The uniform and spherical LiNi0.5Co0.2Mn0.3O2 particles were successfully coated with AlF3. The structures and electrochemical properties of AlF3-coated LiNi0.5Co0.2Mn0.3O2 were characterized by various techniques. When the coating amount was 0.5 mol%, the cathode showed enhanced cycling performance and rate capability compared to the pristine LiNi0.5Co0.2Mn0.3O2. The AlF3-coated LiNi0.5Co0.2Mn0.3O2/Li cell had capacity retention of 98% after 100 cycles even at 4C over 2.8–4.5 V, while the pristine LiNi0.5Co0.2Mn0.3O2/Li exhibited capacity retention of only 95%. Moreover, the rate capability and cyclic performance at elevated temperature (55 °C) were also improved. Electrochemical impedance spectroscopy testing revealed the improved electrochemical performance, which could be considered that the AlF3 coating layer can suppress the increase of impedance during the charging and discharging process by preventing directly contact of the highly delithiated active material with electrolyte.

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1. Introduction

Lithium-ion batteries have revolutionized portable appliances and become dominant power sources for notebook computers, cell phones, and digital cameras because of their high volumetric and gravimetric energy densities [1–5]. Recently, more efforts have focused on improving the performances of lithium-ion batteries to replace the nickel metal hydride batteries for hybrid electric vehicles (HEVs), plug-in hybrid vehicles (PHEVs) and full electric vehicles (EV) [6]. The technological drawbacks of the current cathode materials lie in solving the low rate capability and inadequate cycling stability at elevated temperature [7]. To resolve these problems, great efforts for developing new cathode materials with excellent electrochemical performance and low cost have been made in recent years [8,9]. Among the existing materials, the lithium transition metal oxides, Li[NiCoMn]O2 have been deemed to be promising cathode materials for HEV, PHEV and EV applications because of their relatively high reversible capacity, low cost and low toxicity [10–13]. However, they have also shown poor cycling stability at high rate or high cutoff voltage at elevated temperatures [14,15].

To discharge higher capacity, the cell should charge up to higher cutoff voltage. But its capacity fading becomes more serious than that over 2.8–4.3 V because of the transformation of structure from hexagonal cell with P31 12 to fcc lattice of α-NaFeO2 and dissolution of the Co and Mn [14]. The surface coating has been proved to be an effective method to reduce the electrolyte decomposition, suppress cation dissolution during cycling and enhance structural stability at high cutoff voltage. Metal oxides [16–18], such as Al2O3, ZrO2, TiO2, ZnO, MgO, SiO2 and phosphates [19], have been reported to be effective coating materials for improving the electrochemical performance of cathodes. Al2O3-coated LiCoO2 exhibited no decrease in its original specific capacity and excellent capacity retention [16], which originated from the disappearance of the phase transition from a hexagonal to monoclinic phase by Al2O3 coating. Al2O3 coating for the improvement of the electrochemical performance of LiNi0.5Co1.5Mn1.5O2 [20] and LiMn2O4 [21] had also been reported. During the electrochemical cycling, the metal oxide coating layers, such as Al2O3, scavenged HF species from the electrolyte and formed stable metal fluoride layer which could result in less decomposition of the cathode particles. Thus the metal fluorides, typically AlF3, look to be promising coating materials. Lee et al. [22] found that the enhanced electrochemical properties and thermal stability of AlF3-coated Li1.1Al0.05Mn1.85O4 were due to the fact that AlF3 layer can suppress the decomposition of LiPF6 salt and the dissolution of Mn. In this research, we investigate the effects of AlF3 coating on the structural and electrochemical properties of...
LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$. The AlF$_3$-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ cathode material exhibits the highly enhanced cycling performance and rate capability compared with the pristine at high cut-off voltage (4.5 V) and high temperature (55 °C).

2. Experimental

The spherical hydroxide precursor Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$(OH)$_2$ was prepared by co-precipitation method. An aqueous solution (1.5 mol L$^{-1}$) of NiSO$_4$, CoSO$_4$, and MnSO$_4$ (cations ratio of Ni:Co:Mn = 5:2:3) was pumped into a specially designed reactor under nitrogen atmosphere. At the same time, NaOH solution (3.0 mol L$^{-1}$) as a precipitation agent and desired amount of NH$_4$OH solution as a chelating agent were also separately fed into the reactor. The reaction temperature was kept at 55 °C and pH was adjusted by NaOH solution to 11. The resulted spherical precipitated particles Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$(OH)$_2$ were washed, filtered and dried. The Ni$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$(OH)$_2$ powders were mechanically ground with Li$_2$CO$_3$ by ball milling for 2 h, sintered at 550 °C for 6 h and then at 870 °C for 7 h to form LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ material. The heating and cooling rate of the heat treatment were 4 and 2 °C/min, respectively.

To coat the surface of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ with AlF$_3$, aluminum nitrate nonahydrate and ammonium fluoride were separately dissolved in distilled water firstly. 9.655 g LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ powders were immersed into the aluminum nitrate solution (0.05 mol L$^{-1}$). Then, the ammonium fluoride solution (0.05 mol L$^{-1}$) was added in the mixture. The molar ratio of Al to F was adjusted to 1:3 and the amount of AlF$_3$ in the solution was set at molar ratios of n(AlF$_3$)/n(LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$) = 0.25%, 0.5%, 1%, 2%, respectively. The mixture was stirred constantly at 50 °C for 4 h followed by slow evaporation of solvent at 80 °C for 24 h. The resulting LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ powders were sintered at 400 °C for 5 h in flowing nitrogen to avoid the formation of Al$_2$O$_3$.

The crystal structure of the powders was identified by powder X-ray diffraction (XRD, Rigaku D/max-b) using Cu Kα radiation in the 2θ range of 10–90° at a continuous scan mode with a step size of 0.02° and a scan rate of 5°/min. The particle morphologies of the bare and AlF$_3$-coating LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ powders were observed with a scanning electron microscope (SEM, EVO 18). Particle size distribution was estimated by low-angle laser light scattering (LALLS) measurements (Malvern Mastersizer 2000). The composition and spatial distribution of transition metal elements on the surfaces of powders were measured by Energy dispersive X-ray spectroscopy (EDS, EVO 18).

The electrochemical properties were performed by means of two-electrode coin-type half cells, which consisted of positive electrode (80 wt% LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$, 15 wt% acetylene black and 5 wt% polyvinylidene fluoride), a Celgard 2400 separator, and a lithium foil as negative electrode. 1 mol L$^{-1}$ LiPF$_6$ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1:1:1, by volume) was used as an electrolyte. The cells were assembled in an argon filled glove box where both the moisture and oxygen contents were less than 1 ppm. The electrochemical impedance spectroscopy (EIS) analysis was measured at a CHI660C Electrochemical Workstation (Shanghai Chenhua) over the frequency range from 0.1 MHz to 0.005 Hz with the amplitude of 10 mV.

3. Results and discussion

The XRD patterns of the bare and AlF$_3$-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ were presented in Fig. 1. The XRD patterns confirmed that these five samples had a well-defined layer structure based on a hexagonal α-NaFeO$_2$ structure with space group R $\bar{3}$ m without obvious impurities and secondary phases. The diffraction peaks of the patterns were quite narrow, which represented that the synthesized materials had high crystallinity. AlF$_3$ phase was not observed in the XRD patterns because small amount of AlF$_3$ coating existed on the surface of the LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ particles. The appearance of significant peak splitting of (006)/(102) and (108)/(110) indicated the formation of highly ordered layered structures. The intensity ratio of I$_{003}$/I$_{104}$ is sensitive to the cation distribution in the lattice and the degree of cation mixing of the materials. When the ratio is higher, disorder degree of the cations is lower, and the electrochemical performance is relatively better. Generally, when the ratio >1.2, the materials have a good layered structure with small cation mixing [23]. As illustrated in Fig. 2, with increasing AlF$_3$ content, the I$_{003}$/I$_{104}$ value increased firstly and then decreased. 0.5 mol% AlF$_3$-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ had the largest value of ratio of I$_{003}$/I$_{104}$, about 1.35, which was expected to show the best electrochemical performance.

The morphologies of cathode materials have a strongly correlation with the electrochemical properties in rechargeable lithium batteries. Materials with spherical and uniform particle size distribution exhibit good overall battery performance due to the uniform depth of charge and discharge of each particle. The spherical particle could also lead to the enhanced tap density and

![Fig. 1. XRD patterns of the bare and different (x) AlF$_3$-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$, where x=0.25, 0.5, 1, and 2 mol%.](image-url)

![Fig. 2. I$_{003}$/I$_{104}$ value for different (x) AlF$_3$-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$, where x=0.25, 0.5, 1, and 2 mol%.](image-url)
energy density. The SEM images (Fig. 3) of the bare and 0.5 mol% AlF₃-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ indicated that the synthesized materials showed spherical secondary particles. There was no significant difference between the bare and 0.5 mol% AlF₃-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂. From the particle size distribution of the bare LiNi₀.₅Co₀.₂Mn₀.₃O₂ (Fig. 4), it can be concluded that the as prepared LiNi₀.₅Co₀.₂Mn₀.₃O₂ are distributed in a narrow diameter range with the average particle size of 10.283 μm. The composition and distribution of elements on the surface of 0.5 mol% AlF₃-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ were examined by EDS, as shown in Fig. 5. According to Fig. 5, Al and F were distributed uniformly on the surface of particles of 0.5 mol% AlF₃-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂.

Fig. 6 showed the initial charge/discharge profiles of the bare and various amounts of AlF₃-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ electrodes at 0.2 C (36 mA g⁻¹) over 2.8–4.5 V. All the cells displayed the typical electrochemical behavior with a very smooth and monotonous voltage plateau in the initial charge/discharge process which was very similar to the voltage profiles reported by other workers [24]. The bare LiNi₀.₅Co₀.₂Mn₀.₃O₂ exhibited a discharge capacity of 175.6 mAh g⁻¹. With increasing AlF₃ content, the discharge capacities of the electrode increased firstly then decreased. They were 175.6, 178.4, 173.7 and 145.1 mAhg⁻¹ for 0.25, 0.5, 1 and 2 mol% AlF₃-coated samples, respectively. When the coating amount up to 2 mol%, the discharge capacity decreased remarkably and the polarization increased distinctly. It is speculated that too much inactive AlF₃ coating resulted in the increase of the contact resistance and charge transfer resistance.

The rate capability, one of the important battery performances, was revealed in Fig. 7. The cells were firstly charged at 0.2 C (36 mA g⁻¹) until the voltage reached 4.5 V and then discharged at 0.2 C (36 mA g⁻¹), 1 C (180 mA g⁻¹), 2 C (360 mA g⁻¹), 4 C (720 mA g⁻¹), 6 C (1080 mA g⁻¹) for every five cycles, then discharge at 0.2 C (36 mA g⁻¹) (Fig. 7a). As can be clearly seen from Fig. 7b, appropriate AlF₃ could improve the rate property. When the coating amount was 0.5 mol%, the cell showed the highest discharge capacity at the various rates. The capacity of the 0.5 mol% range with the average particle size of 10.283 μm. The composition and distribution of elements on the surface of 0.5 mol% AlF₃-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂ were examined by EDS, as shown in Fig. 5. According to Fig. 5, Al and F were distributed uniformly on the surface of particles of 0.5 mol% AlF₃-coated LiNi₀.₅Co₀.₂Mn₀.₃O₂.

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**Table 1**

<table>
<thead>
<tr>
<th>Samples</th>
<th>After 1 cycle</th>
<th>After 60 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R_s (Ω)</td>
<td>R_i (Ω)</td>
</tr>
<tr>
<td>Bare</td>
<td>2.876</td>
<td>24.56</td>
</tr>
<tr>
<td>0.5 mol% AlF₃-coating</td>
<td>3.045</td>
<td>18.76</td>
</tr>
</tbody>
</table>
Fig. 5. SEM image (a), and EDS dot-mappings for composition Mn (b), Co (c), Ni (d), F (e) and Al (f) of 0.5 mol% AlF$_3$-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$.

Fig. 6. The first charging and discharging curves of the bare and different (x) AlF$_3$-coated LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ electrodes over 2.8–4.5 V, where x = 0.25, 0.5, 1, and 2 mol%.

AlF$_3$-coated electrode was 153.3 mAh g$^{-1}$ at 6 C, about 86.4% of that at 0.2 C, while the bare electrode discharged a capacity of 142 mAh g$^{-1}$ at 6 C, about 80.8% of that at 0.2 C. These results revealed that the rate capability of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ could be enhanced by AlF$_3$ coating. That may be ascribed to the decrease of cation mixing and polarization.

The influence of AlF$_3$ coating on the cycling performance of LiNi$_{0.5}$Mn$_{0.2}$Co$_{0.3}$O$_2$ was also investigated. The cells were firstly charged to 4.5 V at 4 C, and then kept charging at 4.5 V until the current density was 10 mA g$^{-1}$, then they were discharged to 2.8 V at 4 C. As shown in Fig. 8, the AlF$_3$-coated electrode exhibited good cycling performance and its capacity retention was 98% after 100 cycles, while the bare electrode displayed a obvious capacity fading from 154 to 137.7 mAh g$^{-1}$ with capacity retention of only 89%. The cycling performances of the bare and AlF$_3$-coated cathode were also investigated at 1 C over 2.8–4.5 V at 55 °C (Fig. 9). The 0.5 mol% AlF$_3$-coated LiNi$_{0.5}$Mn$_{0.2}$Co$_{0.3}$O$_2$ had a higher capacity and improved capacity retention. It displayed 91% retention of the initial discharge capacity at the 50th cycle, while the bare one retained only 85% at the same condition. As a result, the AlF$_3$ coating could distinctly improve the cycling performance of the cathode materials.
Fig. 7. Discharge capability as a function of cycle number (a), and discharge current (b) for the bare and different (x) AlF3-coated LiNi0.5Co0.2Mn0.3O2 electrodes at various discharge rates over 2.8–4.5 V, where x = 0.25, 0.5, 1, and 2 mol%.

EIS measurements were carried out for both samples at 1 C over 2.8–4.5 V, as illustrated in Fig. 10. There were two semicircles in the EIS for the electrodes, one in the high-to-medium frequency region and the other in the low frequency region. According to the previous reports [25], the high-to-medium frequency semicircle is connected with the Li-ion migration through surface films that cover cathode particles (R_f). The low-frequency semicircle reflects the charge-transfer process (R_{ct}). The impedance parameters were calculated by the simplified equivalent circuit (Fig. 10c). As illustrated in Table 1, it could be seen that the R_f and R_{ct} increased dramatically during cycling for the bare cathode, particularly the R_{ct}, which was added up to about 25 times of the initial value after 60 cycles. However, the R_{ct} for the modified cathode only increased to about 2.7 times. It revealed that the AlF3 coating could suppress the increase in the R_{ct}, which could be caused by the
undesirable side reaction between the electrolyte and the cathode during cycling, thus contributing to the improved cycling property.

4. Conclusion

The uniform and spherical LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 coated with AlF_3 was successfully prepared and their excellent electrochemical performance had been demonstrated. The AlF_3 coating could minimize the undesirable side reaction between the highly delithiated active material and electrolyte, suppress the increase of impedance during cycling. The modified LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 showed enhanced cycling performance and rate capability, which delivered the discharge capacity of 149.7 mAh g^{-1} after 100 cycles even at 4C over 2.8–4.5 V, almost 98% of the initial capacity, while the discharge capacity and retention of the pristine material exhibited only 137.7 mAh g^{-1} and 89%, respectively. Even at elevated temperature (55 °C), the modified LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 also exhibited better capacity retention. Therefore, surface modification by AlF_3 is an effective method to improve the performance of LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 cathode materials for lithium-ion batteries.

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References