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Synthesis, characterization and electrochemical performance of AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ as cathode for Li-ion battery

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Abstract: Li-rich layered transitional metal oxide $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ was prepared by sol−gel method and further modified by AlF_3 coating via a wet process. The bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and high resolution transmission electron microscope (HRTEM). XRD results show that the bare and AlF_3-coated samples have typical hexagonal α-$NaFeO_2$ structure, and AlF_3-coated layer does not affect the crystal structure of the bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$. Morphology measurements present that the AlF_3 layer with a thickness of 5−7 nm is coated on the surface of the $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ particles. Galvanostatic charge−discharge tests at various rates show that the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ has an enhanced electrochemical performance compared with the bare sample. At 1*C* rate, it delivers an initial discharge capacity of 208.2 mA·h/g and a capacity retention of 72.4% after 50 cycles, while those of the bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ are 191.7 mA·h/g and 51.6 %, respectively.

Key words: lithium-ion battery; $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$; AlF_3 surface coating; capacity retention

1 Introduction

In order to meet the requirement for electric vehicles (EVs) or hybrid electric vehicles (HEVs), lower cost, higher capacity and better safety are needed urgently for lithium-ion battery [1,2]. As one of the vital components of lithium-ion battery, cathode material largely determines the electrochemical performance of battery [3]. Recently, lithium-rich layered oxide $\chi Li_2MnO_3\cdot(1-\chi)LiMO_2$ (M=Mn, Ni, Co) has drawn particular attention due to its high reversible capacity and good thermal stability[1], which are the most competitive features over conventional cathode materials, such as $LiCoO_2$ and $LiMn_2O_4$ for use in automotive applications. However, it suffers from some practical problems for commercial application, including poor rate capacity and bad cycling performance [4]. To overcome above drawbacks, surface coating is often used. Many inorganic compounds, such as metal oxides [5−7], fluorides [8−11] and phosphates [12], have been used to improve the electrochemical performance of cathode materials. Recently, AlF_3 coating was reported to be a very effective way to improve the electrochemical performance of $LiCoO_2$ [13], $LiNi_{0.5}Mn_{1.5}O_4$ [14], $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ [15], etc. Generally, the improved electrochemical performance is attributed to the several reasons as follows: 1) the AlF_3 layer can protect the electrode surface from HF attack in the electrolyte and suppress the dissolution of transition metal ions into the electrolyte, thereby reducing the charge transfer resistance [13,15]; 2) the coating layer can suppress the volume changes of electrode and thus prevent the cathode particles from being pulverized during cycling [15−17]. However, the exact role of AlF_3 layer in Li-rich layered oxides is more complicated due to its special charge−discharge mechanism. By understanding the effect of AlF_3 coating layer on the electrochemical performance of Li-rich layered oxides, the rate and cycling properties of Li-rich layered oxides can be improved effectively. Thus, it can be largely used in the electric vehicle field.

In this work, AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ was prepared and characterized with respect to the bulk structure, surface state and electrochemical performance. Compared with the bare sample, the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ exhibits an obviously improved cycling performance and rate capacity. The

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influence of the AlF_3 coating on the Li-rich layered oxide is particularly addressed.

2 Experimental

2.1 Preparation and characterization

The Li-rich layered oxide, $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$, was synthesized by sol−gel method, using citric acid (CA) and acetic salts as starting materials. Stoichiometric $Mn(CH_3COO)_2{\cdot}4H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, and $Co(CH_3COO)_2{\cdot}4H_2O$ were dissolved in distilled water with 5% excess amount of $Li(CH_3COO){\cdot}H_2O$. Then, the mixed solution was added dropwise to the citric acid solution with constant stirring. The solution pH was adjusted to 6 by using ammonium hydroxide. Subsequently, the solution was heated at 80 °C to obtain a dry solid. The resulting precursor was dried at 120 °C for 12 h and then calcined at 450 °C for 5 h to remove the organic impurities under air atmosphere. After being cooled to room temperature, the powder was pressed into pellets and sintered at 850 °C for 10 h to obtain the final product.

AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ was obtained through a wet coating process. The bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ powders were immersed into $Al(NO_3)_3$ aqueous solution. Then a NH_4F aqueous solution was added slowly, in which the molar ratio of Al to F was controlled to be 1:3. The mixed solution was stirred at 80 °C for 5 h, followed by drying at 60 °C in a vacuum oven. Finally, the mixture was sintered at 400 °C for 5 h under Ar atmosphere. The nominal amount of AlF_3 was about 0.5% (volume fraction) of the parent material.

The crystalline structure of the samples was confirmed by X-ray diffraction (XRD, D/maxш, Rigaku) with a range of 2θ from 10° to 90°. The morphology and composition of the samples were examined with a scanning electron microscope (SEM, Quanta−200) equipped with an energy-dispersive X-ray spectrometer (EDS, EDAX). The AlF_3-coated layer was investigated with a high resolution transmission electron microscope (HRTEM, JEOL−3010).

2.2 Electrochemical measurements

Coin-type (CR2016) half-cells were assembled to evaluate electrochemical properties of the prepared samples. Electrodes were prepared by casting the slurry, with the composition of active materials (80%), conducting agent (Super-P, 10%), and binder PVDF (polyvinylidene fluoride, 10%) onto Al foil. A porous polyethylene (PE) membrane was used as a separator and Li metal foil was used as counter and reference electrodes. The electrolyte was $LiPF_6$ (1 mol/L) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 3:7. Cells were cycled galvanostatically at different constant current rates (1C=200 mA·h/g) between 2.5 and 4.8 V (vs Li/Li^+). Cyclic voltammograms for the samples were obtained in a voltage range of 2.0−4.8 V (vs Li/Li^+) with a scan rate of 0.1 mV/s. Electrochemical impedance measurements were performed over a frequency range from 100 kHz to 0.01 Hz with the amplitude of 5 mV.

3 Results and discussion

3.1 Microstructure

Figure 1 shows the XRD patterns of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ samples. All the diffraction peaks of both samples could be indexed with hexagonal α-$NaFeO_2$ structure with a space group of R_3/m [18]. The clear separations between the adjacent peaks of (006)/(102) and (018)/(110) indicated an ordering structure of R_3/m single phase. The weak peaks at 20°−23° represented the monoclinic Li_2MnO_3-like component (C_2/m) in the structure, caused by the short range ordering of the Li^+, Ni^{2+} and Mn^{4+} in the transition metal layer[19]. Compared with the bare sample, no impurity peaks were observed from the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ patterns due to the amorphous and low content AlF_3. The lattice parameters of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ samples were calculated according to the hexagonal structure with R_3/m space group by using MDI Jade 5.0 software. The refined data of the bare sample were a=2.855 Å, c=14.244 Å, and V=100.59 Å^3, with c/a ratio of 4.988. The values of AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ were a=2.856 Å, c=14.250 Å, and V=100.67 Å^3, with c/a ratio of 4.989. There was no significant difference between lattice parameters of the bare and AlF_3-coated samples, indicating that the AlF_3 coating had little influence on the bulk structure of $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$.

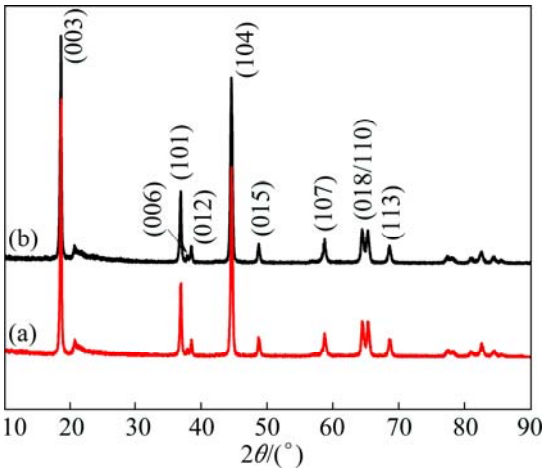

Fig. 1 XRD patterns of bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (a) and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (b)

SEM images of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ are presented in Fig. 2. It can be seen that both of the samples contained aggregates of primary, nano-sized particles. These primary particles were homogeneous and had a small size of 100−200 nm. There is no large difference between the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ due to the nano-thickness of AlF_3-coated layer. More detailed morphology for AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ was observed by HRTEM analysis in Fig. 3(a). Visibly, a AlF_3 layer with a thickness of 5−7 nm appeared in the edge of the coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$. Moreover, EDS analysis of the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ in Fig. 3(b) revealed the presence of Al and F besides Co, Ni and Mn on the surface of AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$.

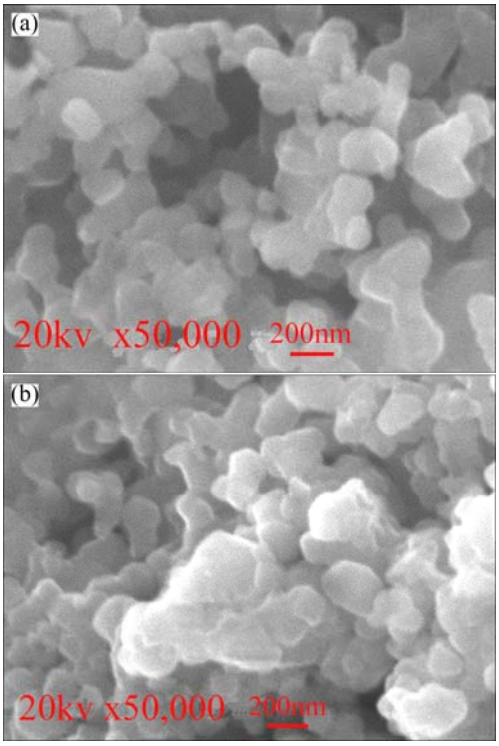

Fig. 2 SEM images of bare (a) and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (b)

3.2 Galvanostatic charge−discharge characterization

Figure 4 shows the initial charge and discharge curves of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrodes at 0.1*C* in the voltage range of 2.5−4.8 V. Both samples exhibited two plateaus during the initial charge, due to the existence of two different lithium de-insertion processes. The first plateau located at 3.8−4.4 V was associated to the lithium removal from the layered component, $LiMO_2$, corresponding to the oxidation of $Ni^{2+}\rightarrow Ni^{4+}$ and $Co^{3+}\rightarrow Co^{4+}$, and the discharge capacity was close to the theoretical capacity (120 mA·h/g). The second plateau, characterized by a relatively flat voltage profile above

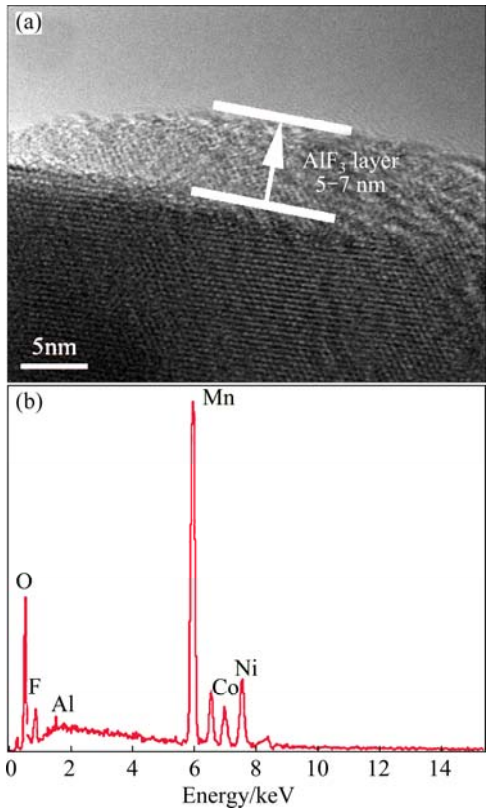

Fig. 3 HRTEM image (a) and EDS result (b) of AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$

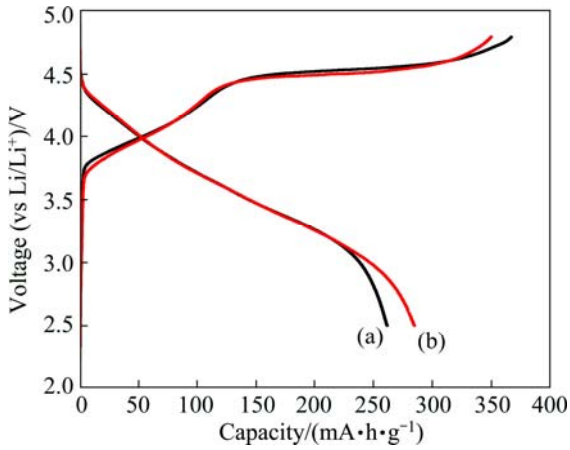

Fig. 4 Initial charge and discharge curves of bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (a) and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (b) electrodes at 0.1*C* rate in voltage range of 2.5−4.8 V at room temperature

4.4 V, originated from the loss of oxygen from the layered Li_2MnO_3 component, which might be transformed to an electrochemical active MnO_2-like phase [20,21]. The corresponding reactions could be represented as follows:

$$LiMO_2 \rightarrow MO_2+Li^+ +e \quad (1)$$

$$Li_2MnO_3 \rightarrow MnO_2+2Li^+ +1/2O_2+2e \quad (2)$$

It could be observed that the initial discharge

capacities of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ were 261.3 mA·h/g and 284.5 mA·h/g, and the initial coulombic efficiencies of the samples increased from 71.18 % to 81.29 %.

Figure 5 shows the discharge profiles of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrodes at different rates (1/20*C*, 1/10*C*, 1/5*C*, 1*C*, 2*C*, 5*C*) between 2.5 and 4.8 V at room temperature. It can be seen that the discharge capacity of the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrode was slightly higher than that of the bare electrode. In detail, the initial discharge capacities of the bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ at 1/20, 1/10 and 1/5, 1, 2 and 5*C* rates were 280.5, 261.3, 249.3, 191.7, 136.5 and 90.9 mA·h/g, respectively, while those of the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ were 296.8, 284.5, 266.9, 208, 166.9 and 110.3 mA·h/g, respectively. Due to the fact that the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ were charged to high cutoff voltage of 4.8 V, where electrolyte decomposition became the main factor affecting their electrochemical performance, the electrolyte decomposition could lead to the formation of LiF-containing film on the electrodes, increasing the interface resistance and deteriorating the electrochemical performance. However, the AlF_3-coated layer may reduce the formation of LiF film, and would thus suppress the cathode−electrolyte interfacial impedance.

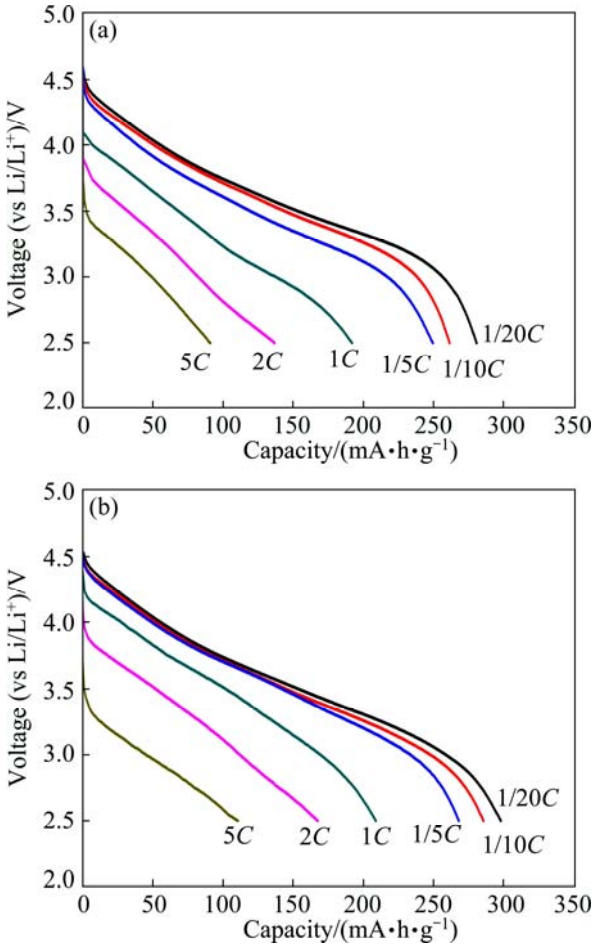

Fig. 5 Discharge curves of bare (a) and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (b) electrodes cycled at different rates in voltage range of 2.5−4.8 V at room temperature

Figure 6 presents the cycling performance of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrodes at 1*C* in the voltage range of 2.5−4.8 V. During the extended cycling, the bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrode exhibited a rapid capacity loss, leading to a capacity retention of only 51.6% after 50 cycles. This poor performance was ascribed to the transition metal dissolution of the electrode surface resulting from HF attack, which causes severe serration of electrode particle surface [22]. However, the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrode demonstrated a greatly improved cycling performance, exhibiting a capacity retention of 72.4% due to the encapsulation of particle surface of AlF_3 layer. And it is worth noticing that the capacity of the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrode increased during 1−8 cycles before decreasing. This phenomenon could be explained as follows. It is a mandatory process for $\chi Li_2MnO_3 \cdot (1-\chi)LiMO_2$ to be charged above 4.6 V (vs Li/Li^+) to deliver large discharge capacity more than 200 mA·h/g [23]. In the high potential region, the oxygen release as Li_2O from the lattice is unavoidable, accompanied with the generation of oxygen vacancies through ionic rearrangements at the end of the initial charge. The polarization in the high potential region is lower for the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$, resulting in the effective lithium extraction and subsequent insertion. In other words, the existence of the AlF_3-coated layer can retain more oxygen vacancies generated in the initial charge process, which is responsible for more lithium-ion insertion and the capacity increase during the subsequent discharge process.

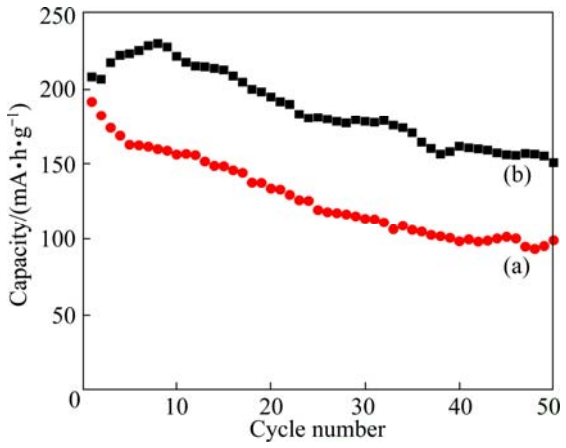

Fig. 6 Cycling performance of bare (a) and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (b) electrodes at 1*C* in voltage range of 2.5−4.8 V

3.3 Cyclic voltammetric (CV) analysis

To explore the improved electrochemical performance of AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$, cyclic voltammetry tests were performed to compare the electrochemical reaction kinetics of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$. Figure 7 displays the CV curves (initial and the second cycle) of the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ at 0.1 mV/s in the voltage range of 2.0−4.8 V (vs Li/Li^+). Both of the samples showed the characteristic CV curves of the $\chi Li_2MnO_3\cdot(1-\chi)LiMO_2$ type materials, which had a large oxidation peak around 4.6 V [24]. The peak was the result from irreversible removal of Li_2O from the Li_2MnO_3 component and the formation of an electrochemically active MnO_2 component. The disappearance of the peak during the second cycle confirmed its irreversibility. The redox around 3.0 V could provide the proof for the formation of MnO_2. It has been reported that MnO_2 had electrochemical reactivity with lithium in the voltage between 2.0 and 3.0 V [25]. As shown in Fig. 8, the couple was clearly observed for the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$, but it was weak for the bare one. The redox peaks of Mn^{3+}/Mn^{4+} are higher and broader in AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ than in the bare electrode. The results implied that the pre-active MnO_2 of the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ sample was better than the bare one. Thus, the AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrode exhibited better performance than the bare one.

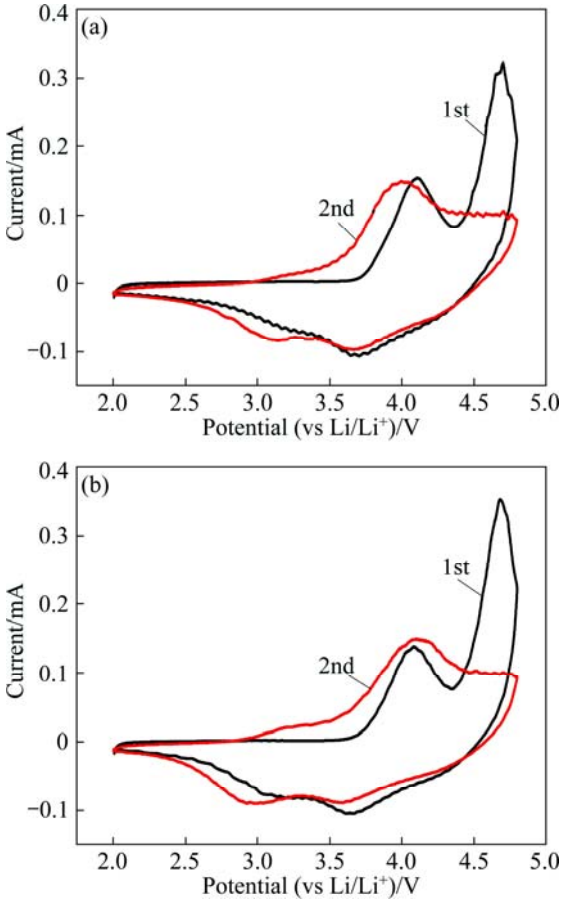

Fig. 7 Cyclic voltammetry curves of bare (a) and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ (b) at scan rate of 0.1 mV/s in voltage range of 2.0−4.8 V (vs Li/Li^+)

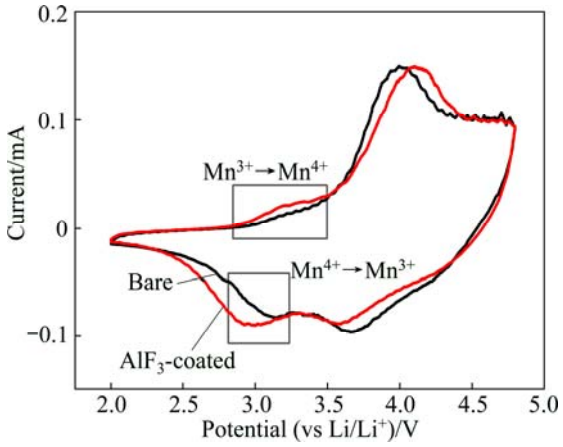

Fig. 8 Comparison of bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ at the second cyclic voltammetry

3.4 Electrochemical impedance spectroscopic analysis

To correlate the electrochemical performance with interfacial impedance, electrochemical impedance spectroscopy was performed for the bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrodes. Both of the electrodes were tested after 30 charge−discharged cycles at 0.1*C* rate. Nyquist plots of the two electrodes are compared in Fig. 9. The plots of both electrodes consisted of two semicircles, one in the high to medium frequency region, the other in the medium to low frequency region and a straight line in the low-frequency region. The semicircle in the high to medium frequency region was related to the surface film resistance (R_{sf}); the semicircle in the medium to low frequency resulted from the charge transfer resistance (R_{ct}); the straight line in the

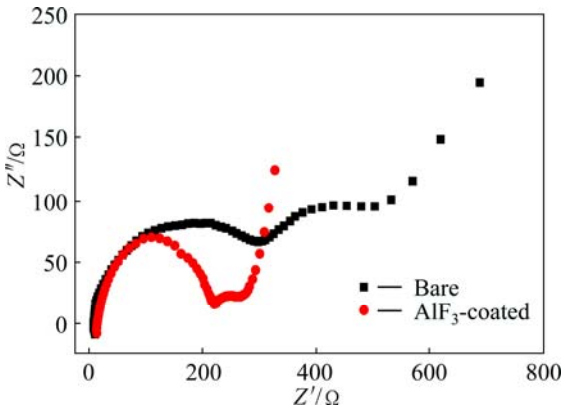

Fig. 9 Electrochemical impedance spectra (EIS) of bare and AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrodes

low-frequency region corresponded to a semi-infinite Warburg diffusion process (solid state diffusion of lithium ions through the bulk of the electrode) [26]. In Fig. 9, it is shown that the total resistance of the bare electrode was much larger than that of AlF_3-coated one. Especially, the charge-transfer resistance was notably reduced after AlF_3 coating. It seemed that the AlF_3-coated layer on the surface of $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ could lower the activity of interface between electrode and electrolyte, facilitating lithium-ion conduction by reducing charge-transfer resistance. Then, the better lithium-ion conduction would improve the cycling performance of AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ electrodes as described in Fig. 6.

4 Conclusions

1) Uniform and thin AlF_3 layer with a thickness of 5−7 nm is coated on the surface of $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ particles by a wet process.

2) The AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ has better electrochemical performance than the bare $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$. At 0.1*C* rate, the initial coulombic efficiency of the $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ is improved from 71.18 % to 81.29 % by AlF_3 coating. And the capacity retention is improved from 51.6% to 72.4 % after 50 cycles at 1*C* rate.

3) EIS results show that the improved electrochemical performance of AlF_3-coated $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ can be explained by the lower charge transfer resistance. CV tests also indicate the better pre-active of MnO_2 by AlF_3 coating.

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AlF_3 包覆锂离子电池正极材料 $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ 的制备、表征及电化学性能

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摘 要：采用溶胶−凝胶法合成锂离子电池正极材料 $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$，并用 AlF_3 对这种材料进行表面包覆改性。采用 X 射线衍射(XRD)、扫描电子显微镜(SEM)、高分辨率透射电子显微镜(HRTEM)等表征材料的结构和形貌。结果表明，合成的 $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ 具有典型的层状 α-$NaFeO_2$ 结构，AlF_3 均匀包覆在 $Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$ 材料表面，包覆层厚度为 5~7 nm。电化学测试表明，包覆 AlF_3 后材料的电化学性能得到提高，在 1*C* 倍率下，包覆的 AlF_3 材料的首次放电容量为 208.2 mA·h/g，50 次循环后容量保持率为 72.4%，而未包覆 AlF_3 的材料的首次放电容量和容量保持率分别为 191.7 mA·h/g 和 51.6%。

关键词：锂离子电池；$Li_{1.2}(Mn_{0.54}Ni_{0.16}Co_{0.08})O_2$；$AlF_3$ 表面包覆；容量保持率

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