

Electrochemical investigation on nanoscale CoO as additive to the positive electrodes for Ni/MH rechargeable batteries

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Received 27 March 2006; received in revised form 22 May 2006; accepted 23 May 2006

Available online 10 July 2006

Abstract

The addition of CoO to the positive electrodes of Ni/MH rechargeable batteries provides excellent performance in terms of specific capacity and mean discharge voltage. CoO increases remarkably the active material utilization due to the formation of CoOOH conductive network. In this paper, an extensive study is focused on the addition of nanoscale CoO to the positive electrodes for Ni/MH batteries in comparison with usual submicron CoO particles. The electrochemical impedance spectroscopy is performed to reveal the advantages of nanoscale CoO to the electrodes. The results indicate that both the ohmic resistance of the electrode and the impedance of the electrochemical reaction decreased in the case of adding nanoscale CoO. Further study by charge–discharge cycling shows that the electrodes with nanoscale CoO have higher discharge capacity and higher mean discharge voltage, and the batteries with such electrodes present enhanced high-rate discharge capability.

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Keywords: Electrode materials; Nanostructured materials; Electrochemical reactions; Electrochemical impedance spectroscopy

1. Introduction

Cobalt oxide (CoO) is regarded as a necessary additive to the positive electrodes of nickel–metal hydride (Ni/MH) batteries. The active material β -Ni(OH)₂ is a kind of semi-conductor and its poor conductivity leads to a limited exchange current density, which handicap the utilization rate of β -Ni(OH)₂ and high-rate discharge ability of the nickel–metal batteries [1–3]. CoO adding to the positive electrodes dissolved in alkaline electrolyte to form blue Co(II) complex ion and then precipitated on β -Ni(OH)₂ particles as β -Co(OH)₂ while standing. After charging, such β -Co(OH)₂ converted to conductive β -CoOOH. The conductive network of β -CoOOH shortens the ‘ring path and the exchange current density is greatly improved [4,5]. It has been proved that the batteries with CoO in the positive electrodes had higher specific capacity, higher mean discharge voltage and better high-rate discharge performance [6].

The scales of the usual submicron CoO used in nickel–metal hydride batteries distribute from 0.1 to 0.5 μ m. These uneven

particles are not so dispersive when mixed with active material β -Ni(OH)₂, which handicap the formation of an integrated β -CoOOH conductive network. Nowadays researchers dedicate to synthesizing nanometer materials by reason of their tiny sizes and their unique characters such as abundant surface area. In this work, nanoscale CoO particles were synthesized by decomposing of CoCO₃ nanorods. The performance of the positive electrodes with nanoscale CoO were studied compared with those with usual submicron CoO in order to investigate the applicability of nanoscale CoO to the sealed Ni/MH batteries.

On the other hand, electrochemical impedance spectroscopy (EIS) technique is extensively used to reveal the electrode process kinetics and to investigate its surface reactions. Many EIS studies on Ni/MH batteries have been reported [7–9] and the results showed that the decrease in discharge capacity was due to the deactivation of the surface, which leads to an increase in the charge-transfer resistance of the battery. In this work, EIS of two groups of positive electrodes were measured to reveal the advantages of nanoscale CoO to the electrodes. In addition, the effect of the nanoscale CoO on the rate discharge capability was investigated based on the measurement of the sealed batteries at different discharge rates.

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2. Experimental

CoCO₃ nanorods were synthesized by the liquid deposition method. 0.1 M Na₂CO₃ and 0.1 M Co(NO₃)₂ solution, which were individually dissolved in distilled water, mixed under a rotary speed of 4000 rpm/min and reacted fully for about 30 min to form CoCO₃ deposition. Thus-prepared CoCO₃ nanorods were put into the sealed chamber of an airtight furnace equipped with a manometer and a vacuum pump. The CoCO₃ nanorods decomposed to nanoscale CoO particles when the chamber temperature was maintained at 400 °C. To accelerate the reaction rate, the decomposed CO₂ was extracted out by the vacuum pump every 10 min. The CoCO₃ nanorods and the nanoscale CoO particles were characterized by X-ray diffraction (XRD, Thermo X' TRA X-ray diffractometer with Cu Kα₁ irradiation) and transmission electron microscope (TEM, Philip 200 UT).

Two groups of positive electrodes of Ni/MH batteries were prepared by paste methods. One group is with 8 wt.% as-prepared nanoscale CoO; the other is with 8 wt.% usual submicron CoO provided by Ningbo Yanmen Corporation. These positive electrodes were tested in three-compartment systems with Hg/HgO reference electrodes and nickel counter-electrodes. The electrolyte was a solution of 6 M KOH. The charge–discharge measurement was conducted with a cell-performance testing instrument (DC-5). The simulated batteries were charged at 0.1 C for 12 h and discharged at 0.1 C to a limited voltage of 0.1 V. The EIS were measured after the fourth charge–discharge cycle when the electrodes were activated fully. The measurement was made at 20% state of charge (SOC), using a CHI-60 electrochemical analyzer. The voltage vibration amplitude of EIS measurement was set as 5 mV and the frequency range was set from 10⁵ to 10⁻² Hz.

These two groups of positive electrodes, together with a commercial AB₅-type hydrogen storage alloy (Mm(Ni_{3.4}Mn_{0.4}Al_{0.3}Co_{0.7})) as the negative electrode material, were sealed to fabricate Ni/MH batteries with designed capacities of 2200 mAh. Before testing of the rate discharge capability, the sealed batteries were charged and discharged at 0.2 C-rate for five times for activation. In the subsequent tests, the batteries were charged at 1 C-rate for 1.2 h, together with 10 mV of potential fall as a termination condition, and then were discharged at 1, 3, 5 and 10 C-rate, respectively. The corresponding cut-off voltages were set as 1.0, 0.9, 0.8 and 0.7 V. We record the capacities as C_n (n = 1, 3, 5 and 10). Then the batteries were discharged at 0.2 C–1.0 V without charge and the remanent capacity was recorded as C_{0.2}. The rate discharge capability was evaluated by the formula C_n/(C_n + C_{0.2}).

3. Results and discussion

Fig. 1 shows a group of TEM images of CoO particles. As shown in Fig. 1(a), the CoCO₃ nanorods with diameters of about 110 nm and lengths of several microns decomposed to CoO nanoscale particles, which have diameters of 50–80 nm. An agitation process with a supersonic cleaner was necessary to get more dispersive nanoscale CoO particles (Fig. 1(b)). Fig. 1(c) shows a TEM image of usual CoO particles. The usual submicron CoO particles present diameters from 100 to 500 nm. These two kinds of CoO particles together with CoCO₃ nanorods are characterized by XRD, as shown in Fig. 2. From the XRD patterns, the CoCO₃ nanorods exhibit a hexagonal structure with parameters $a = 4.6673$ and $c = 14.9256$. While the nanoscale CoO particles decomposed from the nanorods present a cubic structure with parameter $a = 4.2677$, which is slightly smaller than the commercially CoO particles with parameter $a = 4.2651$.

The effects of the CoO sizes on the EIS of the electrodes are shown in Fig. 3. The both Nyquist plots in Fig. 3 can be divided into two parts. At high frequency the plots start as a semicircle, and followed with the frequency decrease they change to a straight line. It is well known that the semicircle reflects the electrochemical reaction impedance of the electrode and the intersection point of the semicircle with the axis reflects the

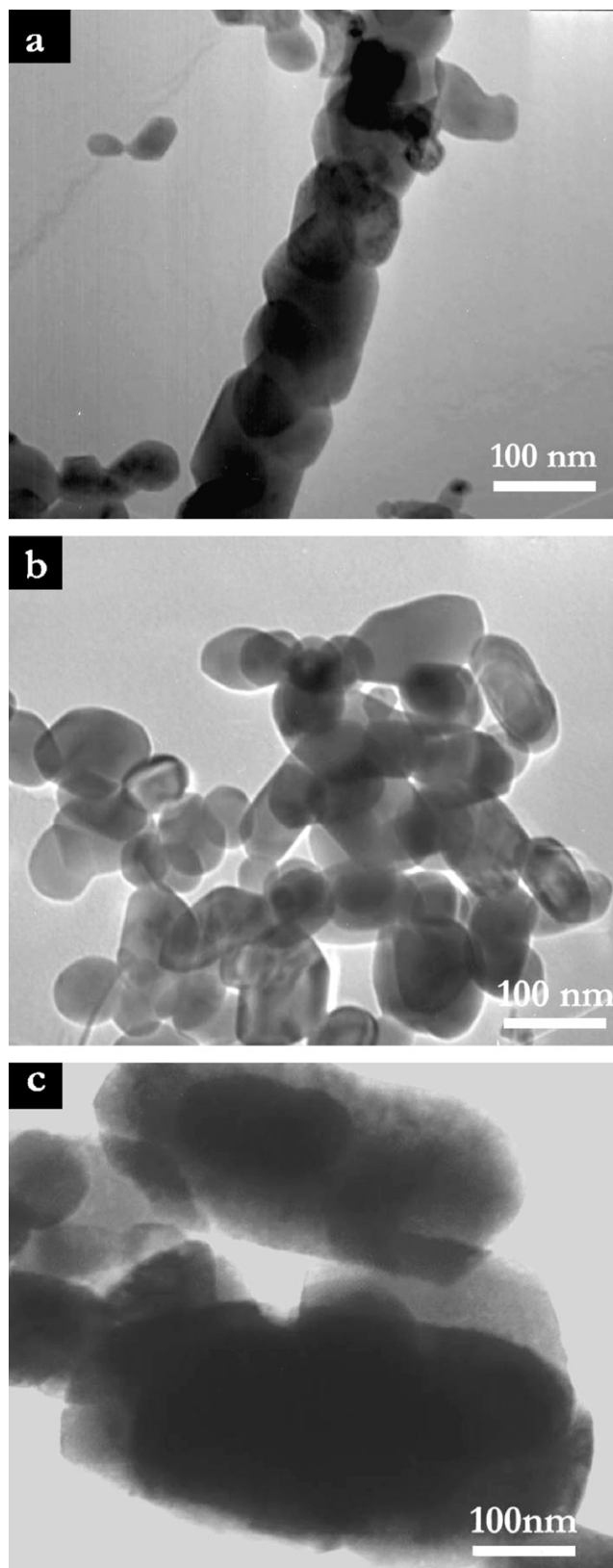


Fig. 1. TEM images of CoO particles: (a) a CoCO₃ nanorod decomposing to nanoscale CoO particles; (b) dispersive nanoscale CoO particles; (c) usual submicron CoO particles.

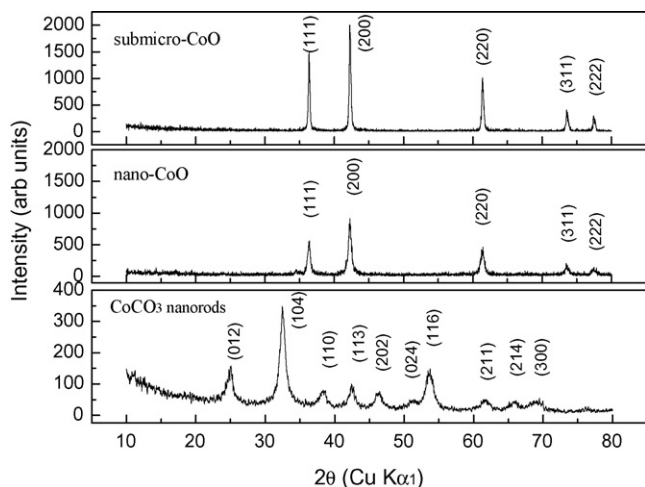


Fig. 2. Powder XRD patterns of CoCO_3 nanorods, nanoscale CoO and submicro-CoO.

total ohmic resistance, while the straight line indicates the diffusion of the electroactive species. As shown in Fig. 3, the plot for the electrode with nanoscale CoO has an advanced intersection and exhibits a smaller semicircle compared to the other plot. At the low frequencies, the linear parts of the plots are even parallel. In our opinion, an advanced intersection means lower total ohmic resistance and smaller diameter of the semicircle represents lower electrochemical reaction impedance. So the plots indicate that the electrode with nanoscale CoO has smaller ohmic resistance and smaller electrochemical reaction impedance.

The equivalent circuit of the $\text{Ni}(\text{OH})_2$ electrode, which can be expressed by Central Digital Computer code (CDC code) as $R_S(Q_C(R_T Z_W))$, is also shown in Fig. 3. R_S , Q_C , R_T and Z_W designate the total ohmic resistance of solution and electrodes, the capacitance of the double layer, the electrochemical reaction impedance and the Warburg impedance, respectively. These parameters can be calculated through the plots shown in Fig. 3 with ZView software. Some values are listed in Table 1 except the Warburg impedance. The Warburg impedance is determined

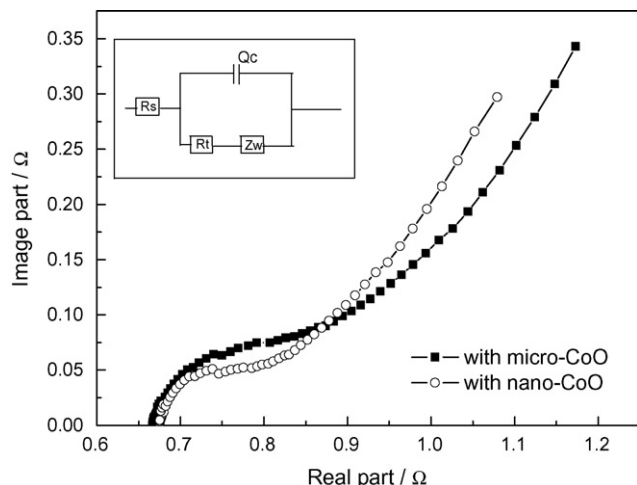


Fig. 3. EIS plots of the positive electrodes for Ni/MH batteries.

Table 1
EIS parameters of the positive electrodes for Ni/MH battery

Positive electrode	Solution resistance, R_S (Ω)	Charge-transfer resistance, R_T (Ω)	Capacitance of the double layer, Q_C (F)
With nano-CoO	0.67415	0.09173	0.18696
With micro-CoO	0.67833	0.10929	0.17148

by the proton transfer process, which is mainly related with the sizes of the $\text{Ni}(\text{OH})_2$. The nanoscale CoO has no effect on the Warburg impedance, so the straight-line parts of the plots in Fig. 3 are even parallel.

According to the reports on the EIS of $\text{Ni}(\text{OH})_2$ electrodes, the semicircle, which represents an electrochemical process occurring at the double layer of the electrode, must not be influenced by the conducting additive, but must be influenced by the actual surface area of the active material [10]. Based on this point, it is concluded that by addition of nanoscale CoO a finer conductive network covering all the $\text{Ni}(\text{OH})_2$ spheres has formed, which not only lowers the ohmic resistance of the electrode but also augments the actual reaction surface area of the active material, and decreases the electrochemical reaction impedance indirectly. In addition, the improvement of the actual reaction surface results in the increase of the utility rate of the active material $\text{Ni}(\text{OH})_2$.

The decay of the specific capacity of these two groups of electrodes is shown in Fig. 4. The specific capacity was calculated by dividing the battering capacity with the total electrode weight except the substrate. The electrode with nanoscale CoO has higher specific capacity. The nanoscale CoO particles replacing usual CoO were more dispersive when agitated in supersonic cleaner and could be mixed with $\beta\text{-Ni}(\text{OH})_2$ more homogeneously. The nanoparticles scattered among $\beta\text{-Ni}(\text{OH})_2$ spheres without effect on volume capacity of the electrodes. Compared with other additives like cobalt [12–14] and cobalt hydroxide [5], which transfer directly to $\beta\text{-CoOOH}$ during charge, CoO

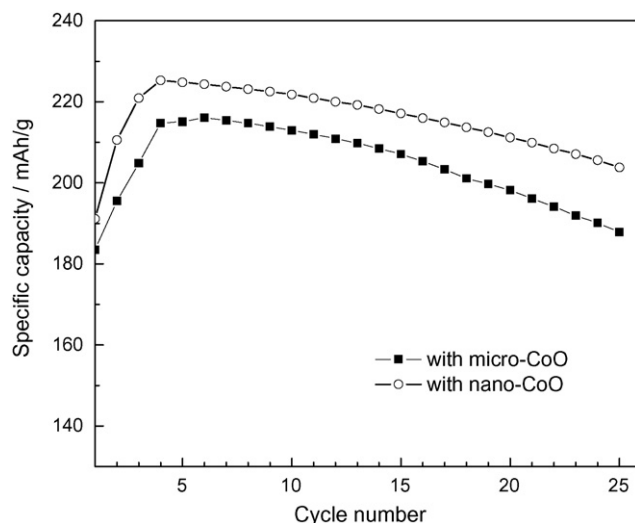


Fig. 4. Variation of specific capacity of $\text{Ni}(\text{OH})_2$ electrodes with nanoscale and submicron CoO at 0.1 C rate.

undergoes a dissolving process resulting in blue Co(II) complex ion in alkaline electrolyte. These Co(II) complex ions precipitate on β -Ni(OH)₂ particles as β -Co(OH)₂ while standing and then converted to β -CoOOH conductive network after first charging process. The standing procedure, as Oshitani reported [4], will last several days for CoO to dissolve thoroughly. The nanoscale CoO is of advantage to dissolve completely due to its tiny size. Therefore a more integrated conductive network can be fabricated after the first charge in the positive electrode with nanoscale CoO. This integrating network improved the real reaction surface and the utility of the active material β -Ni(OH)₂, thus the specific capacity was improved subsequently.

It also can be seen in Fig. 4 that the specific capacity of the electrode with usual CoO deteriorated more seriously than that with nanoscale CoO. It was reported that the open circuit voltage of the batteries is mainly related with the R_S in the equivalent circuit, while the deterioration of the capacity is mainly related with the R_T [11]. Lower is R_T of the electrode with nanoscale CoO, more slightly is the deterioration of the real reaction surface, and more slightly is the decay of the specific capacity.

Fig. 5 shows the typical charge–discharge profiles of the electrodes discharged at 0.1 C. The electrode with nanoscale CoO had lower charge voltage plateau and higher discharge voltage plateau than that with usual submicron CoO. It attributes to the homogenous conductive network transformed from nanoscale CoO. It is known that the voltage of the electrodes lies on total polarization, and the high total polarization leads to low load voltage. The integrated conductive network helps to remove the charge efficiently and diminish the polarization, which lowers the charge voltage plateau and improves the discharge voltage. Higher discharge voltage plateau means more energy the electrodes can release, and it helps to improve the power of the batteries.

The rate discharge capability of the sealed batteries with two kinds of positive electrode, respectively, was presented in Fig. 6. The battery with nanoscale CoO in the positive electrode exhibits rate capability of 95.4% at 1 C. It is slightly higher than the bat-

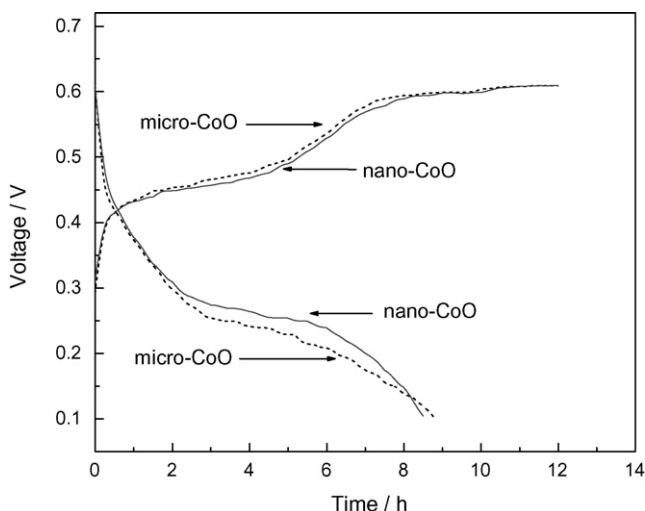


Fig. 5. Charge/discharge profiles of Ni(OH)₂ electrodes with nanoscale and submicron CoO at 0.1 C rate.

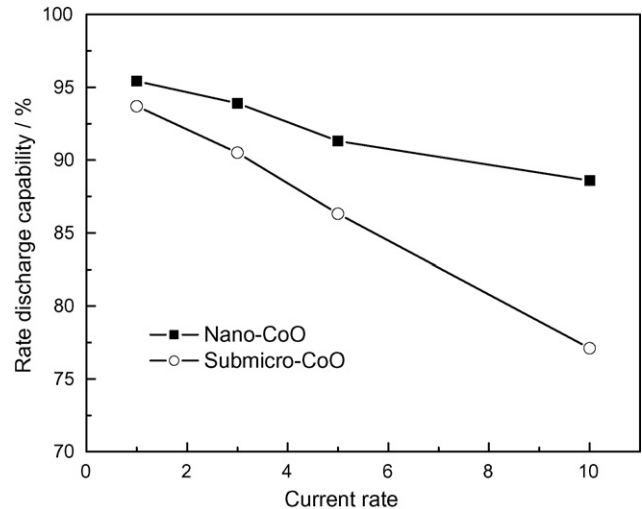


Fig. 6. Rate discharge capability of the two groups of batteries discharged at different current rates (1 C = 2200 mA).

teries with submicron CoO, which presents the rate capability of 93.7%. Followed with the increase of discharge rate, the rate capability of the two kinds of batteries both decreased. Compared to the batteries with nanoscale CoO, the batteries with submicron CoO deteriorated more seriously. Especially at 10 C the rate capability only remains 77% for the batteries with submicron CoO, which is remarkably lower than 89% for the other group of batteries.

Because two groups of batteries have the same negative electrodes, distinguish of the rate discharge capability attributes to the positive electrodes. As we know the discharge kinetics of Ni(OH)₂ electrode is contributed both from proton diffusion and from charge-transfer owing to the rapid discharge process [1]. According to the former analysis, a superior conductive network transformed from nanoscale CoO is formed as current collector between the active materials and the nickel substrate. Though the network has no effect on the proton diffusion process which depends mainly on the sphere sizes and the lattice structure of β -Ni(OH)₂, it assures the fluent transfer of charges. Therefore, the addition of nanoscale CoO improves the discharge kinetics under high-rate discharge condition and it is of advantage to the discharged capacity of Ni/MH batteries even at 10 C.

4. Conclusion

By adding dispersive nanoscale CoO instead of usual submicron CoO to the positive electrodes of Ni/MH batteries, a more integrated conductive network of β -CoOOH can be formed between the active materials and the substrate. As a result, the ohmic resistance of the electrode and the impedance of the electrochemical reaction are decreased. Thus-prepared Ni(OH)₂ electrode has higher specific capacity, high discharge voltage plateau and deteriorates more slightly. The sealed batteries with nanoscale CoO in the positive electrode exhibit a modified rate discharge capability. Compared with usual submicron CoO, the nanoscale CoO is better as additive considering the overall performance of the Ni/MH rechargeable batteries.

Acknowledgement

This work was supported by the Hi-Tech Research and Development Program of China (2003AA302420).

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