Front. Chem. China 2008, 3(1): 64–69
DOI 10.1007/s11458-008-0020-5

RESEARCH ARTICLE

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Effect of TiO_2-coating on structure and electrochemical performance of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$

Abstract $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$, as the cathode material for lithium ion batteries, was modified by TiO_2-coating. The effect of TiO_2-coating on the structure and electrochemical performance of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and galvanostatic charge-discharge tests. The results suggest that a small amount of TiO_2-coating does not change the crystalline structure, but considerably improves the electrochemical performance of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ in terms of capacity delivery and cyclability. XPS measurements confirm that the improved electrochemical performance is most possibly attributed to a decrease in interaction between the layered material and non-aqueous electrolyte during the charge-discharge processes.

Keywords $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$, TiO_2-coating, electrochemical performance, lithium ion batteries

1 Introduction

Since their invention in the 1990s [1], lithium ion batteries have been widely applied in portable electronic devices due to their advantages such as high energy density, long life and high operation voltage. The most common cathode material of commercial lithium ion batteries is $LiCoO_2$. However, disadvantages such as high cost and poor safety have hindered further application, especially on a large scale for these batteries [2]. A lot of research has been done to develop new cathode materials for lithium ion batteries which are less expensive, safer and have a higher energy density than that of $LiCoO_2$.

Translated from *Chinese Journal of Inorganic Chemistry,* 2007, 23(5): 753–758 [译自: 无机化学学报]

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Recently, $LiCo_xNi_yMn_{(1-x-y)}O_2$ [3–5] such as $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ [6], $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ [10–12], and $LiCo_{0.8}Ni_{0.1}Mn_{0.1}O_2$ [13,14], which have a similar crystal structure with $LiCoO_2$, have been investigated and regarded as promising materials to replace $LiCoO_2$ due to their lower cost and better safety. In this kind of material, the major oxide state of Co, Ni, Mn are demonstrated to be +2, +3, +4, respectively [6]. In this case, the average oxide state of Mn is tetravalent so that electrochemically inactive Mn^{4+} provided significant structural stability during electrochemical cycling and better thermal stability than $LiCoO_2$[7–9]. Compared with $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ and $LiCoO_2$,$LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ has a lower cost because of low Co content and better safety because of the higher Mn content. It also has promise not only in cells for portable electric devices, but also in large-scale lithium ion batteries [4,5]. However, $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ has a relatively lower discharge plateau and coulombic efficiency of the first cycle than that of $LiCoO_2$. This material's cycle performance on high cut-off voltage and rate capability also needs to be improved when used in high performance lithium ion batteries for power tools, HEV, EV and other applications.

Metal oxide coating for lithiated transition metal oxides such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ has been investigated. Physical and electrochemical properties were significantly improved by ZnO [15–16], Al_2O_3 [17–18], ZrO_2 [19–20], TiO_2 [20–21], and SiO_2 [22] coating cathode materials. Nevertheless, there are few reports on coating $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$. The authors of this paper have reported that the electrochemical properties of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$, especially rate capability, were improved by Ti, Mg co-doping [23]. Ti^{4+} doping lowered the tap density of the cathode material because it hampered the growth of crystal size, although this problem can be avoided when TiO_2-coating cathode material is prepared. In this paper, the TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ with titanium tetrabutoxide is prepared by a wet chemical process. The improvement in crystal structure and electrochemical property by TiO_2 –coating is also discussed.

2 Experimental

$Co_{0.2}Ni_{0.4}Mn_{0.4}(OH)_2$ was prepared by co-precipitation from a solution containing stoichiometric amounts of nickel/cobalt/ manganese nitrates by the addition of NaOH and a $NH_3{\cdot}H_2O$ solution. The $Co_{0.2}Ni_{0.4}Mn_{0.4}(OH)_2$ was calcined at 500°C first, and then was mixed with stoichiometric amounts of Li_2CO_3. The mixture was sintered at 850−1050°C for 10 h and generated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$. To prepare TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$, the bare cathode material powder was added to an ethanol solution containing titanium tetrabutoxide. This mixture was stirred and evaporated to dryness. The powder was heated at 200−600°C for 2−8 h in the air. By this process, different amounts of TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ material were prepared by controlling the amount of titanium tetrabutoxide. ICP-AES (IRIS Intrepid II, USA) was employed to measure the Ti content of cathode materials.

X-ray diffractometry (XRD, Rigaku Rint 2200) with Cu Kα radiation ($\lambda = 0.15406$ nm) was employed to characterize the crystal structure of cathode materials. It was operated at 40 kV and 30 mA over a 2θ range of 10–80° in continuous scan mode with step size 0.02° and 4.0°/min scan rate. The crystal parameters were calculated by the software Powder X. The particle shape and morphology images of $Co_{0.2}Ni_{0.4}Mn_{0.4}(OH)_2$ and $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ were obtained by scanning electron microscopy (SEM) (HITACHI S-3500N). The tap density of cathode materials was measured using a tap density tester (FTZ-4, 300 times/min for 3000 times tapping).

X-ray photoelectron spectroscopy (XPS, Axis Ultra spectrometer with Al Kα radiation, $h\lambda$ = 1486.71 eV) measurements were performed to get information on the surface of the TiO_2-coated $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$.

The electrode was fabricated by thoroughly mixing the active material (88%) with carbon black (8%) and polythene tetrafluoride (PTFE) (4%), and the mixture was pressed into a 0.2 mm thick patch. The electrode was dried at 120°C for 24 h under vacuum conditions. The model cells were assembled in a dry room (RH% < 3%) using foils of Li metal as counter electrodes, Cegard 2400 polypropylene membrane as a separator and 1.0 $mol{\cdot}L^{-1}$ $LiClO_4$ (PC:DME = 1:1, *v*/*v*) as an electrolyte. The electrochemical performance was characterized under the voltage range 3.0−4.3 V or 3.0−4.5 V at a constant current density of 0.8 $mA{\cdot}cm^{-2}$ (about 0.2 C, 1 C was counted by 160 $mA{\cdot}g^{-1}$) using a LiXing PCBT-110-32D-B secondary batteries tester.

3 Results and discussion

3.1 Morphology and surface structure

Different morphology cathode materials can be obtained by controlling the condition of synthesis. The difference in electrochemical performance can be caused by different surface morphologies. In reference [23], the authors of this paper synthesized $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ with a 200−400 nm size primary particle and delivered a 160 $mAh{\cdot}g^{-1}$ capacity. However, it is difficult to use this material in commercial batteries because it has a large special surface area and low tap density. In this paper, $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ with 2−3 μm primary particles was synthesized as shown in Fig. 1, which has a 2.0 $g{\cdot}cm^{-3}$ tap density and relatively lower special surface area. The primary particle size is very important not only to electrochemical performance but also to the electrode process. However, the material with larger primary particles has a relatively lower special capacity because of two reasons [10,11]. First, larger primary particles perhaps lead to a increase on the diffusive path of Li^+ and electrons. Secondly, it is difficult for the material with larger primary particles to adequately absorb electrolytes.

SEM images of the bare and the TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ are shown in Fig. 1. Distinct changes to the surface morphology of the cathode particles after coating cannot be seen from SEM images due to very low coating content. The test results of ICP-AES showed that the ratios of Ti/(Ni + Co + Mn) across different samples are 0.00%, 0.098%, 0.19%, 0.29% and 0.49%, respectively, which are in good agreement with the initial ration in the mixture.

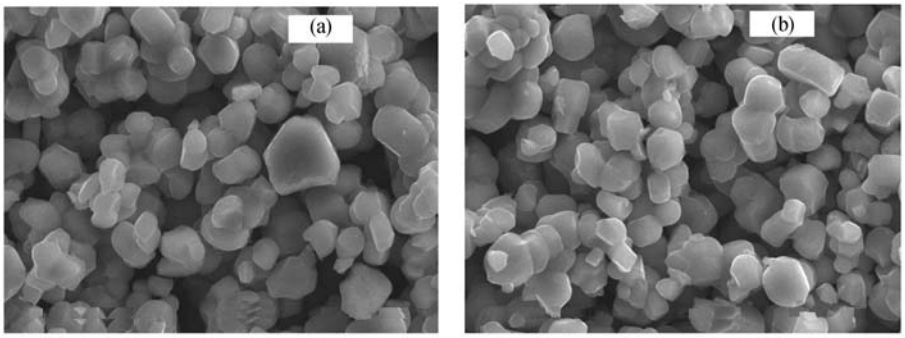

Fig. 1 SEM of (a) bare and (b) 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$

XPS results support evidence of the uniform coating of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ by TiO_2 in Fig. 2. According to Fig. 2, the electron binding energy of Ti2p is 458.25 eV, which is between that of Ti^{4+} (TiO_2, 458.7 eV) and Ti^{3+} (457.69 eV). This result showed that the major portion of the Ti element of the material surface is tetravalent and a small portion is trivalent. Ti(+3) can be attributed to a small amount of $LiTiO_2$ on the surface of the cathode particles [24,25]. The XPS spectra of O1s of bare and 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ are shown in Fig. 2(b). It can be seen that the XPS spectra of O1s are composed of two peaks at 529.3 eV and 531.04 eV, respectively. Compared with bare $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$, the first peak area (peak value = 529.3 eV) of TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ increased to 14655.6 from 10541.6, while the second peak area (peak value = 531.04 eV) decreased to 8420.3 from 14075.3. Usually, a change of the second peak area (peak value = 531.04 eV) is closely related to variety in oxide activity of oxygen on the surface of a cathode material. The result showed that such activity on the surface of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ declined by TiO_2 coating. The decrease in the oxide activity on the surface is an advantage to decrease the undesired reaction between the cathode and electrolyte, which contributes to an improved electrochemical performance of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ [26,27]. Further evidence will be obtained from the results of electrochemical test.

3.2 XRD characterization

The diffraction patterns of bare and coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ can be identified as a pure hexagonal α-$NaFeO_2$ structure with space group $R\bar{3}\ m$ in Fig. 3. Although $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ was coated with TiO_2, there is no significant difference in the crystal structure after the coating as shown in Fig. 3, because the coated amount was very small in the final product and/or the coating material was in an amorphous state when fired at temperatures as low as 400°C [24]. In the hexagonal cell, Li ions occupied the octahedral 3a sites; Ni, Co, and Mn ions occupied the octahedral 3b sites and O occupied the octahedral 6c sites. However, cation mixing often appeared between Li and transition metal ions, which contributed to the deterioration of electrochemical performance [28].

Using the XRD data, the lattice parameters and characteristic peak intensity ratios were calculated in Table 1. The intensity ratio I_{003}/I_{104} has been reported to be closely related to undesirable cation mixing, which is reduced as the value of the ratio increased. The materials with an $I_{003}/I_{104} > 1.2$ ratio have good electrochemical performance. There is no distinct difference on the lattice parameters a and c for $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ by different amounts of TiO_2 coating as shown in Table 1. Although the ratio I_{003}/I_{104} of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ is more than 1.2, the ratio I_{003}/I_{104} is sensitive to the coated amount; the ratio I_{003}/I_{104} increases first and then decreases with increasing coated amounts. This trend is closely related to the electrochemical performance. Therefore, 0.3 mol% TiO_2 coated with the largest value of the ratio I_{003}/I_{104}, up to 2.112, perhaps show the best electrochemical performance. The conclusion will be further supported by data from electrochemical characterizatioin later.

3.3 Electrochemical properties

The dependence of TiO_2 coating amount on the electrochemical properties of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$/Li was examined and shown in Fig. 4. The cells were cycled at 0.2C-rates under a voltage range of 3.0−4.3 V at room temperature. Compared with bare $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$, TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ has a higher capacity and better capacity retention during cycling. The result showed that the change in capacity retention is the same as that of the ratio of I_{003}/I_{104}. Moreover, the 0.3 mol% coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ with the largest I_{003}/I_{104} had the highest discharge capacity, achieving 140 mAh·$g^{-1}$and 142 mAh·g^{-1} after 5 cycles, and the best capacity retention at 98% after 30 cycles. However, at the same test conditions, the discharge capacity of bare $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ is 135 mAh·g^{-1} and stayed at 88 mAh·g^{-1} after 30 cycles. Its capacity retention after 30 cycles is only 65%.

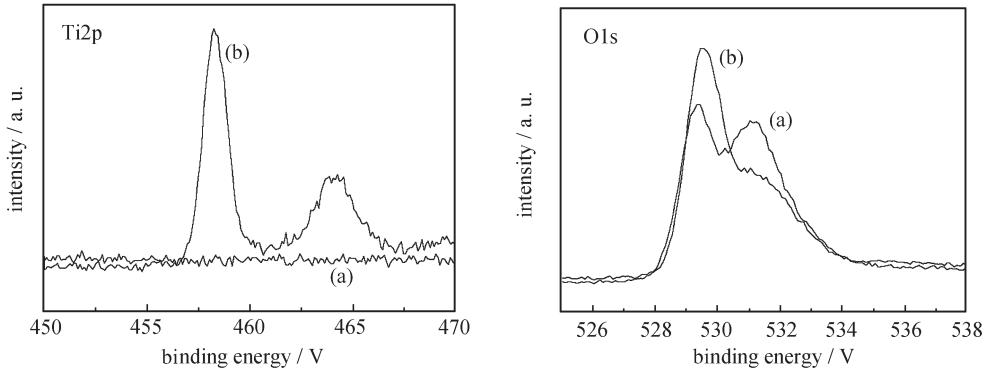

Fig. 2 Ti2p and O1s spectra of (a) bare and (b) 0.3 mol.% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$

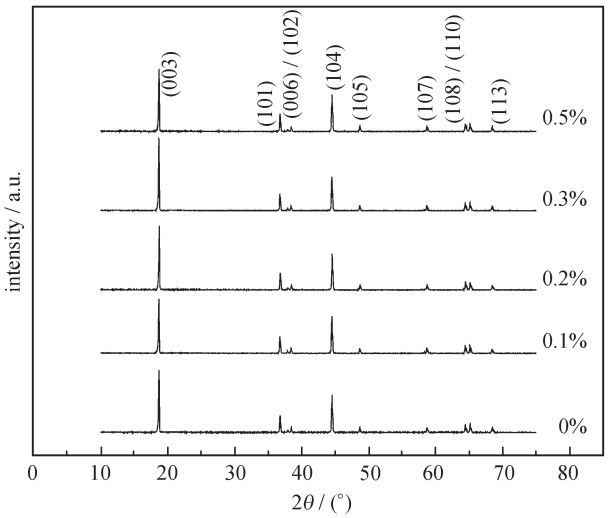

Fig. 3 XRD patterns of TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ materials with different coating amounts

Table 1 Lattice parameters and characteristic peak intensity ratios of samples

Sample	*a*/nm	*c*/nm	*c*/*a*	I_{003}/I_{104}
0.0%	0.2862	1.4228	4.9713	1.758
0.1%	0.2862	1.4229	4.9717	1.454
0.2%	0.2863	1.4232	4.9710	1.830
0.3%	0.2863	1.4230	4.9703	2.112
0.5%	0.2863	1.4233	4.9714	1.767

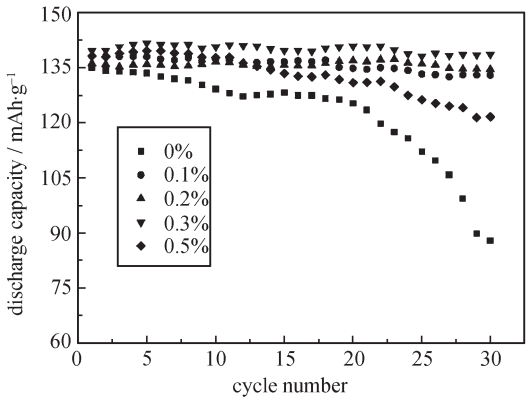

Fig. 4 Cycling performance of TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ materials with different coating amounts

Figure 5 shows the rate discharge curves of the bare and 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$/Li cells by applying different current densities at room temperature between 3.0 and 4.3 V versus Li^+/Li. The cells were charged galvanostatically with 0.2 C, and then discharged at 0.2 C, 0.5 C, 1 C, 2 C respectively. The TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ sample delivered a 140 $mAh \cdot g^{-1}$ capacity at 0.2 C discharging and 115 $mAh \cdot g^{-1}$ at 2 C discharging. The capacity at 2 C is 82% of the capacity at 0.2 C; that of bare material is only 69%. Obviously, the TiO_2-coated sample delivered a better rate capability than bare material.

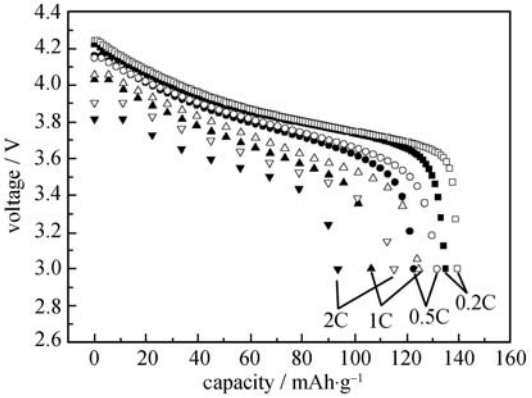

Fig. 5 Performance of rate capability of bare (solid) and 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ (hollow)

Figure 6(1) exhibits cycle performance of the bare and 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$/Li cells by applying galvanostatical charge and discharge at 1C current densities between 3.0 and 4.3 V versus Li. Evidence showed that the TiO_2 coating is effective in improving cycle performance at large current charging and discharging. The differential capacity dQ/dV versus V curves of the second and thirtieth cycle for bare and 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ are shown in Fig. 6(2). The oxide peak value of the curve of 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ in the second cycle is lower than that of bare material. The peak voltage difference between oxide peak and reductive peak reaches 29 mV, while that of bare material is 94 mV. After 30 cycles, the peak voltage difference of the TiO_2-coated sample increased to 55 mV, which is in the range of reversible redox reaction (<56 mV). In comparison, the peak voltage difference of bare material sharply increased to 233 mV. It is obvious that polarization of the cathode during cycling can be suppressed by a TiO_2-coating. The result can be attributed to two reasons. First, this coating layer appears to protect the cathode material from dissolution in the liquid electrolyte and also stabilizes the layered structure of the $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ [29]. Second, the undesirable reaction between cathode and electrolyte decreased as the direct contact area between cathode and electrolyte decreased by TiO_2 coating [30–32]. Certainly, the average voltage of discharge will be promoted and stabilized due to decreasing polarization of the cathode. It can be seen from Fig. 6 that the cycle performance of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ at large current charging and discharging has been improved by a 0.3 mol% TiO_2 coating.

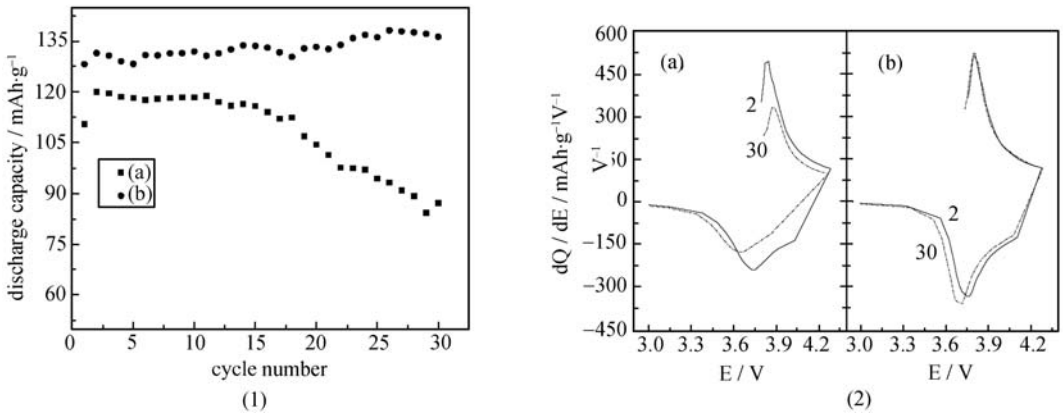

Fig. 6 (1) Cycling performance of (a) bare and (b) 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ (3.0−4.3 V versus Li^+/Li, 1 C charge/discharge); (2) Differential capacity dQ/dV versus V curves of the second (solid line) and thirtieth (dot line) cycle for (a) bare and (b) 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$

Figure 7(1) shows the discharge curve of bare and TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ charged to different cut-off voltages. The discharging capacity of 0.3 mol % TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ increased with the charge cut-off voltage ascending. When it was charged to 4.6 V, TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ delivered 173 $mAh \cdot g^{-1}$ reversible capacity, which is 10% higher than that of bare cathode material. To further study the improvement on cathodes by TiO_2 coating, the cycle performance of bare and TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ were compared at the voltage range of 3.0−4.5 V in Fig. 7(2). It is shown that the discharge capacity of bare $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ retained 53% of the initial capacity after 30 cycles, while the retention ratio of TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ was 93%. This result showed that the cycle performance of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ charged to 4.5 V was improved by TiO_2 coating. The mechanism can be presumed that TiO_2 coating suppressed the undesirable reaction between the surface of the cathode and electrolyte under high charging cut-off voltage, which was attributed to the activity drop of O on the surface of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ as evidenced in the XPS results.

4 Conclusion

Different amounts of TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ have been synthesized with titanium tetrabutoxide by a wet chemical process. XRD data showed that all samples have a pure hexagonal α-$NaFeO_2$ structure, with the intensity ratio of I_{003}/I_{104} first increasing and then decreasing as the amount of TiO_2 coating increased. When $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ was coated by 0.3% TiO_2, the ratio was 2.112, reaching the largest value. An electrochemical property test showed that the cycle performance and rate capability can be improved obviously by TiO_2 coating. 0.3% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ with the largest ratio of I_{003}/I_{104}, showed the best electrochemical performance. According to XPS data, the TiO_2 coating layer appeared to decrease the activity of oxygen on the surface of the cathode materials and avoided the

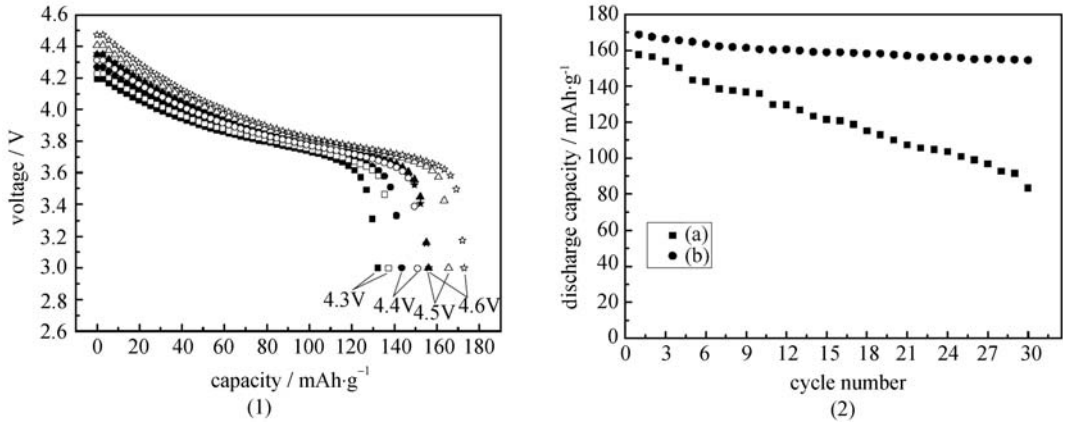

Fig. 7 (1) The discharge profiles of bare (solid) and 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ (hollow) in different cut-off charge voltage; (2) Cycling performance of (a) bare and (b) 0.3 mol% TiO_2-coated $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ in the voltage range 3.0−4.5 V

undesirable reaction between the cathode and electrolyte, which is helpful to stabilize the layered structure during cycling. This is the major cause of improvement in the cycle life and rate capability of $LiCo_{0.2}Ni_{0.4}Mn_{0.4}O_2$ by TiO_2 coating.

Acknowledgements This work was funded by the Electronic Information Industry Development Foundation of Ministry of Information Industry of China (MIIC, contract no. 2004-479).

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