Enhancement of electrochemical performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ by surface modification with MnO_2

Xin Guo ^{a,b}, Li-Na Cong ^{a,b}, Qin Zhao ^{a,b}, Ling-Hua Tai ^{a,b}, Xing-Long Wu ^{a,b}, Jing-Ping Zhang ^{a,b},
Rong-Shun Wang ^{a,b}, Hai-Ming Xie ^{a,b,*}, Li-Qun Sun ^{a,b,*}

^a Institute of Functional Materials Chemistry, Faculty of Chemistry, Northeast Normal University,
Changchun, P. R. China

^b National & Local United Engineering Lab for Power Battery, Northeast Normal University;
Changchun, P. R. China

*E-mail: xiehm136@nenu.edu.cn, sunlq446@nenu.edu.cn.

Tel.: +86-431-85099511; fax: +86-431-85099511.

Abstract

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is successfully coated with MnO_2 by a chemical deposition method. The X-ray diffraction (XRD), scanning electron microscope (SEM) and high resolution transmission electron microscope (HRTEM) results demonstrate that MnO_2 forms a thin layer on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ without destroying the crystal structure of the core material. Compared with pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the MnO_2 -coated sample shows enhanced electrochemical performance especially the rate capability. Even at a current density of 750 mA g^{-1} , the discharge capacity of MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is $155.15 \text{ mAh g}^{-1}$, while that of the pristine electrode is only $132.84 \text{ mAh g}^{-1}$ in the range of 2.5-4.5 V. The cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS) curves show that the MnO_2 coating layer reacts with Li^+ during cycling, which is responsible for the higher discharge capacity of MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Electrochemical impedance spectroscopy (EIS) results confirmed that the MnO_2 coating layer plays an important role in reducing the charge transfer resistance on the electrolyte-electrode interfaces.

Keywords: Lithium ion battery; Cathode material; $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; Surface modification

1. Introduction

Nowadays, rechargeable lithium ion batteries are the leading power sources for portable electronic devices and show great prospect in application of electric vehicles and hybrid electric vehicles, by virtue of their high energy density and power capability [1-9]. One of the principal cathode materials for such lithium ion batteries, LiCoO_2 , has been investigated intensely in the past few years. Despite of its stability and high rate capability, LiCoO_2 is plagued by issues such as the toxicity and high cost of cobalt. Recently, a variety of materials have been developed to substitute all or some of the cobalt with other transition metals [10-13]. One viable LiCoO_2 replacement material is layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ due to its high reversible capacity, superior safety, less toxicity and low cost [14-16]. Unfortunately, there are still two serious shortcomings hindering its further applications. One is the degradation of the reversible capacity upon prolonged cycling. Such phenomenon is attributed to the instability of the electrode surface, leading to severe side reactions between the electrode and electrolyte. The other is the inferior rate capability due to its intrinsic low lithium ion mobility and electronic conductivity.

Surface coating of cathode materials is an effective way to protect the electrode surface from directly contact with the electrolyte, and thus suppress the side-reactions which lead to the deterioration of the cell properties. As coating materials, carbon composites [17-19], metal oxides [20-24], fluorides [25, 26], and phosphates [27, 28] have been shown to improve the cycling stability and rate capability. Nevertheless, all the coated materials used above also lead to the reversible capacity loss because of their inactive characteristics for the lithium insertion/extraction. It is suppose that some electro-active materials, which can provide the conduction path for Li^+ ion transportation from the electrode to electrolyte, should be more favorable for enhancing the electrochemical performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Precisely, MnO_2 is a promising electrochemical active oxide which has been used in catalytic [29-31], supercapacitor [32-34] and especially in lithium ion batteries [35, 36]. It features high theoretical capacity of 1230 mAh g^{-1} , low cost, low toxicity and earth abundance, and there are numerous methods for synthesizing different types of MnO_2 . In this work, with the aim to highly improve the electrochemical properties of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, MnO_2 is introduced as a coating material which can provide Li^+ intercalating sites. Meanwhile, the MnO_2 coating layer can stabilize the bulk particles

as well. The structure, surface character and electrochemical performance of MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are systematically investigated. The difference between $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is also discussed.

2. Experimental

2.1. Synthesis of MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

All reagents used in the experiment were of analytical grade (purchased from Aladdin) without further purification. The $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursor was prepared via co-precipitation. An aqueous solution containing $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ with a concentration of 2.0 mol L^{-1} was pumped into a continuously stirred tank reactor. At the same time, a Na_2CO_3 solution of 2.0 mol L^{-1} and a desired amount of NH_4HCO_3 solution were separately fed into the reactor. The reaction temperature was kept at 50°C and pH was controlled by Na_2CO_3 solution to 8.5. After vigorous stirring for 12 h, the homogenously precipitated carbonate powders were filtered, washed and dried at 110°C overnight. To prepare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders, stoichiometric amounts of the $\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{CO}_3$ precursor and 5 wt% excess Li_2CO_3 (molar ratio of $\text{Li}/(\text{Ni} + \text{Co} + \text{Mn}) = 1.05:1$) were mixed thoroughly by ball milling, calcined and sintered at 500°C for 5 h and then 900°C for 12 h in air.

The surface modification of the synthesized layered oxides was carried out by dispersing 2.0 g $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders in $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.117 g) solution under ultrasound conditions for 1 h, and then the suspension was stirred mechanically while Na_2CO_3 solution of 1.0 mol L^{-1} slowly dropped into it. After a certain reaction time, the precipitated product was filtered and washed with distilled water, dried at 120°C for 10 h and finally heated at 400°C for 4 h in air to form $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample coated with 3 wt% MnO_2 .

2.2. Structural and morphological characterization

X-ray diffractometry (XRD, Rigaku-Dmax2500) was employed to characterize the crystal structure of the sample. XRD data were obtained with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) in the 2θ range of 10 – 80° at a continuous scan mode with a step size of 0.02° and a scan rate of 3° min^{-1} . The morphology of the samples were observed by scanning electron microscope (SEM, quanta250

FEG) and high resolution transmission electron microscope (HRTEM, JEOL 2100F). The electronic states of Ni, Co, Mn and O for the samples were analyzed using X-ray photoelectron spectroscopy (XPS, PHI 5500 system) with Al-K α radiation under ultrahigh vacuum.

2.3. Electrochemical measurements

For fabrication of the positive electrodes, the as-prepared samples were mixed with acetylene black and polyvinylidene fluoride (80:10:10) in *N*-methyl-2-pyrrolidone to obtain a slurry, which was coated onto aluminum foil and dried at 120 °C for 12 hours in a vacuum oven. The electrochemical characterizations were performed using R2025 coin-type cells with Li metal as the negative electrode. The electrolyte solution was a 1M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC = 1:1, volume ratio). All the cells were assembled in an argon-filled glove box with water and oxygen contents below 0.5 ppm. The cells were galvanostatically charged and discharged at various current densities (1 C = 150mA g⁻¹) on a Neware battery tester in the voltage ranges of 2.5-4.3 V and 2.5-4.6 V at room temperature. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the cells were determined with CHI660A electrochemical workstation. The sweep rate of CV was 0.1 mV s⁻¹ in the potential window of 2.0-5.0 V. The amplitude of the AC signal was 10 mV over the frequency range of 100 kHz to 0.1 Hz.

3. Results and discussion

A variety of manganese oxides can be obtained when MnCO₃ is heat-treated at different temperature. It can be confirmed from the XRD patterns (Fig. 1a) that MnCO₃ is converted to MnO₂ at 400 °C. The reaction can be written:

Thus, the MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ is obtained by heat treatment at the same temperature. Fig. 1b shows the XRD patterns of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂. The synthesized materials exhibit a well-defined layered structure based on a hexagonal α -NaFeO₂ with space group R $\bar{3}$ m without any impurity phases. The crystal lattice constants are summarized in Table 1. The results of the coated material show no significant change in the *a* and *c* lattice

parameters and the 2θ values of the peaks. Furthermore, the lattice parameters (a , c) of the two samples show consistency with that of the theoretical and experimental parameter of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ reported [9]. That is, a well layered structure is maintained completely after MnO_2 coating, which ensures the lithium ions migration smoothly.

The morphologies of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ before and after MnO_2 coating are presented in Fig. 2. It is clearly seen from the SEM and TEM images that the surface morphology of the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is smooth and clean without any heterophase particles (Fig. 2a, 2c). By comparison, the surface of the coated sample is rough and covered with nanoparticles, which appeared to be the MnO_2 coating layer (Fig. 2b, 2d). In order to observe the detailed existence of MnO_2 on the surface, HRTEM analysis is also performed. As shown in Fig. 2f, a distinguishable and compact layer can be obviously observed on the surface of the coated sample. The interplanar distances of the parallel lattice is 4.7 Å, which corresponds to the distance of the closely packed (003) plane of the $\text{R}\bar{3}\text{m}$ -layered structure. Thus, a MnO_2 film is successful growth on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particles. The coating layer could reduce the contact area between the electrode and electrolyte, and then it could protect the cathode material from dissolving into the electrolyte.

To explore the composition of the coating layer, XPS measurement is employed, and the partial XPS spectrum of Ni2p, Co2p, Mn2p and O1s are presented in Fig. 3. All of the binding energies in the XPS analysis are corrected for specimen charging by referencing them to the C 1s peak (set at 284.6 eV). No other element peak is detected, indicating that the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are high purity. Both pristine and coated samples have Ni2p_{3/2}, Co2p_{3/2} and Mn2p_{3/2} peaks without remarkable chemical shift of binding energy, indicating that the Ni, Co and Mn ion environment in the structure are not changed. In contrast, the shape of O1s spectra has little changed. The chemical shift of the binding energy of O1s implies that the surface of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is altered by MnO_2 coating. As shown in Fig. 3d, two peaks are observed in the pristine sample. The dominating one is located at 530.17 eV, which can be assigned lattice oxygen in the layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Another small and broad peak located at the higher binding energy of 532.05 eV is likely due to the active oxygen species on the surface or the impurity of adsorbed species, such as Li_2CO_3 . However, the

peak at high binding energy disappears after the coating treatment, suggesting the adsorbed species Li_2CO_3 is consumed by MnO_2 layer during the process of heat-treatment. And then, the nonstoichiometric Li_xMnO_2 oxides are formed on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. Accordingly, the coating layer is likely to be partly Li_xMnO_2 instead of the nominal MnO_2 , which can be further confirmed by the testing of the initial charge/discharge performance.

Fig. 4a illustrates the initial voltage versus capacity curves of the pristine and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ at the constant current density of 15 mA g^{-1} in the range of 2.5-4.3 V. It is worthwhile to note that a small plateau appears at 3.0 V in the charge curve of MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample, which is due to the electrochemical delithiated process of nonstoichiometric Li_xMnO_2 oxides. Correspondingly, a small plateau belonging to the inserted progress of Li^+ to the MnO_2 layer at 2.8 V is also observed in the discharge curve, which will deliver more discharge capacities. It can be seen that the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode delivers a discharge capacity of $161.99 \text{ mAh g}^{-1}$, whereas the coated electrode exhibits a discharge capacity of $166.65 \text{ mAh g}^{-1}$. Significantly, as shown in Fig. 4b, the coated electrode delivers a discharge capacity of $153.66 \text{ mAh g}^{-1}$ even at a high rate of 300 mA g^{-1} , whereas only $141.07 \text{ mAh g}^{-1}$ specific capacities can be obtained for the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode at the same rate. Moreover, the MnO_2 -coated electrode can still have a very stable capacity delivery with a capacity retention of 88.23 % over 100 cycles at 300 mA g^{-1} (vs. to the initial discharge capacity), while only 71.62 % capacity retention for the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode can be obtained. Discharge capacity and capacity retention of a cathode are controlled by surface property. So the enhanced electrochemical properties of the MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ should be attributed to the stabilization of cathode surface by MnO_2 coating. It can also be confirmed in Fig. 4c and 4d that the coated electrode shows much better voltage platforms at the following cycles.

To further evaluate the superiority of the MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material, the cells are tested in a high voltage range of 2.5-4.5 V. Fig. 5a displays the initial charge/discharge profiles of the as-prepared materials at 15 mA g^{-1} . As expected, the initial discharge capacity of the MnO_2 -coated electrode is up to $195.86 \text{ mAh g}^{-1}$, while the pristine electrode presents a lower discharge capacity of $189.86 \text{ mAh g}^{-1}$. Fig. 5b shows the rate capability of the pristine and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrodes between 2.5 V and 4.5 V. At the same current density,

the MnO₂-coated electrode shows a higher discharge capacity than that of the pristine. The discharge capacity gap between the pristine and coated materials is more remarkable with the rate increasing. For example, the reversible capacity of the MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrode has been measured as high as 155.15 mAh g⁻¹ at 750 mA g⁻¹, while that of the pristine electrode merely is 132.84 mAh g⁻¹. Moreover, the coated sample shows excellent capacity retention at each rate step. The stable film layer facilitates the electron transfer at the surface of electrode, which leads to an enhanced rate capability of the MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂.

Cyclic voltammetry (CV) is a useful technique to study the electrochemical performance and electrode kinetics of oxide materials. Fig. 6 shows the CV curves of the cells with the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ samples as the working electrodes. The cells are tested at a scan rate of 0.1 mV s⁻¹ in the range of 2.0-5.0 V. As for the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrode, the main peak at 3.9 V and another low-intensity peak at 4.6 V are corresponding to the redox couples of Ni²⁺/Ni⁴⁺ and Co³⁺/Co⁴⁺, respectively. In the case of MnO₂-coated electrode, the peaks belonging to the redox reaction of Mn⁴⁺ to Mn³⁺ at around 3.0 V are observed. The CV of the MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ at low anodic and cathodic peaks around 3.0 V can be attributed to the oxidation and reduction of MnO₂ during electrochemical reaction. This result is well consistent with the charge/discharge profiles. Overall, the MnO₂ layer reacts with Li⁺ and converts to nonstoichiometric Li_xMnO₂ oxides, which should be the reason for the higher discharge capacity of the MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrode. Besides, the CV curves of MnO₂-coated electrode overlap much better, also suggesting the superior electrochemical cycle stability.

To understand the electron transfer process of the pristine LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes, electrochemical impedance spectroscopy (EIS) has been performed. Fig. 7 shows the impedance spectrum measured using the coin cells after the 100th charge-discharge cycles. Both Nyquist plots have the high frequency semicircles and low frequency tails. Generally, an intercept at the Z_{real}-axis in high frequency region corresponded to ohmic resistance (R_e) of the battery, which contains the resistance of electrolyte, separator, electrode, etc. The semicircle in the high frequency is related to charge transfer resistance (R_{ct}) and the double layer capacitance (CPE). The low frequency tail represents the Warburg impedance

(Z_w), which is associated with Li^+ ion diffusion process in the solid phase of electrode. All the sections correspond to the partitions in the equivalent circuit, which is used to fit the EIS data to give a quantitative result to further understand the effect of MnO_2 coating. It directly demonstrates that the MnO_2 -coated electrode has much lower charge resistance ($R_{ct} = 235 \Omega$) than the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($R_{ct} = 592 \Omega$). This result clearly indicates that the improvement of the electrochemical performance is due to the presence of MnO_2 coating layer, which effectively suppresses the chemical instability ascribed to surface reaction between electrode and electrolyte.

4. Conclusions

In summary, the MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material is successfully synthesized via a simple chemical deposition method. Compared with the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the coated electrode shows higher discharge capacity, longer cycle life and better rate capability. These improvements are mainly attributed to the electrochemical activity MnO_2 coating layer, which could not only provide more lithium ions insertion/extraction sites, but also act as a protective layer to avoid the directly contact between the cathode materials and the electrolyte and further minimize the side reactions.

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Figure Captions

Fig.1. XRD patterns of (a) the thermal decomposition products of MnCO_3 at different temperatures and (b) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders.

Fig.2. SEM, TEM and HRTEM morphologies of (a, c, e) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and (b, d, f) MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders.

Fig.3. XPS spectra of the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (a) Ni 2p; (b) Co 2p; (c) Mn 2p and (d) O 1s.

Fig.4. (a) The initial charge-discharge curves of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrodes at 15 mA g^{-1} from 2.5 to 4.3 V; (b) cycle performance upon 100 cycles at a rate of 300 mA g^{-1} ; (c) and (d) corresponding discharge curves at different cycles of the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

Fig.5. (a) The initial charge-discharge curves of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and MnO_2 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrodes at 15 mA g^{-1} from 2.5 to 4.5 V; (b) rate properties at the current density of 15, 30, 75, 150, 300 and 750 mA g^{-1} , respectively; (c) and (d) corresponding the first discharge profiles at various current densities of the pristine $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and

MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂.

Fig.6. Cyclic voltammograms of (a) LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and (b) MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes between 2.0 and 5.0 V.

Fig.7. Nyquist plots of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrodes at 100th cycle. Inset shows the equivalent circuit.

Table 1:

Crystal cell parameters of the pristine and MnO₂-coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂.

Sample	<i>a</i> -Axis(Å)	<i>c</i> -Axis(Å)	<i>c/a</i>	Unit volume(Å ³)
Pristine	2.871	14.250	4.96	101.76
3% MnO ₂	2.865	14.246	4.97	101.24

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7