Short communication

# Electrochemical and thermal characterization of AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ cathode in lithium-ion cells

H.-B. Kim [a], B.-C. Park [a], S.-T. Myung [b], K. Amine [c], Jai Prakash [d], Y.-K. Sun [a],*

[a] *Department of Chemical Engineering, Center for Information and Communication Materials, Hanyang University, Seungdong-Gu, Seoul 133-791, Republic of Korea*
[b] *Department of Chemical Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan*
[c] *Electrochemical Technology Program, Chemical Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*
[d] *Department of Chemical and Environmental Engineering, Illinois Institute of Technology, 10 West 33rd Street, Chicago, IL, USA*

## Abstract

Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ particles are modified with AlF$_3$ as a new coating material. Even though the initial discharge capacity of the coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ is almost the same as that of the pristine material, the capacity retention and the thermal stability, in a highly oxidized state are both significantly improved. This effect is attributed to the thin AlF$_3$ coating layer protecting the oxidized cathode particles from attack by hydrogen fluoride in the electrolyte.
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## 1. Introduction

Present-day Li-ion batteries commonly use LiCoO$_2$-based cathode materials. Due to the high cost of LiCoO$_2$ and environmental issues concerning Co, there have been extensive efforts to replace this material with a less expensive alternative such as LiNiO$_2$. The latter has several disadvantages, however, such as low-thermal instability and surface transformation resulting from reaction with the electrolyte during cycling [1–3]. Many research groups have substituted Ni by other metals in order to overcome the above problems [4–6]. One of the most promising materials is Li[Ni$_{1-x}$M$_x$]O$_2$ (M = Co and Al) [7–9]. The substitution of Ni by Co and Al improves the structural stability of the oxide, but the thermal instability of Li$_{1-\delta}$[Ni$_{1-x-y}$Co$_x$Al$_y$]O$_2$ remains an issue. It has been observed that commercial Li-ion cells using a Li$_{1-\delta}$[Ni$_{1-x-y}$Co$_x$Al$_y$]O$_2$ cathode suffer from violent thermal runaway at around 210 °C.

One approach to improve the electrochemical and thermal properties of the cathode materials is to coat their surfaces with metal oxides (e.g., Al$_2$O$_3$, ZrO$_2$, ZnO, MgO) [10–12]. Although coating technology has been found to be very effective in enhancing the electrochemical performance of cathode materials, the reason for this improvement is still not fully understood. Extensive studies have been carried out to develop new coating species and coating methods [13,14]. Recently, our group reported that an aluminum fluoride (AlF$_3$) coating on LiCoO$_2$ and Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ oxide improves both cycling performance and rate capability at a high cut-off voltage, i.e., above 4.5 V [15,16]. This study reports the effect of AlF$_3$ coating on the electrochemical and thermal properties of Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$.

## 2. Experimental

To coat the surface of Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ with AlF$_3$, ammonium fluoride (Aldrich) and aluminum nitrate nonahydrate (Aldrich) were separately dissolved in distilled water. The Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ powder was immersed in the aluminum

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* Corresponding author. Tel.: +82 2 2220 0524; fax: +82 2 2282 7329.
*E-mail address:* yksun@hanyang.ac.kr (Y.-K. Sun).

nitrate solution followed by slow addition of the ammonium fluoride solution into the mixture. The molar ratio of F to Al was maintained at 1:7 and the amount of $AlF_3$ in the solution corresponded to 0.25 mol% of the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ powder. The solution containing the active material was stirred constantly at 80 °C for 24 h; this was accompanied by a slow evaporation of solvent. The resulting $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ powders were heated at 400 °C for 5 h in flowing nitrogen to avoid the formation of $Al_2O_3$.

The surface of the $AlF_3$-coated powder was examined by means of transmission electron microscopy (TEM, JEOL 2010). Charge–discharge tests were performed with 2032 coin type cells. The cell consisted of a pristine or $AlF_3$-coated cathode and a lithium metal anode separated by a porous polypropylene film. For fabrication of the cathode, the prepared powders were mixed with carbon black and polyvinylidene fluoride (85:7.5:7.5) in N-methylpyrrolidinon. The slurry thus obtained was coated on Al foil and roll-pressed at 120 °C in air. The electrolyte solution was 1 M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate (1:1 in volume, Cheil Industries Inc., Korea).

For differential scanning calorimetry (DSC) studies, fully charged cells were transferred to an argon-filled glove box and then opened to recover the electrodes. The excess electrolyte was removed from the surface of the electrode and the electrode materials were recovered from the current-collector. A stainless-steel sealed pan with a gold-plated copper seal was used to collect 5–7 mg of the charged cathode. The weight of each sample (pan + sample) was measured before and after each DSC experiment to verify that the system was hermetically sealed. The weight was constant in all cases, which indicated that there were no leaks during the experiments. The DSC runs were performed at a scan rate of 10 °C $min^{-1}$. The enthalpy of the reaction was determined by integrating a peak of interest in the plot of power versus time.

## 3. Results and discussion

Transmission electron images of the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ powders are shown in Fig. 1. The pristine material has a very smooth surface. On the other hand, a nanoscale-$AlF_3$ homogeneous layer with a thickness of 10 nm is clearly seen on the surface of $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ particles as shown in Fig. 1b. Though not presented here, the powder X-ray diffraction patterns show no changes in the structure for the pristine ($a = 2.862(3)$ Å, $c = 14.171(7)$ Å) and coated materials ($a = 2.862(2)$ Å, $c = 14.171(7)$ Å), which implies that the $AlF_3$ is amorphous and is not incorporated into the $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ host structure. The grainy uniform contrast of the $AlF_3$ coating layer further indicates that the $AlF_3$ coating layer is amorphous or has low crystallinity [15].

The voltage versus capacity profiles of Li/pristine and $AlF_3$-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ during 50 cycles are given in Fig. 2. The cells were first activated by applying a current density of 0.2 C-rate (36 mA $g^{-1}$) for two cycles and then cycled at 0.5 C-rate (90 mA $g^{-1}$) between 3.0 and 4.3 V versus Li/$Li^+$. For discharge curves at the 0.2 and 0.5 C-rates, it can be clearly observed that a slight capacity variation occurs for the $AlF_3$-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$. By contrast, there is an abrupt capacity loss with the pristine sample. The initial discharge capacity of the pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ is 183 mAh $g^{-1}$, whereas the $AlF_3$-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ delivers a capacity as high as 188 mAh $g^{-1}$. The cycling behaviour of the $AlF_3$-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ is quite stable showing good capacity retention (96% of its initial capacity after 50 cycles). On the other hand, the pristine electrode showed a gradual decrease in capacity, resulting in relatively poor capacity retention (86.5% of its initial capacity). The pristine $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ electrode also showed a significant voltage drop during cycling compared with the first discharge curve shown in Fig. 2a. Recently, we reported that the $AlF_3$ coating on $LiCoO_2$ and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ was also effective in enhancing the electrochemical properties (such as capacity retention and rate capability) at a high cut-off voltage of 4.5 V versus Li metal [14,15]. The much improved cycling behaviour of the $AlF_3$-coated materials is attributed to the lower and stable interfacial resistance between the cathode and the electrolyte. It is suggested that the reason for the stable interface between the cathode and the electrolyte is that the $AlF_3$ coating layer acts as a stabilizer and hence protects the oxide structure from damage during
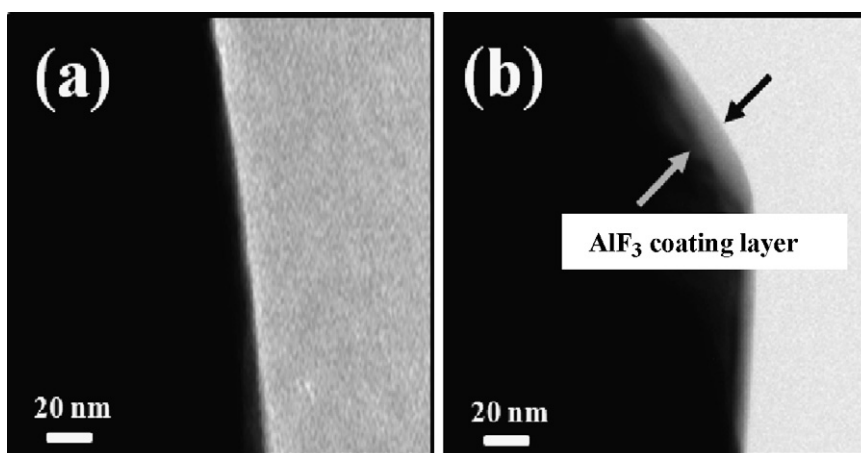


Fig. 1. Transmission electron micrographs of (a) pristine and (b) $AlF_3$-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ powders.
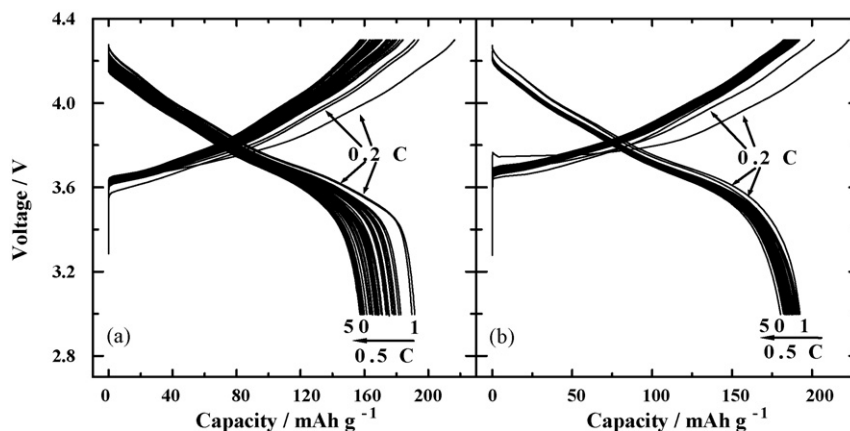
Fig. 2. Charge–discharge curves of (a) pristine and (b) AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ as a function of cycle number.

repetitive Li$^+$ de-lithiated intercalation into the host structure.

The rate capability of the cathode materials is an important variable in judging their use in commercial lithium secondary batteries. Fig. 3 shows the discharge curves for the Li/pristine and AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ cells as a function of various C-rates (36–900 mA g$^{-1}$) between 3.0 and 4.3 V. The cells were charged galvanostatically with a current density of 36 mA g$^{-1}$ (0.2 C-rate) before each discharge test and then discharged at current densities from 36 mA g$^{-1}$ (0.2 C-rate) to 900 mA g$^{-1}$ (5 C-rates). It is clearly observed that the AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ cell has improved capacity retention over the tested C-rate range. Also, the capacity retention of the AlF$_3$-coated oxide cathodes is improved significantly. For example, AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ shows a capacity retention of 96.5 and 75.8% at the 1 and 5 C-rates, respectively, compared with corresponding values of 96 and 59% for pristine Li[Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$]O$_2$. From these results, it is reasonable to conclude that a uniform AlF$_3$ coating layer on Li[Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$]O$_2$ plays a significant role in facilitating Li$^+$ transport from the electrolyte to the cathode as a result of the reduced interfacial resistance [14]. Also, a thin AlF$_3$ coating layer prevents the cathode particles from coming into direct contact with HF in the electrolyte and thus suppresses the decomposition of the cathode active material [16].
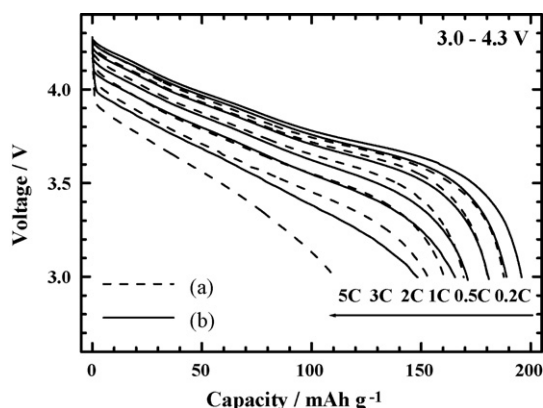


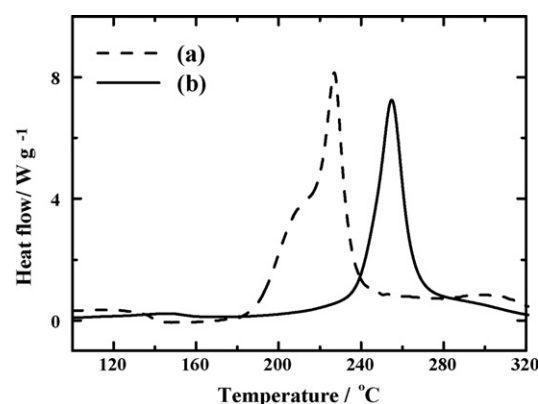Fig. 3. Discharge curves for (a) Li/pristine and (b) AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ cells as a function of C-rate.



Fig. 4. Differential scanning calorimetry curves of (a) Li/pristine and (b) AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ cells charged to 4.3 V.

The thermal stability of cathode materials, especially in a highly de-lithiated state, is an important concern for their practical application. Fig. 4 presents the DSC data of Li/pristine and AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ cells charged to 4.3 V. Cells using the pristine oxide show a large exothermic peak at 227 °C with an onset of decomposition near 180 °C; the reaction heat generation is 2152 J g$^{-1}$. The thermal stability of the AlF$_3$-coated Li$_{1-\delta}$[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$, on the other hand, is greatly improved; the onset of decomposition is shifted to 235 °C. The exothermic reaction heat generation is 1656 J g$^{-1}$, which is significantly smaller than for the pristine oxide cathode. As discussed before, the improved thermal stability of the AlF$_3$-coated Li$_{1-\delta}$[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ can be attributed to a thin AlF$_3$ coating layer, which plays a protective role in preventing the cathode particles from being attacked by HF in the electrolyte solution and hence suppresses the release of oxygen from the host lattice [15,16].

## 4. Conclusions

Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ particles have been coated with AlF$_3$ as a new coating material to improve their electrochemical performance. The AlF$_3$-coated Li[Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$]O$_2$ has capacity retention of 96% during 50 cycles, while the pristine oxide exhibits a capacity retention of only 86.5%. Also, rate

capability and thermal stability at a highly oxidized state of the $AlF_3$-coated $Li[Ni_{0.8}Co_{0.15}Al_{0.05}]O_2$ are remarkably enhanced. The improved electrochemical performance is attributed to the thin $AlF_3$ coating layer de-lithiated preventing the highly de-lithiated cathode from being in direct contact with the liquid electrolyte and thus suppressing decomposition of cathode active material by HF in the electrolyte.

## Acknowledgement

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