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## Short communication

# Effect of TiO<sub>2</sub>-coating on the electrochemical performances of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>

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## 1. Introduction

Lithium secondary batteries have become the main rechargeable power source for mobile electronics in the past decade. Many lithium transition metal composite oxides such as LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub>, and LiNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> have been extensively investigated as alternative cathode materials to LiCoO2. Recently, LiCo1/3Ni1/3Mn1/3O2 has attracted many attentions as one of the most promising cathode materials for lithium-ion batteries due to its high capacity, good cycling ability, and excellent thermal stability. However, its rate capability and cycling performance at high current density are not satisfactory [1–5]. The origin of these problems are mainly related to its low electronic conductivity, the surface reactivity between the highly delithiated cathode and the electrolyte, and the dissolution of transition metal ions into the electrolyte [6-10]. One approach to overcome these problems is to coat the active materials with metal oxides or other materials to improve the properties of the interface between electrodes and electrolyte. This treatment could prevent dissolution of transition metals and unwanted reactions between cathode and electrolyte, since direct contact between electrodes and electrolyte is restricted by an inactive coating layer. There are several reports about coating LiCo1/3Ni1/3Mn1/3O2 with small amounts of metal oxides or other materials such as Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, AlF<sub>3</sub> and C [6,11–13]. TiO<sub>2</sub>-coating has been proposed to improve

ABSTRACT

A novel method to improve the cycling performance of LiCo1/3Ni1/3Mn1/3O2 in lithium-ion batteries by TiO<sub>2</sub>-coating with an in situ dipping and hydrolyzing method was presented in this work. The microstructure of the  $TiO_2$ -coated  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  was characterized by XRD, SEM and TEM, and their electrochemical performances were evaluated by EIS and galvonostatic charge-discharge test. SEM and TEM images show that the TiO<sub>2</sub> are pasted on the surface of the LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> with nano-size. The XRD patterns indicate that the crystal structure of the TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> shows no obvious change compares with the bare material. The TiO2-coated LiCo1/3Ni1/3Mn1/3O2 possesses improved cycle performance and rate capability. The capacity retention of 1.0 wt.% TiO<sub>2</sub>-coated material is more than 99.0% after 12 cycles at 3.0 C while that of the bare sample is only 86.6%. The capacity of coated material at 5.0 C remains 66.0% of the capacity at 0.2 C, while that of the bare  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  is only 31.5%.

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the electrochemical properties of some cathode materials such as  $LiCoO_2$  and  $Li_{1-x}Ni_{0.8}Co_{0.2}O_2$  [14,15]. It can suppress the phase transition of LiCoO<sub>2</sub> during charge–discharge, leading to an enhanced cyclic performance [14,16]. Moreover, it could also improve the thermal stability and interface stability of Li<sub>1-x</sub>Ni<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> [15,17].

In this study, we had synthesized TiO2-coated LiCo1/3Ni1/3  $Mn_{1/3}O_2$  material via an in situ dipping and hydrolyzing method. The effects of TiO<sub>2</sub>-coating on the structural and electrochemical properties of  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  were investigated in detail. Primary results show that TiO<sub>2</sub>-coating is an effective method to improve the rate capability and cycling performance of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> in lithium-ion batteries.

### 2. Experimental

Commercial powdery LiCo1/3Ni1/3Mn1/3O2 (obtained from Beijing Ge Lin Power Ltd.) was used as bare material. The TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> was prepared by an in situ dipping and hydrolyzing method. LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> was firstly dispersed in ethanol, then the calculated tetrabutyl titanate  $(C_{16}H_{36}O_4Ti)$ was added. After stirred for 0.5 h, 10 ml deionized water was added. Then the mixture was stirred at 70-80 °C to vaporize the ethanol/water completely. After calcined the dried mixture at 500 °C for 6 h, the TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> was obtained.

X-ray diffraction (XRD) patterns of the samples were obtained on a D Max-RD12Kw with Cu K  $\alpha$  radiation. The microscopic features of the samples were observed with a scanning electron microscope (SEM; S-3500N). A transmission electron microscopy (TEM) study was performed using a JEOL JEM-1200EX transmission electron microscope.

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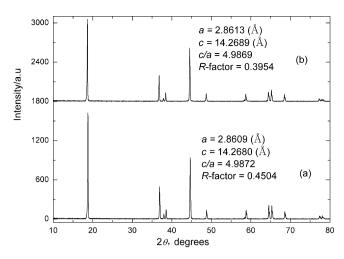


Fig. 1. XRD patterns of (a) bare and (b)  $1.0 \text{ wt.\% TiO}_2$ -coated  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ .

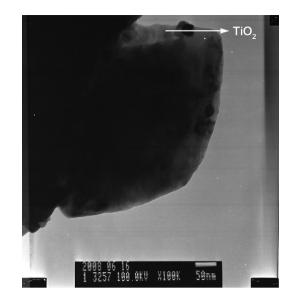
A mixture of 85.0 wt.% bare or TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, 10.0 wt.% acetylene black and 5.0 wt.% PVDF were pasted onto a aluminum foil current collector as cathode electrodes. Then the electrodes were dried at 80 °C for 8 h. The coin cells were assembled using Li-metal foil as the negative electrodes and 1 M LiPF<sub>6</sub>/EC + DMC (1:1 in volume) as the electrolyte in an argon-filled glove box. The galvonostatic charge–discharge were carried out on a Land CT2001A cell tester at room temperature between 2.8 and 4.5 V (versus Li/Li<sup>+</sup>). The cells were charged at 0.2 C and then discharged at 0.2, 1.0, 2.0, 3.0, 4.0, and 5.0 C, respectively.

The electrochemical impedance spectroscopy (EIS) of the cells was conducted on an electrochemical workstation CHI604c. The amplitude voltage was 5 mV and the frequency range was from 0.001 Hz to 0.1 MHz.

#### 3. Results and discussion

#### 3.1. Structure and morphology

Fig. 1 shows the XRD patterns of the bare and 1.0 wt.% TiO<sub>2</sub>coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> materials. For comparison, the bare LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> was also treated at the same temperature (500 °C). Both of the samples have a well-defined  $\alpha$ -NaFeO<sub>2</sub> structure, and there are no obvious changes in the  $2\theta$  position and no other impurity phases after coating. The absence of diffraction patterns corresponding to TiO<sub>2</sub> may be due to very low concentrations of it. The lattice parameters inserted in Fig. 1 are calculated by a least square method from the XRD patterns. The obtained lattice parameters are *a* = 2.5819 and *c* = 14.1786 for the bare LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>



**Fig. 3.** TEM image of 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>.

and a = 2.5887 and c = 14.2386 for the TiO<sub>2</sub>-coated one. The XRD patterns of the coated particles show no basic change in the lattice parameters. It is indicated that the structure of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> is not affected by the TiO<sub>2</sub>-coating during the heat treatment process and TiO<sub>2</sub> only forms a thin layer on the surface. It could be due to the coated amount of TiO<sub>2</sub> is very small in the final product and the coated material was calcined at relatively low temperature for a short period. *R*-factor is regarded as an indicator of hexagonal ordering: the lower the *R*-factor, the better the hexagonal ordering and then the better electrochemical performance [18]. The value of *R*-factor for the coated sample is 0.3954 which is lower than that of the bare one (0.4504). Therefore, the electrochemical behaviors of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> are improved by coating. This result is further proved by the following tests.

The SEM images of the bare and 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> materials are presented in Fig. 2. The bare material is composed of granules with a smooth surface. After coated with TiO<sub>2</sub>, the granules became larger and roughly, with many nano-sized TiO<sub>2</sub> particles on the surface. Fig. 3 shows the TEM photograph of the 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> materials magnified to 100,000 times. The TiO<sub>2</sub> layer is clearly display as a compact film on the surface of the LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> grains and the thickness of it is about 40–50 nm. From above results, it could be concluded that the TiO<sub>2</sub> are only coat on the surface of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, not enter the crystal structure.

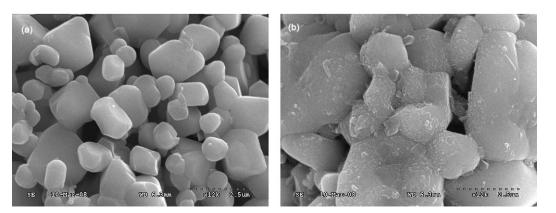


Fig. 2. SEM images of (a) bare, (b) 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, respectively.

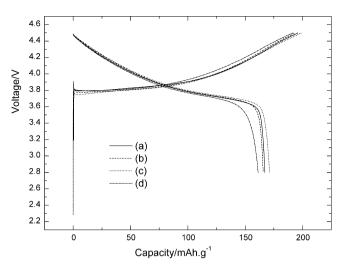


Fig. 4. Initial discharge curves of the (a) bare; (b)  $0.5\,wt.\%$ ; (c)  $1.0\,wt.\%$  and (d)  $2.0\,wt.\%\,TiO_2$ -coated  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2.$ 

## 3.2. Electrochemical behavior

#### 3.2.1. Initial discharge capability

The first charge-discharge curves of the bare and TiO<sub>2</sub>-coated LiCo1/3Ni1/3Mn1/3O2 between 2.8 and 4.5V under a current density of 20 mAg-1 are showed in Fig. 4. The discharge capacity of 0.5 wt.% TiO<sub>2</sub>-coated material is 165.7 mAh g<sup>-1</sup>, charge and discharge voltage and capacity are similar to that of the bare  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  (167.1 mAh g<sup>-1</sup>). The 1.0 wt.% TiO<sub>2</sub>-coated one shows highest discharge voltage and lowest charge voltage and its first discharge capacity reaches to  $171.2 \,\mathrm{mAh \, g^{-1}}$ . When the coating amount increases to 2.0 wt.%, the discharge capacity decreases to 161.3 mAh g<sup>-1</sup>. Obviously, the 1.0 wt.% TiO<sub>2</sub>-coated material delivers a little higher capacity than that of the bare one, the similar results could also be found in Al<sub>2</sub>O<sub>3</sub>-coated Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub> [19] and TiO<sub>2</sub>-coated Li[Li<sub>0.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>]O<sub>2</sub> [14]. The result is regarded due to a suppression of the reaction between the cathode surface and the electrolyte and an optimization of the SEI layer, so the TiO<sub>2</sub>-coating could facilitate the Li<sup>+</sup> diffusion [14]. Groner et al. [20] reported that electron migrations can be somewhat faster by the tunneling effect when the pore size of coating layer is less than several nanometers. The TiO<sub>2</sub>-coating layer would be an amorphous state because the coating media hardly show crystallinity when it is fired at the temperature as low as 500 °C. Therefore, the thin and porous TiO<sub>2</sub>-coating layer would bring the high capacity. These results are perfectly proved by the EIS test latter. The obtained capacity is greatly dependent on the coating concentration of TiO<sub>2</sub>. As the coating concentration becomes higher, the presence of excess coating material between the particles could lower the particle-to-particle electronic conductivity [14].

## 3.2.2. Cycling performance

Fig. 5 present the cycling performances of the bare and TiO<sub>2</sub>coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>. The cells were charged to 4.5 V at 0.2 C, then discharged to 2.8 V at 0.2, 1.0, 2.0 and 3.0 C, respectively. Obviously, the cycling performance of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> can be greatly improved by TiO<sub>2</sub>-coating with an optimal amount of 1.0 wt.%. The initial discharge capacity of the bare LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> decreases gradually during charge–discharge cycling and it drops to 97.9% of its initial discharge capacity after 12 cycles at 0.2 C. For the 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>, the capacity retention ratio increases to 98.8% of its initial capacity after 12 cycles at 0.2 C. As the discharge current increases to 2.0 C

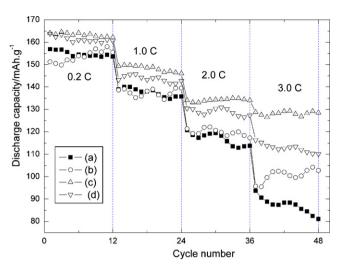


Fig. 5. Cycling performance of the (a) bare; (b) 0.5 wt.%; (c) 1.0 wt.% and (d) 2.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> cathode at different current rates.

and 3.0 C, the discharge capacity of the 1.0 wt.%  $TiO_2$ -coated sample remains 99.9 and 99.8% of its initial discharge capacity after 12 cycles, respectively. The values are much higher than that of the bare sample which are 94.4 and 86.6%. The presence of  $TiO_2$  layer could prevent the increase in the total resistance and suppress the decomposition of the electrolyte solution on the charged particle surface, therefore improve the cyclic performance of the  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  [14,16]. This result is proved by EIS test later. Additionally, the presence of an inert oxide coating on the cathode particle could limit the direct contact of the active material with the electrolyte, and thus prevented dissolution of cobalt and manganese in the electrolyte [21,22].

#### 3.2.3. Rate capability

The rate capabilities of the bare and 1.0 wt.%  $\text{TiO}_2$ -coated  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  are presented in Fig. 6. The cells were charged at 0.2 C and then discharged at 0.2, 1.0, 2.0, 3.0, 4.0 and 5.0 C, respectively. Obviously, the 1.0 wt.% TiO\_2-coated sample delivers higher capacity than the bare one at the same currents. As the current density increases, the discharge capacity of the two samples all decrease due to polarization [11]. However, the 1.0 wt.% TiO\_2-coated sample shows better rate capability. The bare material reaches 120.6 and 49.5 mAh g<sup>-1</sup> at 2.0 and 5.0 C, which are only 76.9 and 31.5%

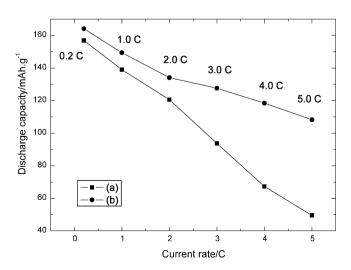


Fig. 6. Rate capability of (a) bare and (b) 1.0 wt.%  $TiO_2$ -coated  $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$  material.

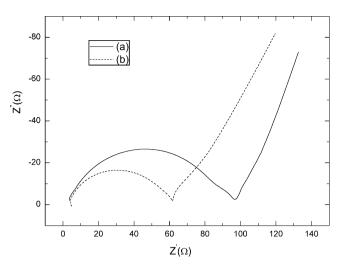


Fig. 7. Impedance spectra (Z' vs. Z") of (a) bare and (b)  $1.0\,wt.\%$  TiO\_2-coated LiCo\_{1/3}Ni\_{1/3}Mn\_{1/3}O\_2.

of the discharge capacity of 156.9 mAh g<sup>-1</sup> at 0.2 C. The 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> shows a high discharge capacity of 134.1 and 108.3 mAh g<sup>-1</sup> at 2.0 and 5.0 C, remaining 81.7 and 66.0% of the capacity of 164.1 mAh g<sup>-1</sup> at the 0.2 C. The enhanced rate capability indicates that the TiO<sub>2</sub> layer could fasten the Liion diffusion. The improved rate capability of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> may be attributed to the enhanced cathode/electrolyte interface stability and stabilized cathode structure [11].

#### 3.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy of the fully charged coin cells (4.5 V) is measured to investigate the interface reaction and the process of lithium deintercalation/intercalation [24]. The EIS profiles of the bare and 1.0 wt.% TiO<sub>2</sub>-coated samples are presented in Fig. 7. As shown in Fig. 7, all profiles are composed of a high-frequency semicircle and a straight line in the low-frequency region. In general, the high-frequency semicircle reflects the surface film forms on the surface of electrodes, i.e. the so-called solid electrolyte interface (SEI). The low-frequency tail is associated with the diffusion effects of Li-ion on the interface between the active material particles and electrolyte, which is called Warburg diffusion [22,25,26]. The numerical value of the semicircle diameter on the Z' axis is approximately equal to the charge transfer resistance ( $R_{ct}$ ) [26]. Obviously, the  $R_{ct}$  of the 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> is significantly smaller than that of the uncoated one. This suggests that TiO<sub>2</sub>-coating could greatly increase the diffusion coefficient of lithium-ion during charge-discharge process. By general conception, TiO<sub>2</sub> is an electric insulator which should block the direct interconnections between active particles and an electrolyte solution, so this would deteriorate the charge transfer from active particles to the current collector, causing an increase in R<sub>ct</sub>. However, the results are different from this expectation. Similar results have been reported in the literature for the case of  $Al_2O_3$  coating [19]. It is regarded that the lower impedance of the coated active material might depend on the thickness of the coating layer. The thickness of the coating layer and the uniformity are critical conditions to have better battery performances [19]. Therefore, it is concluded that the thin (nano-sized) amorphous TiO<sub>2</sub> layer does not disturb the Li<sup>+</sup> intercalation reaction at the interface between electrode and electrolytic interface. Additionally, electron migrations can be somewhat accelerated by the tunneling effect when the pore size of the coating layer is less than several nanometers [20]. On the other hand, the oxide-coated layer could isolate the electrode and the electrolyte then prevent the reaction between them. So the oxidation of the electrolytes is suppressed by TiO<sub>2</sub>-coating and less decomposition products is formed than that of the bare one [23]. The lower impedance could also be ascribed to the positive effects on the electrode/electrolyte interface and the less amount of decomposition of active material by HF [27]. The TiO<sub>2</sub> layer enhances the kinetics of the lithium intercalation then result in the enhancement of electrochemical performance at high rate. The coating layer protects the surface of cathode material from the harmful passive surface film formation during electrochemical cycling. Therefore, the enhanced cycling stability of TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> could be attributed to the improved interface stability [18].

## 3.4. Cyclic voltammetry (CV)

Cyclic voltammetry of the bare and 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> between 2.5 and 4.8 V at a scan rate of 0.1 mV s<sup>-1</sup> for the first three cycles are shown in Fig. 8.

For the bare  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , the first cycle anodic peaks center at 3.64 and 4.60 V which correspond to the  $\text{Ni}^{2+}/\text{Ni}^{4+}$  and  $\text{Co}^{3+}/\text{Co}^{4+}$  [3]. The cathodic peaks center at 4.06 and 4.73 V. In the following two cycles, the anodic peaks are almost at the same voltage, but the cathodic peaks shifts to lower voltage and the cathodic areas decrease sharply compared with the first cycle. The CV peaks of the 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> are much steady

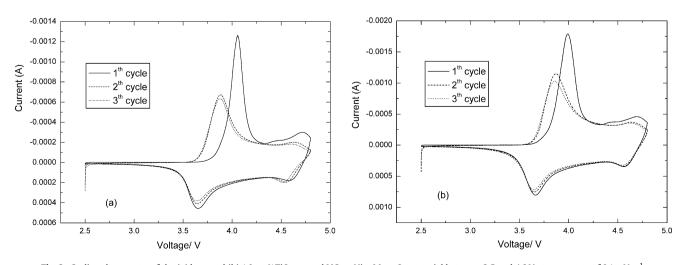


Fig. 8. Cyclic voltammetry of the (a) bare and (b) 1.0 wt.% TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> material between 2.5 and 4.8 V at a scan rate of 0.1 mV s<sup>-1</sup>.

than that of the bare material, which indicate that the cycle performance is improved after  $TiO_2$ -coating.

#### 4. Conclusions

TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> has been synthesized with an in situ dipping and hydrolyzing method for Li-ion batteries. The TiO<sub>2</sub>-coating layer is on the surface of the LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> with nano-size. Although the crystal structure of the TiO<sub>2</sub>-coated LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> shows no obvious change compared with the bare material, its discharge capacity, cycle performance and rate capability have been improved significantly. The coated TiO<sub>2</sub> layer on the surface of LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> by suppressing the dissolution reaction of manganese ions and cobalt ions, and increase the diffusion coefficient of lithium ions during charging and discharging, resulting in the improvement of the electrochemical properties the LiCo<sub>1/3</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>.

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## References

- [1] T. Ohzuku, Y. Makimura, Chem. Lett. (2001) 642-643.
- [2] M.-H. Lee, Y.-J. Kang, S.-T. Myung, Y.-K. Sun, Electrochim. Acta 50 (2004) 939–948.
- [3] K.M. Shaju, G.V. Subba Rao, B.V.R. Chowdari, Electrochim. Acta 48 (2002) 145–151.

- [4] N. Yabuuchi, T. Ohzuku, J. Power Sources 146 (2005) 636-639.
- [5] S.-T. Myung, M.-H. Lee, S. Komaba, N. Kumagai, Y.-K. Sun, Electrochim. Acta 50 (2005) 4800–4806.
- [6] S.B. Jang, S.-H. Kang, K. Amine, Y.C. Bae, Y.-K. Sun, Electrochim. Acta 50 (2005) 4168–4173.
- [7] H. Wang, L. Zhu, M. Chen, J. Rare Earth 25 (2007) 124-128.
- [8] S.H. Park, C.S. Yoon, S.G. Kang, H.-S. Kim, S.-I. Moon, Y.-K. Sun, Electrochim. Acta 49 (2004) 557–563.
- [9] M. Kagayama, D. Li, K. Kobayakawa, Y. Sato, Y.-S. Lee, J. Power Sources 157 (2006) 494-500.
- [10] Y.-K. Sun, C.S. Yoon, I.-H. Oh, Electrochim. Acta 48 (2003) 503-506.
- [11] Y. Kim, H.S. Kim, S.W. Martin, Electrochim. Acta 52 (2006) 1316-1322.
- [12] Y.-K. Sun, S.-W. Cho, S.-W. Lee, C.S. Yoon, K. Amine, J. Electrochem. Soc. 153 (2007) A168–A172.
- [13] H.-S. Kim, M. Kong, K. Kim, I.-J. Kim, H.-B. Gu, J. Power Sources 171 (2007) 917–921.
- [14] G.T.-K. Fey, C.-Z. Lu, T. Prem Kumar, Y.-C. Chang, Surf. Coat. Technol. 199 (2005) 22–31.
- [15] Z.R. Zhang, J. Li, Y. Yang, Electrochim. Acta 52 (2006) 1442–1450.
- [16] G.T.-K. Fey, C.-Z. Lu, J.-D. Huang, T.P. Kumar, Y.-C. Chang, J. Power Sources 146 (2005) 65–70.
- [17] H. Liu, Z. Zhang, Z.L. Gong, Y. Yang, Solid State Ionics 166 (2004) 317-325.
- [18] J.R. Dahn, Solid State Ionics 44 (1990) 87-97.
- [19] S.T. Myung, K. Izumi, S. Komaba, Y.-K. Sun, H. Yashiro, N. Kumagai, Chem. Mater. 17 (2005) 3695–3704.
- [20] M.D. Groner, J.W. Elam, F.H. Fabreguette, S.M. George, Thin Solid Film 413 (2002) 186–197.
- [21] H.-W. Ha, N.-J. Yun, M.H. Kim, M.H. Woo, K. Kim, Electrochim. Acta 51 (2006) 3297–3302.
- [22] H.-W. Ha, N.J. Yun, K. Kim, Electrochim. Acta 52 (2007) 3236-3241.
- [23] G.T.-K. Fey, P. Muralidharan, C.-Z. Lu, Y.-D. Cho, Electrochim. Acta 51 (2006) 4850–4858.
- [24] M.D. Levi, K. Gamolsky, D. Aurbach, U. Heider, R. Oesten, Electrochim. Acta 45 (2000) 1781–1789.
- [25] Z.R. Zhang, H.S. Liu, Z.L. Gong, Y. Yang, J. Power Sources 129 (2004) 101–106.
- [26] Q. Cao, H.P. Zhang, G.J. Wang, Q. Xia, Y.P. Wu, H.Q. Wu, Electrochem. Commun. 9 (2007) 1228–1232.
- [27] S.-T. Myung, K. Izumi, S. Komaba, H. Yashiro, H.J. Bang, Y.-K. Sun, N. Kumagai, J. Phys. Chem. C 111 (2007) 4061–4067.