

# Improvement of the Electrochemical Properties of Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> by AlF<sub>3</sub> Coating

Yang-Kook Sun,<sup>a,\*,z</sup> Seung-Taek Myung,<sup>b</sup> Byung-Chon Park,<sup>a</sup> and Hitoshi Yashiro<sup>b,\*</sup>

<sup>a</sup>Department of Chemical Engineering, Hanyang University, Seoul 133-791, South Korea <sup>b</sup>Department of Chemical Engineering, Iwate University, Morioka, Iwate 020-8551, Japan

An ~10 nm AlF<sub>3</sub> layer was coated on the surface of a Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> positive electrode material for lithium-ion batteries, and the effects of this coating on battery performances and thermal stability of the cathode materials were studied. Although no significant bulk structural differences were observed between the coated and pristine material, a slightly higher capacity was seen for the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrode, and the rate capability was also greatly enhanced by the AlF<sub>3</sub> coating. These improvements are mainly attributed to the suppression of the transition metal dissolution benefited from the AlF<sub>3</sub> coating. This suppression contributed to the reduction in the charge-transfer resistance. Time-of-flight secondary ion mass spectroscopic analysis showed that insulating LiF, as a product of decomposed LiPF<sub>6</sub>, was deposited on the surface of pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. The deposition of LiF was greatly suppressed by AlF<sub>3</sub> coating on the outer surface of Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. The protection of the artive material by the AlF<sub>3</sub> coating substantially improved the capacity, capacity retention, and rate capability of the batteries. It also enhanced the thermal stabilities of the positive electrode material.

Manuscript submitted April 11, 2008; revised manuscript received June 13, 2008. Published July 29, 2008.

Since 1990, lithium-ion batteries with high energy and power output have become an important power source for portable devices, such as cellular phones and laptop computers. As the field of lithium battery systems has expanded, extensive research efforts have been initiated to develop new positive electrode materials with higher energy and higher power outputs. The fabrication of electrodes using commercialized LiCoO<sub>2</sub> positive electrodes for Li-ion batteries has been improved to satisfy the power requirements of new devices. However, physical and mechanical improvements of this type of electrode are limited, and ultimately new power sources will be required. Furthermore, the structural instability<sup>1</sup> and poor thermal properties<sup>2</sup> of  $Li_{1-\delta}COO_2$  in a highly delithiated state must be improved if this material is to be adopted in more electronic or vehicle applications. Therefore, the development of new positive electrode materials is required to address these issues.

Derivatives of Li[Ni<sub>x</sub>Co<sub>1-2x</sub>Mn<sub>x</sub>]O<sub>2</sub> (x = 0-0.333) represent some of the more recently developed positive electrode materials. These derivatives have stable electrochemical performance during the reversible lithium extraction/insertion process.<sup>3-5</sup> The structural stability of  $Li[Ni_{0.5}Mn_{0.5}]O_2$  is due to the presence of tetravalent Mn ions in the structure. The Mn<sup>4+</sup> ions remain electrochemically inactive during cycling in the voltage range of 2.7-4.6 V.6 However, Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> shows a relatively poor rate capability at higher currents due to its lower electronic conductivity compared to LiCoO<sub>2</sub> and Li[Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>]O<sub>2</sub>.<sup>7</sup> Therefore, intensive research efforts have been focused on improving the rate capability of  $Li[Ni_{0.5}Mn_{0.5}]O_2$  with a partial cobalt substitution in the metal ion layer of the host structure.<sup>8</sup> Li[Ni<sub>x</sub>Co<sub>1-2x</sub>Mn<sub>x</sub>]O<sub>2</sub> (x = 0-0.333) showed a stable cycling performance and improved rate capability in the conventional voltage window (3.0-4.3 V). However, when Co-substituted Li[Ni<sub>x</sub>Co<sub>1-2x</sub>Mn<sub>x</sub>]O<sub>2</sub> (x = 0-0.333) was cycled in the higher voltage range to increase energy density, the structural instability in the highly delithiated state brought about a drastic capacity fade during cycling.

Recently, we reported that the coating of AlF<sub>3</sub> on LiCoO<sub>2</sub> and Li[Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>]O<sub>2</sub> effectively improved their electrochemical properties.<sup>10,11</sup> We previously showed that an Al<sub>2</sub>O<sub>3</sub> coating layer on Li[Li<sub>0.05</sub>Ni<sub>0.4</sub>Co<sub>0.15</sub>Mn<sub>0.4</sub>]O<sub>2</sub> particles gradually transformed to AlF<sub>3</sub> through an intermediate complex of an Al–O–F compound, as confirmed by time-of-flight secondary-ion mass spectroscopy

# Experimental

Spherical Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> was synthesized via coprecipitation. Details of the synthetic process are reported in our previous paper.<sup>14</sup> To prepare the AlF<sub>3</sub>-modified Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>, ammonium fluoride (Aldrich) and aluminum nitrate nonahydrate (Aldrich) were first separately dissolved in distilled water. Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> powders were immersed in the aluminum nitrate nonahydrate solution, and the ammonium fluoride solution was then slowly added to the solution. Ammonia solution was used to adjust the pH during precipitation of the powder. The solution containing the active material was constantly stirred at 80°C for 5 h. After filtering, the active materials were washed with deionized water and dried at 120°C. The Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> powders obtained were heated at 400°C for 5 h under a nitrogen atmosphere to avoid the formation of Al<sub>2</sub>O<sub>3</sub>.

Powder X-ray diffraction (XRD, Rigaku Rint-2000) employing Cu K $\alpha$  radiation was used to characterize the powders. Transmission electron microscopy (TEM, 200 kV, Hitachi, H-800) was used to observe the coating layer.

Charge–discharge tests were performed with 2032 coin-type cells. The cell consisted of a positive electrode and a lithium metal negative electrode separated by a porous polypropylene film. For fabrication of the positive electrode, a mixture of 20 mg of positive electrode materials and 5 mg of conducting binder (3.3 mg of Te-flonized acetylene black and 1.7 mg of graphite) was pressed on a 2.0 cm<sup>2</sup> stainless screen at 500 kg cm<sup>-2</sup>. The electrolyte used was a mixture of 1 molar dm<sup>-3</sup> LiPF<sub>6</sub> in ethylene carbonate and diethyl carbonate (1:1 in volume). AC-impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range from 1 MHz to 1 mHz with an amplitude of 10 mV<sub>rms</sub> (root mean square).

To measure the extent of Ni and Mn dissolution, cells charged to 4.5 V were carefully disassembled and then active materials were stored in electrolyte at 90°C for 7 days. The amounts of dissolved Ni and Mn were measured by atomic absorption spectroscopy (AAS, Analytik Jena AG, Vario 6).

To confirm the presence of by-products on the surface of the active materials after extensive cycling, the cycled active materials were examined using a TOF-SIMS (ULVAC-PHI TFS2000, Perkin Elmer) surface analyzer operated at  $10^{-9}$  Torr equipped with a liq-

<sup>(</sup>TOF-SIMS).<sup>12,13</sup> This indicates that, although an oxide electrode material is coated with other amphoteric oxides, they finally transform to stable metal fluorides. For this reason, we intentionally applied an AlF<sub>3</sub> nanolayer coating on Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> and observed the resulting electrochemical behavior.

<sup>\*</sup> Electrochemical Society Active Member.

<sup>&</sup>lt;sup>z</sup> E-mail: yksun@hanyang.ac.kr



Figure 1. XRD patterns of (a) pristine and (b) AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>.

uid Ga ion source and pulse electron flooding. During the analysis, the targets were bombarded with 15 keV Ga beams, with the pulsed primary ion current varying from 0.3 to 0.5 pA. The total collection time was 300 s over a 12  $\times$  12  $\,\mu m$  area.

For differential scanning calorimetry (DSC) experiments, cells were charged to 4.3 V vs Li and opened in an Ar-filled dry box. A stainless steel sealed pan with a gold-plated copper seal (which can withstand 150 atm of pressure before rupturing and has a capacity of 30  $\mu$ L) was used to collect 3–5 mg samples. Measurements were carried out in a Pyris 1 differential scanning calorimeter (Perkin Elmer) using a temperature scan rate of 1 °C min<sup>-1</sup>. The weight was constant in all cases, indicating that there were no leaks during the experiments.

# **Results and Discussion**

Figure 1 shows powder XRD patterns of the as-synthesized  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$  and  $\text{AlF}_3$ -coated  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ . Both materials have well-ordered R3m layer structures. The trace of the superstructure at 21° in 20 is also seen for both materials, implying that there was  $\text{Ni}^{2+}$  (0.69 Å)<sup>15</sup> and  $\text{Mn}^{4+}$  (0.535 Å)<sup>15</sup> ordering in the transition metal layer. After heat-treatment at 400°C in a N<sub>2</sub> atmosphere, there was no appearance of aluminum fluoride-induced product (Fig. 1b). The calculated lattice parameters for the pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> were similar to each other, indicating that no significant structural change occurred as a result of surface modification by AlF<sub>3</sub>.

To estimate the thickness of the coating layer, bare and coated materials were examined using TEM. As can be seen in Fig. 2a, the bare material exhibits a smooth edge line. For the coated sample, a thin coating layer is observed on the surface of  $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ , as seen in Fig. 2b. Based on TEM images, the thickness of the coating layer was around 10 nm. Due to the lower crystallinity and smaller amount of the AlF<sub>3</sub>, this compound was hardly observed in the XRD pattern in Fig. 1b. Approximately 2 mol % AlF<sub>3</sub> was coated on the surface of Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>.

To investigate the effectiveness of the surface modification, charge–discharge experiments were performed by applying currents of 34 mA g<sup>-1</sup> (0.2 C rate) and 85 mA g<sup>-1</sup> (0.5 C rate) across the positive electrode at 30°C. The corresponding results are shown in Fig. 3. The voltage for the coated sample was slightly lower on charging compared with that for the pristine sample. Meanwhile, the corresponding voltage on discharge was slightly higher for the coated sample. The same tendency was also observed at higher currents, as seen in Fig. 3. These results indicate that the AlF<sub>3</sub> coating on the surface of Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> reduces cell impedance during Li<sup>+</sup> extraction and insertion. For this reason, the surface-modified electrode delivers a slightly higher discharge capacity (Fig. 3). Similar behavior was also observed in the Al<sub>2</sub>O<sub>3</sub>-coated oxide electrode, which we previously reported.<sup>12</sup>



Figure 2. TEM bright-field images of (a) pristine and (b) AlF\_3-coated Li[Ni\_{0.5}Mn\_{0.5}]O\_2.

Further cycles were performed for both samples at a current density of 85 mA  $g^{-1}$  (0.5 C rate) at 30°C. Figure 4 presents the corresponding continuous discharge capacities of the pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. The pristine material retained about 75% of its initial discharge capacity throughout the 100 cycles. The capacity after 100 cycles was 120 mAh g<sup>-1</sup>. In contrast, the capacity retention of the coated active materials at the 100th cycle was about 86% (143 mAh g<sup>-1</sup>) of the initial capacity.



Figure 3. (Color online) Initial charge and discharge curves of pristine and  $AlF_3$ -coated  $Li[Ni_{0.5}Mn_{0.5}]O_2$ .



Figure 4. Comparison of cyclability of pristine and  $\rm AlF_3\text{-}coated$   $\rm Li[Ni_{0.5}Mn_{0.5}]O_2.$ 

Figure 5 shows the discharge capacities of the Li/Li[Ni<sub>0.5</sub> Mn<sub>0.5</sub>]O<sub>2</sub> and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> cells at various currents (34–850 mA g<sup>-1</sup>) between 3.0 and 4.5 V vs Li. The cells were charged galvanostatically with a constant current of 20 mA g<sup>-1</sup> before each discharge test, and were then discharged at different current densities ranging from 34 mA g<sup>-1</sup> (0.2 C rate) to 850 mA g<sup>-1</sup> (5 C rates). At a low current density (34 mA g<sup>-1</sup>), the two electrodes showed similar discharge capacities, although the nominal discharge voltage was slightly higher for the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>, as shown in Fig. 5a. At increased current density,



Figure 5. (Color online) Comparison of rate capability of (a) pristine and  $AlF_3$ -coated  $Li[Ni_{0.5}Mn_{0.5}]O_2$  and (b) the corresponding efficiency.



Figure 6. (Color online) Comparison of HPPC test results for pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>: (a) ASI and (b) pulse power capability.

the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrode exhibited much higher discharge capacities than the pristine electrode. For example, as shown in Fig. 5a, the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> delivered a discharge capacity of 130 mAh g<sup>-1</sup> at higher current (850 mA g<sup>-1</sup>), whereas the pristine electrode delivered around 50 mAh g<sup>-1</sup> at the same current density, which corresponds to 30% of its capacity at 34 mA g<sup>-1</sup> (0.2 C rate). From the above tests, it is clear that AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> has a higher capacity, retention, and rate capability than uncoated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>.

The Hybrid Pulse Power Characterization (HPPC) test was used during the discharge procedure.<sup>16</sup> The HPPC sequence was carried out by first applying a 10 s discharge pulse followed by 40 s rest period. After the rest period, the cell was subjected to a group of regenerative pulses for 10 s at a 10 C rate (1700 mA  $g^{-1}$ ). The cell was subsequently discharged to 10% of capacity at a 1 C rate followed by an hour rest period to allow the cell to return to a charge equilibrium condition before applying the next HPPC sequence. Figure 6 compares the area specific impedance (ASI) values for 10 C rate pulse discharges as a function of depth of discharge of the C/pristine and C/AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> cells as evaluated by the HPPC test. The ASI values of the AlF\_3-coated Li[Ni\_{0.5}Mn\_{0.5}]O\_2 electrode indicate a lower impedance during discharge and regeneration (Fig. 6a). Pulse powers higher by a factor of 2 were obtained by surface treatment of  $Li[Ni_{0.5}Mn_{0.5}]O_2$  with AlF<sub>3</sub>, as shown in Fig. 6b. Therefore, surface treatment by AlF<sub>3</sub> is effective for improving battery performance.

To understand the improved cell performance of the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>, ac impedances for the pristine Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> were measured after 20 cycles in the fully charged state (4.5 V vs Li), as shown in Fig. 7. The equivalent circuit was proposed in our previous report.<sup>10</sup> Cole–Cole plots



**Figure 7.** (Color online) Cole–Cole plots for (a) pristine and (b)  $AlF_3$ -coated  $Li[Ni_{0.5}Mn_{0.5}]O_2$  at the 20th charge.

for both electrodes present two semicircles, one in the high to medium frequency region and the other in the low-frequency region. The semicircle in the high to medium-frequency range is attributed to contact resistance of the active particle surface  $(R_{sf})$ , while the semicircle in the low-frequency range is associated with the chargetransfer resistance  $(R_{ct})$  coupled with a double-layer capacitance. The  $R_{\rm sf}$  component is larger for the AlF<sub>3</sub>-coated material, as shown in the inset of Fig. 7. It is likely that the insulating properties of AlF<sub>3</sub> could result in an increase in the impedance in the higher frequency region. In contrast, the charge-transfer resistance  $(R_{ct})$  due to the interface between the positive electrode and the electrolyte was significantly reduced by the AlF<sub>3</sub> coating (Fig. 7). We expect that the presence of an insulating AlF3 layer disturbs Li<sup>+</sup> movements, resulting in a higher  $R_{ct}$  for the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> because insulating AlF<sub>3</sub> particles can block the continuous connection of active materials. However, tendencies contrary to what we predicted were observed, as observed in rate capability tests (Fig. 5), HPPC tests (Fig. 6), and Cole-Cole plots (Fig. 7).

Ni and Mn dissolution can occur in the higher voltage region. To estimate the amount of Ni and Mn dissolution, half cells using a Li metal negative electrode were charged to 4.5 V and were carefully disassembled in a glove box. The recovered active materials were stored in the electrolyte at 90°C for 1 week and the electrolytes were then examined by AAS. Figure 8 shows the amounts of Ni and Mn that dissolved into the electrolyte from the pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrodes after high-temperature storage. As shown, the amounts of dissolved Ni and Mn from pristine



Figure 8. Amount of Ni and Mn dissolved for delithiated pristine and  $AlF_3$ -coated  $Li[Ni_{0.5}Mn_{0.5}]O_2$  stored at 90°C for 7 days.

Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> were approximately 146.4 and 84.6 ppm, respectively, after storage. In contrast, the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> showed greatly reduced Ni and Mn dissolution into the electrolyte, with amounts of only 39.6 and 18.6 ppm, respectively. Thus, it is clear that there was a significant suppression of Ni and Mn dissolution in the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrode during storage at 90°C.

Dissolution of transition metal elements has been shown to lead to capacity fade during cycling.<sup>10,11,17</sup> The electrolyte used in this experiment was a LiPF<sub>6</sub> salt-containing composite solvent. The LiPF<sub>6</sub> can decompose, and this reaction is facilitated at higher potentials, such as 4.5 V vs Li, according to the following reactions suggested by Aurbach et al.<sup>18</sup> and Edström et al.<sup>19</sup>

$$\text{LiPF}_6 \rightarrow \text{LiF} \downarrow + \text{PF}_5$$
 [1]

$$PF_5 + H_2O \rightarrow POF_3 + 2HF$$
 [2]

 $POF_3 + 3Li_2O \rightarrow 6LiF \downarrow + P_2O_5 \downarrow \text{ (or } Li_xPOF_v\text{)}$  [3]

As can be seen from these reactions, the decomposed LiPF<sub>6</sub> salt produces LiF and HF as by-products. The LiF would be deposited on positive or negative electrodes in the cell, while the HF formed would continuously attack the oxide electrode material, resulting in partial dissolution of the active material during cell operation. The dissolved transition metal ions would adhere onto the surface of the positive and negative electrodes and affect cell impedance. Once the dissolved ions are deposited on the surface of the negative electrode, the ions are reduced to metal. Then, the newly formed metal blocks Li<sup>+</sup> movement, which causes an increase in cell impedance. We therefore ascribe the relatively higher cell impedance observed to adhesion of dissolved transition metal ions onto the surface of the positive electrode (Fig. 7).

If decomposition of the active material progresses by HF attack, by-products are inevitably formed. To confirm the formation of byproducts, TOF-SIMS analysis was carried out for the surfaces of the cycled positive electrodes (100 cycles). Ga<sup>+</sup> sputtering was carried out for 3 s, resulting in etching of the top 0.8 Å of the outer surface to remove the air-contaminated layer during sampling. Figures 9a and b show Li-F fragments for the extensively cycled pristine  $Li[Ni_{0.5}Mn_{0.5}]O_2$  and  $AlF_3$ -coated  $Li[Ni_{0.5}Mn_{0.5}]O_2$ , respectively. It is clear that LiPF<sub>6</sub> salt decomposed, resulting in LiF deposition on the surface of the electrode. Direct comparison of the amount of LiF formed is difficult from the spectra. It is likely, however, that more LiF (as a by-product of LiPF<sub>6</sub> salt decomposition) is deposited on the electrode surface of the pristine Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>, because the total count for this material is about five times higher compared to that of the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> (Fig. 9a and b). This LiPF<sub>6</sub> salt decomposition reaction is related to the generation of HF. Increased LiF formation indicates increased HF formation, as shown in Reactions 1 and 2. This consequently results in increased dissolution of Ni and Mn elements of the pristine Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>, as shown in Fig. 8, which is confirmed by the TOF-SIMS spectra in Fig. 9c-f. That is, much higher total counts of Ni-O and Mn-O fragments are seen on the surface of the pristine Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. The following reaction is suggested

$$2\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 \text{ (AlF}_3\text{-coated)} + 2\text{HF} + \text{Li}^+ + \text{e}^- \rightarrow \text{Li}_{1-\delta}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 + \text{NiO} + \text{MnO} + \text{LiF} + \text{H}_2\text{O} \quad [4]$$

The NiO and MnO formed are energetically unstable because they have relatively high Gibbs free energies of formation, NiO  $(-211.7 \text{ kJ mol}^{-1})^{20}$  and MnO  $(-369.9 \text{ kJ mol}^{-1})^{.20}$  These materials consecutively react with HF, and the divalent oxides are partially transformed to NiF<sub>2</sub> or MnF<sub>2</sub>, as shown in Fig. 9g-j. Though the Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> is coated with AlF<sub>3</sub>, NiF<sub>2</sub> and MnF<sub>2</sub> are formed on the outer surface of AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> by the following reactions

$$NiO + 2HF \rightarrow NiF_2 + H_2O$$
 [5]



Figure 9. Comparison of TOF-SIMS fragments for extensively cycled pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrodes: Li–F fragments of (a) pristine and (b) AlF<sub>3</sub>-coated, Ni–O fragments of (c) pristine and (d) AlF<sub>3</sub>-coated, Mn–O fragments of (e) pristine and (f) AlF<sub>3</sub>-coated, Ni<sub>2</sub>–F fragments of (g) pristine and (h) AlF<sub>3</sub>-coated, and Mn<sub>2</sub>–F fragments of (i) pristine and (j) AlF<sub>3</sub>-coated.

$$MnO + 2HF \rightarrow MnF_2 + H_2O$$
 [6]

From the TOF-SIMS analysis, it is apparent that dissolution of transition metals is related to the formation of insulating by-products on the surface of the active materials. In particular, the amount of LiF deposited was significantly reduced. These by-products disturb Li<sup>+</sup> diffusion, and are responsible for poor battery performance in terms of capacity, retention, and rate capability.

Extensively cycled active particles were studied by TEM, and the results are shown in Fig. 10. As can be seen in Fig. 10a, the uncoated particle was severely damaged during cycling. In a magnified image, the smooth edges observed in Fig. 2a are hardly observable in Fig. 10b. This disruption of particle morphology is mainly due to the dissolution of metal elements during cycling. In contrast, the cycled AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> particles still show smooth edge lines with clear coating lines (Fig. 10c), and the AlF<sub>3</sub> coating layer is still present on the surface of Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> in a magnified image (Fig. 10d).

The thermal stability of the uncoated pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrodes was measured by DSC. Figure 11 shows the DSC profiles of the uncoated pristine and AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrode at 4.5 V. The onset temperature of thermal decomposition was increased by AlF<sub>3</sub> coating. The AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> electrode showed a major exothermic peak at 297.9°C while the uncoated electrode had a major exothermic peak at 284.1°C. In addition, the total heat associated with each exothermic peak was greatly reduced by AlF<sub>3</sub> coating. When the charge potential was 4.5 V, the uncoated and Al-coated electrode produced 2893 and 1515 J g<sup>-1</sup>, respectively. This result suggests that coating Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> with AlF<sub>3</sub> retards the exothermic reaction with the electrolyte.

Myung et al.<sup>12,13</sup> recently revealed that an  $Al_2O_3$  coating layer on  $Li[Li_{0.05}Ni_{0.4}Co_{0.15}Mn_{0.4}]O_2$  particles gradually transformed to  $AlF_3$  via an intermediate stage (copresence of mixed chemical bonds of Al–O–F and Al–F after 300 cycles at 60°C) on the surface of the  $Al_2O_3$  coating layer. This was proved by TOF-SIMS, which indicated that  $Al_2O_3$  scavenges HF. In this case, the gradual change of



Figure 10. TEM bright-field images of (a) extensively cycled pristine  $Li[Ni_{0.5}Mn_{0.5}]O_2$  particle and (b) its magnified image, (c) extensively cycled  $AlF_3$ -coated  $Li[Ni_{0.5}Mn_{0.5}]O_2$  particle, and (d) its magnified image. The circled parts are magnified.



Figure 11. Comparison of DSC traces of delithiated (a) pristine and (b) AlF\_3-coated Li[Ni\_{0.5}Mn\_{0.5}]O\_2 electrodes.

the Al<sub>2</sub>O<sub>3</sub> layer to AlF<sub>3</sub> was effective in preserving the powder morphology upon cycling. In our work, the AlF<sub>3</sub> was intentionally formed before electrochemical cycling. It is highly probable that the strong AlF<sub>3</sub> coating layer protects the active material from HF attack during cycling. This, in turn, would lead to suppression of insulating LiF deposition on the surface of the active material and dissolution of transition metal elements during cycling, thereby maintaining the original particle morphology. All these factors simultaneously result in lowering of the charge-transfer resistance. For the above reasons, AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> presented a higher capacity, good cyclability, good rate capability, and improved thermal stability compared to pristine Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>.

#### Conclusions

The effects of AlF<sub>3</sub> coating on Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> subjected to high cutoff voltage (4.5 V) cycling were investigated. Although there was no large difference in the structure of Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> after AlF<sub>3</sub> coating, the AlF<sub>3</sub>-coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> showed a greatly enhanced specific discharge capacity, cycling performance, and rate capability compared to pristine Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. Also, reduced resistance properties and improved rate capability were observed by HPPC testing. The improved electrochemical performance could be mainly attributed to the reduced Ni and Mn dissolution of the AlF<sub>3</sub>-coated active material, giving rise to a lower chargetransfer resistance. As confirmed by TOF-SIMS, Ni and Mn were somewhat dissolved from the active materials whether the materials were coated or not. The by-products formed were NiO, MnO, NiF<sub>2</sub>, MnF<sub>2</sub>, and LiF, and significantly more of these by-products were formed with pristine Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub>. Because the AlF<sub>3</sub> coating layer covers the active materials, the amount of LiF deposited on the surface of coated Li[Ni<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> was significantly smaller than on the uncoated surface. The protection of the active material by AlF<sub>3</sub> coating is substantially effective to improve the capacity, capacity retention, rate capability of the batteries, and the thermal stabilities of the positive electrode material as well.

## Acknowledgment

This work was supported by University IT Research Center Project.

Hanyang University assisted in meeting the publication costs of this article.

# References

- 1. T. Ohzuku and A. Ueda, J. Electrochem. Soc., 141, 2972 (1994).
- G. G. Amatucci, J. M. Tarascon, and L. C. Klein, J. Electrochem. Soc., 143, 1114 (1996).
- 4. T. Ohzuku and Y. Makimura, *Chem. Lett.*, **30**, 744 (2001).
- Z. Lu, D. D. MacNeil, and J. R. Dahn, *Electrochem. Solid-State Lett.*, 4, A200 (2001).
- W.-S. Yoon, C. P. Grey, M. Balasubramanian, X.-Q. Yang, and J. McBreen, *Chem. Mater.*, **15**, 3161 (2003).
- K. Shizuka, T. Kobayashi, K. Okahara, K. Okamoto, S. Kanzaki, and R. Kanno, J. Power Sources, 146, 589 (2005).
- B.-C. Park, H. J. Bang, C. S. Yoon, S.-T. Myung, J. Prakash, and Y.-K. Sun, J. Electrochem. Soc., 154, A520 (2007).
   G.-H. Kim, J.-H. Kim, S.-T. Myung, C. S. Yoon, and Y.-K. Sun, J. Electrochem.
- Soc., **152**, A1707 (2005).
   Y.-K. Sun, J.-M. Han, S.-T. Myung, S.-W. Lee, and K. Amine, *Electrochem. Com-*
- *mun.*, **8**, 821 (2006). 11. B.-C. Park, H.-B. Kim, S.-T. Myung, K. Amine, I. Belharouak, S.-M. Lee, and
- Y.-K. Sun, J. Power Sources, 178, 826 (2008).
  S.-T. Myung, K. Izumi, S. Komaba, Y.-K. Sun, H. Yashiro, and N. Kumagai, Chem.
- Mater, 17, 3695 (2005).
   S.-T. Myung, K. Izumi, S. Komaba, H. Yashiro, H. J. Bang, Y.-K. Sun, and N. Kumagai, J. Phys. Chem. C, 111, 4061 (2007).
- M.-H. Lee, Y.-J. Kang, S.-T. Myung, and Y.-K. Sun, *Electrochim. Acta*, 50, 939 (2004).
- 15. R. D. Shannon, Acta Crystallogr. A, 32, 751 (1976).
- 16. PNGV Battery Test Manual, Revision 3, DOE/ID-11069 (2003).
- S.-T. Myung, K. Hosoya, S. Komaba, H. Yashiro, Y.-K. Sun, and N. Kumagai, Electrochim. Acta, 51, 5912 (2006).
- 18. D. Aurbach, J. Electrochem. Soc., 136, 906 (1989).
- 19. K. Edström, T. Gustafsson, and J. O. Thomas, Electrochim. Acta, 50, 397 (2004).
- J. A. Dean, Lange's Handbook of Chemistry, 4th ed., p. 6, McGraw-Hill Inc., New York (1992).