

AlF₃-Coating to Improve High Voltage Cycling Performance of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ Cathode Materials for Lithium Secondary Batteries

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Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ powders were modified by coating their surface with amorphous AlF₃ as a new coating material. The AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ electrode showed improved cycle performance and rate capability under a high cutoff voltage range of 4.5 and 4.6 V. AC impedance results showed that the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ has stable charge transfer resistance (R_{c1}) regardless of the cycle number. Electron diffraction analysis also showed that no structural transition of the primary particles was observed for the AlF₃-coated electrode. Electrochemical impedance spectroscopy and electron microscopy indicate that AlF₃ coating plays an important role of stabilizing the interface between cathode and electrolyte. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2422890] All rights reserved.

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In recent years, the lithium transition-metal oxides, Li[Ni_xCo_{1-2x}Mn_x]O₂ have received considerable interest as a candidate to replace the commercial cathode material (LiCoO₂) for lithium secondary batteries. Among them, Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ has been studied extensively as a promising cathode material due to its many advantages such as a high discharge capacity, high rate capability, and good structural stability. In attempts to increase the reversible capacity of the cathode material, the upper cutoff voltage limit has been progressively raised. The increased upper voltage limit resulted in a moderate increase in the specific discharge capacity as expected. However, the electrode, charged to a high voltage (>4.5 V) lead to a significant deterioration of the cycle performance.^{1,2} The origin of this capacity fading was related to the increase in the surface reactivity between the highly delithiated and instable cathode and the electrolyte, resulting in significant interfacial impedance rise. In addition, operating at high voltage can lead to either an increase in cobalt dissolution into the electrolyte in case of cobalt based cathodes,^{3,4} or structural changes of the host material.

To solve this problem, various metal oxides were coated on $LiCoO_2$.⁶⁻¹¹ It is well known that a metal-oxide-coated $LiCoO_2$ has a high reversible capacity and improved cycle characteristics. Although the reason for the enhanced electrochemical performance is not well understood, the coating technology is being used for commercialized batteries due to the enhanced electrochemical performance. For example, Cho et al.' reported that an Al₂O₃ coating on LiCoO₂ effectively suppressed the lattice-constant changes and thereby resulted in zero-strain cathode material. Meanwhile, Chen and Dahn¹² proposed that oxide coating might inhibit side reactions involving oxygen loss from Li_xCoO₂ to the electrolyte and hence improve the cycling stability. Recently, Sun et al.¹³ first reported that LiCoO₂ with AlF₃ coating had improved electrochemical properties at a high cutoff voltage, which originated from the lower charge transfer resistance and reduced cobalt dissolution. In addition, Fumihiro et al. 14 found that anion substitution for O in $\rm LiCoO_2$ substantially suppressed the Co dissolution, even at the moderately high upper voltage limit of 4.3 V. In a previous study,¹⁵ Kim et al. reported that a fluorine-substituted Li[Ni1/3Co1/3Mn1/3]O2 exhibited stable cycling performance and improvement of high rate capability compared to the bare Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂, which resulted from the smaller *c*-axis variation and fluorine coating effect.

In this work, we report the effect of surface modification of

 $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ by AlF₃ on electrochemical performance at a high cutoff voltage. We also investigate the reason for the improvement of electrochemical performance of AlF₃ coating by comparing the structural and interfacial properties of pristine and AlF₃-coated $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$.

Experimental

Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ powders were synthesized by the coprecipitation method because this method gives rises to highly homogeneous [Ni_{1/3}Co_{1/3}Mn_{1/3}](OH)₂ hydroxide powders; therefore, simple calcination of the hydroxide and lithium salt can result in a phase-pure product with high homogeneity. The detailed procedure for preparing the [Ni1/3Co1/3Mn1/3](OH)2 powders was reported previously.¹⁶ A mixture of the dehydrated [Ni_{1/3}Co_{1/3}Mn_{1/3}](OH)₂ and LiOH·H₂O was heated at 950°C for 15 h, then annealed at 700°C for 5 h in air. To coat the surface of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ with AlF₃, ammonium fluoride (Aldrich), and aluminum nitrate nonahydrate (Aldrich) were separately dissolved in distilled water. After the prepared Li[Ni1/3Co1/3Mn1/3]O2 powders were immersed into the aluminum nitrate nonahydrate solution, the ammonium fluoride solution was slowly added to the solution. The molar ratio of Al to F was fixed at 3 and the amount of AlF₃ in the solution corresponded to 2 mol % of the Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2 powders. Afterward, the solution containing the Li[Ni1/3Co1/3Mn1/3]O2 powder was continuously stirred at 80°C for 5 h and then filtered by distilled water. The resulting Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ powders were heated at 400°C for 5 h in flowing nitrogen to avoid the formation of Al_2O_3 .

For fabrication of the cathode, the prepared powders were mixed with carbon black and polyvinylidene fluoride (94:3:3) in *N*-methylpyrrolidinon. The slurry thus obtained was coated onto Al foil and roll-pressed at 120° C in air. The electrodes were dried at 120° C overnight in vacuum state prior to use. Preliminary cell tests were done using a 2032 coin-type cell adopting Li metal as the anode. The electrolyte solution was 1 M LiPF₆ in ethylene carbonate–diethyl carbonate (1:1 in volume, Cheil Industries, Inc., Korea).

Powder X-ray diffraction (XRD) (Rint-2000, Rigaku, Japan) measurement using Cu K α radiation was employed to identify the crystalline phase of the synthesized powders and AlF₃-coated powders. From the XRD patterns, lattice parameters were calculated by a least-squares method. High-resolution transmission electron microscope (HR-TEM, JEM2010, JEOL) was employed to characterize the prepared powders and cycled electrodes. AC impedance mea-

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Figure 1. Powder XRD patterns of (a) pristine and (b) $\rm AlF_3\text{-}coated$ $\rm Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2.$

surements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range from 1 MHz to 5 mHz with the amplitude of 10 mV_{rms}.

Results and Discussion

Figure 1 shows XRD patterns of the pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ powders. Both powders were confirmed to be well-defined hexagonal α -NaFeO₂ structure with a space group of $R\bar{3}m$. No impurity peaks corresponding to Al-related compounds were observed from the XRD patterns shown in Fig. 1b. The lattice constants of the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ powder were a = 2.864(6) and c = 14.277(8) Å, respectively, as calculated by a least square method. The values are close to those of the pristine material, a = 2.867(5), c = 14.250(4) Å, indicating that the AlF₃ was not incorporated into the host structure as no changes were seen in the structure.

Figure 2 presents TEM images of the pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂. The images reveal that each AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ individual particle consists of primary particles with sizes of 100–1000 nm. Figure 2a shows a TEM of a typical primary particle from the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ powders. Magnified images around the edge of the particle clearly reveal that it is uniformly encapsulated by a 5 nm thick AlF₃ film. The grainy uniform contrast of the AlF₃ film confirms that the AlF₃ coating layer is amorphous. The TEM images provide conclusive evidence that the primary particle is coated by the AlF₃ film. In comparison, the bright field TEM of an uncoated primary Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ particle shown in Fig. 2b did not have an extra film on the particle surface, as one would expect.

Figure 3 shows the initial charge/discharge curves of the Li/ pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cells by applying a constant current of 16 mA/g between 3.0 and 4.5 V vs Li/Li⁺. Both cells show very stable and smooth charge/discharge curves, and the curves for both cells nearly coincide even up to the cutoff voltage of 4.5 V. This result indicates that the coating medium of AlF₃ was not introduced into the bulk of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ structure. The charge curve for the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ electrode is slightly higher than that of the pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂. This result also indicates that a resistive coating layer exists on the surface of AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ particle.

Figure 4 shows the discharge capacity of Li/pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cells over 50 cycles in the range of 3.0–4.5 and 3.0–4.6 V at a current rate of 80 mA/g (0.5 C-rate), respectively. For the 3.0–4.5 V range, the pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ delivered the same discharge capacity of



Figure 2. TEM images of (a) AIF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ with magnified images around the edge and (b) pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂.

172–173 mAh/g. The pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ showed a gradual decrease in capacity, leading to a capacity retention of 75% after 50 cycles. Meanwhile, the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ showed remarkably enhanced capacity retention of 93% after same cycling period. Similarly to the 3.0–4.5 V range, the capacity retention of the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ in the voltage range of 3.0–4.6 V was significantly improved (92% capacity retention) compared to pristine cathode (72% capacity retention).

The rate capability properties also display advantages of the AlF₃ coating. Figure 5 shows the discharge capacities for the Li/pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cells as a function of current density (32–640 mA/g) between 3.0 and 4.5 V vs Li/Li⁺. The cells were charged galvanostatically with a current density of 16 mA/g (0.1 C rate) before each discharge test and then discharged



Figure 3. Initial charge and discharge curves of Li/pristine Li[Ni $_{1/3}$ Co $_{1/3}$ Mn $_{1/3}$]O₂ and Li/AlF₃-coated Li[Ni $_{1/3}$ Co $_{1/3}$ Mn $_{1/3}$]O₂ cells.



Figure 4. Cycling performance of Li/pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ and Li/AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cells cycled at (a) 3.0–4.5 and (b) 3.0–4.6 V range.

at current densities from 32 (0.2 C rate) to 640 mA/g (4 C rate). At low current density (32 mA/g), the two electrodes showed similar electrochemical performance. With increased current density, the AlF₃-coated Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂ electrode clearly exhibited a higher discharge capacity than the pristine electrode. For example, the AlF₃-coated Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O₂ delivered a discharge capacity of 127 mAh/g with good cyclability at 640 mAh/g, whereas the pristine electrode reached 102 mAh/g at the same current density. Another interesting feature is different capacity retention behavior of the two electrodes. The capacity of the pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ electrode exhibited an accelerated deterioration with cycling while the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ electrode showed excellent capacity retention. This could be due to both intrinsic poor rate capability and decreased cycling behavior of pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ electrode at higher cutoff voltage above 4.5 V as observed in Fig. 4.



Figure 5. Rate capability of Li/pristine Li $[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ and Li/AlF₃-coated Li $[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cells at various current densities.



Figure 6. Nyquist plots of (a) the Li/pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ and (b) the Li/AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cell at 1st, 10th, 30th and 50th cycle.

To explore the reason for the enhanced electrochemical properties of the AlF3-coated Li[Ni1/3Co1/3Mn1/3]O2, electrochemical impedance spectroscopy (EIS) was carried out for the pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ at different cycle numbers in the charged state to 4.5 V vs Li/Li⁺. Nyquist plots derived from the analyses are shown in Fig. 6. The insets in Fig. 6a and b present expanded views for the high-to-medium frequency region. The equivalent circuit used in this study was reported in our previous The open symbols and continuous lines represent experistudy. mental data and fitted results with the equivalent circuit, respectively. These simulated lines correspond well to the observed plots. The Nyquist plots for both electrodes present two semicircles, one in the high-to-medium frequency region and the other in the low frequency region. The semicircle at high-to-medium frequency is attributed to resistance of surface film (R_{sf}) that covers cathode particle. The semicircle at low frequency is associated with the chargetransfer resistance (R_{ct}) coupled with a double-layer capacitance. Tables I and II give R_{sf} and R_{ct} as a function of cycle number for the pristine and AlF₃-coated LiCoO₂ electrodes, respectively. The R_{sf} for the both electrode drastically decreases after the first cycle. This decline could be due to the improvement of ionic conductivity for the lithium ion, although the passivation film or the reduction of electrode/electrolyte reactivity. The $R_{\rm sf}$ of AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ was about one and one-half times larger than that of pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ at the first cycle as well as subsequent cycles. For example, R_{sf} value of AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ changed from 16.9 Ω at the first cycle to 3.7 Ω after 30 cycles, whereas that of pristine decreased from

Table I. Surface film resistance (R_{sf}) for pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ cells with cycle number.

	$R_{sf}(\Omega)$			
Cycle number	Pristine Li[Ni _{1/3} Co _{1/3} Mn _{1/3}]O ₂	$AlF_{3}\text{-coated} \\ Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2}$		
1	10.5	16.9		
10	2.99	3.85		
20	2.38	3.45		
30	2.00	3.69		
40	1.76	3.63		
50	1.81	4.26		

10.5 Ω at the first cycle to 2 Ω after 30 cycles. These results indicate that the AlF₃ coating influences the formation of passivation film on the cathode particle surface. The large $R_{\rm sf}$ of AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ at the first cycle is attributed to more resistive and thicker surface film compared to the other cycle numbers.

In contrast to the $R_{\rm sf}$ trends, the $R_{\rm ct}$ value of pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ greatly increased with increasing cycles, even though the $R_{\rm ct}$ of the first cycle was nearly same for the both pristine and AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂. The $R_{\rm ct}$ value of the pristine was 11.1 Ω after the first cycle, drastically increased with cycling, and reached to 230.9 Ω after 50 cycles. On the other hand, the $R_{\rm ct}$ value of AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ remained within 5.3–6.03 Ω , except for the first cycle (10.35 Ω), as shown in Fig. 6 and Table II. Different from the $R_{\rm sf}$, $R_{\rm ct}$ of the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ remained constant in spite of successive cycling except for the first cycle, while the $R_{\rm ct}$ of pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ rapidly increased with cycling.

It is known that resistive surface films hinder the charge transfer kinetics. However, in our study, although the surface film resistance of the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ is larger than that of the pristine electrode, a stable surface film on the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ particle might have prevented interfacial degradation between the electrolyte and cathode material at a high voltage (4.5 V). Recently, Miyashiro et al.⁹ reported that the enhanced cycling properties of ZrO₂-coated LiCoO₂ for the high cutoff voltage of 4.6 V were not due to the structural change of the host but to the improved interfacial properties at the LiCoO₂ surface. More recently, Sun et al.¹³ also reported that the excellent capacity retention of AlF₃-coated LiCoO₂ at the 4.5 V cutoff voltage originated from the lower charge transfer resistance and reduced cobalt dissolution. It is clear that AlF₃ coating greatly reduces the increase of charge transfer resistance.

Figure 7a shows a TEM of a primary particle from the AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ electrode after electrochemical cycling. The image indicates a 20 nm thick AlF₃ film preserved on the particle surface even after 50 cycles. Again, the uniform grainy

Figure 7. TEM (a) image of primary particle from the cycled AlF_3 -coated $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ electrode and (b) magnified image of the circled region in (a).

contrast of the AlF₃ film indicates that the film remained amorphous during cycling. The coating thickness also appears to have remained uniform; however, the magnified image in Fig. 7b shows that the AlF₃ film thickness is strikingly different from one face of the particle to another. While 2 nm thick AlF₃ film is well maintained along the left face of the particle, the AlF₃ film thickness on the right face is limited to \sim 3 nm. This observation suggests that, although further investigation is needed, the AlF₃ coating may preferentially either be coated or deteriorate along a certain crystallographic direction of the primary particle.

Electron diffraction analysis of the cycled electrodes demonstrated that the integrity of the layered structure during cycling was also improved by the AlF_3 coating. For the pristine sample, it appears that some of primary particle underwent a phase transition to a cubic spinel structure during cycling, as evidenced by a 100 zone diffraction pattern of the cubic spinel structure in Fig. 8a obtained from the cycled electrode that was not coated with AlF_3 . In comparison, no such phase transition was noticed for the observed primary particles of the AlF_3 -coated electrode. All of the observed particles from the AlF_3 -coated electrode exhibited symmetries consistent with the hexagonal structure of layered

040 044 004 003 (a) (b)

Figure 8. Electron diffraction analysis of the (a) pristine $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ and (b) AlF_3 -coated $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cells after 50 cycles.

Table	II.	Charge	transfer	resistance	$(R_{\rm ct})$	for	pristine	and
AlF ₃ -c	oateo	l Li[Ni _{1/}	3Co1/3Mn	_{1/3}]O ₂ cells	with c	ycle	number.	

 $P(\mathbf{0})$

Cycle number	Pristine Li[Ni _{1/3} Co _{1/3} Mn _{1/3}]O ₂	$\label{eq:alF3-coated} \begin{split} AlF_3\text{-coated}\\ Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2 \end{split}$			
1	11.1	10.35			
10	26.5	6.03			
20	43.6	4.18			
30	102.8	5.66			
40	155.7	5.04			
50	230.9	5.30			

Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂. As an example, the 100 zone diffraction pattern of the hexagonal Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ structure obtained from the AlF₃-coated electrode after cycling is shown in Fig. 8b. Although the role of AlF₃ coating for the improved electrochemical properties of layered Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ has not been fully investigated, the this coating brought about stabilization of the host structure as well as lowering of the charge transfer resistance.

Conclusions

Layered Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ was coated with AlF₃ to investigate its cycling performance at high cutoff voltage (>4.5 V). A uniform and thin AlF₃-coating layer of 5–10 nm formed on the surface of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂, and the layer had an amorphous structure. The AlF₃-coated Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ electrode had much enhanced cycling stability and rate capability compared to pristine Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂. The AlF₃-coated electrode showed only 7–8% capacity loss after 50 cycles at high cutoff voltage of 4.5 and 4.6 V, while the pristine samples suffered 25–28% capacity loss. Such excellent properties could have originated from the lower and stable charge transfer resistance between cathode and electrolyte and from the stabilized host structure of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂.

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