

Effects of carbon nanotubes on the high-rate discharge properties of nickel/metal hydride batteries

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Abstract

The sealed Ni/MH batteries with carbon nanotubes (CNTs) in the positive electrodes were assembled. The overall characteristics of Ni/MH batteries were investigated at different charge–discharge cycles at room temperature. The high-rate discharge performance of the Ni/MH battery was improved by the addition of CNTs in the positive electrode. Under high-rate discharge conditions, the batteries with CNTs added in the positive electrodes exhibited much better cycling stability, higher discharge voltage, and high-rate capability. The increase in internal resistance of the batteries with CNTs was lower than that of the batteries without CNTs during charge–discharge cycles. The addition of 0.5 wt.% CNTs was proved a desired amount to modify the batteries performance at the high discharge rates. Too much CNTs contributed no effect in the improvement of overall performance of the batteries.

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1. Introduction

The use of nickel–metal hydride (Ni/MH) batteries has spread quickly in many portable electronic equipments. Although Ni/MH batteries are commercially available, intensive research efforts still aimed to improve the energy density and stability of the batteries. Many studies of Ni/MH batteries nowadays focus on its use in electric tools, electric aeromodelling, electric vehicles (EVs) and hybrid vehicles. In such situations, the characteristics of the advanced battery under high-rate discharge conditions are undoubtedly the key factors for its use.

The capacity of Ni/MH batteries depends on the specific capacity of the positive electrode and the utilization of active material because of the positive electrode capacity limitation. The active material Ni(OH)₂ or NiOOH in the positive electrode is a semiconductor, which is different from the conductive hydrogen storage alloy of the negative electrode. There are relatively higher resistances among the active material particles, the electrolyte, and the substrates. Therefore, increased conductivity of the active material in the positive electrode is very important for improvement of the reliability, safety, and high-rate discharge properties of

the batteries on the basis of an optimized negative electrode. Different additives were used with the aim of improving the performance of the active materials, in terms of conductivity for positive electrode and to avoid the active materials shedding during cycling [1–6]. A properly amount of Co, CoO, Co(OH)₂, Ni, and conductive carbon black were added in the positive electrode as conductive agents, which enhance the conductive properties to some degree. The nickel hydroxide doped with cobalt was prepared according to a novel electrolysis [7]. It was reported that electroless cobalt depositing on the spherical nickel hydroxide particles have made contributions to the improvement of the performance of Ni/MH batteries [8]. But the electroless cobalt layers were found to dissolve and shed from the nickel hydroxide particles after a few high-rate charge/discharge cycles.

Carbon nanotubes (CNTs) have excellent mechanical properties with high elastic modulus of 1.8 TPa [9] and bending strength of 14.2 GPa [10], good tenacity [11], and good electrical conductivity [12–14]. Due to their nanometer size and many predominant properties, including highly accessible surface area, high electrical conductivity, chemical stability, and mechanical strength, it is suggested that carbon nanotubes are of good additives in the positive electrode of Ni/MH batteries.

In this study, the purified CNTs were added into the positive electrode, and the type-AA batteries were assembled. The influence of CNTs on the overall performance of Ni/MH

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batteries at high discharge current density was discussed in order to investigate the applicability of CNTs to sealed Ni/MH rechargeable batteries.

2. Experimental

2.1. Synthesis of carbon nanotubes

Multi-walled carbon nanotubes were synthesized by chemical catalytic pyrolysis of acetylene, in which $\text{Co}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ were employed as catalyst. An acetylene–nitrogen mixture ($\text{C}_2\text{H}_2:\text{N}_2 = 1:3$) was introduced into the quartz chamber at a flow rate of 600 ml min^{-1} at 923 K for 30 min. As-prepared CNTs were purified by immersing in a nitric acid for 48 h and then washed with de-ionized water. The diameter of the CNTs ranged from 20 to 50 nm.

In order to improve the dispersion of CNTs in the nickel hydroxide electrodes, the purified CNTs were mechanically ball milled for 8 h with a planetary ball mill machine in an aether liquid at a rotating speed of 430 rpm. The weight ratio of steel balls to purified CNT is 50:1. CNT samples were characterized by transmission electronic microscope (TEM, Philips 200 UT). As shown in Fig. 1, the CNTs had been shortened and dispersed after ball milling.

2.2. Preparation and test of sealed Ni/MH rechargeable batteries

$\beta\text{-Ni}(\text{OH})_2$, CoO, and Co powders were mixed together according a proper composition, followed by adding different amounts of CNTs (0.5, 1, and 2 wt.%) in the mixture. A

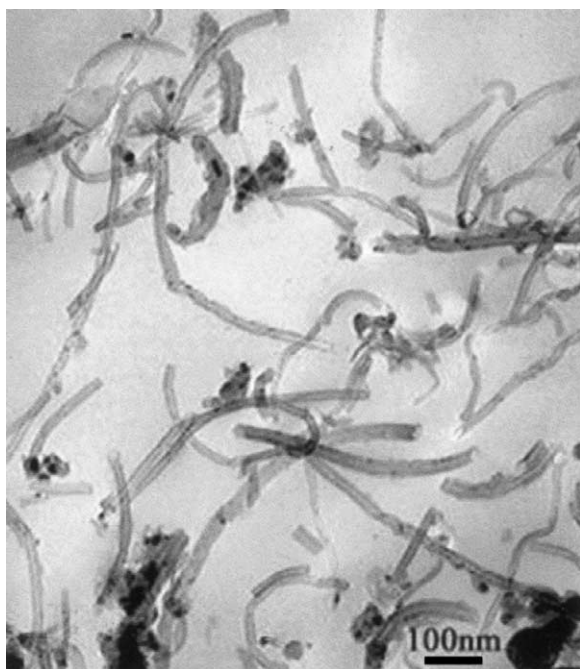


Fig. 1. A TEM image of CNTs after ball milling.

Table 1
Three-cycle activation process

Cycle	Charge rate (C)	Charge time (h)	Discharge rate (C)	Discharge time (h)
1	0.1	16	0.2	3.5
2	0.25	5.5	0.2	5.0
3	0.5	2.4	0.5	2.0

milling procedure is needed to assure the homogeneous of the mixture. Followed by a addition of properly amount of binders (PVA and CMC) and water, a homogeneously paste with adequate rheological properties was made. The foam nickel substrate was taken out from the paste bath and the paste was smeared into it. The mass of active material of the positive electrode was controlled by paste concentration. Afterwards, the positive electrodes were dried at 80°C and rolled to a thickness of 0.62–0.63 mm.

A commercial AB_5 -type hydrogen storage alloy with the standard composition $\text{Mm}(\text{Ni}_{3.4}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.7})$ was used for the negative electrode material. The negative electrodes were prepared by roll-pressing the alloy powder on a copper mesh to form its sheet with a thickness of 0.29–0.30 mm. The ratio of the capacity of positive and negative electrodes was about 1:1.6, that would assure the capacities of the batteries controlled by the positive electrodes. A solution of 6M KOH with 1 M NaOH and 0.5 M LiOH, was used as electrolyte, impregnating the electrodes and separator. The type-AA batteries with a design capacity of 1400 mAh (at 0.2 C discharge rate) were assembled. After the batteries were sealed, the activation process was conducted according to the conditions shown in Table 1. For comparison, a similar type of Ni/MH battery without CNTs in the positive electrode was also assembled.

In the charge–discharge cycle tests, the batteries were charged at 1 C-rate for 1.2 h (controlled by $-\Delta V = 10 \text{ mV}$). The batteries were discharged at 1, 3, 5, and 10 C-rate, respectively. The respective cut-off voltages of discharge were 1, 0.9, 0.8, and 0.7 V. There was 10 min of rest time between charge and discharge. The charge–discharge cycle tests of Ni/MH batteries were performed using a computer controlled cycling equipment (Guangzhou Qingtian BS-9365) at room temperature ($25 \pm 2^\circ\text{C}$). The internal resistances of the batteries were measured during the charge–discharge cycles when the batteries were at 100% DOD state.

3. Results and discussion

3.1. Cycle stability under high-rate discharge conditions

Fig. 2 shows the comparison of the cycle stability of batteries with different CNT contents in the positive electrodes under different discharge conditions. At 1 C discharge rate,

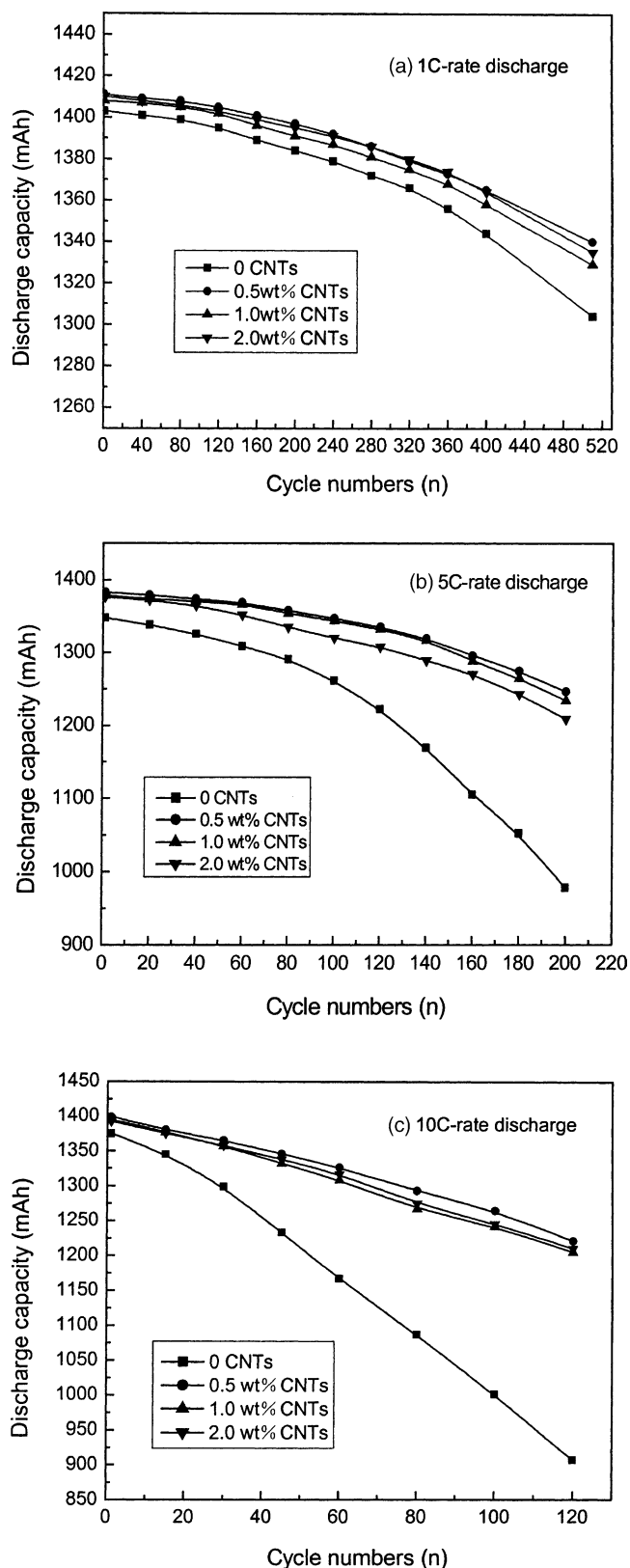


Fig. 2. Cycling stability of batteries with different CNT contents in the positive electrodes under different discharge rate conditions.

all the batteries exhibited good cycling stability, the batteries reached 98.1% capability after 200 charge–discharge cycles and 92.9% capability after 510 charge–discharge cycles. As shown in Fig. 2a, the batteries with CNTs added in the positive electrodes show a little better performance at the normal discharge rate. From Fig. 2b, there are obviously differences between the batteries with CNTs and without CNTs in the positive electrodes at 5 C discharge rate. After 200 cycles, the batteries with 0.5 wt.% CNTs in the positive electrode remained 89.5% discharge capability, while the batteries without CNTs remained only 72.6% discharge capability. At 10 C discharge rate, the batteries with CNTs also revealed superior cycling stability to the batteries without CNTs (Fig. 2c). These results indicated that the addition of CNTs to the positive electrode improved the cycling stability of Ni/MH battery at high-rate discharge significantly.

It is well known that during the charge and discharge process, the positive electrode is expanding and shrinking, which result in its lower mechanical strength, losing of the active material from the substrate, higher internal resistance, and capacity degeneration [15]. Contrast with other carbon materials, such as graphite and conductive carbon black, the volume of CNTs monomer is much smaller, the specific surface is much higher [16]. It is suggested that the dispersion of CNTs in the positive electrode is more homogeneously and effectively. The continuous conductive meshwork made by CNTs is of advantage to the stability of the β -Ni(OH)₂ electrode during charge and discharge procedures. Because of the highly mechanical strength and lowly expansion coefficient along the axial direction of the CNTs [9,10,17], the network fabricated by CNTs can also depress the expanding of the positive electrodes and avoid shedding of active material from the positive electrodes.

In addition to expanding and shrinking, the rising of temperature during high-rate charge and discharge process would induce an increase in internal resistance of the battery. Low internal resistance reduced the losing of energy during charge–discharge cycles and increased the charge–discharge efficiency. Fig. 3 shows the variation of internal resistance of batteries with different CNT contents in the positive electrodes at different discharge rates. It can be seen that the internal resistance of the batteries is all in the range of 13.3–13.8 m Ω , and the resistance differences of batteries with CNTs and without CNTs are not obvious before cycling tests. During the charge–discharge cycles, the increase in internal resistance was depressed when CNTs added in the positive electrodes. After cycling at high discharge rates, as shown in Fig. 3b and c, the resistance differences of the batteries with CNTs and without CNTs are more obviously. Because of the highly accessible electrode–electrolyte interface, the good electrical conductivity and the nanostructure of CNTs, enough tiny regions for current collection would form in the electrode. The efficiency of charge–discharge was enhanced accordingly, so the overcharged and overdischarged could be depressed to some degree. As known,

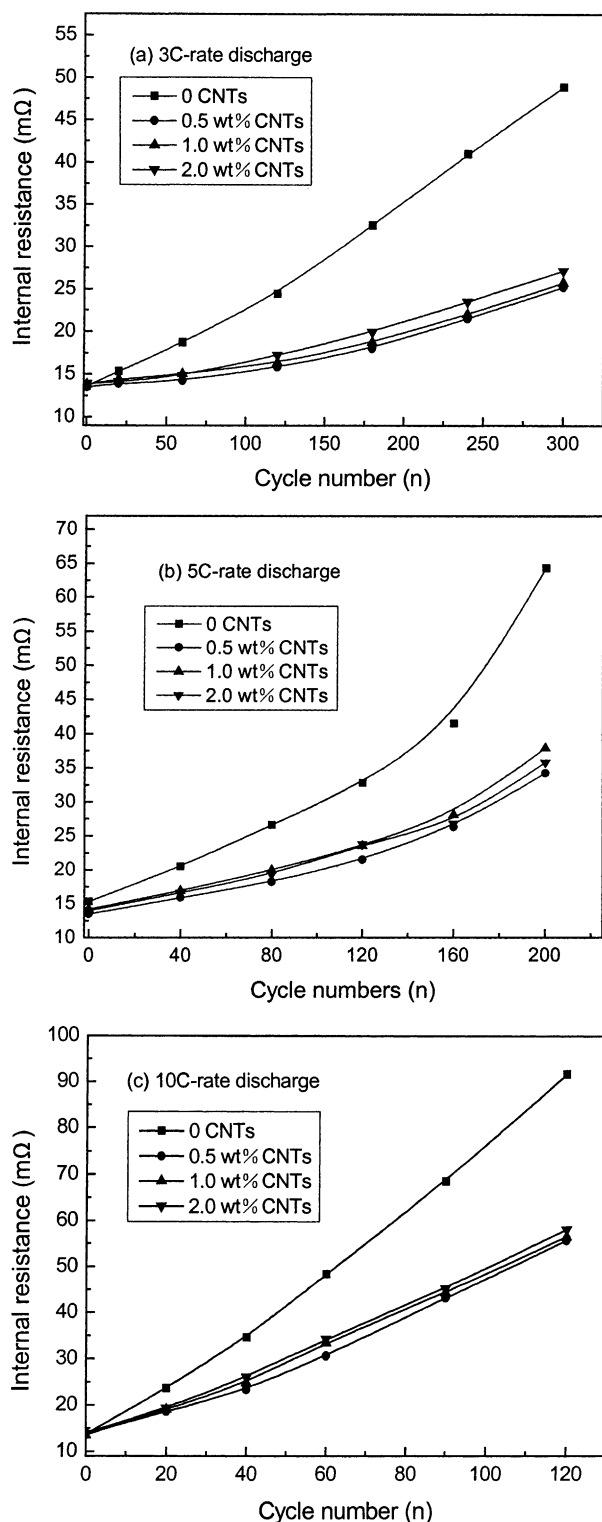


Fig. 3. Variation of internal resistance of batteries with different CNT contents in the positive electrodes under different rate discharge conditions.

O₂ evolved on the positive electrode when overcharged or charged with high-density current. The internal resistance of the Ni/MH battery also increased due to the oxidation of hydrogen alloys in the negative electrode. The addition

Table 2
Discharge middle voltage of batteries with different CNT contents in the positive electrodes

CNT contents (wt.%)	1 C-rate (V)	3 C-rate (V)	5 C-rate (V)	10 C-rate (V)
0	1.232	1.161	1.128	1.038
0.5	1.244	1.183	1.152	1.078
1.0	1.243	1.181	1.148	1.074
2.0	1.241	1.181	1.150	1.075

of CNTs in the nickel hydroxide electrodes increased the electrochemical reaction surface of the active particles and reduced the evolving of O₂. Thus the increase in the internal resistance for the Ni/MH batteries with CNTs was lower. As shown in Fig. 3, the batteries with 0.5 wt.% CNTs exhibit the lowest internal resistance at the same cycling tests, indicating that only a little amount of CNTs can modify the internal resistance.

3.2. Discharge potential analysis

Table 2 shows the discharge middle voltages of batteries with different CNT contents. The discharge middle voltages are the average data that observed at the first 30 charge–discharge cycles. The discharge middle voltage is an important parameter of the rechargeable batteries. Higher discharge middle voltage associates with higher discharge potential and better performance in discharging. As shown in Table 2, addition of CNTs in the positive electrode has enhanced the discharge middle voltage obviously, especially being discharged at high rates. The average value of middle discharge voltage of the battery with 0.5 wt.% CNTs was about 1.183 V at 3 C-rate discharge, 1.152 V at 5 C-rate discharge, and 1.078 V at 10 C-rate discharge, respectively.

Fig. 4 shows the comparison of the discharge curves of batteries with 0.5 wt.% CNTs and without CNTs at 5 and 10 C rates. Because the batteries with different CNT contents had very similar characteristics in discharging, only the batteries with 0.5 wt.% CNTs were compared with the batteries without CNTs. From Fig. 4a and b, the high-rate discharge properties of the batteries with CNTs are better than those of the batteries without CNTs. This can also attributed to the larger reaction surface and lower internal resistance of Ni/MH battery with CNTs in the positive electrode.

3.3. High-rate capability analysis

The high-rate capability of battery is calculated from

$$\text{high-rate capability (\%)} = \frac{C_{nC}}{C_{nC} + C_{0.2C}} \times 100$$

In the formula, the battery charges with 0.2 C constant current for 6.5 h, rests for 10 min, then discharges with *n* C (where *n* = 1, 3, 5, and 10) constant current to the cut-off voltages of 1.0 V. And the discharge capability is *C_nC*. After

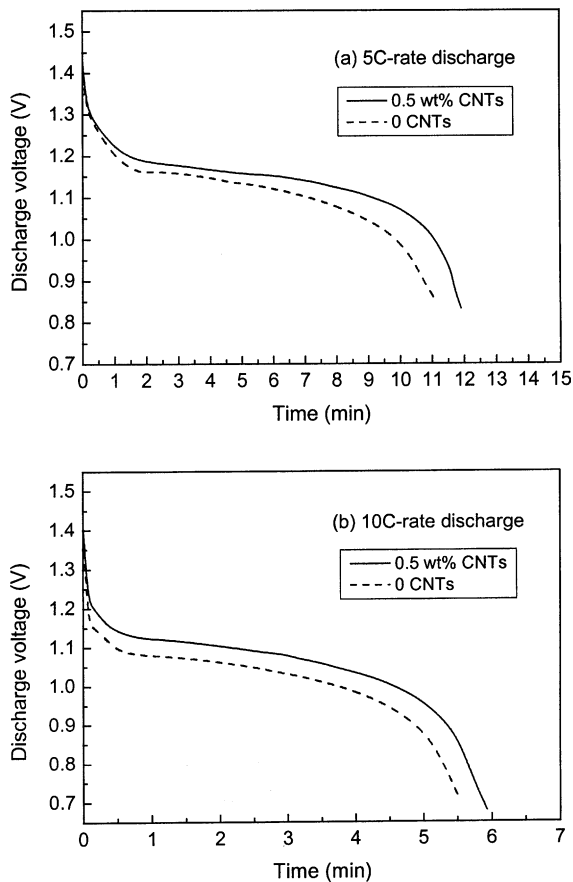


Fig. 4. The comparison of the discharge curves of batteries with 0.5 wt.% CNTs and without CNTs at 5 and 10C rates (the discharge curves were observed at the 30th charge–discharge cycle).

each discharge at nC rate and 20 min rest, the battery further discharges at 0.2C rate down to 1.0V, the discharge capability is $C_{0.2C}$.

Fig. 5 shows the comparison of high-rate capability of the batteries with CNTs and without CNTs. The Ni/MH batteries

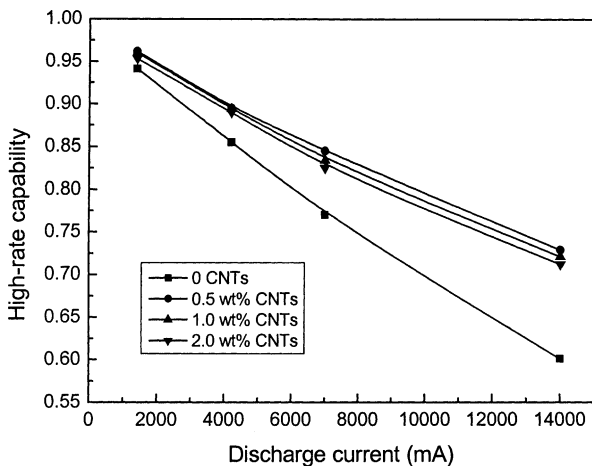


Fig. 5. High-rate capability of batteries with different CNT contents in the positive electrodes.

with CNTs have higher high-rate capability. The addition of 0.5 wt.% CNTs was proved a desired amount to modify the batteries performance at high discharge rates. Too much CNTs contributed no effect in the improvement of high-rate capability and stability of the batteries.

According to the discharge kinetics of the nickel electrode reported by Zimmerman and Effa [18], the kinetics of the nickel electrode was controlled by solid-state proton diffusion under normal rate discharge conditions. As the nickel electrode was discharged, the conductivity of the active material decreased until eventually mixed kinetics was observed where the electrode impedance had significant contributions from both proton diffusion and charge transfer resistance. Further discharge resulted in formation of a semiconductor layer at the active material interface, and then the kinetics of the nickel electrode was controlled by charge-transfer resistance. Under the high-rate discharge conditions, it is concluded that the kinetics of the nickel electrode is dominantly controlled by charge-transfer resistance because of the rapid discharging process. A conductive agent with stable electrochemical properties is of important for providing enough current collectors in the positive electrodes, thus decreasing the charge transfer resistance. Due to their excellent electronic conductivity, highly accessible surface area and unique structure, the addition of CNTs is beneficial to the electrochemical reaction and comprehensive high-rate discharge performance of Ni/MH battery.

4. Conclusions

- (1) The high-rate discharge performance of Ni/MH battery was improved by the addition of CNTs in the positive electrode. Under high-rate discharge conditions, the batteries with CNTs showed better cycling stability, higher discharge voltage plateau, lower internal resistance, and better high-rate capability. The increase in internal resistance of the batteries with CNTs was lower than that of the batteries without CNTs during the same charge/discharge cycles.
- (2) At normal discharge rate ($\leq 1C$), addition of CNTs in the positive electrode contributed little influence to the performance of the batteries.
- (3) The addition of 0.5 wt.% CNTs was proved a desired amount to modify the batteries performance at high discharge rates. Too much CNTs contributed no effect in the improvement of cycle stability, internal resistance, discharge potential, and high-rate capability of the batteries.

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