The Cycle Life Performance of MH-Ni Batteries for High Power Applications*

HOU Xian-lu[1*], *XUE Jian-jun*[1], *NAN Jun-min*[2], *XIA Xin-de*[1], *YANG Min-jie*[2], *CUI Yan*[3]
(1. Great Power Battery Co. Ltd. No. 1 Industrial Estate of Panyu, Guangzhou 511483, China;
2. South China Normal University, Guangzhou 510631, China;
3. School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China)

Abstract: Because of few environment pollution of Ni/MH battery compared with Ni/Cd battery, the demand of the high-rate cylinder nickel metal hydride battery is growing in high power applications, and the annual consume amount is above 5 hundred millions. But now some performances of Ni/MH battery can't meet the requirement for usage of electrical tools, especially the poor charge&discharge cycle life. So the development of high-rate nickel metal hydride battery with high performance is very important both in the scientific research and the market applications. The mainly contents in this paper are the study of effects on the charge&discharge cycle life and degradation of sub-C type Ni-MH power batteries. The change of impedance, temperature, and weight loss are investigated in the process of cycle life test. The cause for increase of battery internal resistance is also analysis by SEM method. We think increase of the internal resistance of battery is the main problem to the poor cycle life at high rate, besides the performance deteriorates of the electrode materials. Swell occurred on positive and pulverization on negative electrode at high rate current, make the pore space increased and the electrolyte depleted. The restrains of swelling and the increase of capacity of negative electrode can improve the performance of cycle life.

Key words: nickel metal hydride battery; cycle life; impedance; high power
CLC number: TM912.2　**Document code**: A　**Article ID**: 0529-6579 (2005) S2-0077-04

1　Introduction

In light of the ever increasing calls for environment preservation together with demands for the careful use of natural resources, industries in the automotive and energy sectors have been involved in the development of electric vehicle (EVs) and hybrid electric vehicle (HEVs)[1]. During the course of this development, the battery technologies have evolved dramatically. Visions for the battery of the future have shifted from a conventional lead—acid battery to high performance batteries. Among the high performance batteries, nickel metal hydride (Ni-MH) battery is superior in terms of performance, reliability and safety[2].

On the other hand, the demand battery for power tools is growing in whole world. Now, the annual consume amount is above 5 hundred millions. But a majority of which is nickel-cadmium battery. As it exhibits higher energy storage capabilities than nickel-cadmium at reasonable cost and does not show any safety issue. the nickel-metal hydride (Ni—MH) electrochemical system is predominant in a large range of portable appliances. One of the key points for the commercial success of Ni-MH batteries is life duration, especially for the power tools application.

2　Experimental details

2.1　Preparations of batteries

A hydrogen storage alloy powder having a composition of $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ (SANTOKU JAPAN) was used as the negative material of battery. Herein, Mm is a Misch metal composed of 45% by weight of Ce, 30% by weight of La, 5% by weight of Nd and 20% by weight of other rare earth elements. The alloy powder was immersed for 0.5 hour in an aqueous KOH solution having a specific gravity of 1.30 g/mL which had been heated at temperatures 80 ℃, then, washed with water and dried. The dried alloy powder was mixed with an aqueous solution containing 5% by weight of polyvinyl alcohol, and the mixture was kneaded to give a paste. This paste was applied on a substrate made of a punched metal, dried, and pressed to obtain a negative electrode comprising the hydrogen storage alloy.

The sub-C size batteries were manufactured having a

* 收稿日期：2005—07—10
基金项目：广州市经委重大专项基金资助项目（0612B2002044）
作者简介：侯宪鲁（1978 年生），男，工程师；E-mail：houxian-lu@163.com

nominal capacity of 3 A·h using the resulted negative electrode. The positive electrode of the cell was obtained by filling a paste comprising nickel hydroxide into a substrate made of a foamed nickel sheet by an ordinary method, and drying and pressing it. As a separator, polyamide non-woven fabric which had been subjected to a treatment to introduce sulfonic acid groups was used. An electrolyte was used which was prepared by dissolving LiOH at a concentration of 20 g/L into an aqueous KOH solution having a specific gravity of 1.30 g/mL, followed by sealing this case at the top thereof with a sealing plate.

The batteries first underwent five activation cycles by charging at 300 mA (0.1C) for 6 hours and discharging at 300 mA (0.1C) to 1.0 V. Four batteries which discharging capacity is 3 000 mA·h were tested.

2.2 Test condition

The cycle test condition A: The battery underwent 500 cycles by charging at 1500 mA (0.5C) for 2.5 hours or to $-\Delta V=10$ mV and discharging at 1500 mA (0.5C) to 1.0 V. The cycle test condition B: the battery underwent cycles by charging at 3000 mA (1C) to $-\Delta V=10$ mV and discharging at 30 A (10) to 0.8 V. All batteries were tested on BS9300 Series Recharge Battery Test Device (Guangzhou Kinte Industrial Co Ltd).

The temparature of battery at charge&discharge was recorded by the Hydra 2625 A data logger (FLUKE, US); the impedance and weight of battery were both tested during cycle life.

Both before cycling and after cycling, the positive electrode and negative electrode were characterized by the scanning electron microscopy (SEM). After cycling, the materials of positive and negative electrode were characterized by XRD using Cu Kα radiation.

3 Results and discussion

3.1 The cycling capacities

As Fig. 1 shown, the battery that tested according to condition A died at 120 cycles, while the cycle life of the battery which tested according to condition A attach to 500 cycles. There were some differences between two cycle life of battery according to different testing conditions. The cycle life of battery discharging at 10C is so short those doses not satisfy the actual needs. In order to know the cause, the impedance, temperature and weight of batteries were investigated.

3.2 The changing of impedance, temperature and weight

As shown in Fig. 2, the impedance of battery began to increase after 100 cycles. If the impedance would reach 10 mΩ, it was difficult that discharging of Sub-C size battery at 10C. Thus the high impedance was the key points for the degradation. During charge & discharge cycles, the electrolyte was redistributed among the positive and negative electrodes and separator due to an increase in surface area and pore volume and swelling of positive electrode. An extensive research on the electrolyte distribution during charge & discharge cycling of Ni/MH battery was carries out by Singh[3]. The electrolyte level of MH electrode did not apparently change during cycle on the whole, while that of positive and separator had an apparent change. Namely, the electrolyte level of the positive electrode increased and the electrolyte level of separator decreased. Therefore, it might be believed that the quick increase in ohmic resistance in the later stage of cycle would be caused by the separator had already dried out. After the degradation, the Ni/MH batteries were disassembled and it was found that the separator had already dried out. The corrosion of the alloy in the electrolyte consumed a small amount of water[4], which accelerated the drying out of the separator. While the over high cell internal pressure made the gas in battery release out, leading to the electrolyte losing. As shown in Table 1, the weight of batteries decreased little by little during charge&discharge cycle. And the weight losing rate of the battery A (charging at 1C and discharging at 10C) quicker than the battery B (charging at 0.5C and discharging at 0.5C).

The temperature of battery in charge &discharge cycle was a key factor that restricted the batteries' cycle life. Figure 3 shows the temperature change of battery at the course of charging, resting and discharging.

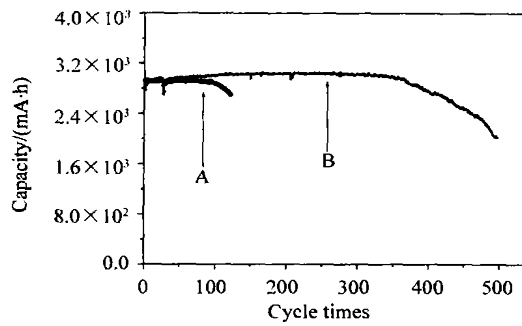

Fig 1 The cycling capacities of battery tested as different conditions

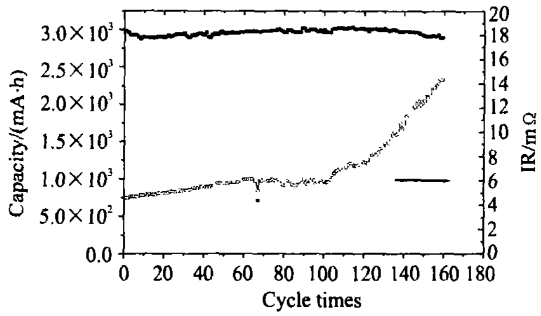

Fig 2 The change of internal resister of battery in cycle life

Tab. 1 The weight of batteries during charge&discharge cycle

Cycle times	Initial	50	100	150	200	250	300	350	400	450	500
Weight(A)/g	56.50	56.49	56.49	56.48	56.48	56.46	56.44	56.40	56.35	56.33	56.30
Weight(B)/g	56.73	56.68	56.62	56.60	—	—	—	—	—	—	—

In testing, the charging current is 3A (1C) and the discharging current is 30A (10C), and the resting time after charging is 20 minutes and the resting time after discharging is 30 minutes. In one charge&discharge cycle, the temperature of battery was above 50 ℃ for 20 minutes. The higher temperature leads to a decrease in the hydrogen storage capacity in the MH alloy because of the increase of the absorption-desorption plateau pressure. Furthermore, the higher temperature leads to an increase in the charge-transfer and mass transfer reactions at the MH electrode/electrolyte interface and in the bulk MH alloy.

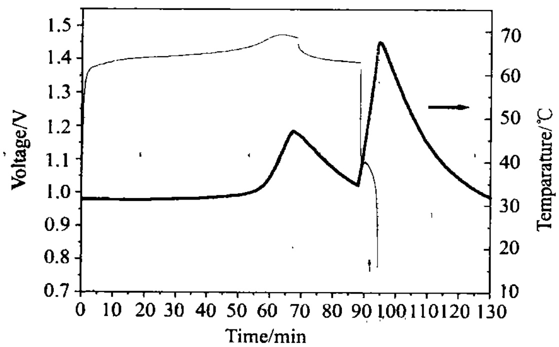

Fig 3 The curves of charging & discharging and temperature of battery in one cycle

Which may accelerate corrosion of MH alloy and the decomposability of water in electrolyte at the MH electrode surface. Thus, the higher temperature can increase the internal pressure and decrease the water in electrolyte in battery. Charging and discharging at high rate current can make the increase of battery impedance.

In a word, the higher temperature and large current can accelerate the increase of the battery impedance, which is the key factor for degradation of battery discharging at high rate.

3.3 The form of the positive electrode and negative electrode

Fig. 4 displays the morphologies of the positive and negative electrodes. After cycling, the both positive electrodes had swelled and the pore volume increased according to two testing conditions. But the negative electrode after 120 cycles discharging at 10C had split and the pore volume increased. While the negative electrode after 500 cycles discharging at 0.5C had been corrupted and lost its performance. Thus the degradation failure of the MH alloy leads to the degradation of battery in the charge&discharge cycle at low rate, but the materials wasn't failure when the batteries' life ended in the charge&discharge cycle at high rate.

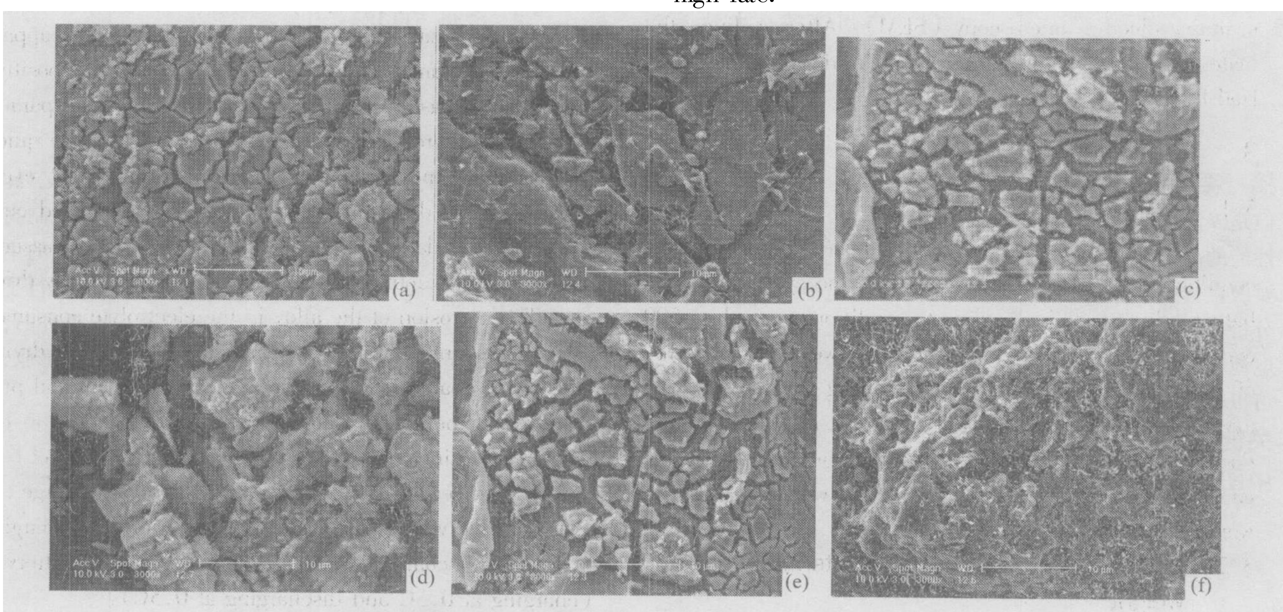

Fig 4 The SEM photos of the positive and negative electrodes:
(a) the positive electrode before cycling; (b) the negative electrode before cycling; (c) the positive electrode after 120 cycles discharging at 10C; (d) the negative electrode after 120 cycles discharging at 10C; (e) the positive electrode after 500 cycles discharging at 0.5C; (f) the negative electrode after 500 cycles discharging at 0.5C

As Fig. 5 shown, XRD spectra both displays the structural characteristics of the MH alloy was not change after charge &discharge cycle at high rate. So the materials are not the key point for the degradation of Ni-MH batteries in the cycles discharging at high rate current.

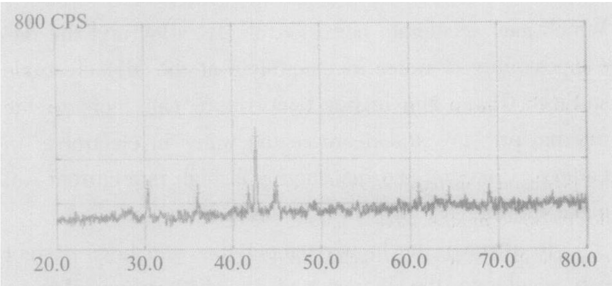

Fig 5 XRD spectra of the MH alloy after 120 cycles discharging at 10C

4 Conclusions

Ni/MH batteries have a poor charge & discharge cycle life at high rate discharging as compared with lower rate discharging. Both before cycling and after cycling, the positive electrode and negative electrode were characterized by SEM and XRD respectively. The materials did not fail after 120 cycles at high rate discharging. During charge & discharge cycles, in higher temperature, the electrolyte was redistributed among the positive and negative electrodes and separator due to an increase in surface area and pore volume and swelling of positive electrode. Which make the battery impedance increase and lead to the degradation of Ni-MH batteries. The restrains of swelling and the increase of capacity of negative electrode can improve the performance of cycle life.

References:

[1] LAURE L G, PATRICK B. Life duration of Ni-MH cells for high power applications [J]. Journal of Power Sources, 2002, 105: 134—138.

[2] TOMOHIKO I, NOBUYUKI S, JUNICH M, et al. Multi—step constant—current charging method for an electric vehicle nickel/metal hydride battery with high-energy efficiency and long cycle life [J]. Journal of Power Sources, 2002, 105: 6—12.

[3] SINGH D. Characteristics and effects of γ-NiOOH on cell performance and a method to quantify it in nickel electrodes [J]. J Electrochem Soc, 1998, 145 (1): 116—120.

[4] XU G R, TANG Y G. Study on the reasons of failure for MH/Ni battery [J]. Battery Bimonthly, 2003, 33 (4): 238—239.

高功率型镍氢电池的循环性能

侯宪鲁[1]，薛建军[1]，南俊民[2]，夏信德[1]，杨敏杰[2]，崔 燕[3]

（1. 广州市鹏辉电池有限公司，广东 广州 511483；
2. 华南师范大学，广东 广州 510631；
3. 天津大学化工学院，天津 300072）

摘 要：由于没有镉污染，对环境友好，用于高功率设备的镍氢电池的需求量增长很快，目前每年的需求量约为 5 亿只。但是镍氢电池的一些性能还不能完全满足电动工具的使用要求，突出表现在电池大电流充放循环寿命较差。因此，研制高性能的高倍率镍氢电池不仅具有重要的研究意义，也有很大的应用价值。本文研究影响 SC 型动力电池循环寿命衰减的主要因素，测量了在大电流循环过程中镍氢电池的内阻、温度及重量变化，并运用 SEM、XRD 对电池内阻升高的原因进行了分析。我们认为电池内阻升高是镍氢电池大电流循环寿命差的主要原因，分析发现在镍氢电池进行大电流充放电循环时，电池正极膨胀，负极微粉化，电池内部孔隙率增加，致使电解液干涸，电池内阻升高。通过增加负极容量，抑制正极膨胀，可以有效改进镍氢电池大电流充放时的循环性能。

关键词：镍氢电池；循环寿命；内阻；高功率
中图分类号：TM912.2