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Influence of carbon coating prepared by microwave pyrolysis on properties of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

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Abstract: A novel synthesis method of carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode material for lithium-ion battery was reported. The carbon coating was produced from a precursor, glucose, by microwave-pyrolysis method. The prepared powders were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and charge/discharge tests. XRD results indicate that the carbon coating does not change the phase structure of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ material. SEM results show that the surface of spherical carbon-coated material becomes rough. Electrochemical performance results show that the carbon coating can improve the cycling performance of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. The specific discharge capacity retention of the carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ reached 85.0%−96.0% at the 50th cycle at 0.2*C* rate, and the specific discharge capacity retention is improved at a high rate.

Key words: lithium-ion battery; cathode material; carbon coating; microwave pyrolysis method; electrochemical performance

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1 Introduction

Lithium ion battery has become the state-of-power sources for portable appliances such as cellular phones, notebook computers, digital cameras and also a prime candidate for hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) for reasons of high power density, high energy density, safety and cycling performance [1−3]. Literatures related to lithium transition metal oxides and their derivatives, such as $LiMn_2O_4$, $LiCoO_2$ and $Li(Ni,Co)O_2$, have been extensively reported, which are commercially available as 4 V class cathode materials for lithium ion batteries. Among them, $LiCoO_2$ is widely used as positive electrode in commercial lithium secondary batteries. However, utilization of $LiCoO_2$ has the drawback due to the scarcity of cobalt, being expensive and toxic. The cathode material synthesized by OHZUKU and MAKIMURA [4], $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, attracts lots of attention for its lower cost, less toxicity and higher capacity, which is superior to the commercial material of $LiCoO_2$. It was reported that even 200 mA·h/g can be attainable by charging up to 2.8 and 4.6 V, with superior cycle performance [5]. Although $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ exhibits excellent performance comparatively, it has drawbacks, such as low electronic conductivity, low tap density and relatively low cycling performance at high-rate, which impede its industrial acceptance. Some measures have been reported to improve the cycle performance of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, such as doping small amounts of additional ions [6−8], and modification of the surfaces [9−11]. In particular, a thin carbon coating on particles is known to be effective not only in enhancing the conductivity of the cathode material but also in protecting the particles from

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chemical attack by the electrolyte. However, only a few studies on the carbon-coated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ material were reported. Diverse methods of carbon coatings, such as carbon black compounds or pyrolysis of adsorbed organic compounds [12,13], were employed. Nevertheless, all of these methods need some hours for providing carbon coating on the particles at an elevated temperature. It is well known that microwave process is widely used to synthesize many inorganic materials and advanced sinter materials [14,15], such as $LiMn_2O_4$ [16−18], $LiNiO_2$ [19], $LiFePO_4$ [20] and $LiCoO_2$ [21], due to its short reaction time, low energy consumption, high efficiency of synthesis and product crystal structure [22].

In this study, in order to decrease the process time, reduce the synthesis cost and improve the cycle performance of cathode material, carbon was coated on the surface of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ powder by microwave pyrolysis method in a novel microwave reactor (as shown in Fig. 1). Coin cells were prepared with the carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ powder and lithium metal, and their electrochemical performance was measured.

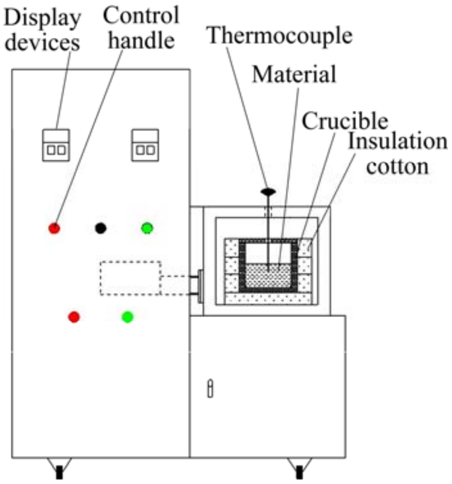

Fig. 1 Schematic of microwave reactor

2 Experimental

2.1 Sample preparation

The spherical $(Ni_{1/3}Mn_{1/3}Co_{1/3})(OH)_2$ (Lanzhou Jinchuan) and Li_2CO_3 (China Lithium, 99.9%) powders with molar ratio of 1:1.06 were ball-milled thoroughly. The excess amount of Li was used to compensate for the loss of Li during calcination. The powder after drying at 323 K was sintered in the microwave reactor at 1243 K for 30 min. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ powder was mixed with glucose of 2% or 3% in mass fraction by mechanically mixing for 16 h, and then pyrolyzed in flowing nitrogen in a microwave reactor at 673 K for 15 min.

2.2 Experimental equipment

Experiments were carried out using a novel microwave reactor. The schematic is shown in Fig. 1. The microwave reactor with a frequency of 2450 MHz and a maximum power output of 1500 W was made by Kunming University of Science and Technology, China.

2.3 Characterization

X-ray diffraction (XRD) data for the finely ground samples were collected at 298 K using a Bruker D8 X-ray diffractometer with Cu K_α radiation (λ=1.5406 Å). It was operated at 40 kV and 300 mA in the 2θ range of 10°−80° in the continuous scan mode with the step size of 0.01° and the scan rate 1.0 (°)/min. The particle shapes and morphologies of the bare and carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ materials were obtained using scanning electron microscopy (SEM, Philips XL-30E). Rigaku ZSX100e X-ray fluorescence spectrometer was applied to multi-element determination in the bare and carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ materials. The electrodes were fabricated from a 85:10:5 (mass fraction) mixture of active materials, acetylene black as the current conductor and polyvinylidene difluoride (PVDF) as the binder. The PVDF was dissolved in *n*-methyl pyrrolidinone before the active material and the conductor mixture were added. After homogenization, the slurry was evacuated for 20 min to remove the residual air. The slurry was then coated on a thin aluminum foil (20-μm thick) and dried overnight at 60−70 °C. The electrode was pressed under a pressure of 10 MPa and punched into 12-mm diameter disks. The electrochemical cells were prepared as 2025-coin cell hardware with lithium metal foil as both the counter and reference electrodes. The cells were assembled in a Ar-filled glove box. The electrolyte used for analysis was 1 mol/L $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1).

3 Results and discussion

3.1 Structure

Figure 2 shows the XRD patterns and Miller indices of the bare and carbon-coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$. In Fig. 2, the XRD patterns of the two materials indicate a single phase of α-$NaFeO_2$ structure with space group of $R\overline{3}m$. The splits in the (006/012) and (108/110) are around at 38° and 65° doublets, indicating the formation of a highly ordered layered structure. The ratios of intensities of the $I_{(003)}/I_{(104)}$ of the bare and carbon-coated material are 1.60759 and 1.83147, respectively, above the values reported for compounds like $LiNi_{1-x}Co_xO_2$ to deliver good electrochemical performance [23]. No other impurity phases were observed in the XRD patterns for the carbon-coated material, which suggests that the structure of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is not affected by the carbon coating. The structural parameters of the two samples are summarized in Table 1 according to the XRD data and the hexagonal crystal spacing calculation equation:

$$\frac{1}{d^2}=\frac{4(h^2+hk+k^2)}{3a^2}+\frac{2l}{c^2} \tag{1}$$

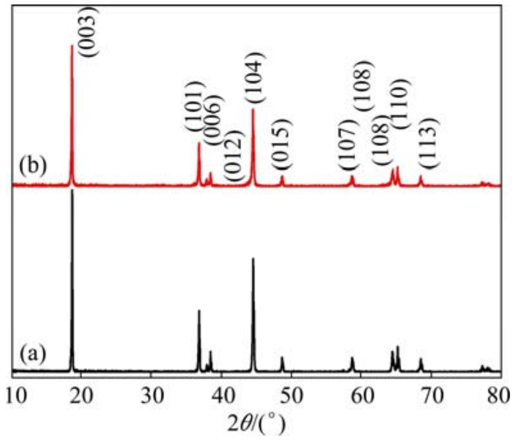

Fig. 2 XRD patterns of bare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (a) and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (b)

Table 1 Lattice structural parameters of bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

Sample	a/Å	c/Å	c/a	$I_{(003)}/I_{(104)}$
Bare	2.858193	14.22028	4.975269	1.60759
Carbon-coated	2.859432	14.19277	4.963491	1.83147

3.2 Morphology

The SEM images of the bare and carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particles are shown in Fig. 3. For the bare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, the rod-shaped particles with a submicron size are agglomerated to form a sphere-shaped particle with diameter of 10−14 μm. A smooth and clean surface is observed in the bare particles. After coating carbon, the surface of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particles is rough. Similar SEM images were also observed in ZrF_x-coated $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ [24] and the carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ [25]. Compared with the average size of the primary grain of bare particles, that of the carbon-coated material increased from 540 nm to 750 nm. The primary grain of the carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particles treated by microwave is more distinct than that of the bare one.

3.3 Elemental analysis

Table 2 shows the X-ray fluorescence results of 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and 3% carbon coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. The XRF analysis indicates that O, Ni, Co, Mn and C are in the carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ particle. The practical contents of carbon are 1.9106% and 2.9968% after microwave pyrolysis of 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and 3% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, respectively.

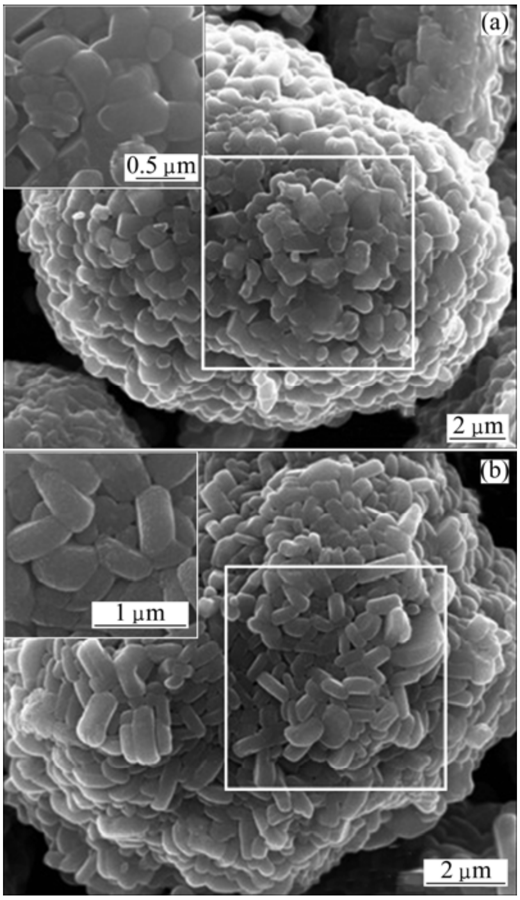

Fig. 3 SEM images of bare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (a) and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (b)

Table 2 XRF results of 2% carbon and 3% carbon coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

Sample	w(O)%	w(Ni)%	w(Co)%	w(Mn)%	w(C)%
2% carbon	41.5288	18.8922	18.5518	17.8886	1.9106
3% carbon	41.6463	18.8708	18.4789	17.8127	2.9968

3.4 Electrochemical performance

Figure 4 shows the discharge curves of bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes cycled between 2.75 and 4.3 V at 0.2C rate. The specific discharge capacities for the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode without carbon coating are 161.7 mA·h/g at the first time and 137.4 mA·h/g at the fiftieth time at 0.2C rate, while they are 159.3 mA·h/g at the first time and 152.9 mA·h/g at the fiftieth time at 0.2C rate for the 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode. As can be seen, the first specific discharge capacity of carbon-coated sample at 0.2C reduces slightly because a layer of barrier, carbon, is covered on the positive electrode material surface, which blocks cathode materials to contact with electrolyte.

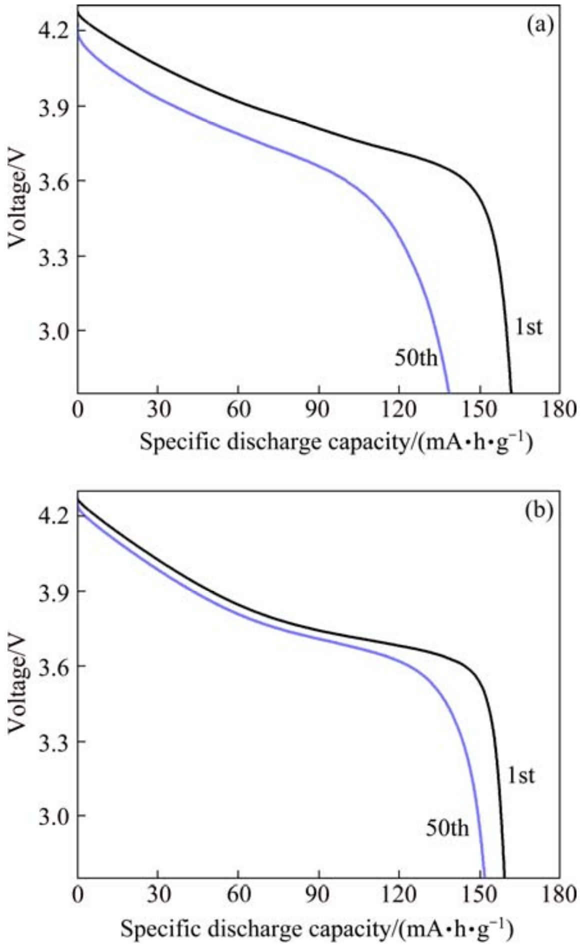

Fig. 4 Discharge curves of bare (a) and 2% carbon-coated (b) $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes tested at 0.2*C* rate in 2.75−4.3 V

Figure 5 shows the discharge curves of bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes cycled between 2.75 and 4.3 V at 2*C* rate. The specific discharge capacities for the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode without carbon coating are 105.5 mA·h/g at the first time and 86.4 mA·h/g at the 50th time at 2*C* rate, while they are 130.8 mA·h/g at the first time and 112.6 mA·h/g at the 50th time at 2*C* rate for the 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode.

Comparison of the cycling performance between the bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes at 0.2*C* rate are shown in Fig. 6. The specific discharge capacity of the bare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode at 0.2*C* rate at the first circle is about 161.7 mA·h/g, while the 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode exhibits comparable specific discharge capacity of 152.9 mA·h/g. However, after the 50 cycles the specific capacity retentions of the bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes are 84.8% and 95.5%, respectively.

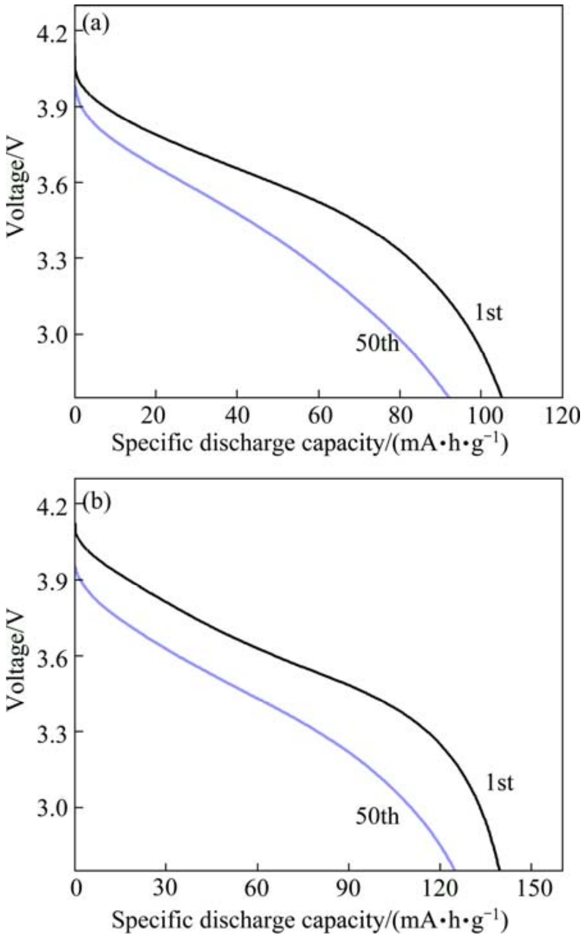

Fig. 5 Discharge curves of bare (a) and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (b) $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes tested at 2*C* rate in 2.75−4.3 V

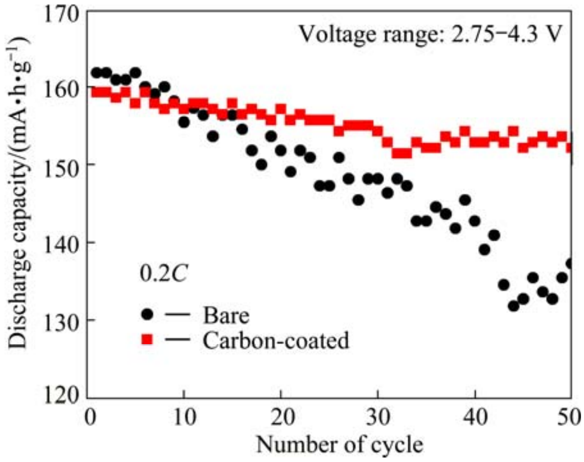

Fig. 6 Cyclic performance of bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes in 2.75−4.3 V at 0.2*C* rate

Figure 7 shows the specific discharge capacities and cyclic properties of the bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes at 0.2*C*, 2*C*, 4*C* and 8*C* rates in the voltage range of 2.75−4.3V. At 2*C* rate, after the 50 cycles the specific capacity retention of 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode is 86.1%, while that of the bare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode is 81.9%.

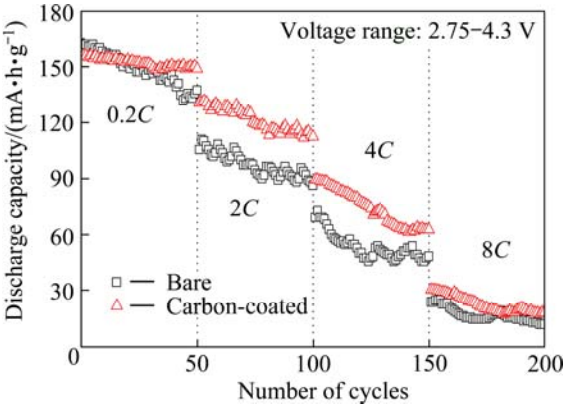

Fig. 7 Specific discharge capacities and cyclic performance of bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes in 2.75−4.3 V at 0.2*C*, 2*C*, 4*C* and 8*C* rates

Figure 8 displays the capacity retention (ratio of the discharge capacity at an assigned discharge rate to the discharge capacity at a 0.2*C* rate) as a function of the rate. After 50 cycles the specific capacity retention of the bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes are 69.7% and 69.9% at 4*C* rate, respectively. At 8*C* rate, after 50 cycles the capacity retentions of the bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes are 50.0% and 59.8%, respectively. The specific capacity retention of the carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode is better than that of bare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode at any discharge rates because the carbon coating blocks the contact between cathode materials and electrolyte, which reduces the corrosion of positive electrode material.

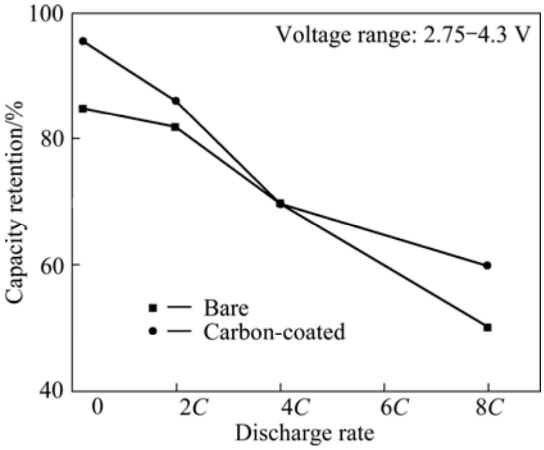

Fig. 8 Specific capacity retentions of bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes as function of discharge rate

Although the specific discharge capacities of the bare and 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrodes decrease with the increase of charge-discharge cycles, the specific capacity retention of the 2% carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode remains better than the bare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode. The result affirms that the carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode exhibits good discharge rate capability and cycle performance. Perhaps, it could be attributed to the increase in electronic conductivity of the carbon-coated material, reducing the cell polarization and oxygen evolution from the cathodes at the end of charge [25]. The carbon coating could act as a protection layer of positive material, which restrains the dissolution of metal ions and reduces the impedance of the charge transfer [26]. The improved electronic conductivity of the carbon-coated material surface may contribute to the improvement in electrical contact of the material among particles, thereby improving the electrochemical performance of the material [27].

4 Conclusions

1) The carbon-coated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ material was successfully synthesized by microwave-pyrolysis method using glucose as carbon source. The carbon coating does not change the phase structure of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ material.

2) The experimental results show that the carbon coating enhances the rate capability and cycling performance of the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ electrode.

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微波热解法制备的炭涂层对 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ 性能的影响

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摘 要：报道了炭包覆锂离子电池正极材料 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ 的新工艺。炭涂层由前驱体葡萄糖通过微波热解而形成。采用 X 射线粉末衍射(XRD)、扫描电镜、X 射线荧光测试和恒流充放电测试来表征所制备的材料。XRD 结果表明，炭包覆没有改变 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ 材料的相结构。SEM 结果表明，炭包覆的 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ 颗粒表面变得粗糙。充放电测试结果显示，炭包覆的 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ 的循环性能与未包覆的相比得到提高。炭包覆的 $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ 在 0.2*C* 倍率下循环 50 次的容量保持率由 84.8%提升到 95.5%，且高倍率下材料的容量保持率得到提高。

关键词：锂离子电池；正极材料；炭涂层；微波热解；电化学性能

(Edited by Hua YANG)