

Enhanced electrochemical properties of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathode by surface coating using LaF_3 and MgF_2

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Abstract LaF_3 and MgF_2 were introduced for the surface modification of an $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrode. The rate capability, cyclic performance, phase stability at a high voltage range, and thermal stability of pristine and coated electrodes were characterized. Surface modification with both coating materials, LaF_3 and MgF_2 , enhanced the rate capability and cyclic performance. The LaF_3 and MgF_2 coatings also suppressed the structural instability during cycling in the high voltage range (4.8–3.0 V). This implies that both fluoride coating layers successfully protected the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrode from the acidic electrolyte. However, the MgF_2 coating improved the thermal stability of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrode more effectively than the LaF_3 coating.

Keywords Surface coating · Electrochemical properties · Cathode · Lithium battery

1 Introduction

Over the last two decades, lithium rechargeable batteries have played a significant role in our lives. Nowadays, they are being applied in new developments such as electric vehicles (EVs), plug-in hybrid electric vehicles (PHEVs), robots, and electric power storing systems [1–6]. LiCoO_2 was one of the earliest cathode materials developed, and it continues to be a main component for cathodes in rechargeable lithium batteries owing to its easy preparation, high

voltage, and good cycle properties. However, many researchers have made efforts to find substitutes for LiCoO_2 to increase the energy density and decrease the toxicity of Co [7–13]. $\text{Li}(\text{Ni},\text{Co},\text{Mn})\text{O}_2$ is one of the most promising new cathode materials owing to its high capacity and stable cyclic performance [14–17]. However, several problems with this material still need to be overcome, such as its inferior rate capability and thermal stability. One possible method for improving the electrochemical properties of a cathode is surface coating. Coating materials such as oxides [18–21], phosphates [22–26], and fluorides [27–30] have been used to improve the properties of cathode materials. However, the coating effect is highly dependent on the coating material [31, 32]. Some coating materials are very effective in improving the electrochemical and other properties, whereas others are not. Thus, the selection of a good coating material is essential for coating treatments of cathode materials.

In this study, LaF_3 and MgF_2 was introduced as a coating material for $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathodes. La and Mg doping reportedly improve the discharge capacity and cyclic performance of cathodes [33, 34]. Moreover, other fluorides such as AlF_3 have been successfully introduced as a coating material in various cathode materials [27–30]. In this work, we fabricated LaF_3 - and MgF_2 -coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathodes and investigated their electrochemical and structural properties.

2 Experimental

Pristine $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ powder from ECOPRO was used. For synthesizing the LaF_3 coating, lanthanum nitrate hexahydrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$] (Aldrich, 99.99 %) and ammonium fluoride [NH_4F] (Aldrich, 98 %+) were separately

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dissolved in distilled water and then stirred continuously for 30 min. The active material $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ was slowly poured into the LaF_3 solution. After 30 min, the mixture was dried at 100 °C. The powder was annealed at 400 °C for 3 h in air and then slowly cooled to room temperature. To prepare the MgF_2 coating solution, magnesium nitrate hexahydrate $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{NH}_4)_2\text{HPO}_4$ (Aldrich, 99 %) and ammonium fluoride $[\text{NH}_4\text{F}]$ (Aldrich, 98 %+) were separately dissolved in distilled water and stirred continuously for 30 min. Subsequently, $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ powder was added to the coating solution, which was mixed thoroughly for 30 min. The slurry was dried in an oven at 100 °C for 12 h and heated in a furnace at 400 °C for 3 h in air. The starting ratio of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ to the coating materials was 99.75:0.25. X-ray diffraction (XRD) patterns of the powders were obtained using a Philips X-ray diffractometer, and the surface morphologies of the samples were analyzed using a transmission electron microscope (TEM, JEOL-JEM 2100 F) operated at 200 kV.

The electrochemical performances of the coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathodes were examined using two-electrode test cells (with 2032 configuration) consisting of a cathode, metallic lithium anode, polypropylene separator, and an electrolyte of 1 M LiPF_6 in EC/DMC (1:1 vol%). The cathode contained 80 wt% active materials, 12 wt% carbon black, and 8 wt% PVDF binder. The components were ball-milled to achieve homogeneous mixing, coated on aluminum foils, and dried at 90 °C for 2 h. The cells were subjected to galvanostatic cycling using a WonATech system at various C rates (200 $\text{mA} \cdot \text{g}^{-1}$ was considered as 1 C rate). Impedance measurements were carried out using an electrochemical workstation (CHI instrument, CHI 660A) through the application of an AC voltage at an amplitude of 5 mV over a frequency range 0.1–100 KHz. Samples of the cathode were prepared for differential scanning calorimetry (DSC, Mettler Toledo) as follows. Cells containing sample electrodes were charged to 4.6 V with a current density of 0.2 C, and the potential was held until the current density reached 4 $\text{mA} \cdot \text{g}^{-1}$. The cells were then disassembled in a dry room to remove the charged positive electrode. The positive electrode (4 mg), including the electrolyte, was sealed in a high-pressure DSC pan. The heating rate and temperature range for the DSC tests were 5 °C min^{-1} and 25–400 °C, respectively.

3 Results and discussion

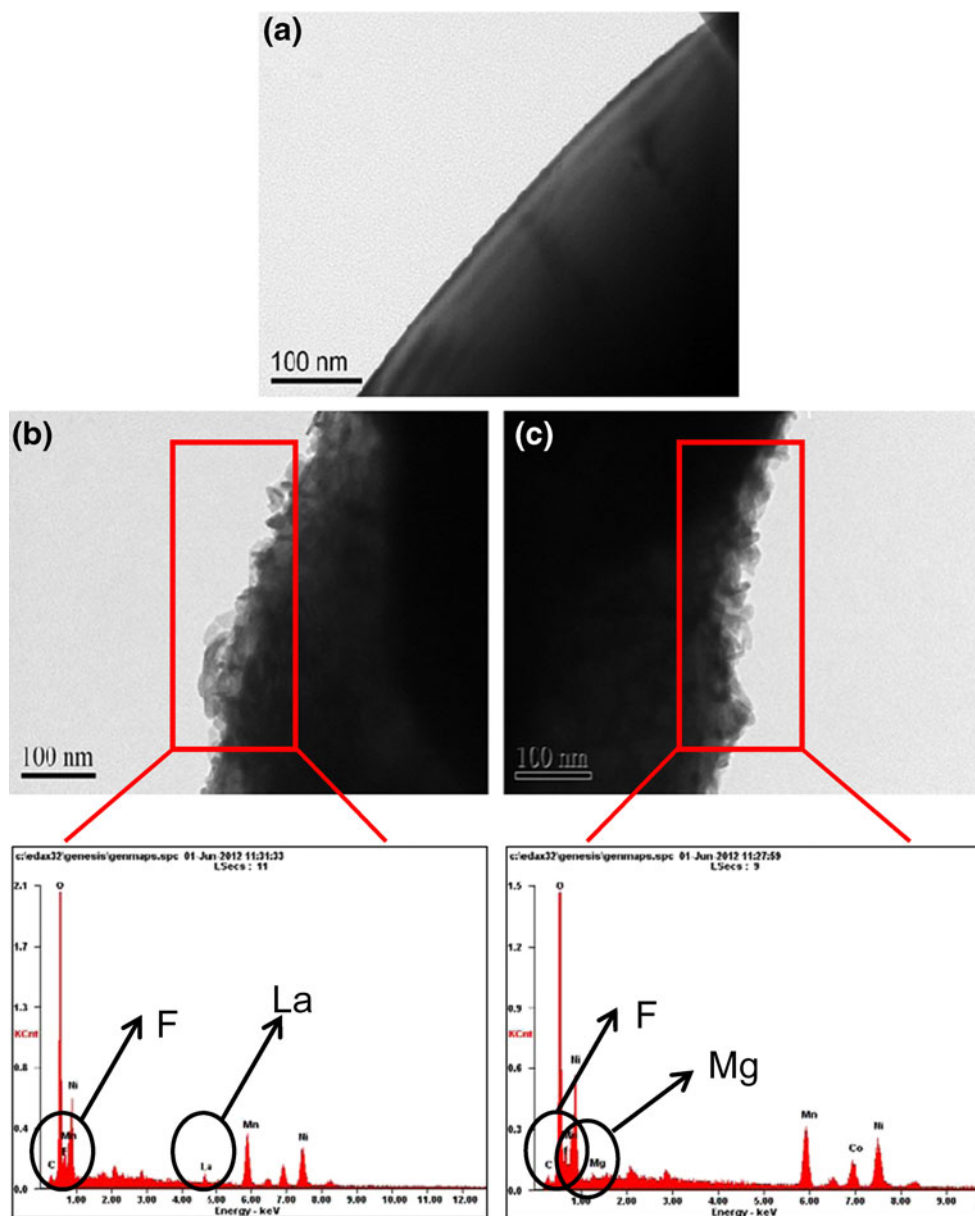
The shapes of the pristine and coated samples were investigated by transmission electron microscopy (TEM). Figure 1 presents the TEM images of the pristine, LaF_3 -coated, and MgF_2 -coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ powders. The pristine sample exhibited a smooth surface without any heterophase

particles. On the other hand, the coated samples were covered with a rough and porous coating layer composed of nanostructured particles; this shows that the coating layers successfully formed on the surface of powder. The coating layers were relatively homogeneous. As shown below Fig. 1(b and c), the coating elements (La, Mg, and F) were distinctly detected via energy-dispersive X-ray spectroscopy (EDS), which confirmed the formation of a LaF_3 (Fig. 1(b)) and MgF_2 (Fig. 1(c)) coating layer on the surface of the pristine cathode.

To examine the coating effects, the electrochemical properties of the samples were measured at various C rates. Figure 2 shows the discharge capacities of the pristine and coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes at 0.5, 1, 2, 3, and 6 C rates for voltage range 4.6–3.0 V. The pristine and coated samples showed similar discharge capacity at a rate of 0.5 C. As the C rate increased, the discharge capacities of the pristine and coated samples decreased; this was due to the high resistance at high charge-discharge rates. However, the LaF_3 - and MgF_2 -coated samples maintained a relatively higher discharge capacity than the pristine sample at high C rates. This means that the rate capability of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes was improved by the LaF_3 and MgF_2 coatings. Figure 3 presents the fifth discharge profile (which may show the median value of each rate) of the pristine and coated electrodes at rates of 1, 3, and 6 C rates. According to the voltage profiles at the 1 C rate, the coated sample showed superior capacity to the pristine sample. In the voltage profiles of the 3 and 6 C rates, of more significance was that the LaF_3 and MgF_2 coatings were found to be effective in enhancing the rate capability. Basically, the coating materials are non-conductive for lithium ions and electrons, so they may inhibit the diffusion of lithium ions and electrons. However, it should be noted that the cathode was attacked by the acidic electrolyte during cycling and formed an unwanted surface layer because of the dissolution of the transition metal ions such as Co, Ni, Mn in the electrolyte at the interface of the cathode. This interface layer is a major obstacle to the diffusion of lithium ions and electrons during the charge and discharge process. The surface coating may suppress the formation of an unwanted surface layer originating from the dissolution of cations (e.g., Co, Ni, and Mn) and/or protect the cathode from attacks by HF in the electrolyte [18, 19, 31]. In particular, the metal fluoride layers have been reported to be highly effective for protection against HF attacks during cycling [31]. Therefore, the stable LaF_3 and MgF_2 coating layers are considered to effectively protect the cathode surface from the acidic electrolyte and facilitate the diffusion of lithium ions and electrons, leading to an enhanced rate capability of the coated electrode.

The impedance spectroscopy result supports the above explanation. Figure 4 shows the Nyquist plots of the pristine

Fig. 1 TEM images of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ powder: (a) pristine; (b) LaF_3 -coated powder; (c) MgF_2 -coated powder (EDS spectra of coating layers are shown below (b) and (c))

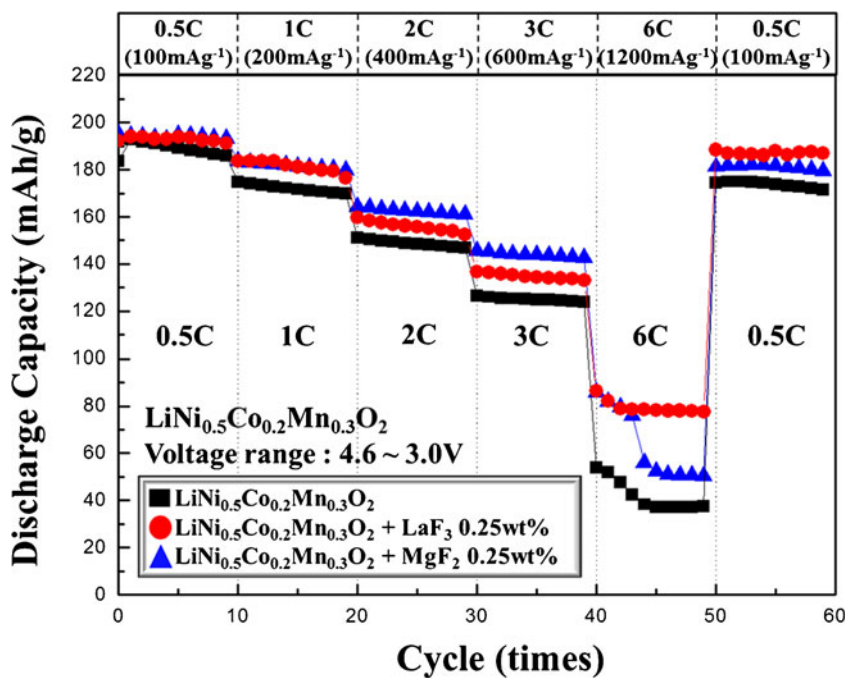


and coated samples before the electrochemical tests. In the Nyquist plots, the semicircles of the coated electrodes with both fluorides were smaller than that of the pristine electrode. In general, the semicircle in the Nyquist plot represents two resistance factors: the impedance values related to the solid electrolyte interface and the charge-transfer resistance [35]. The smaller semicircle of the coated sample implies that the LaF_3 and MgF_2 coating layers decrease the impedance values related to the impedance factors. This result correlates with the improved rate capability of the coated electrodes.

Figure 5 presents the cyclic performances of the pristine and coated electrodes. To investigate the coating effect on the cycling behavior under severe measurement conditions, the upper cut-off voltage was increased to 4.8 V. The $\text{Li}[\text{Ni}$,

Co , $\text{Mn}]\text{O}_2$ cathode with a layered structure was unstable at a high voltage range above 4.6 V, therefore rapid capacity fading was expected during cycling in the high voltage range 4.8–3.0 V [17, 36]. As shown in Fig. 5, the discharge capacity of the electrodes dropped over the course of 50 cycles. However, the LaF_3 - and MgF_2 -coated samples clearly exhibited a superior cyclic performance. The MgF_2 coating layer, in particular, appears to be effective in improving the cyclic performance in the high voltage range. The stable cyclic performance of the coated electrode may be attributed to the protection of the coating layer against the attack of the reactive electrolyte. The electrodes were collected after being cycled 50 times in the voltage range 4.8–3.0 V (all the samples were fully discharged state to 3.0 V), and their structures were characterized by XRD analysis to examine

Fig. 2 Discharge capacities and cyclic performances of pristine and coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes in a voltage range of 4.6–3.0 V at C rates of 0.5, 1, 2, 3, and 6 C



the the effect of the coating layer on the phase stability. The diffraction patterns of the pristine sample prior to cycling

can be perfectly indexed as a typical hexagonal $\alpha\text{-NaFeO}_2$ structure with O3 stacking (Fig. 6(a)). However, after

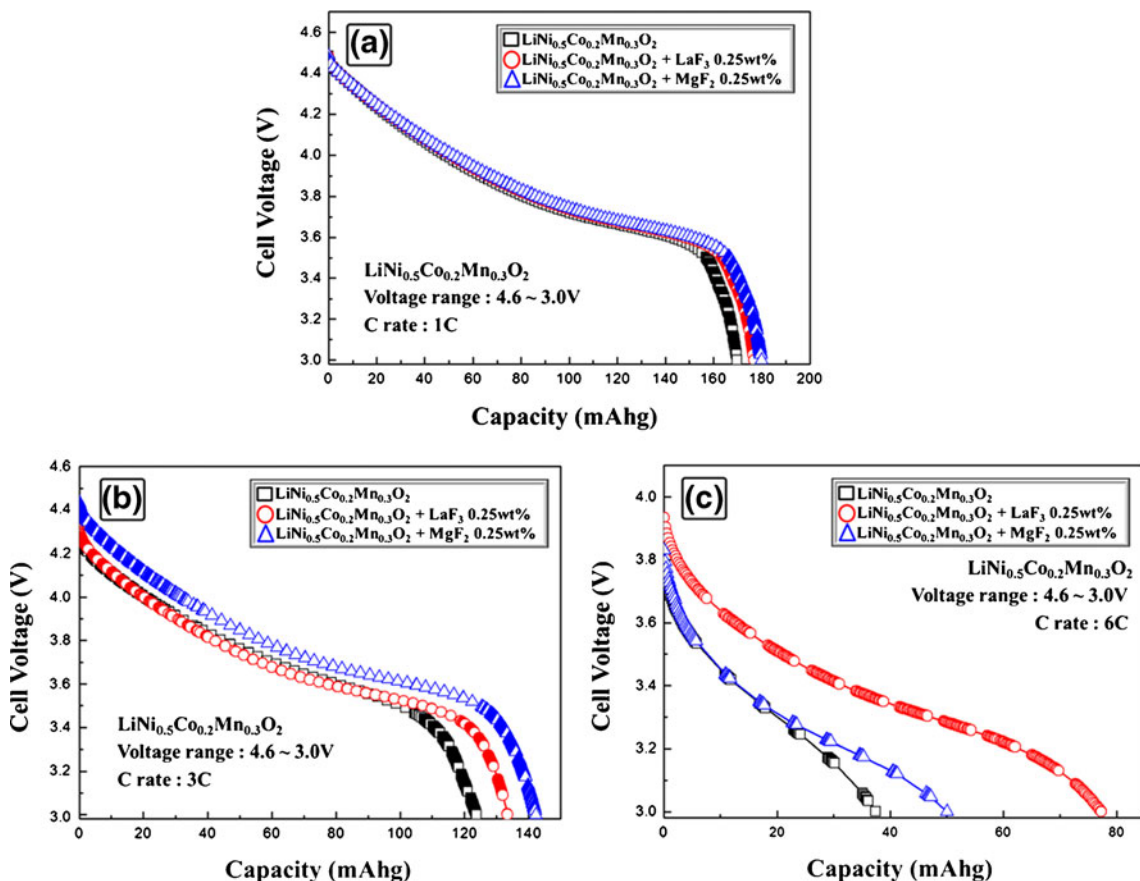
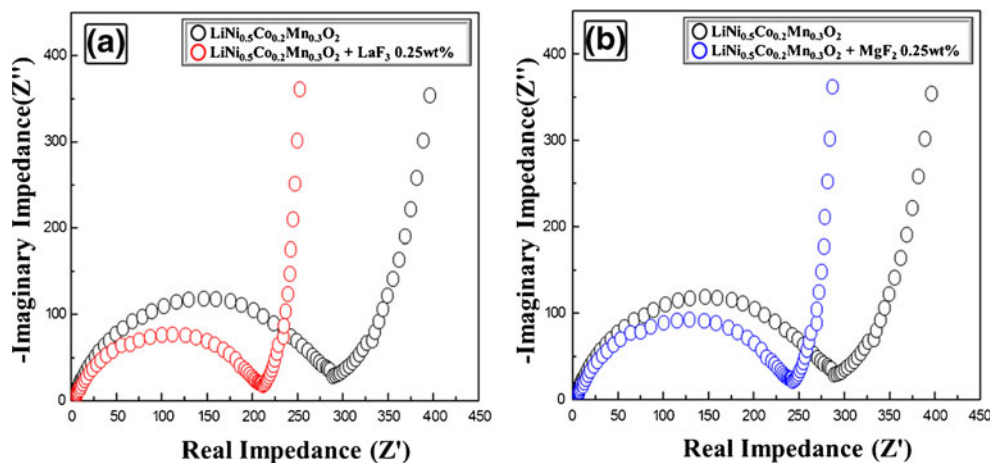


Fig. 3 Fifth discharge profiles of pristine and coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes in a voltage range of 4.6–3.0 V at (a) 1, (b) 3, and (c) 6 C rates

Fig. 4 Nyquist plots of (a) LaF_3 -coated and (b) MgF_2 -coated electrodes before the electrochemical test compared with that of the pristine electrode

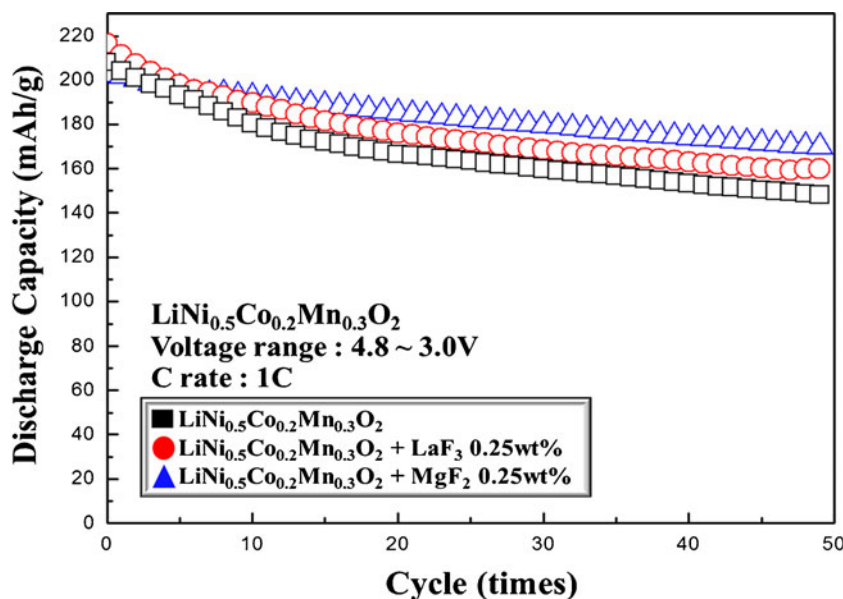


cycling, a significant change was observed in the diffraction patterns, as shown in Fig. 6(b). Specifically, several unknown peaks (marked with *) were detected, implying that the typical $\alpha\text{-NaFeO}_2$ structure changed during cycling at the high voltage range (over 4.6 V). The unknown peaks may be associated with a phase with P3 stacking, which is easily formed due to loss of oxygen at highly charged state [17]. The XRD patterns of the LaF_3 - and MgF_2 -coated samples were almost identical to that of the pristine sample before cycling (not shown in the figure). When the coated samples were cycled 50 times in the voltage range 4.8–3.0 V, some noticeable changes were also detected in the XRD patterns. For the LaF_3 -coated sample, the intensity of the (015) diffraction peak decreased slightly after cycling. In the diffraction pattern of the MgF_2 -coated electrode, the (110) diffraction peak split slightly after cycling. However, it should be noted that the coated samples appeared to relatively maintain their phases during cycling, as compared with the cycled pristine sample. This result shows that the

LaF_3 and MgF_2 coatings effectively suppress phase transition during cycling at a high voltage range (over 4.6 V), which explains the enhanced cyclic performance of the coated samples, as shown in Fig. 5.

The thermal stability of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrode before and after coating was investigated using DSC analysis in the following test. The electrodes were charged to 4.6 V before analysis and sealed in a high-pressure DSC pan. Figure 7(a) shows the DSC profile of the pristine electrode. The pristine sample showed a thermal reaction with the electrolyte at approximately 230 °C, and heat was generated until ~320 °C. Three exothermic peaks were detected at approximately ~250, ~275, and ~290 °C. The total heat generated was ~186 Jg^{-1} . As shown in Fig. 7(b), the exothermic peak of the LaF_3 -coated sample shifted to a lower temperature (~200 °C). Although the total amount of heat generated was somewhat reduced to ~177 Jg^{-1} , the LaF_3 coating did not seem to effectively improve the thermal stability. In contrast, the thermal stability of the

Fig. 5 Cyclic performances of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes in a voltage range of 4.8–3.0 V at a 1 C rate



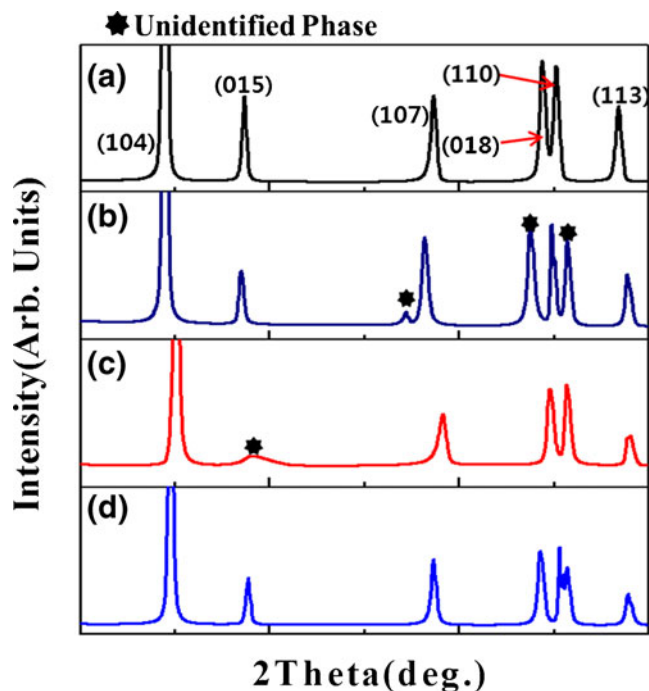
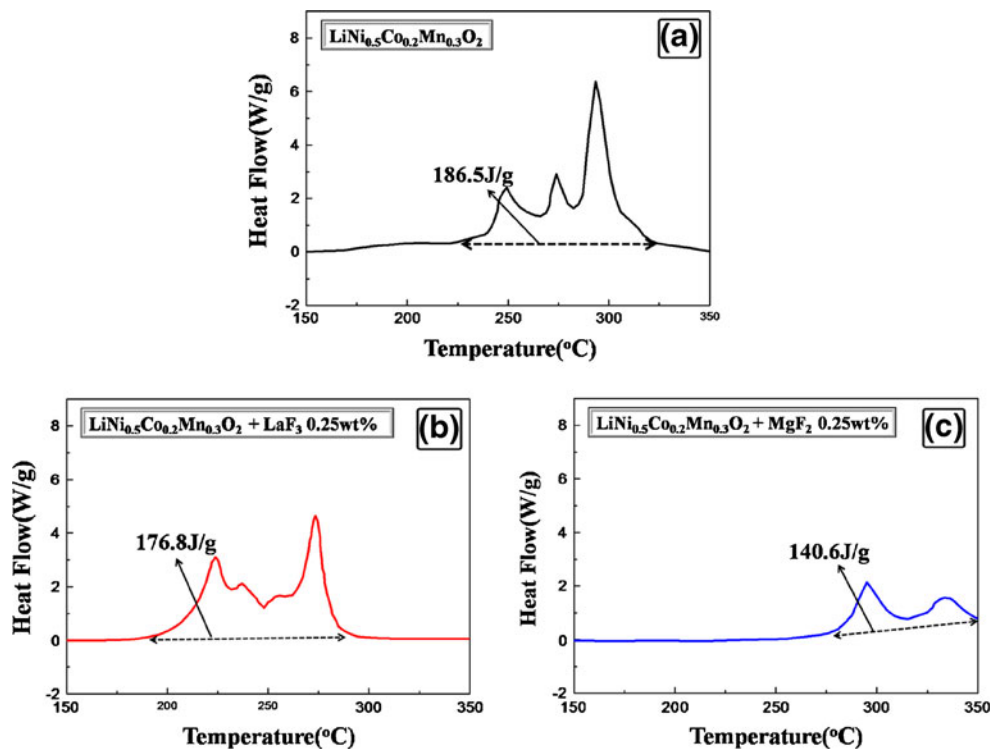


Fig. 6 XRD patterns of pristine and coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes: (a) pristine sample before cycling, (b) pristine sample after cycling, (c) LaF_3 -coated sample after cycling, and (d) MgF_2 -coated sample after cycling

$\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrode was significantly enhanced by the MgF_2 coating. The exothermic peak of the MgF_2 -coated sample shifted to a higher temperature ($\sim 280^\circ\text{C}$),

Fig. 7 DSC scans of pristine and coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes in fully charged state (cut-off voltage of 4.6 V): (a) pristine sample, (b) LaF_3 -coated sample, and (c) MgF_2 -coated sample



and heat generation in that region also decreased to $\sim 141 \text{ Jg}^{-1}$. As shown in Figs. 2 and 3, both LaF_3 and MgF_2 coatings effectively improved the rate capability. However, as shown in Figs. 5 and 7, the MgF_2 coating was more effective at enhancing the cyclic performance and thermal stability than the LaF_3 coating. Considering that Mg is a cheap element, MgF_2 is a promising coating material for improving the electrochemical properties of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ electrodes.

4 Conclusion

The surfaces of the commercial $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathode were coated with two series of fluoride materials (LaF_3 and MgF_2). The TEM images showed that the surface of each coated sample was tough and had nanoparticles attached. Examination of the results of the galvanostatic charge-discharges at various C rates indicated that both coating samples enhanced the rate capability of the electrodes. Impedance values confirmed that both fluoride coatings reduced the resistance of the cells. The MgF_2 -coated electrode provided a more advanced cyclic performance in the high voltage range than the LaF_3 -coated electrode. In particular, the LaF_3 coating was not effective in improving the thermal stability of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathode. The MgF_2 -coated electrode, on the other hand, significantly enhanced the thermal stability according to DSC analysis. These results imply that MgF_2 is a promising coating

material for improving the electrochemical properties of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cathodes.

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