

## The Effects of LaF<sub>3</sub> Coating on the Electrochemical Property of Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> Cathode Material

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The effect of LaF<sub>3</sub> coating on the structural and electrochemical properties of Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> cathodes was investigated using XRD, SEM, TEM, and a cyclor. The coating layer consisted of nano-sized particles attached nonuniformly to the surface of pristine powder. Despite the surface coating treatment, phase difference by LaF<sub>3</sub> coating was not detected. The discharge capacities of coated electrodes were a little lower than that of pristine sample at a 1 C rate. However, as the C rate increases, the capacity retention of the coated sample becomes obviously superior to that of the pristine sample. The cyclic performances of the electrodes in the voltage range of 4.8 ~ 3.0 V were also improved by the surface coating. Such enhancement is attributed to the presence of the LaF<sub>3</sub> coating layer, which effectively suppressed the reaction between electrodes and electrolytes on the surface of the Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrode.

**Key Words:** Surface coating, Electrochemical property, Cathode, Lithium battery

### Introduction

Lithium ion batteries are representative system for electrochemical energy storage. At present, lithium ion batteries serve as an essential electric source for cellular phones, PDAs, and lap-top computers. Moreover, they have also been considered as a possible power source for new applications such as electric vehicles (EVs), hybrid electric vehicles (HEVs), and electric power tools.<sup>1-3</sup> Cathode material is a key factor determining capacity, cyclic performance and thermal stability. Since the commercialization of lithium ion batteries, LiCoO<sub>2</sub> has been used as a cathode material due to its stable property. However, to satisfy various needs of new application fields of lithium ion batteries, the introduction of new cathode materials having high capacity, long cycle life and low cost is inevitable. Li(Ni, Co, Mn)O<sub>2</sub> is one of the most promising new cathode materials since its electrochemical properties are comparable or superior to other alternative cathode materials.<sup>4,5</sup> However, this material has some problems such as inferior rate capability due to low electronic conductivity, and the significant capacity fading during cycling was investigated when the upper cutoff voltage was increased to more than 4.6 V.<sup>4,5</sup> One approach to improve the electrochemical properties is to substitute transition metal ions for other elements such as Mo,<sup>6</sup> Cr,<sup>7</sup> and Zr.<sup>8</sup> These elements may stabilize the layered structure, and prevent unwanted reactions between cathodes and electrolytes. Another way is to substitute fluorine for oxygen to stabilize the host structure.<sup>9-11</sup> This method was also very effective for improving the cycling performance and thermal stability of cathode materials. However, such approaches could cause a lowering of capacity and Li ion diffusion because the substituents are usually electrochemically inactive elements. In contrast, modifying the surface by coating it with stable oxides or phosphates is beneficial with respect to the delivery of the original capacity because there is no reduction of the amount of active elements in the parent structure.<sup>12-17</sup> One point we should

consider is that the coating effect is highly dependent on the coating material. Cho *et al.* and Myung *et al.* reported that the electrochemical properties of coated cathode material is highly attributable to the coating materials themselves.<sup>16-17</sup> So the selection of good coating material is an important factor of coating treatments of cathode materials. Herein, lanthanum fluoride (LaF<sub>3</sub>) was introduced as a coating material for Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> cathodes. A doping of La reportedly improved the discharge capacity and cyclic performance of the cathode,<sup>18</sup> and lanthanum oxide coated cathode material has an excellent thermal stability and enhanced electrochemical properties.<sup>19,20</sup> Moreover other fluoride such as AlF<sub>3</sub> was successfully introduced as a coating material in various cathode materials.<sup>21,22</sup> In this work, we fabricated surface modified Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> cathodes with lanthanum fluoride (LaF<sub>3</sub>). The morphology of coated powder and the electrochemical properties of coated electrodes were the focus of this study.

### Experimental

The pristine Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> powder was a commercial product of Daejung Chemicals & Metals. To prepare the coating solution, La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.99, Aldrich) and NH<sub>4</sub>F (98+%, Aldrich) were dissolved in distilled water, followed by continuous stirring for 2 h at 21 °C. Subsequently, Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> powder was added to the coating solution and mixed thoroughly for 2 h at 80 °C. The slurry was dried in an oven at 100 °C for 12 h and heat-treated in a furnace at 400 °C for 5 h. The estimated concentration of LaF<sub>3</sub> in the Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> powders was varied from 0.25 to 1.0 wt%. X-ray diffraction (XRD) patterns of powders were obtained using a Rigaku X-ray diffractometer in the 2θ range of 10° to 70° with monochromatized Cu-K<sub>α</sub> radiation (λ = 1.5406 Å). The microstructure of the powder was observed using a field-emission scanning electron microscopy (FESEM, JEOL-JSM 6500F). A transmission electron microscopy (TEM,

JEOL-JEM 2100F) study was also carried out with an electron microscope, operating at 200 KV.

For electrochemical testing, the cathode slurry was prepared by mixing the oxide powder, carbon black (Super P), and poly(vinylidene)fluoride (PVDF) at a weight ratio of 80:12:8. After 24 hr of ball mill processing, the viscous slurry was coated onto aluminum foil using a Dr. blade, and then dried at 90 °C in an oven. The coin-type cell (2032 size) consists of a cathode, a Li metal anode, a separator, and an electrolyte. The electrolyte was 1 M LiPF<sub>6</sub> with ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 vol%). Cells were subjected to galvanostatic cycling using a WonAtech system in the voltage range of 4.6 ~ 3.0 V at various rates between 1 ~ 12 C, and in the voltage range of 4.8 ~ 3.0 V at 1 C rates.

### Results and Discussion

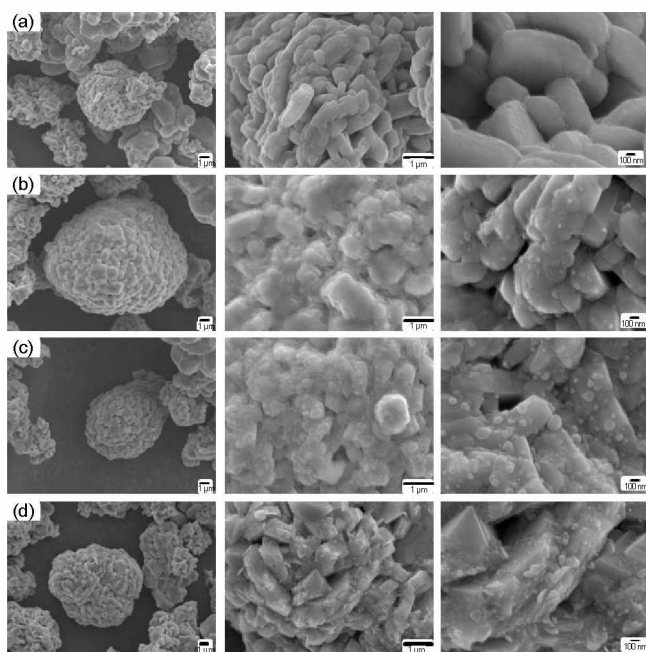
Figure 1 presents scanning electron microscopy (SEM) images of the Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> powders. In all the cases, the Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> powders display sphere shapes of approximately 8 ~ 12 μm. The particles are composed of smooth-edged 0.5 ~ 1.0 μm sized polyhedral primary particles. At low magnification, no significant difference was observed between the coated and uncoated samples. However, at higher magnification, it is revealed that the roughness of the surface increases slightly because of the reaction of the primary particles with nanoparticles. As the amount of LaF<sub>3</sub> coating increased, nano-particles developed on the surface of the coated sample.

The shape of the primary particles and the surface morphology was investigated in detail transmission by electron microscopy (TEM) analysis. Figure 2 shows the TEM images of the pristine and 0.5 wt% coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> pow-

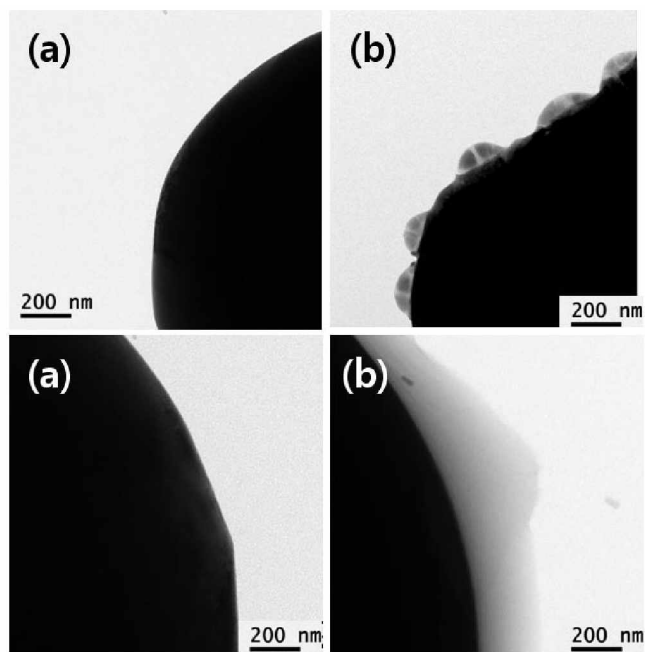
ders. The pristine sample particles exhibit a smooth surface, whereas, the surfaces of the 0.5 wt% coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> particle are covered with a coating layer. Most of the coating layer comprised nano-structured particles of diameter 100 ~ 200 nm, but some parts of it comprised homogeneous film. EDX analysis (the data are omitted) indicates the existence of La and F on the surface of the coated samples. The SEM, TEM and EDX results confirm that the coating layer was successfully formed on the surface of the coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> powders.

Figure 3 shows the X-ray diffraction (XRD) patterns of pristine and LaF<sub>3</sub> coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> powders. The diffraction patterns of all the samples are indexed well with that of a typical layered structure with an  $R\bar{3}m$  space group. The phases of the coated samples were identical to that of a pristine sample. The unique change in the phase caused by the LaF<sub>3</sub> coating was not revealed in the diffraction pattern. This indicates that the surface coating layer was formed as an amorphous phase. The coating sources were heat-treated at 400 °C, which is not high enough for the formation of a crystalline coating phase. It has also been reported that most of the coating layers were amorphous.<sup>12-17</sup> In fact, glassy coating layers are expected to facilitate Li ions transport across the surface because of their open structure. However, the coating layer with a crystalline phase also enhanced the electrochemical properties and the thermal stability of cathode materials, as shown in our previous study.<sup>20</sup>

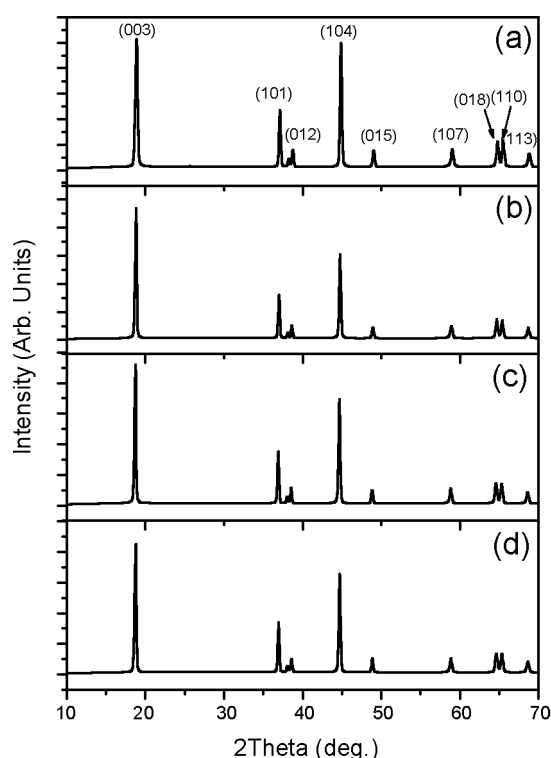
The electrochemical properties of the pristine and coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrodes were determined to investigate the coating effect on the capacity, cyclic performance, and rate capability of the electrodes. Figure 4 shows the discharge capacities of the pristine and coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrodes at 1 C, 2 C, 4 C, 6 C, 8 C, 10 C and 12 C



**Figure 1.** SEM images of (a) Pristine; (b) 0.25 wt%, (c) 0.5 wt%, (d) 1.0 wt% LaF<sub>3</sub> coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> cathode.

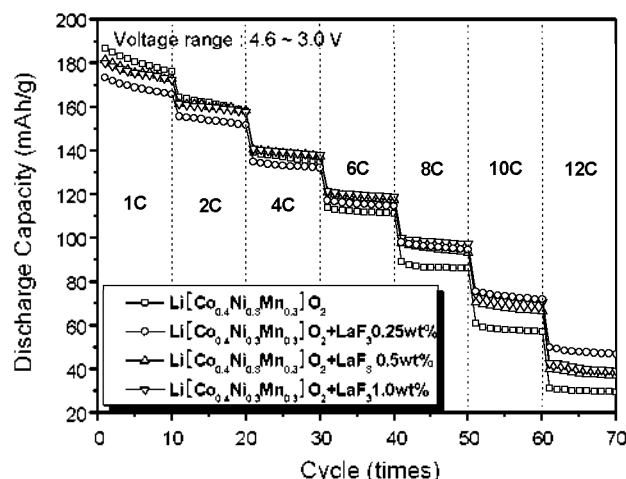


**Figure 2.** TEM images of (a) Pristine; (b) 0.5 wt% LaF<sub>3</sub> coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> cathode.



**Figure 3.** XRD patterns of (a) Pristine; (b) 0.25 wt%, (c) 0.5 wt%, (d) 1.0 wt% LaF<sub>3</sub> coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> cathode.

rates in the voltage range 4.6 ~ 3.0 V. The discharge capacity of the pristine sample was slightly higher than that of the coated sample over several initial cycles at a 1 C rate. However, as the C rate increased, the discharge capacity of the pristine sample rapidly decreased. In contrast, while the discharge capacity of the coated samples was inferior at 1 C rate, the decrease in the discharge capacity at high C rates was relatively lesser. This means that the rate capability of the coated samples is superior to that of the pristine sample. Table 1 summarizes the discharge capacity and capacity retention at various C rates (the values of the first cycle). From the table, it is apparent that the ratio of the discharge capacity at a high C rate to that at a 1C rate was enhanced by coating treatment. For a pristine electrode, the capacity retention at a 12 C rate was only 16.7% that at a 1 C rate. In contrast, the capacity retentions were 28.8%, 22.0%, and 23.8% for samples coated with 0.25 wt%,

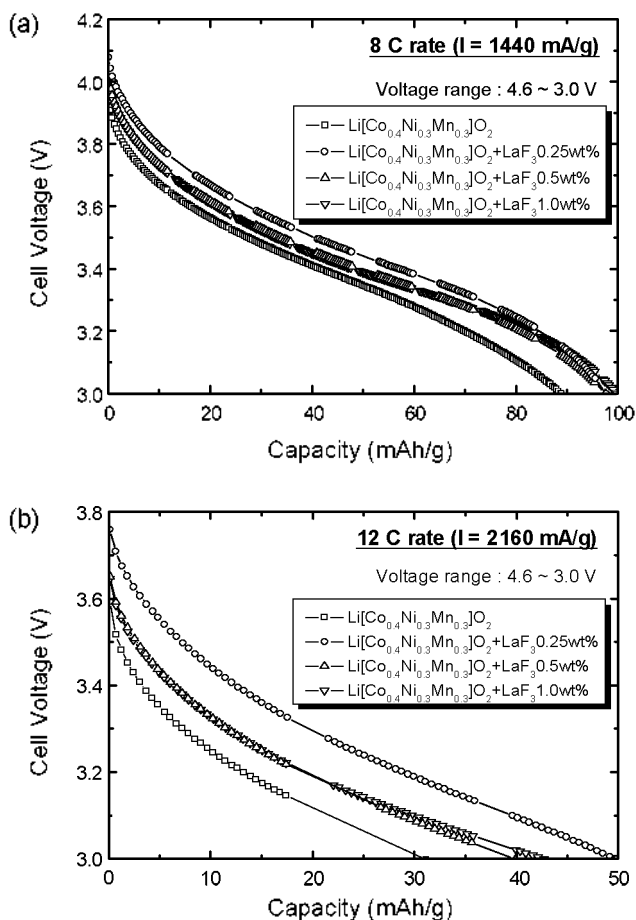


**Figure 4.** Discharge capacities and cyclic performances of pristine and coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrode in the voltage range of 4.6 ~ 3.0 V at 1, 2, 4, 6, 8 and 12 C rates.

0.5 wt%, 1.0 wt%, respectively. Figure 5 shows the initial discharge profiles of the pristine and coated electrodes at 8 C and 12 C rates. The discharge capacities of the pristine electrode were just 89 mAh/g (8 C rate) and 31 mAh/g (12 C rate), respectively. However, the capacity was enhanced by surface coating. A sample coated with 0.25 wt% LaF<sub>3</sub> delivered a higher discharge capacity of 97 mAh/g (8 C rate) and 50 mAh/g (12 C rate). The effect of surface coating on the rate capability was more clearly observed as the C rate increased. Electrodes coated 0.5 and 1 wt% LaF<sub>3</sub> also showed improved discharge capacities, although the improvements were slightly smaller than the improvement in the case of the sample coated with 0.25 wt%. These results prove that the LaF<sub>3</sub> coating can effectively enhance the rate capability of a Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrode. The coating material can protect the core material from direct contact with the acidic electrolyte when the cells are charged to their highest potentials.<sup>23,24</sup> Myung *et al.* proposed a possible explanation for the improvement of battery performance by metal oxide coating.<sup>12,16</sup> They reported that the metal oxide coating layer transformed to a metal fluoride layer during cycling. This is highly effective for offering protection against HF attacks during cycling. Since the metal fluoride layer formed by reactions with HF in the electrolyte can serve as a protecting layer, direct coating with metal

**Table 1.** Discharge capacities and capacity retentions of Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> samples at various C rates (values of the first cycle). (%) means capacity retention compared to the discharge capacity at 1 C rate.

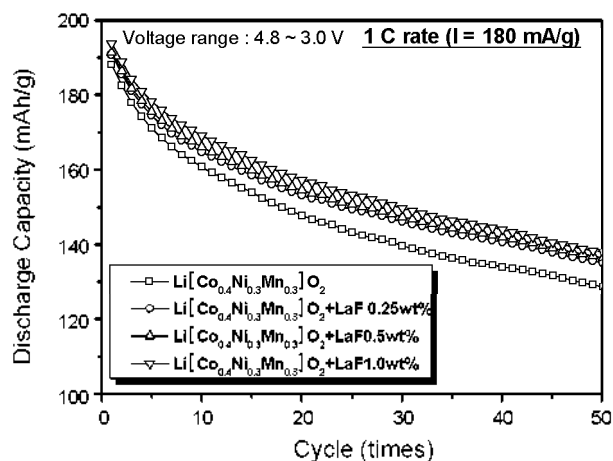
	Pristine (mAh/g)	(%)	LaF <sub>3</sub> 0.25 wt% (mAh/g)	(%)	LaF <sub>3</sub> 0.5 wt% (mAh/g)	(%)	LaF <sub>3</sub> 1.0 wt% (mAh/g)	(%)
1 C	186.46	100.0	172.97	100.0	181.03	100.0	179.74	100.0
2 C	164.02	88.0	155.32	89.8	160.92	88.9	161.06	89.6
4 C	138.64	74.4	134.65	77.8	140.14	77.4	140.57	78.2
6 C	113.75	61.0	116.86	67.6	120.53	66.6	121.13	67.4
8 C	88.95	47.7	97.73	56.5	97.50	53.9	99.83	55.5
10 C	60.78	32.6	75.31	43.5	70.35	38.9	74.31	41.3
12 C	31.15	16.7	49.81	28.8	39.89	22.0	42.71	23.8



**Figure 5.** Initial discharge profiles of pristine and LaF<sub>3</sub> coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrodes in the voltage range of 4.6 ~ 3.0 V at (a) 8 C rate and (b) 12 C rate.

fluorides such as LaF<sub>3</sub> can have a superior effect on the surface protection achieved by the presence of HF in the electrolytes. Therefore, undesired reactions between electrodes and electrolytes are likely to be suppressed by LaF<sub>3</sub> coating treatment.

All of the pristine and coated electrodes presented good cyclic behavior in the voltage range 4.6 ~ 3.0 V. However, the significant capacity degradation during cycling was investigated by increasing the upper cutoff voltage over 4.6 V. Figure 6 shows the cycling behavior of the pristine and coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrodes in the voltage range 4.8 ~ 3.0 V. In order to clearly illustrate the effect of the LaF<sub>3</sub> coating on the cycling behavior, the upper cut-off voltage was increased to 4.8 V. As mentioned earlier, the discharge capacity of the pristine sample was rapidly decreased during cycling. But the cyclic performance of the coated electrode was slightly enhanced. The electrode charged to high voltages is vulnerable because the reactions between the surfaces of the electrode and the electrolyte are activated. That is why the capacity fades rapidly when the cut-off voltage increases above 4.6 V. However, if a stable surface layer is formed by LaF<sub>3</sub> coating treatment, surface reactions can be retarded, and thus, the cyclic performance can be improved. However, the capacity fading of the coated samples was still rapid, therefore, in future studies, coated samples must be used at cut-off voltages



**Figure 6.** Cyclic performance of pristine and LaF<sub>3</sub> coated Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> electrode in the voltage range of 4.8 ~ 3.0 V at a rate of 1 C (specific current = 180 mA/g<sup>-1</sup>).

higher than 4.6 V.

## Conclusions

The surface of a commercial Li[Ni<sub>0.3</sub>Co<sub>0.4</sub>Mn<sub>0.3</sub>]O<sub>2</sub> cathode was modified with LaF<sub>3</sub> coating. The XRD patterns of the coated materials did not show any extraneous peaks corresponding to the coated particles. However, the rough surface of a coated sample comprising nano-particles with diameters 100 ~ 200 nm, and an EDX analysis results indicating the existence of La and F on the surface suggested that the coating layer was successfully formed. Galvanostatic charge-discharge studies at various C rates showed that a LaF<sub>3</sub> coating enhanced the rate capability and cyclic performances of the electrodes. Such enhancement is due to the presence of a stable LaF<sub>3</sub> coating layer, which effectively suppressed the reactions between electrodes and electrolytes on the surface electrode.

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