



Short communication

Surface modification of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with Y_2O_3 for lithium-ion battery

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ABSTRACT

The surface of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material was coated with 1.0 wt.% Y_2O_3 via a simple method to improve the cycling performance for lithium-ion batteries. Cyclic voltammetry showed Y_2O_3 -coating inhibited structural change of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and reaction with the electrolyte on cycling. The Y_2O_3 -coated material showed a higher capacity with good cyclability. The discharge capacity of coated sample was 137.5 mAh g^{-1} at 2.0 mA cm^{-2} while that of bared one was only 116.2 mAh g^{-1} . The rate of capacity decrease after 20 cycles for the coated sample was 0.7%, much smaller than that of the bared one (2.8%). X-ray photoelectron spectroscopy (XPS) data represented that the presence of two different environmental O 1s ions corresponded to the surface-coated Y_2O_3 and core material. ICP-OES and EIS displayed the coating layer could protect the $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ from being corroded by the electrolyte and benefit to decrease the cathode charge-transfer resistance at delithiated state.

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1. Introduction

Since Ohzuku [1] first proposed a layered compound $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, it has attracted significant attention as a promising cathode material. It has high capacity, structural and thermal stability, and excellent cycle performance [2–5]. However, many problems still remained, such as low rate capability and considerable capacity loss at high current density. There are many reasons for these problems, such as electrode direct contact with the electrolyte, mechanical stress caused by their volumetric changes during (de)intercalation of the lithium-ions and the extrication of the conductive additives from the active material [6]. Some researchers believed the presence of an inert oxide coating on the surface of cathode material could prevent dissolution of transitional metal ions due to significantly reduced HF content in the electrolyte [7,8]. The dissolution of Co^{4+} would not only mean a loss of active material, but also the introduction of inactive phases in the cathode [9].

In order to further improve the electrochemical characteristics, two different modification methods have been developed. One is the elemental substitution in crystal lattice to stabilize the crystal structure and restrain the phase transition in redox process. The other is the coating of electrochemically inactive materials on the cathode material to improve the properties of the interface between electrode and electrolyte. Some authors verified that the oxides

coating on the cathode material surface could improve structural stability of the active material and enhance its cyclability [10–12]. The presence of an inert oxide-coating layer on the cathode particles could avoid the direct contact of the active material with the electrolyte, and thus prevent dissolution of cobalt in the electrolyte [13].

Oxides of the rare earth elements possess good thermal stability and form better electrical contact with the supported metal oxides to facilitate electron transfer. In this paper, we attempted to modify the surface of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ by Y_2O_3 -coating. The effects of Y_2O_3 -coating on the electrochemical properties were investigated in detail.

2. Experimental

Commercially $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder was used as the original material and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as the coating reagent. For preparation of 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ sample, the calculated amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water, then 3.0 g of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was added. The mixture was slightly heated at 333 K while being stirred in order to evaporate the solvent. The resulting mixture was heated at 923 K (the decomposition temperature of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is 753 K [14]) for 5.5 h, so the 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material was obtained.

XRD measurement was carried out using a D Max-RD12Kw diffractometer with a Cu target $K\alpha$ radiation. The scan data were collected in the 2θ range of $10\text{--}80^\circ$ in steps of 8° min^{-1} . The TEM image was measured by JEM-1200EX type instrument. The surface

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properties of coated particle were investigated by X-ray photoelectron spectroscopy (XPS) using ULVAC-PHI, INC instrument.

The electrochemical properties of the coated material were examined in the CR2025 coin type cells. The cathode electrodes were prepared by pasting the mixture of 85.0 wt.% bared or Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, 10.0 wt.% acetylene black and 5.0 wt.% PVDF onto a aluminum foil current collector. The electrolyte was 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ (1:1 in volume). The cells were assembled in an Argon-filled glove box, then aged for 12 h before electrochemically cycled between 2.8 and 4.5 V (versus Li/Li^+) using CT2001A Land instrument.

The cyclic voltammogram (CV) was operated at 0.1 mVs^{-1} between 2.5 and 4.8 V. The dissolution of transitional metal ions from $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was measured by inductively coupled plasma-emission spectroscopy (ICP-OES). The electrochemical impedance spectroscopy (EIS) measurements were conducted by a CHI604c impedance analyzer, using an amplitude voltage 5 mV and frequency range was 0.001 Hz to 0.1 MHz.

3. Results and discussion

3.1. X-ray diffraction and morphology

The XRD patterns of bared and 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were presented in Fig. 1. It was observed that Y_2O_3 -coating did not change the structure of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. All the samples had a well-defined α - NaFeO_2 structure. The XRD patterns of the coated particles show there were no change in a and c lattice parameters. This means that Y_2O_3 only forms a thin layer on the surface of the core materials, instead to form a solid solution by interacting with core material during the heat treatment process at 923 K for 5.5 h. Fig. 2 was the TEM photograph of 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ magnified to 70 thousand times. The Y_2O_3 layer was clearly displayed as a compact, uniform film on the surface of the $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ grains. The coating layer could reduce the contact area of active material with the electrolyte and protect the active material from dissolution in the electrolyte.

3.2. Electrochemical behavior

Cyclic voltammetry (CV) is a technique well suited for evaluation of the electrochemical performance and electrode kinetics of oxide material [11]. Thus, cyclic voltammetry curves were

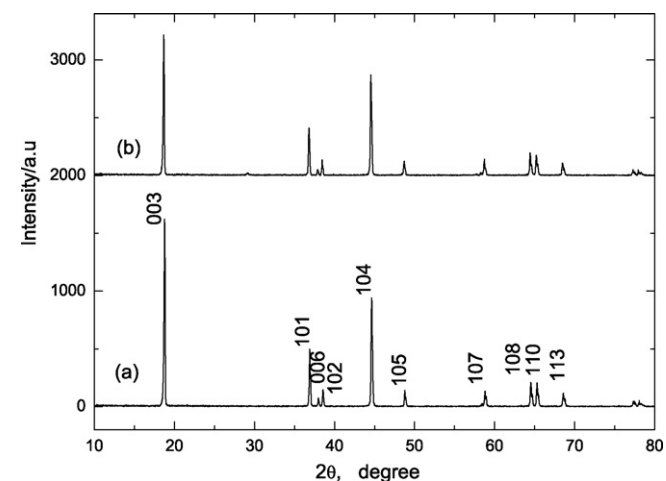


Fig. 1. XRD patterns of (a) bared and (b) 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

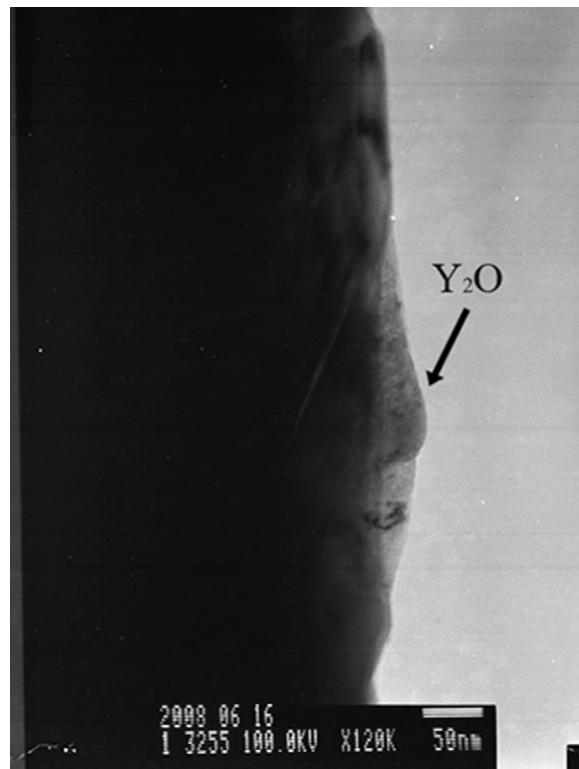


Fig. 2. TEM image of 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

investigated in order to understand the effect of the coating on the phase transitions during charge–discharge processes. Fig. 3a and b showed the cyclic voltammograms of bared and 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, respectively. There was a difference between the first and subsequent cycles. For the bared $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, the first cycle anodic peaks were centered 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 were centered at 4.06 and 4.73 V. In the following two cycles, the anodic peaks were almost at the same voltage, but the cathodic peaks still shifted to lower voltage and the cathodic areas were decreased sharply when compared to the first cycle. In Fig. 3b, the suppressed peaks can be observed. And after the first cycle, the cathodic and anodic peaks were almost unchanged. The CV peaks of Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were much steady than bared material, which indicated that the cyclability of the Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was better than that of the bared one. This showed that the Y_2O_3 -coating could suppress the phase transformation of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle from layered to spinel structure or impede the electrolyte decomposition on the surface of the cathode material. As a result, the cycling performance of Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was improved progressively.

The cycling performance of cells with bared and 1.0 wt.% Y_2O_3 -coated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material operated at 1.0 and 2.0 mA cm^{-2} when cycled between 2.8 and 4.5 V were presented in Fig. 4. When the current density was 1.0 mA cm^{-2} , for the bared electrode material, the discharge capacity decreased gradually with cycling and reached a 130.5 mAh g^{-1} at the end of 20th cycle and there was 7.6% decrease in specific capacity. The Y_2O_3 -coated electrode material reached a 149.0 mAh g^{-1} at the end of 20th cycle, which was only 2.7% decrease. When the current density was 2.0 mA cm^{-2} , the bare material reached a 112.9 mAh g^{-1} at the end of 20th cycle, with 2.8% decreases in specific capacity; while the Y_2O_3 -coated material reaches a

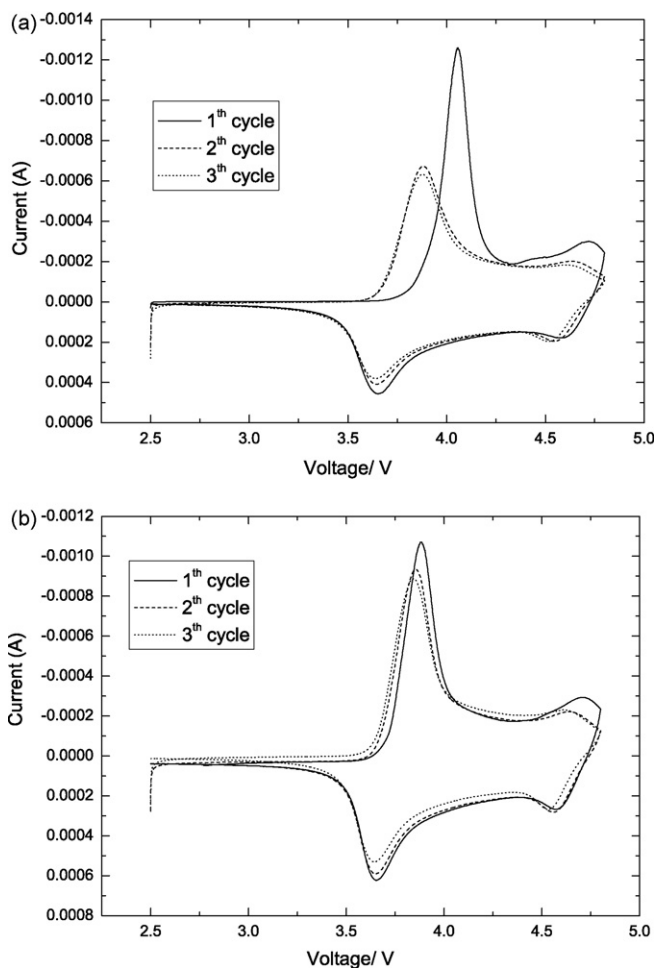


Fig. 3. Cyclic voltammety of the (a) bared and (b) 1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ material between 2.5 and 4.8 V at a scan rate of 0.1 mV s^{-1} .

136.6 mAh g^{-1} at the end of 20th cycle, with 0.7% decreases in specific capacity. This indicated that the Y_2O_3 -coating was not only effective for increasing the discharge capacity, but also effective for decreasing the capacity fade rate, especially at high rate. The mechanism of the capacity fading of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was related to the abnormal increase in the total resistance. This abnormal increase in the total resistance had been attributed to the change in the particle surface and the morphologies of the particles [15]. The Y_2O_3 -coating layer could effectively depression of redox reaction between electrode and electrolyte at delithiated state, thereafter improving the cyclic performance [16]. Y_2O_3 -coating also improved cathode/electrolyte interface stability and stabilized structure of cathode which supported by the following studies.

Discharge capacities of bared and 1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ material at various current densities were

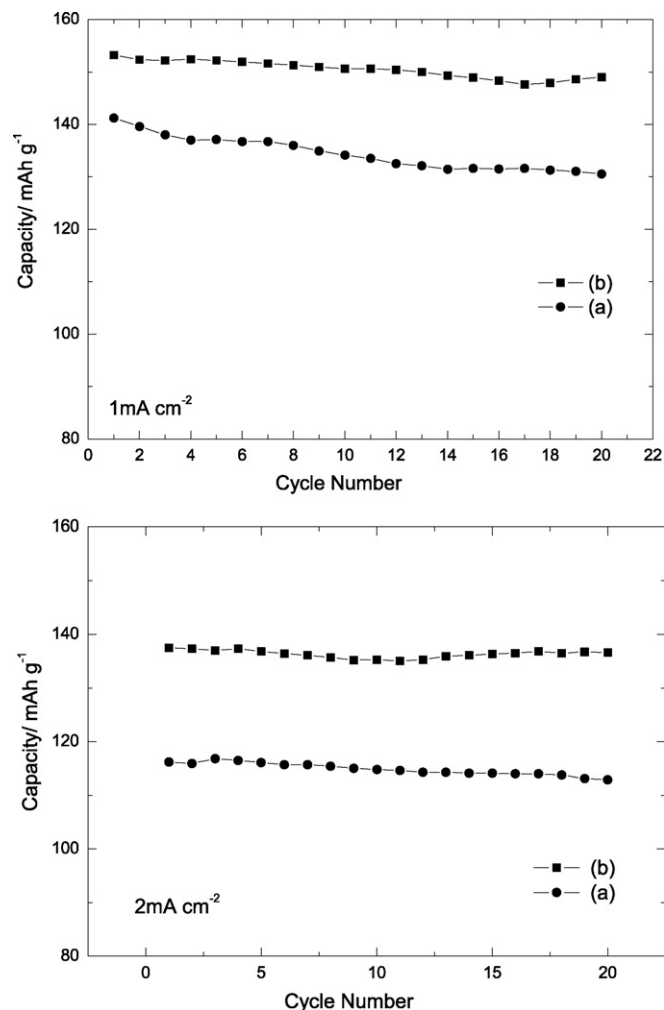


Fig. 4. Cycling stability of the (a) bared and (b) 1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ material at 1.0 and 2.0 mA cm^{-2} current density.

summarized in Table 1. The charging density was equal to discharge density. The discharge capacity of the bared $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ decreased with increasing current density and reached 92.0 and 75.7% at 1.0 and 2.0 mA cm^{-2} compared with the specific capacity of 153.4 mAh g^{-1} at 0.1 mA cm^{-2} , respectively. At the same time, the discharge capacity of the Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ material decreased less than the bared one, reached 92.8 and 83.3% at 1.0 and 2.0 mA cm^{-2} when compared with the specific capacity of 165.1 mAh g^{-1} at 0.1 mA cm^{-2} , respectively. The results revealed that the rate capability of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was significantly improved by the Y_2O_3 -coating. It can be considered that the 1.0 wt.% Y_2O_3 -coating layer improved the Li-ion fast diffusion and the (de)intercalation kinetics, simultaneously minimized the interfacial impedance.

Table 1

Comparison of rate capabilities bared and 1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode cycled between 2.8 and 4.5 V.

Current density (mA cm^{-2})	Bared		1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	
	Discharge capacity (mAh g^{-1})	Ratio (%)	Discharge capacity (mAh g^{-1})	Ratio (%)
0.1	153.4	100.0	165.1	100.0
1.0	141.2	92.0	153.2	92.8
2.0	116.2	75.7	137.5	83.3
3.0	100.4	65.4	125.7	76.1
4.0	79.3	51.7	108.7	65.8

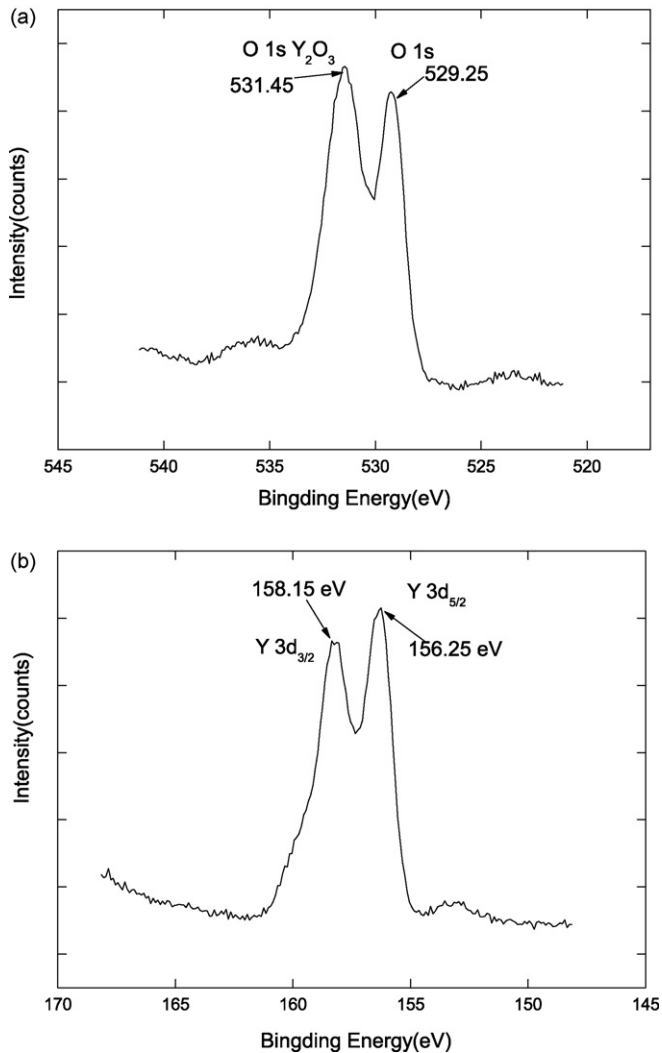


Fig. 5. XPS emission spectra (a) O1s and (b) Y 3d of the 1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$.

3.3. X-ray photoelectron spectroscopy analysis (XPS)

XPS analysis was used to study the surface composition of Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ to verify whether the Y_2O_3 coating had formed a solid solution or remained on the surface of the core material [17]. In Fig. 5a, the observed broad peak consisted of two peaks, of O1s at 531.45 and 529.25 eV, which attributed to the crystal lattice oxygen located at lower binding energy and the surface absorption oxygen located at higher binding energy. The peak at 529.25 eV corresponded to O1s bonded with Co/Ni/Mn-ions in the lattice of the core material [18]; the peak at 531.45 eV corresponded to O1s bonded with Y-ion [19]. From Fig. 5b, the Y spectrum showed characteristic BEs of 158.15 eV ($Y 3d_{7/2}$) and 156.25 eV ($Y 3d_{5/2}$). The line shape and peak positions were in good agreement with report from Cho et al. [20]. This result suggested that the valence of Y was trivalence, thus the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ was coated with Y_2O_3 .

3.4. ICP-OES

The amount of Ni and Mn-ions dissolved after 40 cycles at $400 mA g^{-1}$ in the cells containing coated cathode or bared cathode were tested by ICP-OES. The amounts of transmission metal ions dissolved from the coated material were greatly decreased

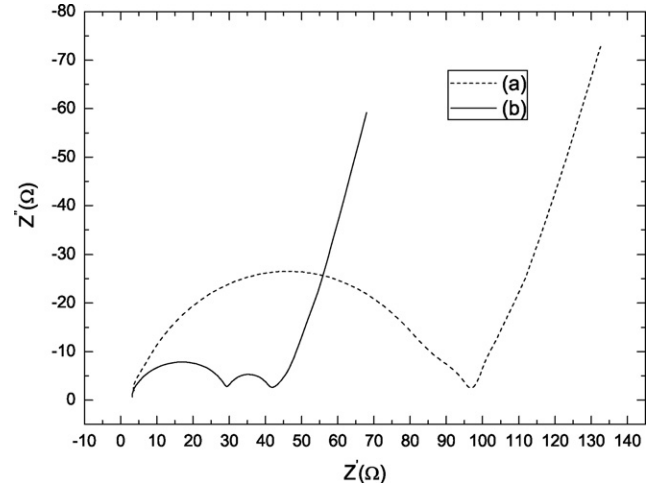


Fig. 6. Impedance spectra (Z' versus Z'') of (a) bared and (b) 1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ when first charged to 4.5 V.

when compared with the bared one. The concentrations of Mn and Ni dissolved from 1.0 g coated materials were only 0.08 and 0.08 mg separately, that of the bared one were 0.26 and 0.33 mg. These results suggested that the coating layer protected the $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ from being corroded by the electrolyte. This contributed to the improvement of cyclability.

3.5. Electrochemical impedance spectroscopy measurements

Fig. 6 compared the EIS profiles of the bared and coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (first charged to 4.5 V). According to Chen et al. [21], cathode impedance, especially charge-transfer resistance, is the main component of the cell impedance and is most responsible for the raise of the cell impedance during storage at room temperature. It was clear to see that there was great difference appeared at the semicircle of the bared and coated material. To the bared one, only a high frequency semicircle followed by an inclined straight line while there was a new depressed semicircle appeared in the relatively low frequency region of the coated one. A high frequency semicircle represents the impedance due to a solid-state interface layer formed on the surface of the electrodes, a low frequency semicircle is related to a slow charge transfer process at the interface and its relative double-layer capacitance at the film/bulk oxide, and an inclined straight line at the low frequency end is related to a combination of the diffusion effects of lithium-ions on the interface between the active material particles and electrolyte [22–24]. The lithium-ions migrated through the interface between the surface layer of the grains and the electrolyte of the coated ones were much faster than that of the bared ones, and the resistance of the surface film on the coated one was only 43.0Ω , however, the bared one was 97.2Ω . It illustrated that Y_2O_3 -coating had a positive effect on decreasing the cathode charge-transfer resistance at delithiated state. This can be interpreted as the formation of surface film is restrained and the decomposition reaction of the electrolytes is suppressed on the coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ surface.

3.6. XRD investigation after cycling

After 40 cycles, cells were disassembled in an Argon-filled glove box, and cathode powder was collected for XRD measurement. Fig. 7 suggested that there was a great difference between the structural changes of the coated and the bared $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ during cycling. Compared with Fig. 1 (XRD of the samples before cycling),

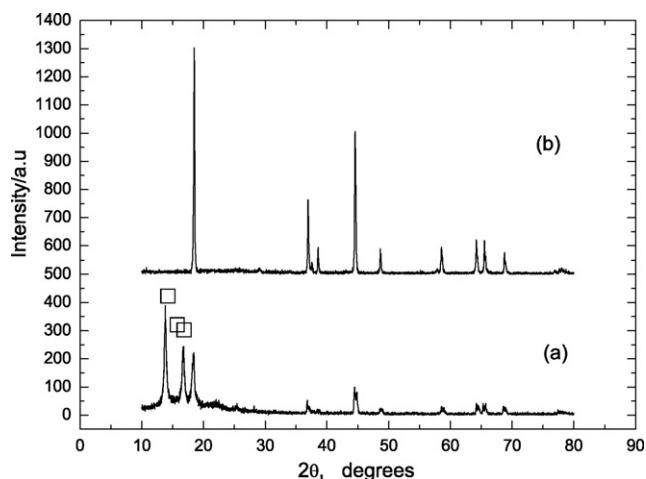


Fig. 7. XRD patterns of (a) bared and (b) 1.0 wt.% Y_2O_3 -coated $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ after 40 cycles.

we found that the coated one showed a reduced lattice parameter change after cycling. However, not only the lattice parameter of the bared one reduced but also the abnormal structure change and many unexpected diffraction peaks (see in Fig. 7) were observed. It was related to the large capacity fade during cycling for the bared one. That imply the structure of the coated one was more stable during cycling. The metal oxide layer cannot only effectively suppress the decomposition of the electrolyte on the charged particle surface, but also partially absorb the stress caused by the volumetric change of the granules during the cycling [15]. According to these results, we believed that the abnormal increase in the charge transfer resistance after long cycling should be originate from structural change.

4. Conclusions

The electrochemical characteristics of $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode material at room and high temperature were improved by coating with 1.0 wt.% Y_2O_3 . The improvements of the discharge capacity and cycling characteristics are due to the coating layer protects the surface of cathode material from harmful reaction with the electrolyte then suppress the phase transformation. The enhanced rate capability could be attributed to the increase in the electri-

cal contact between the cathode grains and minimization of the interfacial impedance.

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