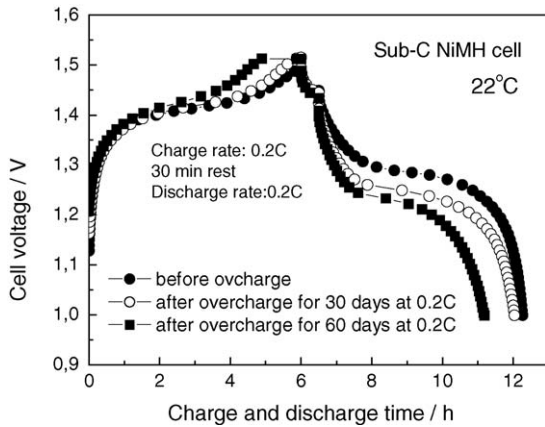


Fig. 2. Charge and discharge curves of sub-C NiMH cells before and after long-term overcharge at a 0.2C rate and 22 °C.

electrodes were washed with distilled water. In order to prevent MH materials from burning in air, the negative electrodes remained in distilled water for several days. Then, a small part of materials scraped from both electrodes was examined by X-ray diffraction (XRD) using Cu $K\alpha_1$ radiation.

Fig. 3 shows the results of XRD measurements. It is clear that the positive material still remain in the β -phase nickel hydroxide. No γ -phase nickel oxide hydroxide was detected, indicating that the positive material is relatively stable in this case. In contrast, the oxidization of misch-metal AB_5 -type hydrogen storage alloy in the negative electrode was found. As seen in Fig. 3, the strong diffraction peaks of misch-metal oxide and nickel oxide were detected. During overcharge in the NiMH cells, O_2 molecules produced in the positive electrodes should be consumed in the negative electrodes via a recombination reaction: $O_2 + 4MH = 4M + 2H_2O$ (M and MH denote the hydrogen storage alloy and the metal hydride, respectively). The formed hydrogen storage material (M) can be charged back to metal hydride (MH) in the overcharge state: $M + H_2O + e = MH + OH^-$. In view of points, the sealed NiMH cells can sustain overcharge through such a recombination cycle, and keep a low internal pressure and prevent the cell damage.

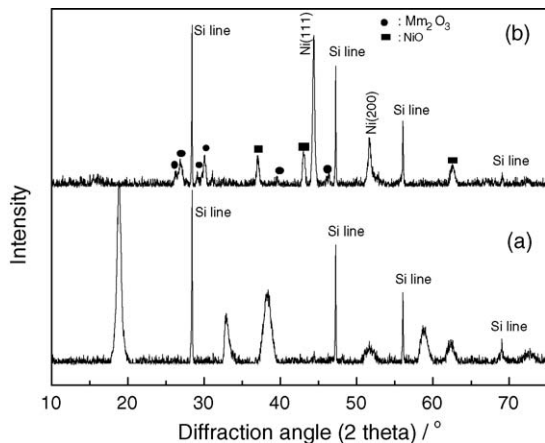


Fig. 3. XRD patterns of positive (a) and negative (b) electrodes after 60-day overcharge at a 0.2C rate using Cu $K\alpha_1$ radiation (1.54056 Å); silicon is used as standard lines.

In our case of long-term overcharge (60 days), however, we observed the formation of two oxides (misch-metal oxide and nickel oxide) in the negative electrodes. The formation of these metal oxides was probably relative to side reactions of oxidation/corrosion happening on the negative electrodes under the conditions of continuous O_2 -diffusion supply, especially in the case of using a less electrolyte (see in the Section 3.3). These oxides formed on the metal hydride electrodes resulted in surface passivation of metal hydride and reduction of hydrogen storage capacity. Consequently, we observed larger polarization of NiMH cells during charge–discharge processes and deterioration of capacity-rate performance.

3.2. High temperature performance

In applications of EV or HEV, fast charge–discharge and poor thermal management of battery stack require that the NiMH batteries must run in a wide-temperature range of 0–60 °C. Fig. 4 presents the performance of sub-C NiMH cells at various temperatures. It could be seen that the electrochemical capacity decreased remarkably as the environmental temperature rose, in particular at temperatures of >50 °C. The performance degeneration is ascribed to the lower charge efficiency of NiMH cells at elevated temperatures. The charge curves at various temperatures are shown in Fig. 5. As seen, the charge curves at 22 °C had a relatively flat charge voltage in the first 5 h of charge time, and then the voltage started to rise rapidly and subsequently reached another flat near to the charge terminate. The quick rise of charge voltage near to the charge terminate indicates that the NiMH cell has been close to a full charge state and further charge mainly leads to evolution of oxygen gas on the positive electrode. When the operational temperature reached >50 °C, the quick rise of charge voltage near to the charge terminate disappeared. This indicated that the oxygen gas evolution accompanies with the charge process from the initial stage, leading to the low charge efficiencies. In the case of 60 °C, we found that the charge voltage was flat in the first 2 h of the charge processes and started down slightly afterward. This phenomenon could be related to oxygen gas evolution readily at temperature of 60 °C. The produced O_2 molecules then diffused to the negative electrode

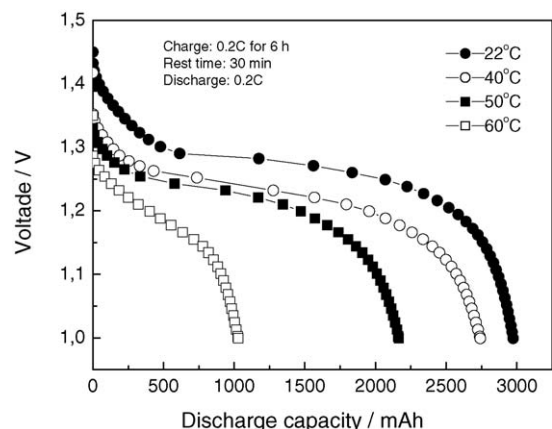


Fig. 4. Discharge curves of NiMH cells at different temperatures.

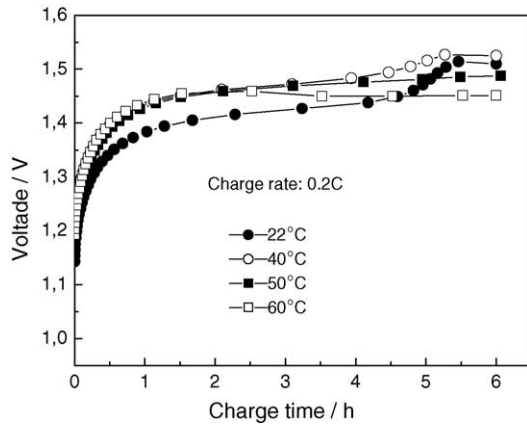


Fig. 5. Charge curves of NiMH cells at 0.2C rates and different temperatures.

where they were recombined into water with hydrogen stored in the MH electrodes. At the same time, they could oxidize the hydrogen storage materials and consequently lowered the cell voltage. These factors resulted in the low charge efficiencies and poor performances of NiMH cells at elevated temperatures. Therefore, how to improve the performance of NiMH cells at elevated temperatures is an important issue. The charge efficiencies of positive electrodes play an important role for improving the performances of NiMH batteries at elevated temperatures. Some studies [8–15] have indicated that addition of cobalt oxide, cobalt hydroxide or rare-earth element oxides benefits to improve the charge efficiency and suppress the oxygen evolution on positive electrodes at elevated temperatures.

The cycling stability of NiMH cells at elevated temperatures is also an important parameter for practical uses. Herein, we examined the cycling performance of NiMH cells at 50 °C under repeating charge–discharge using 0.2C rates. Fig. 6 gives the measured results. The NiMH cells exhibited good stability in the first 40 cycles. Afterwards, the loss in capacity increased. The elevated temperature and alkaline environment facilitate the misch-metal AB₅-type alloys to be corroded, particularly when the NiMH cells suffered from a 100% depth of discharge (DOD). To check the negative material, the NiMH cell after 100 cycles at 50 °C was opened in a 50% charged state. The phase

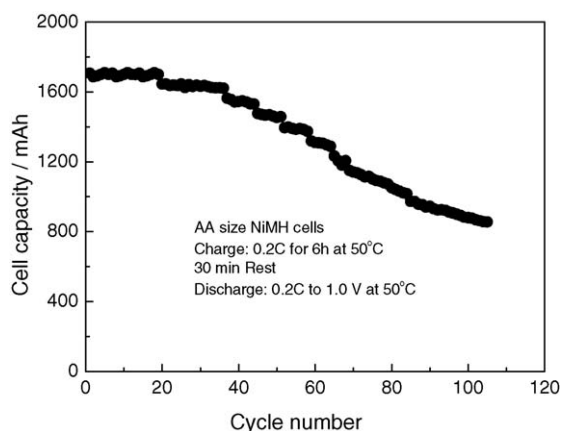


Fig. 6. Cycling stability of NiMH cells at elevated temperatures.

composition of negative materials was investigated. As shown in Fig. 7, the diffraction peaks of misch-metal hydroxide phase were detected. This indicates that the original single phase of AB₅-type hydride alloys has been decomposed after repeated cycles at elevated temperatures. The formation of misch-metal hydroxide resulted in reduction of the electrochemical capacity of hydrogen storage in the negative electrodes. However, it should be noted that the aging mechanism of negative electrodes in this section is different from that of long-term overcharge (60 days) at 22 °C, where two oxides (misch-metal oxide and nickel oxide) were found instead of misch-metal hydroxide. But, the real aging mechanism is more complex, and is still not clear so far.

For the positive electrodes, we also observed the strong diffraction peaks of gamma-phase nickel oxide hydroxide, as shown in Fig. 7. This implies that the beta-phase nickel oxide hydroxide has partly changed to a gamma phase. The formation of gamma-phase nickel oxide hydroxide is not desired in the NiMH cells because it has a relatively large volume of unit cell [16,17], which results in a large change of electrode volume during charge–discharge processes. The volume swelling and contract of the positive electrodes damage the conductive network between nickel hydroxide particles and substrates. In addition, more water was needed to intercalate into the gamma-phase nickel oxide hydroxide, leading to redistribution of electrolyte inside NiMH cells and drying out of membranes. Another negative effect of the formation of gamma-phase nickel oxide hydroxide is that both electrodes' capacity balance was shifted, and the charge reserve in the MH electrodes was reduced. These factors led to the acceleration of performance deterioration and reduction of NiMH cell lifespan.

3.3. Electrochemical behaviour of the opened NiMH cells

The sealed NiMH cells usually use a very limited amount of electrolyte. The alkaline electrolyte does not consume during charge or discharge processes from the theoretical points based on the battery reaction: $M + Ni(OH)_2 = MH + NiOOH$. During the practical uses especially in long-term overcharge

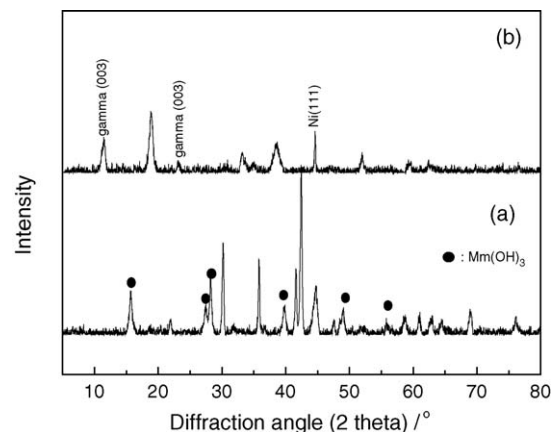


Fig. 7. XRD patterns of negative (a) and positive (b) electrodes after 100 cycles at 50 °C and 0.2C rates.

or under higher temperature environment, however, the alkaline electrolyte inside cells will be consumed due to corrosion/oxidization of hydrogen storage alloys or phase transformation of positive materials. In addition, the use of polyamide separator also facilitates the consumption of electrolyte due to formation of nitrogen species (hydrolysis) and their shuttle effect. If the electrolyte inside NiMH cells reduces, the internal resistance will rise and the charge efficiencies are lowered, leading to performance deterioration of NiMH cells. Fig. 8a shows the relationship of average charge voltage with cycling at temperatures of 50 °C. The charge voltage of sealed NiMH cells increases with increasing the cycle number. This implies that the internal resistance and polarization increased and the charge efficiency reduced with cycling. To check the influence of electrolyte, the tested cell was opened and put it into a container that has a sufficient height of 6N KOH electrolyte to cover the cell. Then, the charge and discharge experiments were resumed at the same conditions. The results are shown in Fig. 8b. For comparison, the charge–discharge curves of the sealed NiMH cell were also presented. As can be seen, the average charge voltage of the NiMH cell in the sealed state after 60 cycles was much higher than that before cycling. After opened the NiMH cell and put it into the electrolyte container, a significant reduction of the charge voltage and increase of discharge voltage were observed. The charge–discharge voltages are close to those before cycling in the sealed state. This indicates that

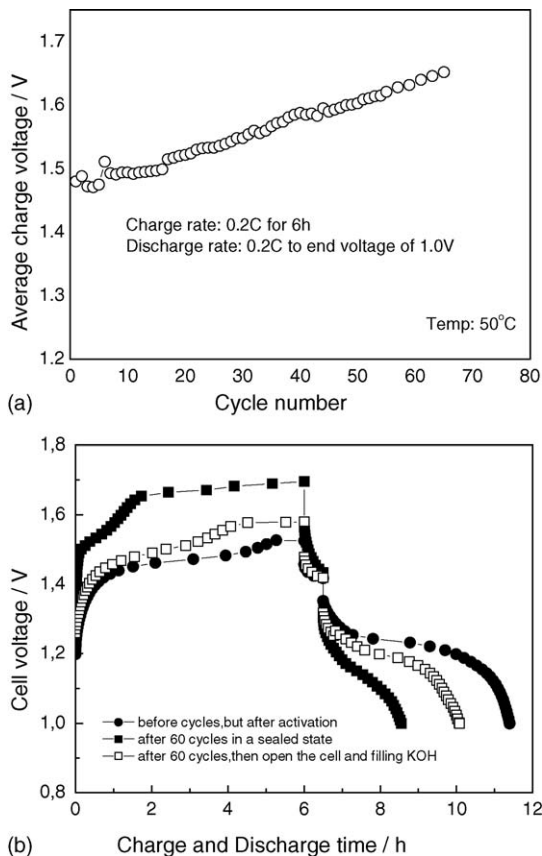


Fig. 8. The average charge voltage of NiMH cells (a). The charge and discharge curves of NiMH cells at various states at 0.2C rates and 50 °C (b).

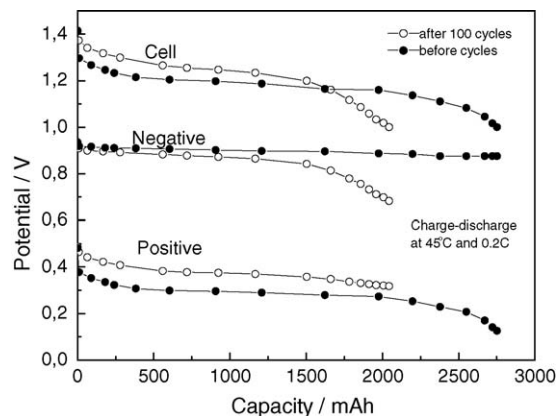


Fig. 9. Performance comparison of NiMH cells and both electrodes before and after 100 cycles.

the electrolyte inside the NiMH cells has been at least partly consumed after cycles at elevated temperatures and long-term overcharge due to oxidation/corrosion of negative materials or formation of gamma phase nickel oxide hydroxide on the positive electrodes.

Fig. 9 shows the discharge curves of cell and both electrodes. Before repeating cycles, the cell capacity is limited by the positive capacity. After 100 cycles, the cell capacity was determined by the negative capacity instead of positive, as shown in Fig. 9. This implies that the hydrogen storage capacity in the negative electrode has declined significantly due to oxidization and corrosion of metal hydrides. This test also indirectly proves our viewpoints that the oxidization and corrosion of negative materials occurred in the sealed state, particularly after cycling at elevated temperatures, leading to consumption of electrolyte and fade of cell lifespan.

4. Conclusion

The rechargeable NiMH batteries are expected to have applications as power sources in EV and HEV, and as backup power sources in the bank, hospital, military and telecomm equipments etc. The NiMH batteries used in such fields must suffer different operational conditions. In this paper, we investigated the influence of long-term overcharge at low rates and higher operated temperatures on cell performance. The main conclusions are as follows.

- (1) The NiMH cells can remain the capacity and capacity-rate performance after 1-month overcharge at a 0.2C rate. After 2-month overcharge, however, the capacity and capacity-rate performance were reduced. XRD examinations of both electrode materials showed that the main cause of performance degradation was due to the formation of metal oxides (misch-metal oxide and nickel oxide) in the negative electrodes.
- (2) The sub-C size NiMH cells in this work showed not good performances at temperatures of 50–60 °C. The performance degeneration was mainly due to the lower charge effi-

ciency at elevated temperatures. In order to keep good performance of NiMH cells at elevated temperatures, improvement of the charge efficiency of positive electrodes is a key issue. In this work, we also found that the metal hydrides in the negative electrode were decomposed into misch-metal hydroxide and the β -phase nickel hydroxide partly changed to γ -phase after repeating cycles at elevated temperatures. The oxidation/corrosion of negative materials and phase transformation of positive materials are supposed the main cause leading to fade of cell lifespan at elevated temperatures.

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References

- [1] J.D. Shepard, L. Brush, in: H.A. Frank, E.T. Seo (Eds.), Proceedings of the 13th Annual Battery Conference on Applications and Advances, Long Beach, California, Jan. 13–16, 1998, pp. 251–253.
- [2] S.R. Ovshinsky, S.K. Dhar, M.A. Fetcenko, D.A. Corrigan, B. Reichman, K. Young, C. Fierro, S. Venkatesan, P.R. Gifford, J. Koch, Proceedings of the 33rd Intersociety Energy Conversion Engineering Conference IECEC336/1-IECEC336/15, 1998.
- [3] H. Honda, K. Shiba, E. Shu, K. Koshiji, T. Murai, T. Nakamura, T. Masuzawa, E. Tatsumi, Y. Taenaka, H. Takano, ASAIO J. Am. Soc. Art. Int. Organs 45 (4) (1992) 339–343.
- [4] H. Kasahara, T. Yao, T. Suzuki, M. Masui, H. Konishi, EP 0926758 A1.
- [5] S. Venkatesan, D.A. Corrigan, M.A. Fetcenko, P.R. Gifford, S.K. Dhar, S.R. Ovshinsky, Proceedings of the 36th Power Sources Conference, 1994, pp. 196–201.
- [6] J.K. Erbacher, S.P. Vukson, in: H.A. Frank, E.T. Seo (Eds.), Proceedings of the 12th Annual Battery Conference on Applications and Advances, Long Beach, California, Jan. 14–17, 1997, pp. 9–15.
- [7] S. Venkatesan, D.A. Corrigan, M.A. Fetcenko, P.R. Gifford, S.K. Dhar, S.R. Ovshinsky, NASA Conference Publication, vol. 3228, 1993, pp. 61–66.
- [8] M. Onishi, T. Tanaka, M. Oshitani, JP 10064535 A2(1998).
- [9] R.D. Armstrong, G.W.D. Briggs, E.A. Charles, J. Appl. Electrochem. 18 (1988) 215.
- [10] M. Oshitani, H. Yufu, K. Takashima, S. Tsuji, Y. Matsumaru, J. Electrochem. Soc. 136 (1989) 1590.
- [11] K. Hong, Y.M. Lin, US Patent 20010012586 A1.
- [12] M. Oshitani, M. Watada, K. Shodai, M. Kodama, J. Electrochem. Soc. 148 (2001) A67.
- [13] Z. Mi, X.P. Gao, C.Y. Jiang, M.M. Geng, J. Yan, C.R. Wan, Electrochim. Acta 49 (2004) 3361.
- [14] X.-Y. Wang, J. Yan, Z. Zhou, J. Lin, H.T. Yuan, D.Y. Song, Y.S. Zhang, L.G. Zhu, Int. J. Hydrogen Energy 23 (1998) 873.
- [15] W.K. Hu, X.P. Gao, M.M. Geng, Z.X. Gong, D. Noréus, J. Phys. Chem. B 109 (2005) 5392.
- [16] W.K. Hu, D. Noréus, Chem. Mater. 15 (2003) 974.
- [17] D. Singh, J. Electrochem. Soc. 145 (1998) 116.