Regulation of the discharge reservoir of negative electrodes in Ni–MH batteries by using Ni(OH)$_x$ (x = 2.10) and γ-CoOOH

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ABSTRACT

In this paper, a novel strategy to regulate the discharge reservoir of negative electrodes in Ni–MH batteries is introduced by using Ni(OH)$_x$ (x = 2.10) and γ-CoOOH. The electrochemical measurements of these batteries demonstrate that the use of Ni(OH)$_x$ (x = 2.10) and γ-CoOOH can not only successfully regulate the discharge reservoir of negative electrodes in Ni–MH batteries to an adequate quantity, but also effectively improve the electrochemical performance of the batteries. Compared with normal batteries, the in-house prepared batteries with a lower discharge reservoir exhibit an enhanced discharge capacity, improved high-rate discharge ability, higher discharge potential plateau and superior cycle stability. The effect of Ni(OH)$_x$ (x = 2.10) and γ-CoOOH on the electrochemical performance of nickel electrode is also investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results suggest that the new method is simple and effective for cost reduction of Ni–MH batteries with improved electrochemical performance.

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1. Introduction

Nickel–metal hydride (Ni–MH) batteries have been intensively studied and widely used in today's power tools and portable applications because of their high specific energy power and specific energy density, fast charge and discharge capabilities, environment-friendly characteristics, long cyclic stability and good security [1–3]. Although Ni–MH batteries are commercially available, further research is still required to improve their power performance for applications in electric vehicles and hydride vehicles [4]. It is also necessary to reduce the cost of Ni–MH batteries in order to further expand their application fields, such as a replacement for nickel–cadmium (Ni–Cd) batteries in power tools, because the latter are cheaper but have cadmium pollution.

It is well known that in the sealed Ni–MH batteries, the capacities of the batteries are usually positive-electrode limited, the capacity of the MH negative electrodes is usual larger than that of the Ni(OH)$_2$ positive electrodes due to proper recombination reactions and for safety reasons. Generally, during the production process of Ni–MH batteries, the capacity ratio of positive and negative electrodes is usually adjusted at 1:(1.35–1.5) to ensure the sealing state and cyclic lifetime. It is noticed that the excessive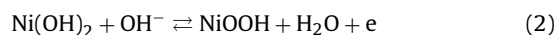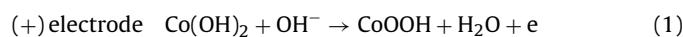 negative capacity has two primary functions: to provide a charge reservoir (R_{ch}) for preventing high pressure generated during charge and overcharge, and to provide a discharge reservoir (R_{dis}) for protecting the negative electrode from oxidation during forced over-discharge.

As illustrated in Fig. 1, the residual non-charged capacity of the negative electrode under fully charged condition of the positive electrode is referred to as the charge reservoir, and the residual charged capacity of the negative electrode under fully discharged condition of the positive electrode is referred to as the discharge reservoir.

Generally, the discharge reservoir is obtained in two ways:

(1) Cobalt and its compounds (CoO and Co(OH)$_2$ etc.) have been widely adopted as an addition to the nickel hydroxide electrode in many commercial Ni–MH batteries [5–8]. Intrinsically, these divalent cobalt oxides have no conductivities, but they can be converted into conductive β-cobalt oxyhydroxide by electrochemical oxidation in the process of initial charging, forming an effective conductive network.

For the positive electrodes mixed with CoO, Oshitani et al. [8] reported that CoO contained in the electrode dissolved in alkaline electrolyte to form blue Co(II) complex ion and then precipitated on nickel hydroxide particles as β-Co(OH)$_2$. After initial charging, such β-Co(OH)$_2$ converted to β-CoOOH. The reactions that occur on the positive and negative electrodes are as follows:

$$(+)\,\text{electrode} \quad \text{Co(OH)}_2 + \text{OH}^- \rightarrow \text{CoOOH} + \text{H}_2\text{O} + \text{e} \tag{1}$$

$$\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + \text{e} \tag{2}$$

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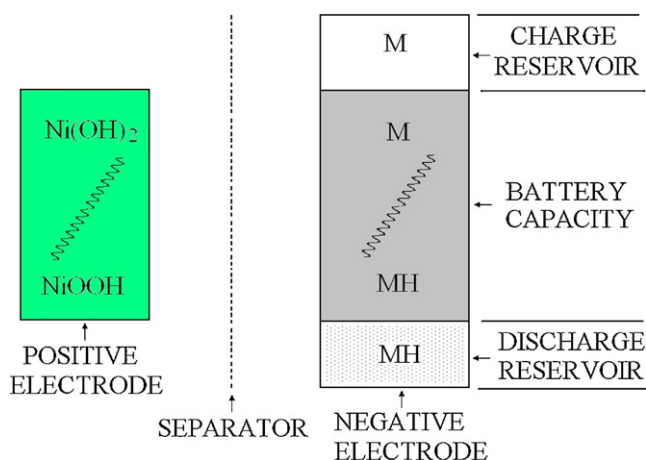
Fig. 1. The schematic diagram of the capacity distribution between the positive $Ni(OH)_2$ electrode and negative MH electrode of a Ni–MH battery.

$$(-)\,\text{electrode} \quad M + H_2O + e \rightleftarrows MH + OH^- \quad (3)$$

where M is the hydrogen-absorbing alloy. As CoOOH is considered to be a stable compound that cannot be reduced during usual discharge cycles, metal hydride generated during the formation of CoOOH is conserved and will not be used [8]. The electrical quantity stored in the negative electrode during this process becomes a part of the discharge reservoir (named as R_{dis-1}). In the case that CoO is used at a rate of about one tenth of the weight of nickel hydroxide, the R_{dis-1} is about one tenth of the capacity of the positive electrode.

(2) Reaction (2) is not a complete reversible reaction. The valence (oxidation number) of nickel in nickel hydroxide is initially 2 but rises to approximately 3.2 by charging of the battery, so that nickel hydroxide is changed to a nickel oxyhydroxide. A phenomenon occurs involving the suspension of discharge reaction at a valence of approximately 2.2 when nickel oxyhydroxide is converted back to nickel hydroxide during discharge. Accordingly, the negative electrode has always electricity left therein in an amount corresponding to a valence of 0.2. This remaining electricity makes no contribution to battery capacity. The non-discharged nickel oxyhydroxide thus remains to give another part of the discharge reservoir (named as R_{dis-2}) of about two tenths of the capacity of the positive electrode.

Accordingly, the Ni–MH battery has the total discharge reservoir of about three tenths of the capacity of the positive electrode. The adequate quantity of the discharge reservoir is at most about one tenth of the capacity of the positive electrode. Namely the capacity corresponding to about two tenths of the capacity of the positive electrode is excessive in the negative electrode. In other words, the prior art battery includes a specific quantity of the hydrogen storage alloy that does not contribute to charging and discharging. For a commercial reason, it is of great technological importance to regulate the discharge reservoir and reduce the surplus capacity of the MH electrode with the maintenance of the battery properties.

Recently, Li et al. [9] have reported a method to reduce the consumption of AB_5 alloy in a Ni–MH battery by using cobalt oxyhydroxide coated nickel hydroxide. However, the R_{dis-1} of only about

8% of the capacity of the positive electrode was removed from the metal hydride electrodes by this method and the R_{dis-2} obtained from the incomplete reversible reaction (2) was not taken into account. Hence, the goal of this work is to seek a new method to regulate not only the R_{dis-1} but also the R_{dis-2} to an optimal quantity and to decrease the consumption of alloy in MH electrode with improvement of the battery properties.

On the basis of our previous work [10–12], a new way to regulate the discharge reservoir of negative electrodes for Ni–MH batteries is introduced by using $Ni(OH)_x$ ($x = 2.1$) and γ-CoOOH. The results show that the discharge reservoir of negative electrodes for Ni–MH batteries has been successfully regulated to an optimum quantity. The electrochemical properties of the batteries with a lower discharge reservoir were examined systematically. The effect of $Ni(OH)_x$ ($x = 2.10$) and γ-CoOOH on the electrochemical performance of nickel electrode was also investigated by CV and EIS.

2. Experimental

2.1. Synthesis of $Ni(OH)_x$ ($x = 2.10$) and γ-CoOOH

Synthesis of the $Ni(OH)_x$ ($x = 2.10$) was carried out by a new electrolysis method as described previously [11]. $Ti/SnO_2 + Sb_2O_3/PbO_2$ electrodes and stainless steel were used as anode and cathode, respectively, and the ion exchange film was used as the separating membrane. The electrolyte was composed of 400 mL of 2 M KCl (pH = 10). 40 g spherical $Ni(OH)_2$ powder was added to the electrolyte under stirring at ambient temperature. After electrolysis for a period of time, the black $Ni(OH)_x$ ($x = 2.10$) suspension particles were formed. Then the obtained precipitate was filtered, rinsed with deionization water and dried in a 80 °C vacuum environment for over 6 h to produce the final product. The valence of nickel in nickel hydroxide was determined by iodometry and ethylenediamine tetraacetic acid (EDTA) complexometric titration [11]. The spherical β-$Ni(OH)_2$ used in this work is a commercial product (China, Henan Kelong Co. Ltd.).

The γ-CoOOH with a high valence of 3.40 was prepared as described in Ref. [12].

2.2. Preparation of electrodes and Ni–MH batteries

The paste nickel electrodes were prepared as follows: a mixture containing 92 wt.% $Ni(OH)_2$ and 8 wt.% CoO (the total weight is 6.4 g for electrode A) or a mixture containing 92 wt.% $Ni(OH)_x$ ($x = 2.10$) and 8 wt.% γ-CoOOH (the total weight is 6.1 g for electrode B) were mixed thoroughly and a milling procedure was needed to ensure the uniformity of the mixture. Followed by an addition of a proper amount of binders (PTFE and CMC) and distilled water, a homogenous paste with adequate rheological properties was made. The slurry was poured into a foam nickel sheet and dried at 80 °C in air. Afterwards, the positive electrodes were rolled to a thickness of 0.6 mm. The capacity of the $Ni(OH)_2$ electrodes was about 1500 mAh.

A commercial AB_5-type hydrogen storage alloy with a standard composition $MmNi_{3.4}Co_{0.7}Mn_{0.4}Al_{0.3}$ was used for the negative

Table 1
Three groups of batteries with different positive and negative electrodes.

Battery	Composition	Positive electrode (mAh)	Negative electrode (mAh)	The capacity ratio of positive and negative electrodes
A	92 wt.% $Ni(OH)_2$ + 8 wt.% CoO	1500	2100	1.4
B	92 wt.% $Ni(OH)_{2.1}$ + 8 wt.% γ-CoOOH	1500	2100	1.4
C	92 wt.% $Ni(OH)_{2.1}$ + 8 wt.% γ-CoOOH	1500	1800	1.2

electrode material. A slurry containing 94% alloy powders, 3% nickel powder and 3% PTFE binder was pasted into the foam nickel substrates, and then dried and compressed to obtain the MH electrodes. The capacity of the MH electrodes was about 2100 mAh and 1800 mAh.

A solution containing 6 M KOH, $50\,g\,L^{-1}$ NaOH and $15\,g\,L^{-1}$ LiOH and fluorinated polyolefin poriferous membrane (FS2216, Freudenberg, Germany) were selected as electrolyte and separator, respectively. After being sealed, the AA-type Ni–MH rechargeable batteries with a capacity of 1500 mAh were assembled. As seen in Table 1, three groups of batteries were assembled in this work.

2.3. Test of sealed Ni–MH rechargeable batteries and nickel electrodes

Charge/discharge measurements were conducted using a Land CT2001A battery performance testing instrument (China, Wuhan Jinnuo Electronics Co. Ltd). For activation, five charge discharge cycles at 0.1 C were performed, and the batteries were discharged to 1.0 V. The batteries were then charged at a 0.2 C rate for 7 h and separately discharged at respective 1, 2, and 5 C discharge current rates. The cut-off voltages were set as 1.0, 0.9, 0.8 V, respectively. In the subsequent charge–discharge cycling tests, the batteries were charged at a 1 C rate for 1.2 h, rested for 10 min, and then discharged at respective 1 and 5 C discharge current rates. The cut-off voltages were set as 1.0 and 0.8 V, respectively. The internal resistance of the batteries at 100% depth of discharge (DOD) was measured under alternative current (AC) of 1 kHz by using an internal resistance testing instrument.

R_{dis} tests of the batteries were performed as follows: the battery was charged at a 0.1 C rate for 14 h, rested for 20 min, and then discharged at a 0.2 C rate to a cut-off voltage of 1.0 V. Afterwards, the sealed battery was cut as an open cell, and immersed into the electrolyte in a beaker followed by a 20 min rest. The working electrode was discharged at 0.2 C to the cut-off potential of −0.6 V (vs. Hg/HgO) at 25 °C and the R_{dis} was then obtained.

Electrochemical tests of nickel electrodes A and B were performed in a three-compartment electrochemical cell at ambient temperature. Two nickel ribbon counter electrodes were placed in the side chambers and the working electrode was positioned in the center chamber. A Hg/HgO reference electrode was used via a Luggin capillary, which was made using the same alkaline solution for the working cell. CV and EIS were conducted on a Solartron SI 1260 impedance analyzer with a 1287 potentiostat interface. The CV test scan rate was $2\,mV\,s^{-1}$ and the cell potential ranged from 0.0 V to 0.8 V. For EIS, the impedance spectra were recorded at a 5 mV perturbation amplitude with a sweep frequency range of 10 kHz to 1 mHz.

3. Results and discussion

On the basis of the above discussion about the discharge reservoir of negative electrodes for Ni–MH batteries, the regulation of the discharge reservoir can be carried out in two aspects. On the one hand, R_{dis-1} is completely removed from the metal hydride electrodes by the use of γ-CoOOH, similar to that of Ni(OH)$_2$ coated with CoOOH [9]. For the batteries mixed with CoO, the R_{dis-1} equals the electric quantity consumed during the formation of CoOOH. Thus, the R_{dis-1} can be calculated from the formula as:

$$R_{dis-1} = \frac{(m_{CoO} \times 26.8 \times 1 \times 1000)}{74.9}$$

where m_{CoO} is the quantity of CoO in the positive electrode. On the other hand, R_{dis-2} is reduced to an adequate quantity of about one tenth of the capacity of the positive electrode by using pre-oxidized Ni(OH)$_2$. The valence of nickel in Ni(OH)$_2$ was pre-oxidized from 2
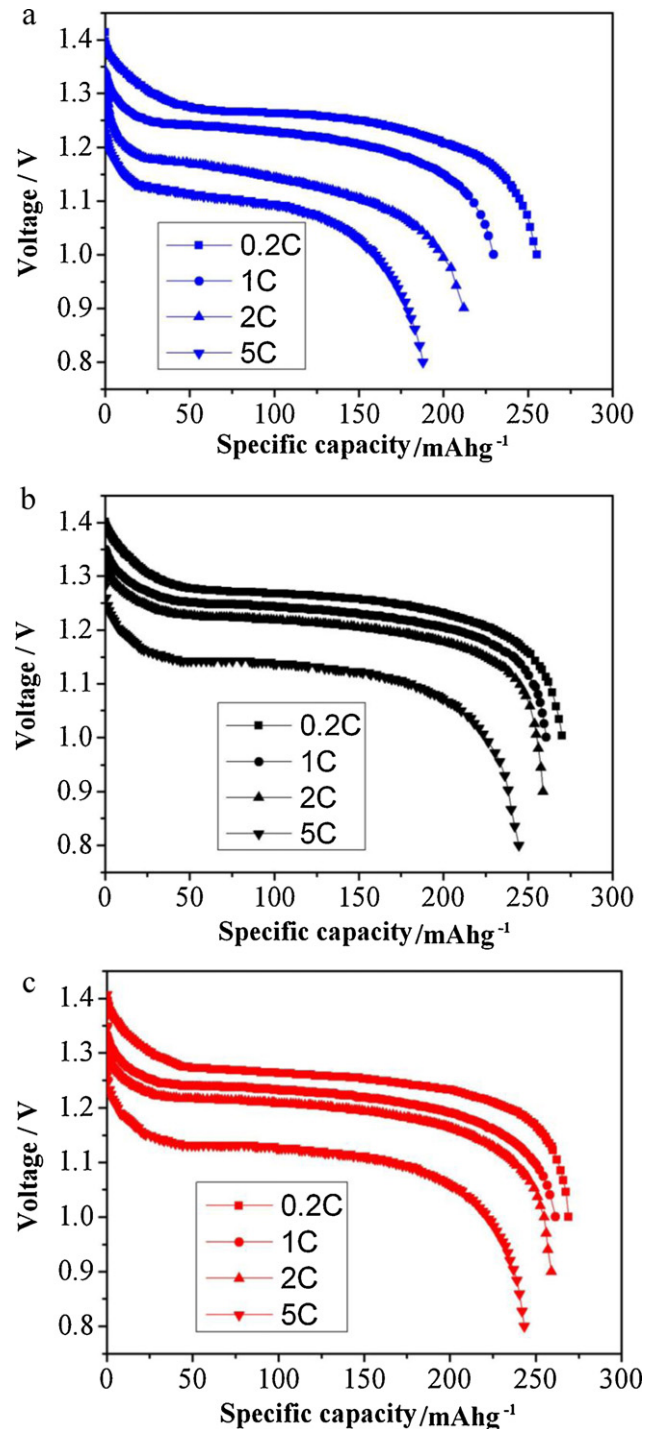

Fig. 2. Discharge curves of batteries A (a), B (b), and C (c) at different discharge rates.

to 2.1. The result of regulation of the discharge reservoir of negative electrodes for Ni–MH batteries A, B, and C is presented in Table 2.

Obviously, it can be seen that the batteries B and C show a lower discharge reservoir of 159 mAh and 144 mAh, whereas the values for the normal battery A is 419 mAh, indicating that the discharge reservoir of batteries B and C is successfully reduced to an adequate quantity of about one tenth of the capacity of the positive electrode by the use of Ni(OH)$_x$ (x = 2.10) and γ-CoOOH. Especially, battery C exhibits a remarkably lower surplus capacity of the MH electrodes than that of batteries A and B and holds an adequate quantity of

Table 2
The result of regulation of the discharge reservoir of negative electrodes for Ni–MH batteries A, B, and C.

| Battery	Surplus capacity of the MH electrodes (mAh)				
	Total[a]	Charge reservoir[b] (R_{ch})	Discharge reservoir (R_{dis})		
			Total	R_{dis-1}	R_{dis-2}
A	598	179	419	183	236
B	590	431	159	0	159
C	294	150	144	0	144

[a] Total reservoir (the surplus capacity of the MH electrode) = the capacity of the MH electrode- the discharge capacity of the Ni(OH)$_2$ electrode (0.2 C).
[b] Charge reservoir (R_{ch}) = total reservoir – discharge reservoir (R_{dis}).

charge reservoir as much as about one tenth of the capacity of the positive electrode.

Fig. 2 depicts the typical discharge curves of Ni–MH batteries A, B and C at different discharge rates. The experimental results are summarized in Table 3. Obviously, batteries B and C exhibit a larger discharge capacity and higher discharge potential plateau than battery A at the same discharge rate (0.2, 1, 2 and 5 C). As the discharge rate increases from 0.2 to 5 C, the specific discharge capacity of battery C decreases from 268.9 to 243.2 mAh g^{-1}, showing that at such a high discharge rate 90.4% capacity is retained. At a 5 C rate, batteries B and C show a higher discharge capacity of 244.5 mAh g^{-1} and 243.2 mAh g^{-1}, whereas the value for battery A is 187.8 mAh g^{-1}, indicating that the high-rate performance of batteries B and C is much better than that of battery A. Table 3 also shows that the specific capacity of Ni(OH)$_2$ of the electrode with CoO is obviously lower than the electrode with the same content

of γ-CoOOH. The utility of Ni(OH)$_2$ is greatly improved by substituting γ-CoOOH for normal CoO, which is in accordance with Ref. [12]. In addition, it can be seen that batteries B and C at 100% DOD exhibit a lower inner resistance of 11.9 and 11.7 mΩ, whereas the value for the normal battery A is 13.2 mΩ. This can be attributed to the preferable conductivity of the adding compounds in the positive electrode. It may also result from a decrease in the internal resistance of the MH electrode with the reduction of R_{dis}, since the electric conductivity of the hydrogen-absorbing alloy (M) is much higher than that of metal hydride (MH) [9]. Compared battery A with B, It can be concluded that the electrochemical performance improvement of the discharge capacity, high-rate discharge ability, and high discharge potential plateau is due to the addition of Ni(OH)$_x$ (x = 2.10) and γ-CoOOH.
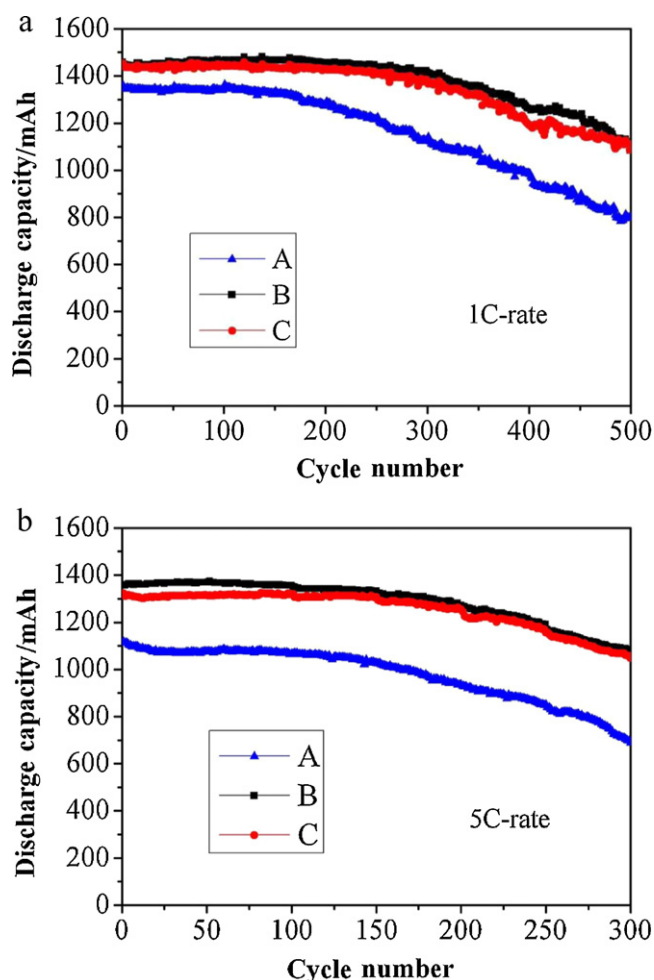
Fig. 3. Cyclic performance of batteries A, B, and C at 1 C and 5 C rates.
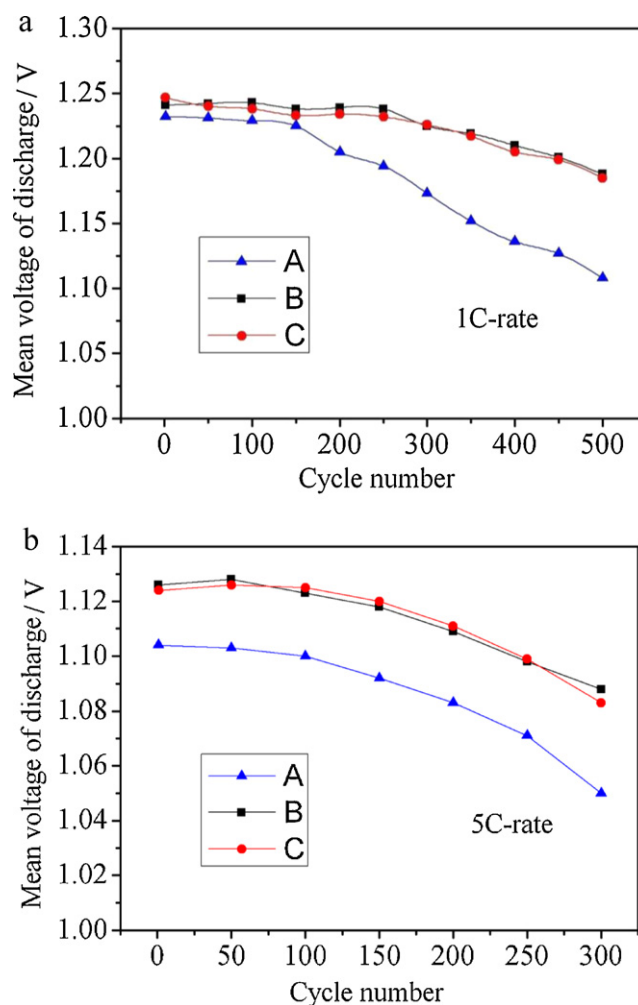
Fig. 4. Variation of the mean discharge voltage with the charge–discharge cycle at 1 C and 5 C rates.

Table 3
Performances of Ni–MH batteries A, B, and C at different current rates.

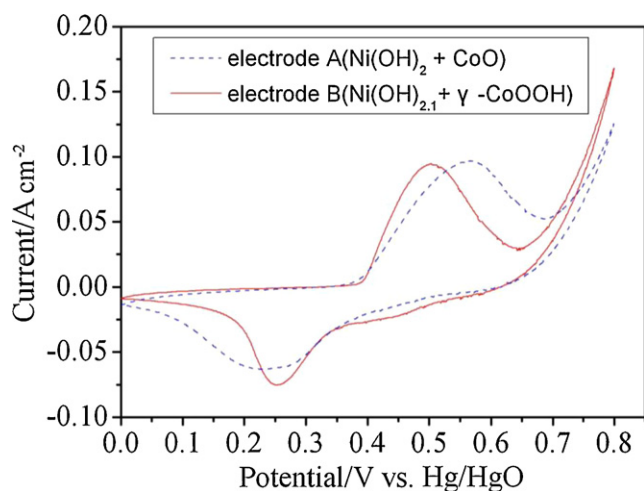| Battery	Battery capacity (mAh)				Specific capacity (mAh g^{-1})				Battery internal Resistance at 100% DOD (mΩ)
	0.2 C	1 C	2 C	5 C	0.2 C	1 C	2 C	5 C	
A	1502	1351	1251	1106	255.1	229.4	212.5	187.8	13.2
B	1518	1465	1453	1372	270.5	261.0	258.9	244.5	11.9
C	1509	1450	1442	1365	268.9	258.4	256.9	243.2	11.7

Fig. 5. CV curves of electrodes A and B at a scan rate of 2 mV s^{-1}.

Fig. 3 illustrates the cyclic performance of Ni–MH batteries A, B, and C at 1 C and 5 C rates. During these cycle processes, batteries B and C show a higher specific capacity and better cycling stability than battery A. The capacity fading of batteries B and C are restricted to a very low level after long-term cycling, while the capacity of battery A diminishes quickly although it contains more hydrogen storage alloy. This indicates that the performance deterioration of the Ni–MH battery during charge-discharge processes is mainly caused by the positive electrode which determines the battery capacity. In general, the capacity fading of the positive electrode for nickel based batteries is associated with the volume expansion or swelling of the Ni(OH)$_2$ electrode because of the formation of γ-NiOOH, which interferes with effective contacts between active material particles and damages the conductive network between
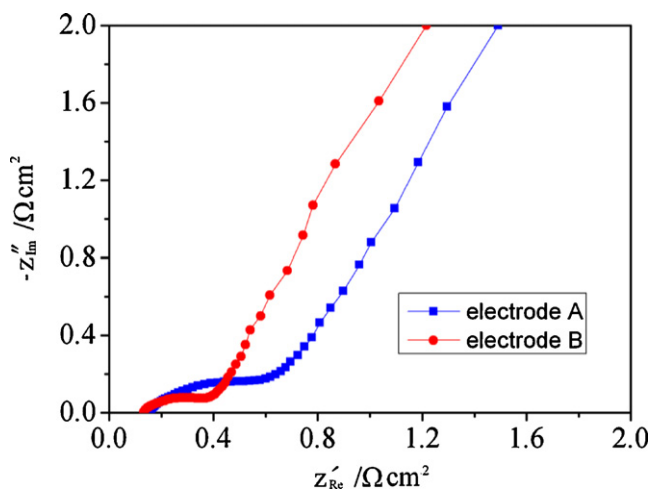

Fig. 6. Electrochemical impedance spectra of electrodes A and B.

Ni(OH)$_2$ particles and substrates [13,14]. To quantitatively characterize the cyclic stability of the batteries, the deterioration rate (R_d) is used, where R_d is equal to $(C_m - C_i)/C_m$ (C_m: maximum capacity; C_i: capacity at a certain cycle). As seen in Fig. 3, the R_d at the 500th cycle (1 C) for batteries A, B, and C are 41.21%, 25.94% and 24.33% and the R_d at the 300th cycle (5 C) are 38.21%, 21.56% and 20.80%, respectively, which indicates that batteries B and C have much better cyclic stability and higher discharge capacity than battery A. Especially, battery C exhibits excellent electrochemical performance, though the capacity of its negative electrode is reduced compared with that of batteries A and B. Moreover, the high power performance of Ni–MH batteries not only depends on the high-rate discharge current, but also depends on the working voltage. High mean discharge voltage means higher discharge potential and more energy that the batteries can store and release [4].

Fig. 4 compares the mean discharge voltage curves of batteries A, B, and C at 1 C and 5 C rates. As shown in Fig. 4, the addition of Ni(OH)$_x$ ($x = 2.10$) and γ-CoOOH to the positive electrode has greatly enhanced the mean discharge voltage, especially at a high discharge rate. Consequently, the overall electrochemical performance of batteries B and C with a lower discharge reservoir is obviously superior to battery A. All the results illustrate that using Ni(OH)$_x$ ($x = 2.10$) and γ-CoOOH can not only effectively enhance the cycling stability, but also remarkably extend the lifespan of the Ni–MH battery at a high discharge rate.

In order to further confirm the effect of Ni(OH)$_x$ ($x = 2.10$) and γ-CoOOH on the electrochemical performance of nickel electrodes, the electrochemical performance of electrode B (mixed with 92 wt.% Ni(OH)$_{2.1}$ + 8 wt.% γ-CoOOH) is further investigated in comparison with electrode A (mixed with 92 wt.% Ni(OH)$_2$ + 8 wt.% CoO) by CV and EIS.

The cyclic voltammograms of electrodes A and B after full activation with a scan rate of 2 mV s^{-1} are illustrated in Fig. 5. The features of the voltammograms are tabulated in Table 4. Obviously, the oxidation potential peak of electrode B shifts to a more negative position at 504 mV and the reduction potential peak moves to a more positive site at 262 mV in comparison with that of electrode A, corresponding to a higher discharge potential plateau on the discharge curves for electrode B shown in Fig. 2. Generally, the average of the cathodic and anodic peak potentials (E_{rev}) can be taken as an estimate of the reversible potential for nickel electrodes, and the potential difference ($\Delta E_{a,c}$) between the anodic (E_a) and cathodic (E_c) peak potentials is a measure of the reversibility of the redox reaction [15,16]. The experimental data show that the redox reactions are quasi-reversible for both electrodes, as indicated by the relatively large $\Delta E_{a,c}$. However, the $\Delta E_{a,c}$ of electrode B is only 242 mV, which is smaller than that of electrode A. This indicates that the charge and discharge processes of electrode B are

Table 4
Potential values of CV features for electrodes A and B.

Electrode	Potential (mV)			
	E_a	E_c	$\Delta E_{a,c}$	E_{rev}
A	246	553	307	399
B	262	504	242	383

more reversible, and therefore more active material can be utilized during these processes, which accords with the charge–discharge results shown in Fig. 2.

Fig. 6 demonstrates the electrochemical impedance spectra for electrodes A and B at steady state. The impedance spectra of both electrodes display a depressed semicircle resulting from charge transfer resistance in the high-frequency region, and a slope related to Warburg impedance in the low-frequency region [17,18]. The impedance of electrode B is much smaller than that of electrode A, which implies that the electrochemical reaction on electrode B proceeds more easily than on electrode A. This is in agreement with the results of the above CV testing.

On the basis of these facts, it can be concluded that $Ni(OH)_x$ ($x = 2.10$) and γ-CoOOH is a key factor for improving the electrochemical performance of the Ni–MH battery, such as the discharge capacity, high-rate discharge ability, and cycle stability. The results also illustrate that using $Ni(OH)_x$ ($x = 2.10$) and γ-CoOOH can not only regulate the discharge reservoir of the negative electrode to an adequate quantity, but also enhance the cycling stability and extend the lifespan of the Ni–MH battery at a high discharge rate. In other words, the new method makes it possible to provide a battery with excellent electrochemical properties, which will not be deteriorated by the reduction in the discharge reservoir, and helps the battery hold an adequate quantity of charge reservoir.

4. Conclusion

The surplus capacity of the MH electrodes in Ni–MH batteries was successfully reduced by the use of $Ni(OH)_x$ ($x = 2.1$) and γ-CoOOH. The electrochemical measurements of the prepared batteries demonstrate that $Ni(OH)_x$ ($x = 2.1$) and γ-CoOOH can not only successfully regulate the discharge reservoir of the negative electrodes in Ni–MH batteries to an adequate quantity, but also effectively improve the electrochemical performance of the batteries. The batteries with a lower discharge reservoir exhibit a high discharge capacity, enhanced high-rate discharge ability and improved cycle stability. Therefore, it is believed that the new method is promising and effective for cost reduction and electrochemical performance improvement of alkaline rechargeable Ni–MH batteries.

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