Electrochemical properties of nanosized Li-rich layered oxide as positive electrode materials for Li-Ion batteries†

Won-Hee Ryu,ab Dong-Han Kim,b Sun-Ho Kang* b and Hyuk-Sang Kwon*a

A nanosized Li-rich layered oxide/carbon composite material is successfully prepared by simple ball milling pulverization of microsphere-shaped Li-rich layered oxide materials with conductive carbon. The nanosized Li-rich layered oxide/carbon composite electrode exhibits a high 1st discharge capacity of 250 mAh g⁻¹ with an excellent rate capability at high current density. The composite also reduces the internal resistance from oxygen release during the electrochemical activation of Li₂MnO₃. The improvement in the electrochemical performance of nanosized Li-rich layered oxide/carbon composite materials primarily occurs because the nanosized particles facilitate the diffusion of Li within the structure and provide innumerable reaction sites with lithium. Furthermore, the electronic conductivity of the active material is effectively enhanced by the carbon coating on the particles. In addition, unique effects of ball milling on the electrochemical properties of the Li-rich layered oxides are observed: (i) pre-activation of the Li₂MnO₃ component and (ii) gradual electrochemical activation under 4.3 V during cycling. Adverse effects on the electrochemical stability of the nanosized Li-rich layered oxide are also discussed, and these adverse effects mainly arise due to (i) the structural deformation of hexagonal ordering, (ii) the growth of the spinel component and (iii) the insufficient formation of a protective NiF₂ layer on the surface of the active material.

Introduction

High demand for plug-in hybrid electric vehicles (PHEV) and electric vehicles (EV) has spurred the development of secondary lithium batteries with high energy/power density and fast charge/discharge properties. Recent studies have focused on maximizing these electrochemical properties for new positive electrode materials.¹,² For example, structurally integrated xLi₂MnO₃ -(1-x)LiMO₂ (M = Co, Ni, Mn) is a promising candidate to replace LiCoO₂ as a positive electrode material because of its high reversibility and improved structural stability at high potentials.³,⁴ The xLi₂MnO₃ -(1-x)LiMO₂ structure can be described as the electrochemically inactive Li₃MnO₃ component that is structurally integrated into the electrochemically active LiMO₂ matrix, where M is, for example, Mn₀.₅Ni₀.₅ or Mn₀.₃₃Ni₀.₃₃Co₀.₃₃.⁵ The presence of the electrochemically inactive Li₃MnO₃ component is known to stabilize the layered structure as a result of the diffusion of Li from octahedral sites in the LiMn₆ ordering phase to tetrahedral sites in the lithium-depleted layer (known as two-dimensional, quasi-spinel-like features).⁶ Furthermore, when charged to high potentials (typically 4.6–4.8 V vs. Li/Li⁺), the Li₂MnO₃ component is activated to MnO₂ by the simultaneous extraction of lithium and oxygen from the structure, thus leading to additional reversible capacity arising from the participation of Mn in the electrochemical redox reactions during subsequent discharge/charge cycles.

While the composite material has some distinct advantages, such as additional reversible capacity and better structural stability, the rate capability is intrinsically limited because of the 2-dimensional lithium pathway of the layered structure. Several recent strategies have aimed to improve the kinetic properties of the Li-rich layered oxide electrodes during Li insertion and extraction. The rate capability of a Li-rich layered oxide was improved using intergrown “layered-spinel” composite materials, which have analogous interlayer spacing between (001) planes of layered Li₂MnO₃ and (111) planes of spinel LiMn₂O₄, primarily because of the three-dimensional movement of lithium in the spinel structure.⁷ Li₁.₃₂Na₀.₀₂Ni₀.₂₅Mn₀.₇₅O₄ (IE-LNMO), prepared by Li ion-exchange of the isostructural sodium layered oxide (Na[M]O₂), was recently reported to show an excellent rate...
capability, even under a high current (1500 mA g⁻¹, 10 C). The larger radius of Na can increase the interlayer slab space while also reducing the site disorder of Ni in the Li layer. Unlike previous approaches, one of the most attractive solutions to improve the rate capability is using nanometer-sized layered electrodes. The rate of Li⁺ insertion/extraction can be significantly increased using nanosized electrode materials by virtue of their large surface area, which provides innumerable reaction sites for Li and a short Li⁺ diffusion length (D = L²/t, where L is the diffusion length, D: diffusion coefficient) within the particles. In addition, internal stress induced by structural changes, such as the evolution of internal oxygen during the process of activation of Li₂MnO₃, can be better relieved using nanostructures.

This work reports on the electrochemical properties of nanosized Li-rich layered oxide as a high energy positive electrode material. Nanosized Li-rich layered oxide materials were easily obtained from the simple pulverization of microsphere-shaped Li-rich layered oxide materials using ball milling. Furthermore, conductive carbon (super-P carbon black) was mixed with the active material during the ball milling process because (1) covering the active material with carbon improves its electronic conductivity by increasing the contact area and (2) the carbon exterior is expected to protect against direct mechanical damage to the surface from ball milling (Scheme 1).

**Experimental**

**Materials preparation and characterization**

The positive active material was 0.5Li₂MnO₃·0.5LiNi₀.₃₄Mn₀.₃₅Co₀.₃₅O₂ (ANL-NMC). ANL-NMC was synthesized from stoichiometric amounts of Li₂CO₃ (Sigma-Aldrich) and Mn₉O₁₄Ni₉O₁₄Co₉O₁₄(OH)₂ precursors. The Mn₉O₁₄Ni₉O₁₄Co₉O₁₄(OH)₂ precursor was prepared using a co-precipitation method. A 2 M aqueous solution of Ni, Co, and Mn sulfate (Mn : Co : Ni = 0.656 : 0.219 : 0.125) was added to a 2 M aqueous solution of NaOH with the desired amount of NH₄OH under a flowing nitrogen atmosphere. The pH, temperature, and stirring speed were controlled at 12 ± 5 °C, and 1000 rpm, respectively, throughout the co-precipitation process. The co-precipitated nickel-cobalt-manganese hydroxide was filtered, dried, and then mixed with appropriate amounts of Li₂CO₃, followed by calcination at 750 °C for 12 h in an air atmosphere.

The as-prepared ANL-NMC powder was mixed with carbon at a weight ratio of 5 : 1 by ball milling with stainless-steel balls in air (Spex8000 Mixer/Mill) for various durations. The powders will be denoted as BMₙ, where n denotes the ball milling time in minutes (n = 10, 30). For comparison, the ANL-NMC powder was also ball milled without adding carbon. As discussed below, the ball milling not only provides sufficient mixing to improve the electrical contact between ANL-NMC particles and carbon, but it also prevents direct mechanical damage to the surface of the layered active material. The surface morphology of the samples before and after ball milling treatment was analyzed using scanning electron microscopy (SEM, Philips, XL30SFEG) and transmission electron microscopy (TEM, FEI, Tecnai F30 S-Twin). The crystal structures of the samples were analyzed by X-ray diffraction (XRD, RIGAKU, D/MAX-RC). The specific surface area of the samples was analyzed using a Brunauer–Emmett–Teller (BET) surface area analyzer (Micromeritics ASAP 2020 M + C). The structural change on the surface of a pulverized particle was investigated by X-ray photoelectron spectroscopy (XPS, Thermo, MultiLab 2000) analysis.

**Materials preparation and characterization**

The electrochemical performance of the as-prepared and ball milled materials was evaluated in coin-type cells (2032, Hohsen). The positive electrode was fabricated by casting a slurry on aluminum foil consisting of 75 wt% active material, 15 wt% carbon, and 10 wt% polyvinylidenedifluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP). In the case of the ball milled samples, no additional carbon was added during the slurry preparation process because they were already mixed with carbon at a 5 : 1 weight ratio. After drying in air at 75 °C, the electrode was pressed to ~40% electrode porosity and then re-dried under vacuum at 75 °C prior to cell assembly in an argon-filled glove box. The average loading density of the active materials was 1.6 mg cm⁻². A Li-metal foil was used as the counter electrode, and 1.2 M LiPF₆ in a 3 : 7 mixture (by volume) of ethylene carbonate : ethyl methylcarbonate (Tomiyama, Japan) was used as the electrolyte. The separator was a Celgard 2325 (25 μm thick). All electrochemical experiments were performed at room temperature.

**Results and discussion**

Fig. 1a and 1b show SEM images of as-prepared and ball milled ANL-NMC samples. As-prepared ANL-NMC particles (Fig. 1a) were observed to have a uniform and spherical shape with a diameter of approximately 20 μm. After ball milling, ANL-NMC particles were fully pulverized (Fig. 1b). Fig. 1c shows the detailed morphology and the selected area electron diffraction (SAED) pattern of a ball milled sample (BM30) obtained using transmission electron microscopy. Crystalline particles and amorphous carbon are observed as spot and ring patterns, respectively, from the SAED pattern at each point, as
shown in Fig. 1c. Although a deviation in the particle size distribution was observed after ball milling, the nanosized Li-rich layered oxide particles, with a mean particle size of 200 nm, were connected and uniformly mixed with nanosized amorphous carbon webs (约20 to 30 nm), as shown in Fig. 1c and 1d. The surface of the partially active material was observed to be well covered with amorphous carbon, which can provide a path for rapid electron conduction during charging/discharging (Fig. 1e). BET analysis was conducted to determine the specific surface area of each sample, as shown in Table 1. The BET surface area of the samples increased with ball milling time.

Fig. 2a shows X-ray diffraction patterns of the as-prepared and ball milled ANL-NMC samples. The diffraction patterns were indexed based on a hexagonal \( \alpha \)-NaFeO\(_2\) structure with the space group \( R\bar{3}m \). As shown in Fig. 2b, the patterns showed small, additional peaks (\( C2/m \)) between 20° and 23° (2\( \theta \)), indicating the presence of the ordering component \([LiMn]_n\) in the transition metal layers. Overall, the diffraction peaks broadened (FWHM increased, see Table 1) with ball milling time due to the decrease in crystalline particle size. In addition, the \( I_{(003)}/I_{(104)} \) ratio decreased, and the \( R \)-factor \( \left[ (I_{(006)} + I_{(102)})/I_{(101)} \right] \) increased with increasing ball milling time. These results demonstrate the structural changes in ANL-NMC during mechanical ball milling.

The 1st and 2nd charge/discharge curves of lithium half cells containing the ANL-NMC, BM10 and BM30 positive electrodes are shown in Fig. 3. The cells were cycled between 2.0 and 4.6 V at room temperature in a constant-current condition with a current density of 15 mA g\(^{-1}\) and a constant voltage of 4.6 V for 3 h during charging. The 1st discharge capacity of the BM30 electrode (250 mAh g\(^{-1}\)) was higher than those of both the BM10 (230 mAh g\(^{-1}\)) and as-prepared ANL-NMC (213 mAh g\(^{-1}\)) electrodes. The discharge capacities of all samples increased after the 2nd cycle because the residual Li\(_2\)MnO\(_3\) phases were activated to the active MnO\(_2\) phase. In addition, the first-cycle coulombic efficiency of the BM30 electrode was 78%, compared with 69% for the ANL-NMC electrode. These improvements are attributed to the larger surface area (more reaction sites) and smaller particle size (facile migration of Li ions in the particles). Furthermore, the initial charging of the ball milled samples was observed to begin at a lower voltage (<3.8 V) than in the ANL-NMC sample (3.9 V). During the 2nd charge/discharge process, the lithium extraction of the ball milled samples also began at a lower voltage, while the discharge capacity increased with increasing ball milling time (Fig. 3b). Previous reports have demonstrated that the charge curve at about 3.4 and 3.8 V represents the extraction of lithium from the spinel component, whereas the

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**Table 1** Properties of the 0.5Li\(_2\)MnO\(_3\)-0.5Li\(_{0.44}\)Mn\(_{0.31}\)Co\(_{0.25}\)O\(_2\) material (ANL-NMC) before and after the ball milling treatment: ball milling time, lattice parameter, \( c/a \), \( I_{(003)}/I_{(104)} \), \( R \)-factor, FWHM\(_{(003)}\), and BET surface area

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Ball milling time (min.)</th>
<th>( a/Å )</th>
<th>( c/Å )</th>
<th>( c/a )</th>
<th>( I_{(003)}/I_{(104)} )</th>
<th>( R )-factor ( (I_{(006)} + I_{(102)})/I_{(101)} )</th>
<th>FWHM(_{(003)})</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANL-NMC</td>
<td>—</td>
<td>2.8512</td>
<td>14.2049</td>
<td>4.9821</td>
<td>1.683</td>
<td>0.3546</td>
<td>0.130</td>
<td>1.239</td>
</tr>
<tr>
<td>BM 10</td>
<td>10</td>
<td>2.8579</td>
<td>14.2929</td>
<td>5.0012</td>
<td>1.236</td>
<td>0.4069</td>
<td>0.190</td>
<td>22.364</td>
</tr>
<tr>
<td>BM 30</td>
<td>30</td>
<td>2.8606</td>
<td>14.3438</td>
<td>5.0143</td>
<td>1.139</td>
<td>0.4193</td>
<td>0.250</td>
<td>28.282</td>
</tr>
</tbody>
</table>
lithium extraction from the layered component, such as LiNi0.44Co0.25Mn0.31O2, starts at a voltage higher than 3.9 V.\textsuperscript{15} The charging reaction at a lower voltage (~3.7 V) for ball milled ANL-NMC indicates the partial transformation to an additional active phase, such as the spinel component.

Fig. 4 shows an open-circuit voltage/constant current voltage (OCV/CCV) plot of ANL-NMC, BM10 and BM30 obtained from a galvanostatic intermittent titration (GITT) experiment.\textsuperscript{16,17} The difference between OCV and CCV reflects the degree of resistance (V = IR) at each point during charging. The CCV plot for ANL-NMC clearly shows an irregularity at high voltages (>4.5 V), highlighted here as the boxed area. The origin of this irregularity is unclear, but it is speculated to be closely related to the evolution of oxygen from the electrochemical activation of Li2MnO3.\textsuperscript{18,19} Conversely, this irregular increase in CCV was not observed for the ball milled sample. This result suggests that the internal resistance induced by oxygen release is effectively reduced by the formation of nanosized particles. Furthermore, the difference between the OCV and CCV decreased at the beginning of charging for the ball milled samples, indicating facile lithium extraction from nanosized particles in the initial stage. In addition, the coating of the nanosized ANL-NMC with conductive carbon helped decrease the ohmic resistance at the beginning of charging.

Fig. 5a shows the cycling behaviour of the ANL-NMC, BM10 and BM30 electrodes between 2.0 and 4.3 V. The capacity of the 1st discharge increased from 76 mAh g\textsuperscript{-1} to 92 mAh g\textsuperscript{-1} as ball milling time increased. Furthermore, the specific capacity of the ball milled samples gradually increased during cycling, reaching 110 mAh g\textsuperscript{-1} after the 50th cycle in the case of BM30. However, the discharge capacity of ANL-NMC maintained its initial discharge capacity of 76 mAh g\textsuperscript{-1}, even after the 50th cycle. This phenomenon, first reported here, indicates that at 4.3 V, the nanosized Li-rich layered oxide was partially electrochemically activated. Fig. 5b shows the 50th charge/discharge curve of the samples and their derivative capacity-voltage (dQ/dV) plots. The charge/discharge profile of the ball milled samples is characteristically similar to that of a layered- and spinel-composite electrode.\textsuperscript{20} Conversely, the charge/discharge profile of ANL-NMC is similar to that of LiNi0.44Co0.25Mn0.31O2, which underwent oxidation and reduction of Ni and Co from 4\textsuperscript{+} to 3\textsuperscript{+}. From the dQ/dV curve shown in the inset of Fig. 5b, the redox peaks of Mn were confirmed at approximately 3.0 V and 2.8 V during charging and discharging, respectively. These peaks correspond to the presence of an Mn-based active phase such as layered LiMnO2 or spinel Li1+yMn2−yO4 in the structure, indicating a transformation from inactive Li2MnO3 to active Mn-based oxide. In addition, the first discharge from the OCV at 2 V was performed for each sample, as shown in Fig. S4, ESI.\textsuperscript{1} In contrast to ANL-NMC, BM30 delivered a discharge capacity of 9 mAh g\textsuperscript{-1}, indicating the presence of an electrochemically active component that is available for a reductive lithiation reaction without the 1st charging process. Interestingly, these results suggest two unique and distinct phenomena: (i) the pre-activation of the Li2MnO3 component by simple ball milling and (ii) gradual electrochemical activation below 4.3 V. These phenomena are triggered from the surface of the pulverized sample. Previous studies have reported that the Li2MnO3 component was chemically activated by acid treatment to combat the irreversible first-cycle capacity loss of these electrodes upon charging to high potentials.\textsuperscript{6,13} These studies indicate that a simple immersion treatment in an acid solution can accomplish the pre-formation of MnO2 from Li2MnO3, reducing the irreversible capacity loss. However, acid treatment harmed the cyclic performance and rate capability due to unexpected H\textsuperscript{+} ion exchange into the structure.\textsuperscript{6,7} In our study, the preparation of nanosized Li-rich layered oxide by ball milling ensures pre-formation of MnO2 without any H\textsuperscript{+} ion exchange.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Fig. 3 (a) 1st and (b) 2nd charge/discharge curves of each sample between 2 and 4.6 V at 15 mA g\textsuperscript{-1}.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Fig. 4 OCV (open circuit voltage) and CCV (closed circuit voltage) plot of (a) ANL-NMC and (b) BM10, which were acquired with a current flux of 15 mA g\textsuperscript{-1} for 30 min. and a 150 min. time interval during the 1st charging.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Fig. 5 (a) Cycling performance of each sample at 2.0 and 4.3 V and (b) the 50th charge/discharge curves and dQ/dV plots (inset) of each sample between 2 and 4.3 V. The cells were cycled at a constant current with a current density of 15 mA g\textsuperscript{-1}.}
\end{figure}
Fig. 6 shows the rate capability of ANL-NMC, BM10 and BM30 collected at various currents from 15 mA g\(^{-1}\) (0.1 C) to 1500 mA g\(^{-1}\) (10 C). The BM10 and BM30 samples exhibited a better rate capability than as-prepared ANL-NMC. The discharge capacity of the BM10 sample at a high current density (1500 mA g\(^{-1}\), 10 C) retained nearly 60% (~140 mAh g\(^{-1}\)) of the discharge capacity at a low current density of 15 mA g\(^{-1}\) (0.1 C). On the other hand, the discharge capacity of the ANL-NMC sample at a high current density (1500 mA g\(^{-1}\)) is nearly 40% (~87 mAh g\(^{-1}\)) of the discharge capacity at a constant current of 15 mA g\(^{-1}\). These results agree well with the specific surface areas and particle sizes of the samples considering the large number of reaction sites for Li and the short diffusion length of Li. Furthermore, the carbon coatings on these active materials improved the electronic conductivity of the ball milled samples. However, in the case of BM30, a sudden deterioration of the rate capability was observed at current densities greater than 750 mA g\(^{-1}\). Similarly, Fig. 7 shows the discharge capacity of each sample during 50 cycles at a current density of 15 mA g\(^{-1}\). The 50-cycle performance of each sample decreased slightly as the ball milling time increased. The slight increase in the discharge capacity of all samples during the initial few cycles is related to the activation of residual Li\(_2\)MnO\(_3\) phase to the active MnO\(_2\). Although nanosized samples exhibited improved specific capacities and rate capabilities, these materials adversely affected the electrochemical stability in severe conditions such as long-term cycling at a high current, where the rate capability of BM30 deteriorated. The negative effects of ball milling on the electrochemical stability can be simply explained by the structural changes of ball milled samples. As shown in Table 1, the R-factor increased from 0.3546 to 0.4193 with increasing ball milling time, indicating lower hexagonal ordering in the layered structure.\(^{21}\) The well-ordered hexagonal layered structure improves long-term cycling. However, direct mechanical damage by ball milling can lead to defective deformation in the layered structure. Similarly, the defective layered structure with lower hexagonal ordering made maintaining structure under long-term cycling difficult, and also made rapid insertion and extraction of Li\(^+\) (high rate) difficult. Therefore, excessive ball milling treatment time (BM30) harmed the cycle performance and the rate capability at severely high rates, as compared to BM10.

To further understand the degradation mechanism of degradation of the nanosized samples, derivative capacity-voltage (dQ/dV) plots for different cycles were examined, as shown in Fig. 8. Two oxidation peaks, at 4.0 and 4.5 V, were found on the 1st charge in the ANL-NMC plot. These are typical of lithium extraction from the LiNi\(_{0.44}\)Mn\(_{0.31}\)Co\(_{0.25}\)O\(_2\) component and the irreversible delithiation from the Li\(_2\)MnO\(_3\) component that accompanies structural rearrangement, respectively.\(^{3,12}\) For the 1st discharge, two broad but weak reduction peaks were observed between 3 and 4 V, indicating reduction of metal ions (Mn\(^{4+}\) → Mn\(^{3+}\) at 3.4 V, Co\(^{4+}\) → Co\(^{3+}\), Ni\(^{4+}\) → Ni\(^{3+}\) at 3.7 V). In the case of BM10 and BM30, lithium extraction occurred beginning at 3.7 V. The dominant peaks of the 1st discharge at 3.4 V are related to the preferential growth of the spinel component.\(^{20}\) During the 50th charging, the ANL-NMC plot showed a broad oxidation peak between 3.2 V and 3.8 V. For the samples treated by ball milling, the two distinct oxidation peaks in the broad peak occurred at 3.0 V and 3.7 V, and the wider reduction peak was observed between 2.9 V and 3.5 V. The dominant growth of the redox peaks at 2.9 V during charging is related to the formation of the spinel component in the Li-rich layered structure.\(^{22-24}\) The increased prevalence of the spinel component may cause internal stress because of the phase transition from tetragonal to cubic. Therefore, capacity loss during cycling is partially due to the phase transition from layered MnO\(_2\) to spinel LiMn\(_2\)O\(_4\). In addition, the oxidation peak of the ball milled sample at 4.5 V increased. Okubo et al. reported a similar phenomenon for nanocrystalline LiCoO\(_2\).\(^{15}\) The cycle performance worsened with decreasing particle size of nanocrystalline LiCoO\(_2\) and was worse than
that of bulk LiCoO₂ because of the ease with which particles reacted with electrolytes at high voltages. Thus, using nanoparticles smaller than a critical size makes it difficult to maintain the cyclability and electrochemical stability at an extremely high rate.

The structural changes on the surface of a pulverized particle were investigated by XPS analysis. Fig. 9 shows the O 1s XPS spectra of the samples. A typical oxide ion (O²⁻) peak in the bulk is observed at 529.2 eV for all samples. An additional peak was observed for the ball milled samples at 531.3 eV, which is known to be from lithium carbonate, and the intensity of this peak increased with increasing ball milling time. Similarly, C 1s spectra revealed that a peak at 285 eV was observed for the ball milled samples at 531.3 eV, which is attributed to carbon atoms in C–H/C–C bonds. An additional peak at 531.3 eV was observed for the ANL-NMC sample (Fig. 10a), which is attributed to carbonates in CO₃²⁻ species (Fig. 10b). This result suggests the formation of a Li₂CO₃ component on the surface due to mechanical pulverization. The spinel component in the structure was formed by the conversion of Li₂MnO₃. Excess lithium in the Li₂MnO₃ would consequently form lithium carbonate on the surface. The lithium carbonate peak at 531 eV did not result from the addition of carbon during ball milling, because the peak was observed in samples ball milled with and without carbon. Although more evidence is needed for verification, we speculate that the C source forming the Li₂CO₃ phase might come from the atmosphere including CO₂ gas. The formation of lithium carbonate is intimately related to the structural change on the surface induced by mechanical ball milling. As evidence for this relationship, the 531 eV peak of samples ball milled for 30 min without carbon was stronger than that for samples ball milled for 30 min with carbon, thus indicating that co-pulverization with carbon effectively relieves direct mechanical damage to the surface by ball milling (Fig. 9). As reported in Table 1, the lattice parameters of both the a and c axes increased after ball milling treatment. The increase in both the a and c axis parameters indicates partial spinel formation in the layered structure because the crystal structure of spinel is based on a cubic lattice (a = b = c) rather than a hexagonal lattice (a = b ≠ c). In addition, increasing

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**Fig. 8** dQ/dV plots for the (a) 1st and (b) 50th cycles of lithium cells with ANL-NMC, BM10, and BM30 positive electrodes.

**Fig. 9** O 1s X-ray photoelectron spectra from ANL-NMC, BM10 with carbon, BM30 with carbon, and BM30 without carbon prepared by ball milling treatment.

**Fig. 10** C 1s X-ray photoelectron spectra from ANL-NMC and BM30 without carbon prepared by ball milling treatment.
ball milling time led to a relatively large decrease in the $I_{(003)}/I_{(104)}$ ratio for all samples, as shown in Table 1. From previously reported results, the decrease in the $I_{(003)}/I_{(104)}$ ratio indicates a significant amount of cation mixing in the layered structure. Therefore, the partial cation rearrangement after ball milling was related to the formation of spinel structure within the layered structure.

To obtain information on the structural and chemical changes on the surface during cycling, ex-situ XPS spectroscopy was performed after the 20th cycle. Yabuuchi et al. reported the formation of oxygen containing species such as lithium carbonate, which accumulated on the electrode surface after cycling. Our experiments also confirmed by products, including sub-peaks corresponding to C–O, C–F, and –CH$_2$–, as shown in Fig. S5, ESI. However, the peaks disappeared after Ar$^+$ etching, indicating that these products were only formed on the surface. Fig. 11 shows ex-situ XPS spectra collected in Ni 2p from ANL-NMC, BM10, and BM30 electrodes after the 20th cycle. The XPS spectra of the electrodes were collected after 30 s Ar$^+$ etching. Although there was no significant difference among the Mn and Co XPS spectra collected from the various samples, the intensity ratio of the two representative Ni 2p peaks was significantly different. These two peaks were determined to be nickel fluoride (NiF$_2$) at 858.8 eV and Ni$^{2+}$ at 855.5 eV. The NiF$_2$ peak was dominant in the ANL-NMC spectrum; however, the NiF$_2$ peak disappeared with increasing ball milling time, and the Ni$^{2+}$ fraction increased. Fig. S6, ESI$^+$ presents F 1s X-ray photoelectron spectra from ANL-NMC and BM30 electrodes during depth profiling 10 nm from the surface. LiPF$_6$ salt absorbed from the electrolyte was found on the surface; however, the LiPF$_6$ peak on the surface of both samples disappeared after Ar$^+$ etching. For ANL-NMC, the main peak identified as LiF shifted from 685.8 eV to 685.4 eV with increasing etch depth, corresponding to NiF$_2$. The F 1s XPS spectra again confirmed the existence of the NiF$_2$ layer. Conversely, only the LiF peak at 685.8 eV remained stationary with increasing etching depth. Therefore, these results indicate that the reaction with the electrolyte leads to the minimal surface formation of nanosized Li-rich layered oxide during cycling. NiF$_2$ originates from the reaction with LiPF$_6$, salt in the electrolyte and is critical to the stability of the cycling performance, as it acts as a protective passivating layer on the electrode surface during cycling. Similarly, Myung et al. suggested that a surface-coated metal oxide (MO$_x$) on the active material gradually transforms to a metal fluoride layer (MF$_x$) on the surface, which helps to protect the active material from metal dissolution by acidic HF species in the electrolyte. In addition, a fluoride substituted positive electrode material has been reported to exhibit stable cycling and enhanced thermal stability, partially due to the formation of metal fluoride on the surface. In the present study, nanosized samples such as BM10 and BM30 were observed to suppress the formation of a protective NiF$_2$ layer on the surface. When exposed to acidic HF, the cycling performance of the nanosized samples deteriorated with increasing ball milling time.

Despite its poor cycling stability, the nanosized Li-rich layered oxide is not only able to significantly improve electrochemical performance (e.g., high 1st discharge capacity, excellent rate capability at high current density even under 1500 mA g$^{-1}$, improved coulombic efficiency), but it can also effectively reduce the internal resistance caused by oxygen release during the electrochemical activation of Li$_2$MnO$_3$ on 1st charging. The simple ball milling strategy used in this work can provide some useful ideas to improve our understanding of the effects of nanosized Li-rich layered oxide materials.

Conclusions

In summary, nanosized Li-rich layered oxide/carbon composite materials were successfully prepared by ball milling with conductive carbon. Using this strategy, nanosized Li-rich layered oxide materials were easily obtained by the pulverization of microsphere-shaped Li-rich layered oxide materials. In addition, coating the active material with carbon significantly enhanced the electronic conductivity. The ball milled samples exhibited better electrochemical performance (e.g., high 1st discharge capacity of 250 mAh g$^{-1}$, excellent rate-capability, even at a high current of approximately 1500 mA g$^{-1}$ and improved coulombic efficiency on 1st cycling) than the as-prepared ANL-NMC. This improvement was primarily due to the short Li$^+$ diffusion length within nanosized particles and because the particles provide innumerable reaction sites for lithium ions. Furthermore, the ball milled samples were found to significantly reduce the internal resistance caused by the release of oxygen during the 1st charging process above 4.5 V. Interestingly, (i) the Li$_2$MnO$_3$ component was pre-activated, and (ii) gradual electrochemical activation under 4.3 V was also observed for the nanosized samples prepared by simple
ball milling. However, a ball milled sample of an insufficient size exhibited a lower rate capability at a current higher than 750 mA g$^{-1}$. Moreover, the cycle performance decreased with decreasing particle size. Degeneration during cycling is related to (i) the structural deformation of hexagonal ordering; (ii) the growth of the spinel component, which causes internal stress by a phase transition from tetragonal to cubic; and (iii) the insufficient formation of a protective NiF$_2$ layer on the surface of the active material.

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Notes and references