

Effect of Carbon Nanotube Dispersion on Electrochemical Behavior of the CNTs/LiCoO₂ Composite Cathode

Guo-ping Wang^{1,*}, Mei Li¹, Yong Qian¹, Li-fang Jia¹, Yu-qiang Tao^{1,*}, Jiang Qi², Xiaoying Lu²

¹ School of Chemistry and Chemical Engineering, University of South China, Hengyang 421001, PR China

² Key Laboratory of Advanced Technologies of Materials, Superconductivity and New Energy R&D Centre, Southwest Jiaotong University, Chengdu 610031, PR China

*E-mail: wgpcd@aliyun.com, taoyuqiang26@qq.com

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Carbon nanotubes (CNTs) are utilized as conductive additives in lithium ion battery. Particularly, the effect of surfactant type on the CNTs' dispersion as well as corresponding electrochemical behavior of LiCoO₂ cathode is investigated. The results demonstrate that the dispersion of CNTs can be improved by both cationic and anionic surfactants, but the resulted electrodes show poor wettability with electrolyte. As a result, the electrochemical performance of corresponding LiCoO₂-based cathode is worsened. Non-ionic polymer polyvinylpyrrolidone (PVP) act as an effective dispersant for promoting the dispersion of CNTs and improving the electrochemical performance of LiCoO₂ cathode. In addition, CNTs after ball-milling show damaged structure and more agglomerates, which are not suitable for forming a continuous conductive network.

Keywords: Carbon nanotubes; Conductive additives; Dispersion; Lithium ion battery

1. INTRODUCTION

The poor conductivity of electrode materials for lithium ion batteries (LIBs) easily results in large internal resistance, serious polarization, insufficient discharge depth, and low charge-discharge efficiency. Accordingly, conductive additives are often introduced into the electrodes to form conductive network. Due to high chemical inertness and electrical conductivity, carbon materials have been widely employed as conductive additives in LIBs [1-4]. The types and dosages of carbon materials have significant influence on the conductivity. Carbon materials often include graphite powders, carbon black, carbon nanofibers and CNTs, etc [5-7]. CNTs have been used as one kind of highly efficient conductive additives in LIBs because of their advantages such as wire-like shape, higher electrical conductivity and

higher crystallinity nano-size in comparison with acetylene black and carbon fiber [8-11]. The wire-like shape of CNTs helps to construct continuous conductive network, and the higher crystallinity makes them display better ability to rapidly transfer electrons and show lower percolation threshold [12]. In one word, by using CNTs, much conductive additives can be saved, and the electrode shows enhanced rate capacity and higher energy density. In addition, hybrid conductive additives containing CNTs have been proven to be effective for improving the rate performance and cyclic stability of LiCoO₂ cathode material [6]. Even so, there is still much space for further improving the performance of lithium ion battery when using CNTs as conducting additives. Owing to their high length-diameter ratio, small particle size and large specific surface area [13-17], CNTs tend to entangle and aggregate together to reduce the total surface energy. If such CNTs aggregates were directly mixed with active electrode materials like LiCoO₂, it would be very difficult to disperse CNTs homogeneously in electrode materials. As the result, the utilization efficiency of both active electrode materials and CNTs is low, resulting in the unnecessary waste of CNTs and decreasing the energy density of LIBs. Therefore, it is necessary to address the agglomeration and entangling of CNTs.

In our previous paper [8], the effects of multi-walled CNTs (MWCNTs)' precursors, diameter, and weight fraction on the electrochemical behavior of CNTs/LiCoO₂ composite cathode were studied. To make full use of LiCoO₂ at high rate, it is necessary to add at least 5 wt.% of MWCNTs with a diameter 10~30 nm.

To further decrease the content of MWCNTs in LiCoO₂-based cathode without negative effect on electrochemical performance, this paper mainly try to improve the dispersion of MWCNTs in the electrode by using surfactants or ball-milling. Firstly, MWCNTs were ultra-sonicated to separate from each other. Then, different kinds of surfactants were added to modify MWCNTs for alleviating the aggregation of MWCNTs. In addition, induced by the fact that the entangling of MWCNTs can be well suppressed by shortening the length, MWCNTs were appropriately cut by ball milling and the influence on the dispersion of MWCNTs was investigated.

2. EXPERIMENTAL

2.1 Materials

MWCNTs and binder LA132 were obtained from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. MWCNTs with a diameter of 10-30 nm, which were prepared as reported [12], were additionally treated in dilute nitric acid to remove metal particles. LiCoO₂ was purchased from BTR Energy Materials Limited Co., Ltd, Shenzhen, China.

2.2 Preparation of CNTs/LiCoO₂ composite electrode and cells

Firstly, MWCNTs were ultrasonicated for 30 min in ethanol/water mixed solution. After that, anionic, cationic and polyvinylpyrrolidone (PVP) surfactants were added into the solution, respectively. Then LiCoO₂ and binder LA132 were added with a LiCoO₂/LA132/MWCNTs mass ratio of 94:3:3.

After homogeneously mixed, the slurry was coated on 20- μm -thick aluminium foil and dried at 100 °C for 24 h under vacuum. Finally, the electrode was rolled to enhance the contact of particles. The thickness of obtained electrode was about 65 μm . For simplicity, the cathodes prepared by using cationic, anionic and PVP as surfactants were marked as CCNTs/LiCoO₂, ACNTs/LiCoO₂, and PCNTs/LiCoO₂, respectively. The electrode prepared without adding surfactants was marked as NCNTs/LiCoO₂.

To further decrease the aggregation of MWCNTs, the commercial MWCNTs were treated by ball-milling. After that, the broken MWCNTs were used as conductive agent using PVP as surfactants to prepared LiCoO₂-based electrode. The process was the same as that of NCNTs/LiCoO₂, and the resulted electrode was marked as PBCNTs/LiCoO₂.

To evaluate the electrochemical performance of the electrodes, coin cells were assembled in an Ar-filled glove box with a humidity rate of less than 5 ppm. In the cell, metal Li sheet served as a counter electrode, and porous polypropylene separator (Celgard no. 2400) was used to separate the LiCoO₂-based composite electrodes from Li sheet. The electrolyte used was 1 M LiClO₄ solution (mixture of ethylene carbonate and diethyl carbonate in a ratio of 1:1 as the solvent). The cells were cycled between 3.0 and 4.3 V versus Li/Li⁺.

3. RESULTS AND DISCUSSION

3.1 Effect of Surfactants on the Electrochemical Properties of CNTs/LiCoO₂

Table 1 shows the electrochemical performance of CCNTs/LiCoO₂, ACNTs/LiCoO₂ and NCNTs/LiCoO₂ electrodes. After adding cationic or anionic surfactant, the specific capacity of CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrodes decreases to some extent at all charge/discharge rates. At lower charged/discharged rate, their capacities worsen gently. Moreover, with the increase of the charge/discharge rate, their capacities worsen more and more seriously. When the charge/discharge rate comes to 3.0 C, CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrodes decline in the capacities by about 30 and 15 mAh g⁻¹, respectively. Our idea is to promote the dispersion of MWCNTs with surfactants and then improve the electrochemical performance of the electrode, but the experimental results don't offer the supporting evidence.

Table 1. The electrochemical performance of NCNTs/LiCoO₂, CCNTs/LiCoO₂ and ACNTs/LiCoO₂

Electrode	Capacity at various charge/discharge rates (mAh g ⁻¹)				
	0.2 C	0.5 C	1.0 C	2.0 C	3.0 C
NCNTs/LiCoO ₂	139.7	131.5	124.9	120.1	113.6
CCNTs/LiCoO ₂	129.5	111.4	99.1	94.8	85.9
ACNTs/LiCoO ₂	130.0	122.9	111.2	107.8	100.8

This is beyond our expectation. The distribution of MWCNTs in the electrode is characterized by SEM. As shown in Fig. 1, the MWCNTs in NCNTs/LiCoO₂ electrode appears to be some thicker and denser, suggesting MWCNTs' severe agglomeration. However, in CCNTs/LiCoO₂ and ACNTs/LiCoO₂, LiCoO₂ granulates are well covered by MWCNTs additive and are linked by MWCNTs to form conducting network. This implying that the used cationic or anionic surfactant do promote the dispersion of MWCNTs to some extent by electrostatic force [18].

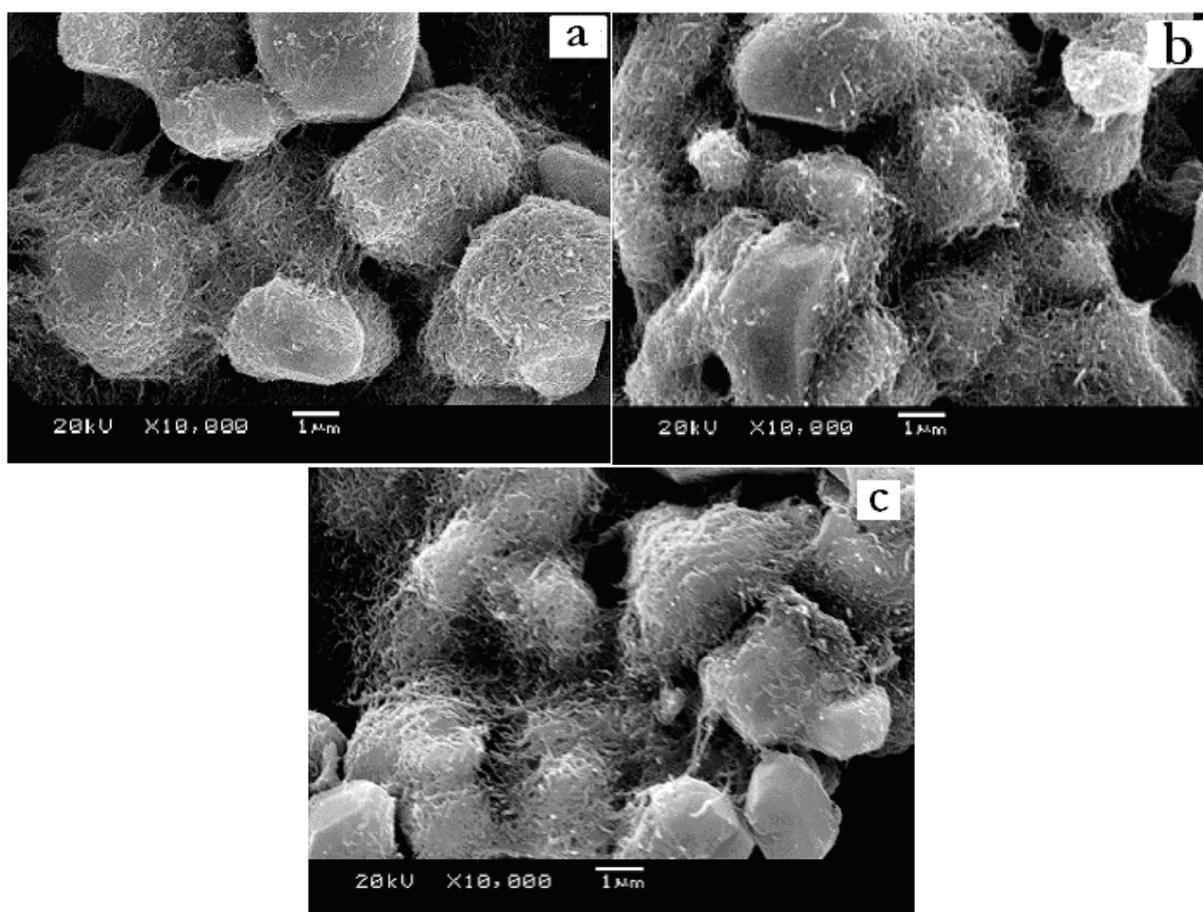


Figure 1. SEM images of (a) NCNTs/LiCoO₂, (b) ACNTs/LiCoO₂ and (c) CCNTs/LiCoO₂.

Since MWCNTs' amount has not been changed and MWCNTs' dispersion has also been improved to some degree, the resistance of the CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrodes at least is not higher than that of NCNTs/LiCoO₂. The electrical resistivity of NCNTs/LiCoO₂, CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrode is 3.75, 3.60 and 2.96 Ω cm, respectively. Obviously, the volume electrical resistivity of CNTs/LiCoO₂ electrodes doesn't increase with the addition of surfactants. Especially for ACNTs/LiCoO₂ electrode, its volume resistivity declines obviously compared with NCNTs/LiCoO₂. Therefore, the worsening electrochemical performance of CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrodes apparently can't be attributed to their poor electronic conductivity. The

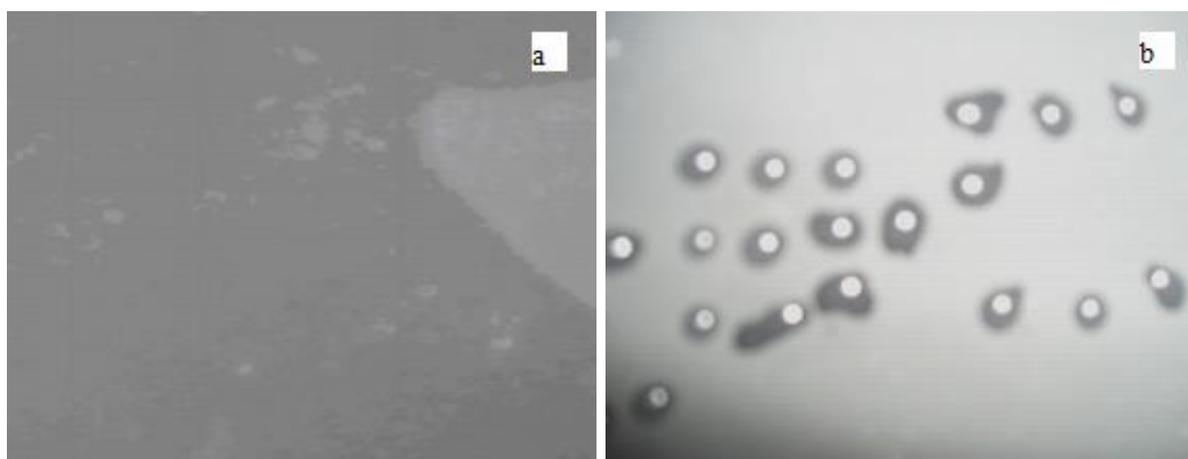
possible reason is that surfactants may result in poor electrolyte wettability on the electrodes, hindering the diffusion of lithium ions in the electrodes [19, 20].

To investigate the wettability of electrolyte on the electrodes surface, the aforesaid electrolyte was dropwise added onto the NCNTs/LiCoO₂, CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrodes with a dropper. Five minutes later, their wettability of electrolyte on the electrodes were observed.

As shown in Fig. 2, for NCNTs/LiCoO₂ electrode, no small electrolyte droplet exists, and the electrolyte has completely spread out in the electrode. However, for CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrodes, small electrolyte droplets are very obvious. This phenomenon indicates that the wettability of the electrolyte on the electrodes seriously worsens when adding cationic surfactant or anionic surfactant, which was also found in LiFePO₄ composite electrodes [21]. The relationship between interface tension and contact angle can be expressed as Young Equation:

$$\sigma_{s-g} - \sigma_{s-l} = \sigma_{g-l} \cos \theta \quad (1)$$

where σ_{s-g} , σ_{s-l} and σ_{g-l} are solid-gas, solid-liquid, and gas-liquid interface tension, respectively. θ is the contact angle. According to Eq. (1), when σ_{s-g} is smaller than σ_{s-l} , the solid-liquid interface tends to diminish, resulting in non-wetting liquid. Adding surfactants may change the relative value between σ_{s-g} and σ_{s-l} . As the result, the driving force of electrolyte wetting on the electrode decreases, and the wetting ability worsens. This in turn increases the diffusion resistance of Li ion and concentration polarization, making the electrodes charge/discharge incompletely and then show lower specific capacity [22, 23]. Especially when charged/discharged at higher rates, such a concentration polarization will be more serious. This is why CCNTs/LiCoO₂ and ACNTs/LiCoO₂ electrodes' specific capacity is much lower than that of NCNTs/LiCoO₂ electrode at higher rates. Additionally, the surfactant probably existed on the surface of the LiCoO₂ and affected the performance of the battery after drying [24].



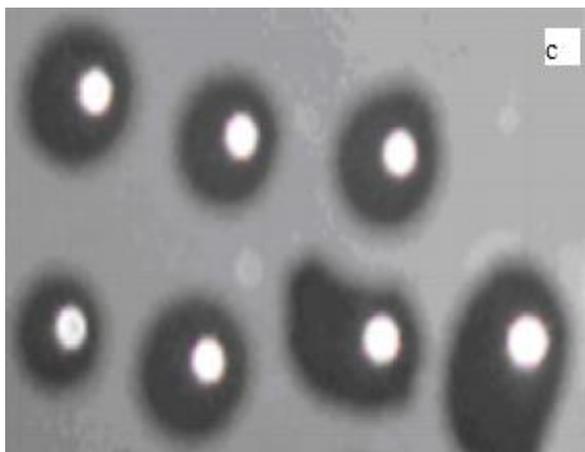


Figure 2. The wetting performance of the electrolyte on the electrode (a) CNTs/LiCoO₂, (b) CCNTs/LiCoO₂ and (c) ACNTs/LiCoO₂.

3.2 Effect of PVP on the Electrochemical Properties of CNTs/LiCoO₂ Electrode

Since the electrolyte wetting ability on CNTs/LiCoO₂ electrode worsens when adding cationic or anionic surfactant, non-ionic polymer PVP was utilized to coat MWCNTs for preventing them from aggregating, and the corresponding PCNTs/LiCoO₂ electrode was prepared. Fig. 3 compares the electrochemical performance of PCNTs/LiCoO₂ and NCNTs/LiCoO₂ at the rate of 1 C.

As shown in Fig. 3, PCNTs/LiCoO₂ electrode displays some higher specific capacity than NCNTs/LiCoO₂. Such result may be ascribed to the addition of PVP. After coated by PVP, MWCNTs' surface energy and the interfacial energy between MWCNTs and LiCoO₂ decreases, and MWCNTs' aggregation is alleviated, improving the dispersion and utilization of MWCNTs [24]. As the result, more electronic channels are established among more LiCoO₂ particles, and more LiCoO₂ particles take part in electrochemical reaction, resulting in a higher specific capacity.

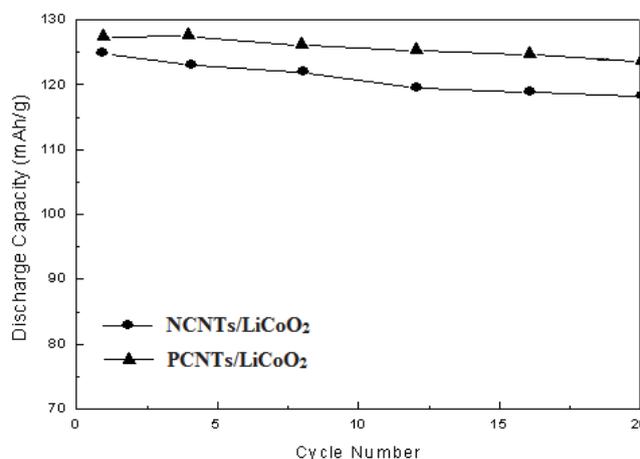


Figure 3. Electrochemical performance of NCNTs/LiCoO₂ and PCNTs/LiCoO₂ electrode at the rate of 1C.

As for MWCNTs' higher dispersion, it can be further testified by settling experiments. Generally, if the ultrasonicated MWCNTs can suspend in the solution for longer time, MWCNTs' agglomeration should be relatively slight and their dispersion should be relatively better. Contrarily, if stratification or settling phenomenon happens, it indicates that MWCNTs begin to agglomerate and their dispersion worsens. The faster the stratification or settlement process is, the more serious MWCNTs' agglomeration is. Fig. 4 shows the settling phenomenon of MWCNTs in ethanol/water solution. Obviously, in the presence of PVP, MWCNTs can keep suspended and the settling phenomenon can't be observed even if the ultrasonic suspension solution has been placed for half a year. However, for the suspension solution in the absence of PVP, MWCNTs begin to delaminate within 30 minutes, and most of MWCNTs settle at the bottom of the test tube within six months. The reason for such phenomenon is that PVP coated on MWCNTs can decrease the surface energy of MWCNTs, enhance MWCNTs' agglomerating steric hindrance [24], and then improve MWCNTs's stability in the solution. Based on the phenomenon, it is concluded that PVP can inhibit MWCNTs from aggregating to some extent, and it is an effective dispersant for MWCNTs.

3.3 Effect of ball-milled MWCNTs

MWCNTs' high length-diameter ratio often leads to entangling. To addressing MWCNTs' entangling problem, MWCNTs were ball-milled, and then the effect of ball-milled MWCNTs on the performance of the electrodes was studied. Because it was difficult to accurately measure the length of MWCNTs, it was estimated by TEM images.

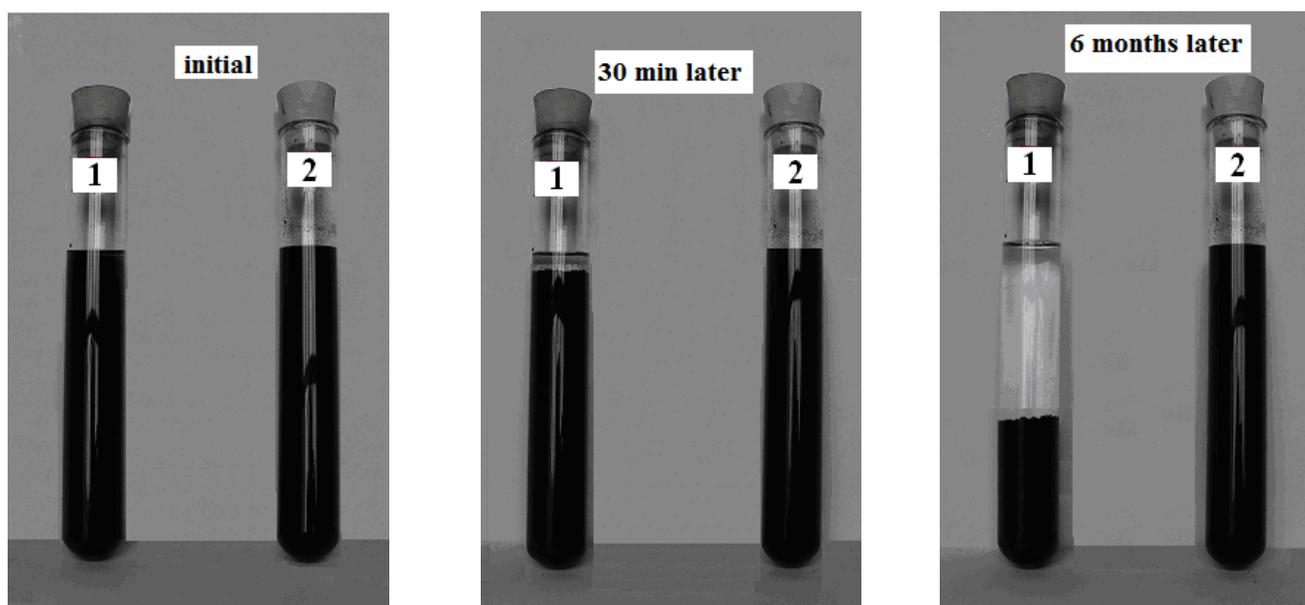


Figure 4. The pictures of MWCNTs' suspension state at different moments after being ultrasonicated in the presence of (1) no PVP and (2) PVP.

As shown in Fig. 5, the longer the ball-milling time is, the shorter MWCNTs are. After ball-milled for 0, 10 and 20 h, MWCNTs' average length is about 10 μm , 500 nm and 250 nm, respectively. Obviously, shorter MWCNTs twine less together. However, it should be pointed out that the surface of ball-milled MWCNTs becomes more blurry, indicating ball-milled MWCNTs' structure may be destroyed. Besides, MWCNTs tend to agglomerate more together when increasing their ball-milling time.

Theoretically, shorter MWCNTs are prone to disperse in the composite electrode, resulting in lower electrical resistivity. However, the electrical resistivity of PBCNTs/LiCoO₂ electrode increases with the extension of the ball-milling time. After balled for 0, 10 and 20 h, the electrical resistivity of PBCNTs/ LiCoO₂ increases from 3.61 to 12.00 and then to 27.50 Ω cm. This result may originate from: (1) as shown in Fig. 5, ball-milling damages the structure of MWCNTs. As the increase of defects in MWCNTs surface, both the amorphous carbon content and MWCNTs' surface energy increase, resulting in more agglomerating and lower electron conductivity [25, 26]. (2) Similar to acetylene black, shorter MWCNTs can't form a continuous conductive network in the composite electrode, which is not conducive to obtaining high conductivity.

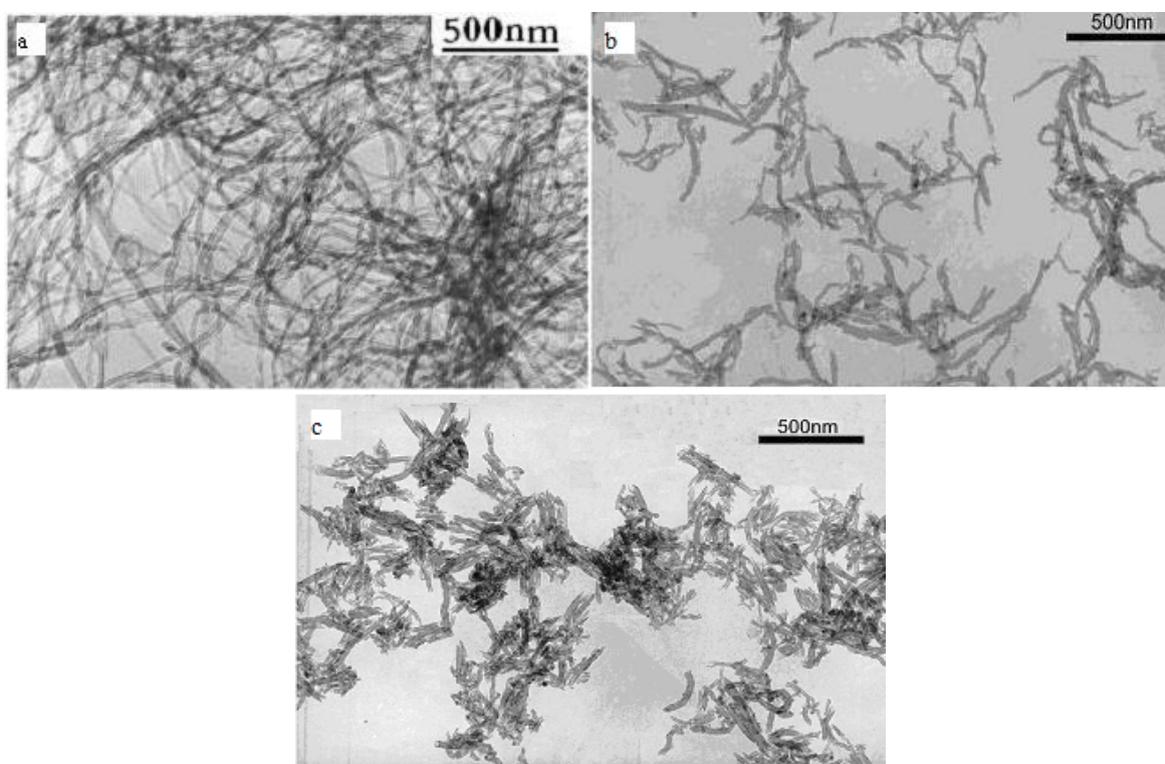


Figure 5. TEM images of MWCNTs ball-milled for (a) 0 h, (b) 10 h and (c) 20 h.

The electrochemical properties of PBCNTs/LiCoO₂ electrodes are shown in Fig. 6. The longer the ball-milling time of MWCNTs is, the worse the electrochemical properties of PBCNTs/LiCoO₂ are. When MWCNTs are not ball-milled, the discharge curves of PBCNTs/LiCoO₂ electrode gradually shift to the lower potential with the increase of the charge/discharge current density from 0.2 to 3 C, and its discharge capacity decreases slightly too. In other words, it shows better rate capability. However, for the electrodes containing ball-milled MWCNTs, their discharge curves rapidly shifted to the lower

potential when increasing the charge/discharge current density, and their corresponding discharge capacity decreases rapidly. This phenomenon implies their larger electrical resistivity, their poor rate capability and more serious polarization. From the above results, it can be concluded that appropriate length of MWCNTs is necessary for MWCNTs' efficient dispersion and the formation of continuous conductive network in composite electrode.

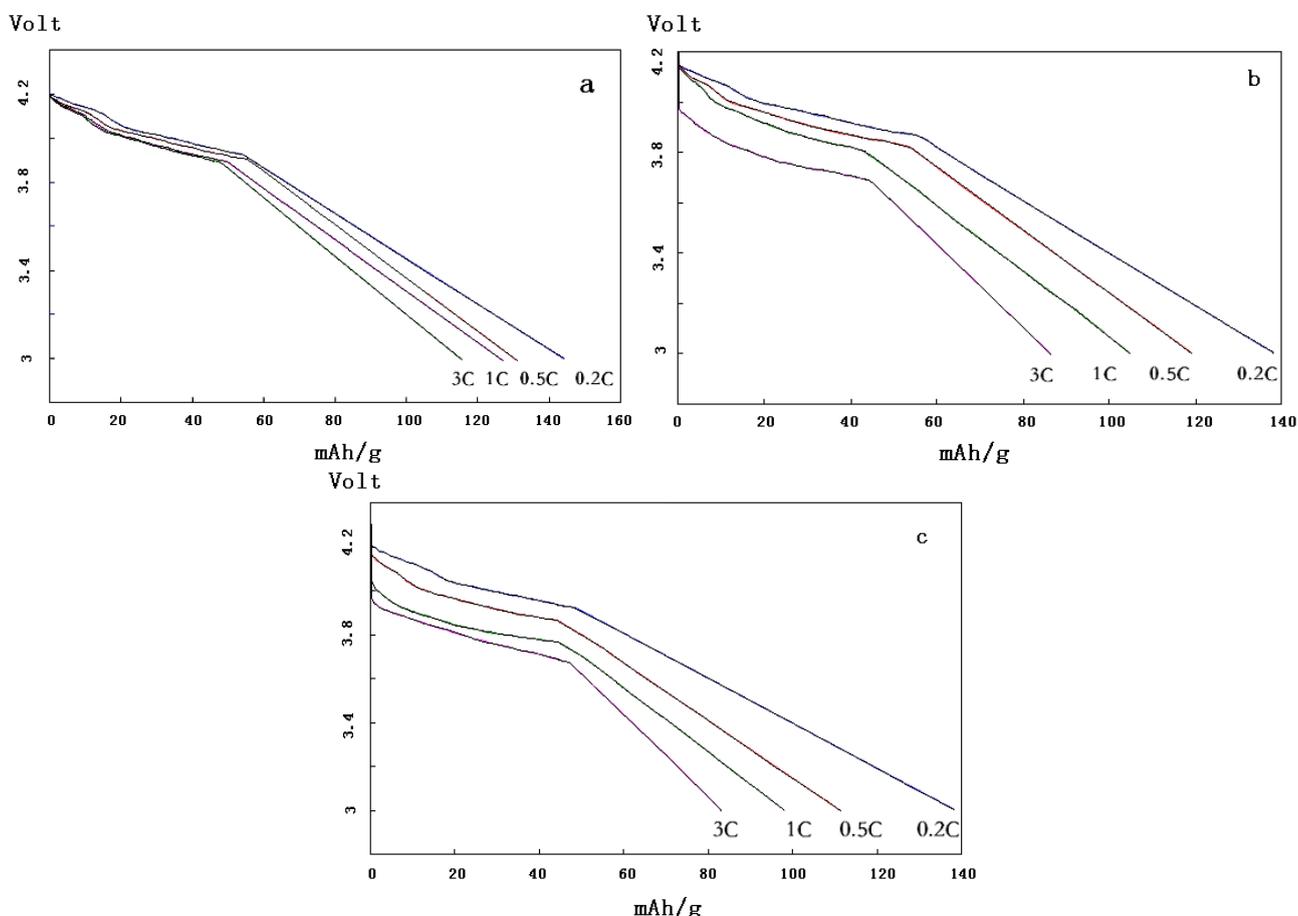


Figure 6. The discharge profiles of PBCNTs/LiCoO₂ as a function of C rate after ball-milling MWCNTs for (a) 0 h, (b) 10 h and (c) 20 h.

4. CONCLUSION

Although cationic and anionic surfactants are helpful for improving MWCNTs' dispersion to some extent, they can result in poor wettability of electrolyte on the electrodes, precluding lithium ions from diffusion within the electrodes. Therefore, using cationic or anionic surfactant is not appropriate in lithium ion battery. By substituting cationic or anionic surfactant with non-ionic polymer PVP, it not only promotes MWCNTs' dispersion but also improves the electrochemical performance of LiCoO₂ composite cathode. PVP can serve as an effective dispersant for MWCNTs.

Extending ball-milling time can make MWCNTs shorter, alleviating MWCNTs' entangling. Nevertheless, such ball-milled MWCNTs can't form effective continuous conductive network. What's more, ball-milling can damage MWCNTs' structure, decreasing its electron conductivity, and ball-

milled MWCNTs tend to agglomerate together. Therefore, it is necessary to prepare MWCNTs with appropriate length from the beginning instead of cutting by ball-milling.

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