

Uniform AlF_3 thin layer to improve rate capability of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material for Li-ion batteries

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Abstract: $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was coated with uniform nano-sized AlF_3 layer by chemical precipitation method to improve its rate capability. The samples were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), charge–discharge cycling, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). Uniform coated layer with a thickness of about 3 nm was observed on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle by TEM. At 0.5C and 2C rates, 1.5% (mass fraction) AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ in 2.8–4.3 V versus Li/Li^+ after 80 cycles showed less than 3% of capacity fading, while those of the bare one were 16.5% and 45.9%, respectively. At 5C rate, the capacity retention of the coated sample after 50 cycles maintained 91.4% of the initial discharge capacity, while that of the bare one decreased to 52.6%. EIS result showed that a little change of charge transfer resistance of the coated sample resulting from uniform thin AlF_3 layer was proposed as the main reason why its rate capability was improved obviously. CV result further indicated a greater reversibility for the electrode processes and better electrochemical performance of AlF_3 -coated layer.

Key words: Li-ion battery; $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; coating; uniform thin AlF_3 layer; rate capability

1 Introduction

Layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, reported firstly by OHZUKU and MAKIMURA[1], has been extensively studied as a promising cathode material for Li-ion battery. Due to its high discharge capacity, stable cycling performance, relatively low cost and high safety[2–4], $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is even considered to be one of the best cathode materials for power source system of hybrid electric vehicle (HEV) or electric vehicle(EV)[5]. However, it shows poorer rate capability, compared with LiCoO_2 , which limits its further application[6–7].

It's well known that surface modification on cathode materials with electrochemically inactive metal oxides such as Al_2O_3 [8–10], ZrO_2 [11], MgO [12], ZnO [13] and Y_2O_3 [14] could significantly improve their electrochemical performance. Among these materials, Al_2O_3 was widely used to coat LiCoO_2 , LiMn_2O_4 , LiNiO_2 or their composite metal compounds. Using time-of-flight secondary ion mass spectrometry (ToF-SIMS), MYUNG et al[15] found that the Al_2O_3 coating layer on $\text{Li}[\text{Li}_{0.05}\text{Ni}_{0.4}\text{Co}_{0.15}\text{Mn}_{0.4}]\text{O}_2$ acted as HF

scavenger, which could reduce HF generation, resulting in less decomposition of the cathode by forming AlF_3 on the surface of Al_2O_3 coating layer. Based on these results, AlF_3 -coated LiCoO_2 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with significant improvement of high voltage cycling behavior were prepared by SUN et al[16–17]. Recently, AlF_3 layer with the thickness of about 10 nm was employed to modify $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ by PARK et al[18] and obvious improvement of electrochemical properties in high voltage region was achieved. Considering that asymmetrical and thick coated-layer will be not propitious for further improvement of electrochemical properties, in this work, accordingly, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was coated by uniform and thin AlF_3 layer with chemistry precipitation method, in order to ameliorate its rate capability. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests were also carried out to explain the reason for the improvement of electrochemical performance.

2 Experimental

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder chosen for this work

was provided by Dongguan Ampere Electronics Technology Co., Ltd (ATL). To prepare AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, aluminum nitrate and hydrogen ammonium fluoride were separately dissolved in distilled water. After $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder was immersed into the aluminum nitrate solution, a certain excessive amount of hydrogen ammonium fluoride was slowly added to the solution with the speed of 1.5 mL/min. At the same time, the solution was heated to 45 °C and constantly stirred by magnetic force stirrer in order to disperse the powder adequately. The amount of AlF_3 in theory in the solution corresponded to 1.5% (mass fraction) of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder. After the solution containing the cathode material was filtered and then washed by distilled water, the powder was dried at 110 °C for 3 h and then was calcined at 600 °C for 4 h to obtain AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ under argon atmosphere.

The crystalline structures of the bare and coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were identified with Rigaku X-ray diffractometer using Cu K_α radiation in the 2θ range of 10°–80° with a step of 0.02°. Transmission electron microscopy was operated by JEOL 200CX instrument and energy dispersive spectroscopy was carried out on Oxford INCA energy system.

Electrochemical tests were operated using CR2032 coin-type cells. This cell consisted of a cathode and a lithium metal anode, separated by a porous polyethylene film (Celgard 2500). The positive electrode was constituted from 85% active material, 10% carbon black as conducting additive, and 5% polytetrafluoroethylene (PTFE) as binder. It was pressed onto a 100 mm² stainless steel mesh used as the current collector at 300 kPa and then dried at 120 °C for 8 h in a vacuum oven in order to remove moisture. A commercial 1 mol/L lithium-hexafluoro phosphate (LiPF_6) solution in a mixture of ethylene-carbonate (EC), dimethyl carbonate (DMC) and propylene carbonate (PC) at a volume ratio of 1:1:1 was used as the electrolyte. The cells were cycled galvanostatically in the voltage range of 2.8–4.3 V versus Li/Li^+ at a desired current density with a Land tester system.

AC impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range from 500 kHz to 10 mHz with an amplitude of 5 mV. Tested cell was charged to 3.95 V versus Li/Li^+ and the voltage was kept stable until the current decreased to less than 50 μA . Cyclic voltammetry was also performed using a Zahner Elektrik IM6 analyzer at a scan rate of 1 mV/s. The scan voltage was from 3.0 to 4.5 V versus Li/Li^+ . Differential scanning calorimetry (DSC/TG) was carried out with a Model STA449C differential scanning calorimeter at a ramp rate of 10 °C/min. The temperature ranged from 45 to 600 °C.

3 Results and discussion

3.1 Physical characteristics of coated and uncoated samples

Fig.1 shows the XRD patterns of the bare, 1.5% and 3.0% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. All three samples had $\alpha\text{-NaFeO}_2$ layered structure and belonged to $R\bar{3}m$ space group. In comparison with the bare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, no diffractions of impurity in both 1.5% and 3.0% AlF_3 -coated sample were observed, which showed that the AlF_3 -coated layer had no influence on the structure of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The absence of diffraction peaks corresponding to AlF_3 may be due to very low concentration of AlF_3 on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle. The lattice parameters of the bare, 1.5% and 3.0% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were calculated as $a=2.863$ Å, $c=14.242$ Å; $a=2.863$ Å, $c=14.245$ Å; $a=0.2864$ Å, $c=14.261$ Å; respectively. There was little change in a lattice parameter, while a little extending in c axis direction existed with the increase of the concentration of coated AlF_3 , which suggested that the phase of AlF_3 -coated layer nearly close to the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ could form the solid solution under 600 °C for 4 h[19].

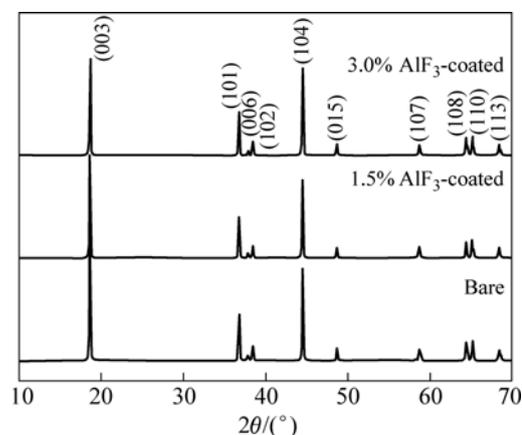


Fig.1 X-ray diffraction patterns of bare and AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

The surface morphology of the 1.5% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder was observed by transmission electron microscopy (TEM). In Fig.2(a), a thin and uniform AlF_3 layer with the thickness of about 3 nm was shown on the particle surface. To the best of our knowledge, the coated layer was much thinner than those reported[8–9, 17]. In our opinion, the thin coated layer would make the lithium ion transfer well and decrease the polarization of the electrode.

Energy dispersive spectroscopy (EDS) result of the AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder is recorded in

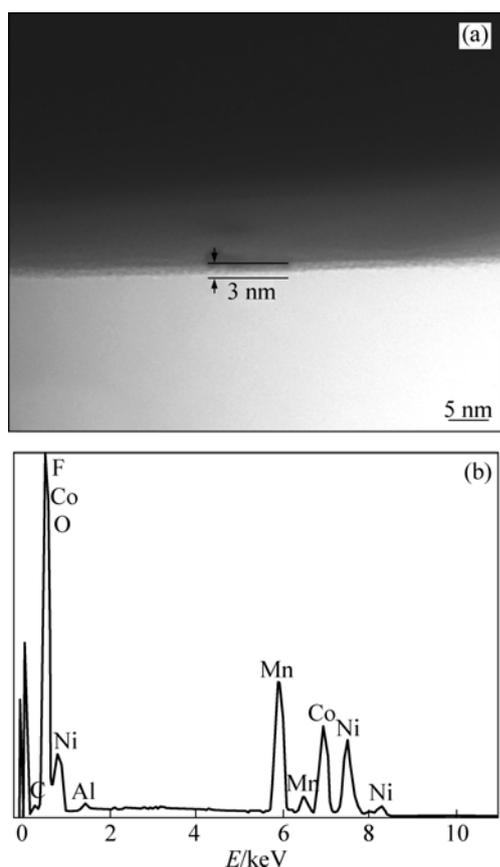


Fig.2 TEM morphology (a) and EDS result (b) of 1.5% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powder

Fig.2(b). The existence of peaks corresponding to F and Al indicated probably the presence of AlF_3 coating layer on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ particle [17].

3.2 Electrochemical performance

Fig.3 indicates the cyclic performance of the bare, 1.5% and 3.0% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ at 0.5C rate (1C rate was defined as 150 $\text{mA}\cdot\text{h}/\text{g}$ in this work) between 2.8 and 4.3 V versus Li/Li^+ . The bare $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ had an initial discharge capacity of 139.6 $\text{mA}\cdot\text{h}/\text{g}$ and exhibited good electrochemical performance at the first 40 cycles. However, capacity fading ratio increased to 13.5% after 80 cycles. On the other hand, although 1.5% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ showed lower discharge capacity (132.3 $\text{mA}\cdot\text{h}/\text{g}$), the capacity after 80 cycles was still 128.2 $\text{mA}\cdot\text{h}/\text{g}$, only with nearly 3% capacity fading. As for 3.0% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$, it demonstrated good cyclic performance, with 2.4% capacity fading after 50 cycles. However, its discharge capacity was less than that of the 1.5% AlF_3 -coated sample by about 6 $\text{mA}\cdot\text{h}/\text{g}$. So, 1.5% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ was chosen to take further test.

Fig.4(a) depicts cyclic stability of the bare and 1.5% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$, operated at 2C rate

between 2.8 and 4.3 V versus Li/Li^+ and the discharge curves after 80 cycles are also given in Fig.4(b). As obviously observed, the AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ had only about 2.4% capacity fade after 80 cycles, while the bare sample suffered from about 46% fading of the initial discharge capacity. For the coated and bare cells, the discharge capacity of 119.7 $\text{mA}\cdot\text{h}/\text{g}$ and 63.6 $\text{mA}\cdot\text{h}/\text{g}$ was observed at the 80th cycle, respectively. Such comparison was also shown by the 80th discharge curves in Fig.4(b). Clearly, AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

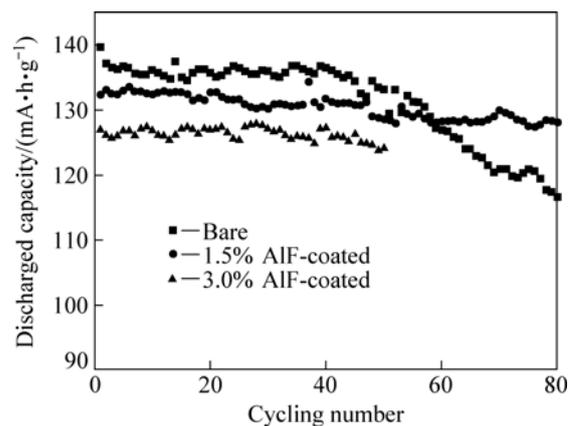


Fig.3 Cyclic performances of bare, 1.5% and 3.0% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ at 0.5C rate

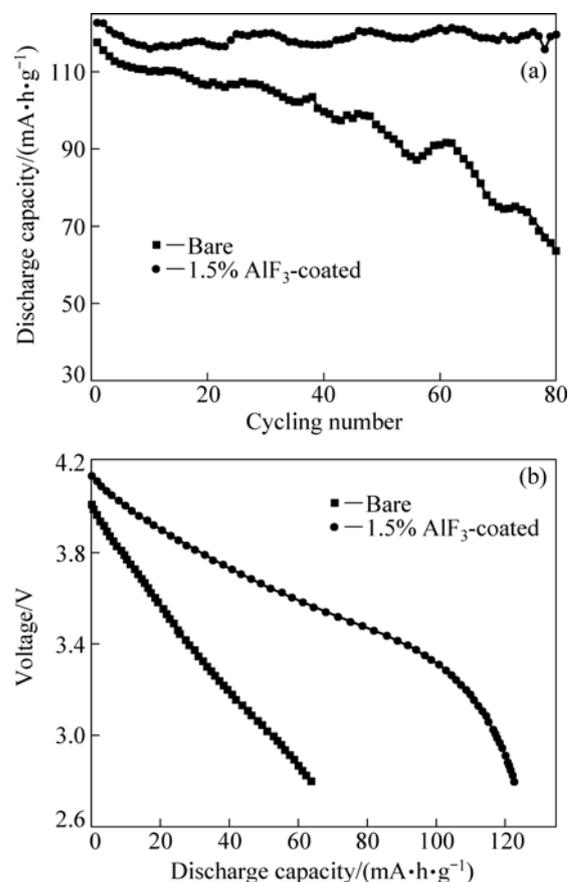


Fig.4 Cyclic performance (a) and discharge curves after 80 cycles (b) of bare and 1.5% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ at 2C rate

indicated much better electrochemical performance at such current density.

Fig.5(a) shows the discharge capacity versus cycle number of the bare and AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ cells operated at 5C rate between 2.8 and 4.3 V versus Li/Li^+ and the discharge curves of both samples at different cycles (1st, 10th, 30th, 50th) are given in Fig.5(b) and Fig.5(c), respectively. As can be seen, discharge curve of the bare sample became steeper with the cycle number increasing, while that of the coated one changed a little, indicating that the AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode had much

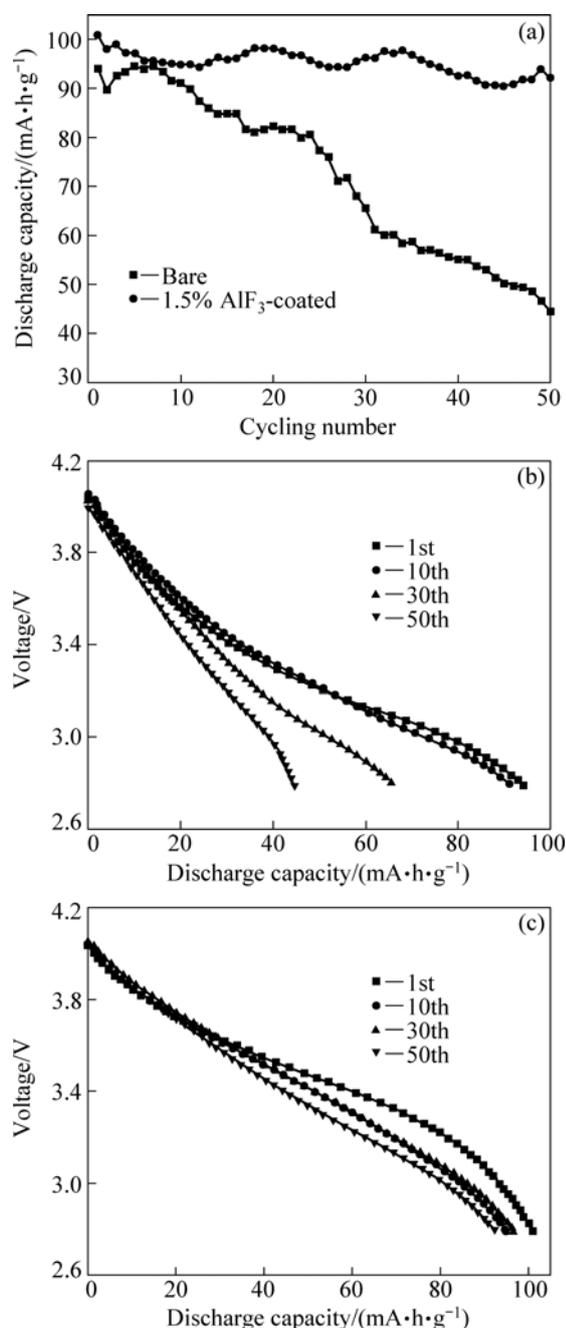


Fig.5 Cyclic performance (a) and discharge curves of bare (b) and AlF_3 -coated (c) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ at different cycles operated at 5C rate

better charge–discharge platform retention than the bare one. From the Fig.5(a), the bare electrode suffered from a severe capacity fading, showing only 52.6% of initial discharge capacity (44.6 mA·h/g) after 50 cycles was retained. As for AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, 91.4% of the initial discharge (99.2 mA·h/g) was maintained. It is very interesting that the initial discharge capacity of the coated electrode at 2C rate or 5C rate was larger than that of the bare one, although it is well known that the discharged capacity often decreased to some extent after being coated[12], just like that at 0.5C rate. Such phenomenon could be explained as follows. The amount of unavailable active material (lithium ion) because of polarization at high current density was reduced effectively, which would enhance the capacity relatively. That is to say, the specific capacity fading of the coated sample resulting from polarization was less than that of the bare one. Apparently, uniform AlF_3 nano-sized layer in this work was a well coated material to improve rate capability for cathode material. Most researchers attributed the performance improvement to the formation of a barrier isolated electrolyte from electrode, which would lower the activity of the second reaction[10, 12]. Besides, SUN et al[20] clarified that the excellent cyclability of ZnO -coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in the 5 V region was due to the reduced HF content and thus suppressed Mn dissolution. MYUNG et al[15] considered that the Al_2O_3 coating layer on $\text{Li}[\text{Li}_{0.05}\text{Ni}_{0.4}\text{Co}_{0.5}\text{Mn}_{0.4}]\text{O}_2$ acted as a HF scavenger, which would reduce HF generation, resulting in less decomposition of the cathode particle by forming AlF_3 on the surface of Al_2O_3 coating layer. It is known the strain and defect resulting from the fast Li^+ extraction and intercalation in the cathode material were considered as the important cause of capacity fading when the battery was charged at high current density[21], which would increase the surface activity of cathode material largely and then result in electrolyte decomposition. In this work, compared with thick layer, uniform and thin AlF_3 layer could not only suppress the electrolyte decomposition and hinder the second reaction in the material surface effectively, but also be better for the improvement of rate capability, since it was much easy for the Li^+ extraction and intercalation when the electrode was charged at high current density. The conclusion above could be approved by the compared results of electrochemical impedance and CV test.

In order to gain further understanding of the role of the AlF_3 -coated layer, Nyquist plots of the bare and AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ at 3.95 V versus Li/Li^+ after different cycles (1 and 50) at 5C rate between 2.8 and 4.3 V versus Li/Li^+ are recorded in Fig.6. In general, each impedance spectrum of the bare and the AlF_3 -coated cells consisted of two overlapped

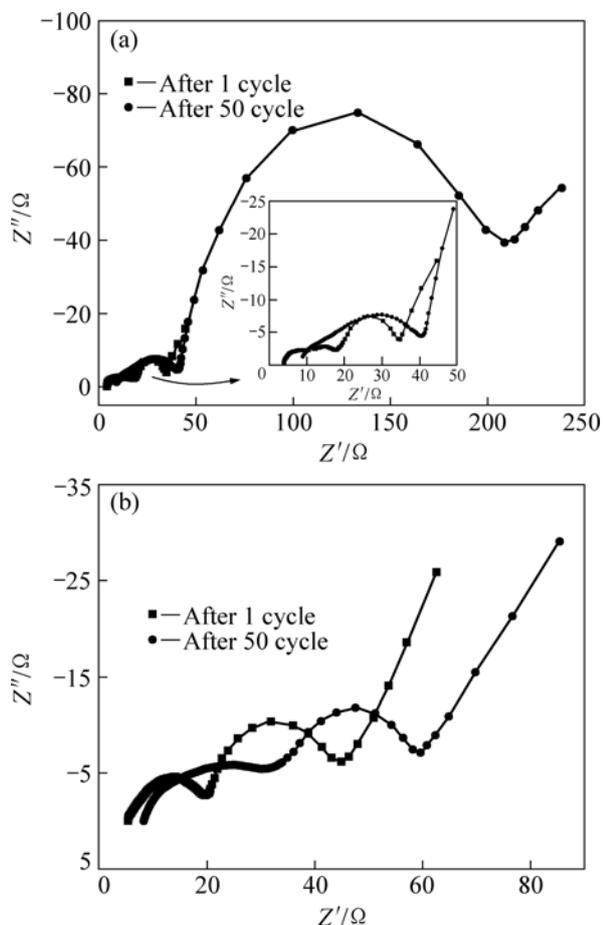


Fig.6 Nyquist plots of bare (a) and AlF_3 -coated (b) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ at 3.95 V versus Li/Li^+ after different cycles at 5C rate

semicircles at the high frequency side and a well defined semicircle at the low frequency followed by a slop line at the very low frequency range. It has been confirmed that the high frequency semicircle was due to the interface parameters such as the porous nature of the electrode, the surface film contribution, and/or the bulk of the material while the low frequency semicircle was considered as the contribution of the charge-transfer process[22]. As for the slop line, it was due to Warburg resistance which reflected Li ion diffusion in the solid-state electrodes. AURBACH et al[23] reported that capacity fading of LiCoO_2 on cycling and storage at elevated temperature was attributed to the increase of surface film resistance rather than the bulk degradation. SUN et al[16] considered that the variation in charge transfer resistance(R_{ct}) was a key to capacity fading for bare and Al_2O_3 -coated electrode. SHAJU et al[24] found the proportional increase in the charge transfer resistance of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode with cycling number. In Fig.6, it is shown that the total resistance of the bare electrode was much larger than that of AlF_3 -coated one.

Especially, charge transfer resistance of the bare electrode drastically increased during cycling, while that of the coated electrode changed a little. From the results above, we concluded that the improvement of rate capability of the AlF_3 -coated cathode material was attributed to the uniform and thin AlF_3 layer, which lowered the activity of interface between active material and electrolyte, and also considerably suppressed impedance growth, especially the charge transfer resistance.

Cyclic voltammetry curves of the bare and AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ at the first 3 cycles, operated at 1 mV/s in the potential range from 3.0 to 4.5 V versus Li/Li^+ are compared in Fig.7. Both studied cells were those after 50 cycles at 5C rate. It was reported that $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ under small current often showed two couple peaks at about 3.9 V and 4.5 V, respectively. One was assigned to the $\text{Ni}^{2+}/\text{Ni}^{3+}$ or $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple and the other was due to $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple[1, 25]. However, the polarization of the bare and coated cells after cycling made the second redox couple nearly disappear and the interval of oxidation and reduction peaks became large. From Fig.7, the oxidation and reduction peaks of the AlF_3 -coated sample were centered at 4.3 and 3.4 V, respectively, but those of the bare one even located at 4.5 V and 3.1 V, respectively, which indicated the polarization of the bare one after such charge–discharge test was very larger than that of the coated one. The reduced interval of each redox couple and little change of peak area further demonstrated a greater reversibility for the electrode processes upon AlF_3 -coated layer. The EIS and CV test results approved that the uniform and thin AlF_3 layer could reduce the polarization of the battery and improve the electrochemical performance when cycling at high rate.

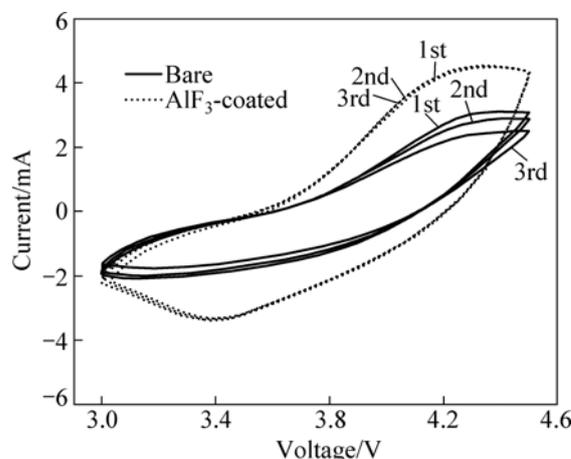


Fig.7 Cyclic voltammetry curves of bare and 1.5% AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ cells with scan rate of 1 mV/s after 50 cycles at 5C rate

4 Conclusions

1) Uniform and thin AlF_3 layer with a thickness of about 3 nm was coated on the surface of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ successfully by chemical precipitation method.

2) At 0.5C rate and 2C rate, the 1.5% (mass fraction) AlF_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2/\text{Li}$ in 2.8–4.3 V versus Li/Li^+ after 80 cycles showed less than 3% capacity fading, while the bare electrode exhibited 16.5% and 45.9% capacity loss, respectively. At 5C rate, capacity retention of the coated electrode after 50 cycles maintained 91.4%, while that of the bare one decreased to 52.6%.

3) EIS result showed that a little change of charge transfer resistance of the coated electrode was the main reason why the rate capability was improved obviously. CV tests also indicated that a great reversibility for the electrode processed upon AlF_3 -coated layer.

4) All the test results approved that the uniform and thin AlF_3 layer could reduce the polarization of the battery evidently and improve the electrochemical performance when cycling at high rate.

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