

Supporting Information

Electrochemical Properties of Nanosized Li-rich Layered Oxide as Positive Electrode Materials for Li-Ion Batteries

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S.1 SEM images of as-prepared and ball milled ANL-NMC samples (BM10 and BM30) are shown in Figure S1. No significant effects of ball milling time are observed, but BM30 particles were pulverized to a greater degree than BM10 without partial agglomeration.

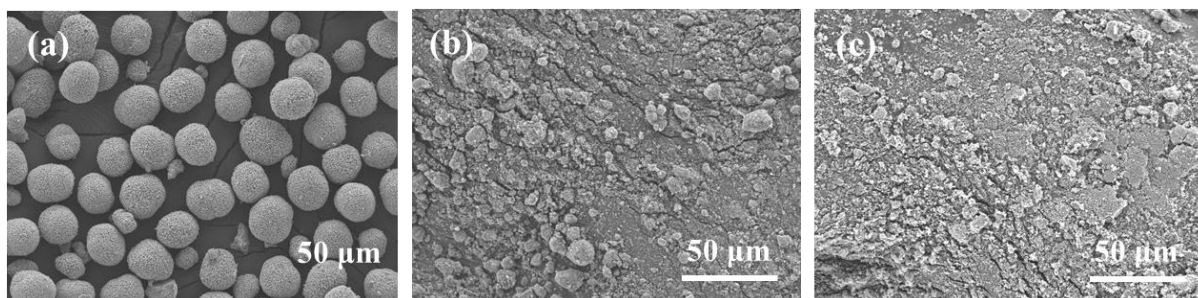


Figure S1. Surface morphologies of (a) ANL-NMC, (b) BM10, and (c) BM30.

S.2 Similar to BM30, the BM10 sample with a mean particle size of 200 nm was connected and uniformly mixed with nanosized amorphous carbon webs (~ 20 to 30 nm). Relatively short ball milling times of 10 and 30 min were sufficient to prepare the nanosized Li-rich layered oxide/C composites.

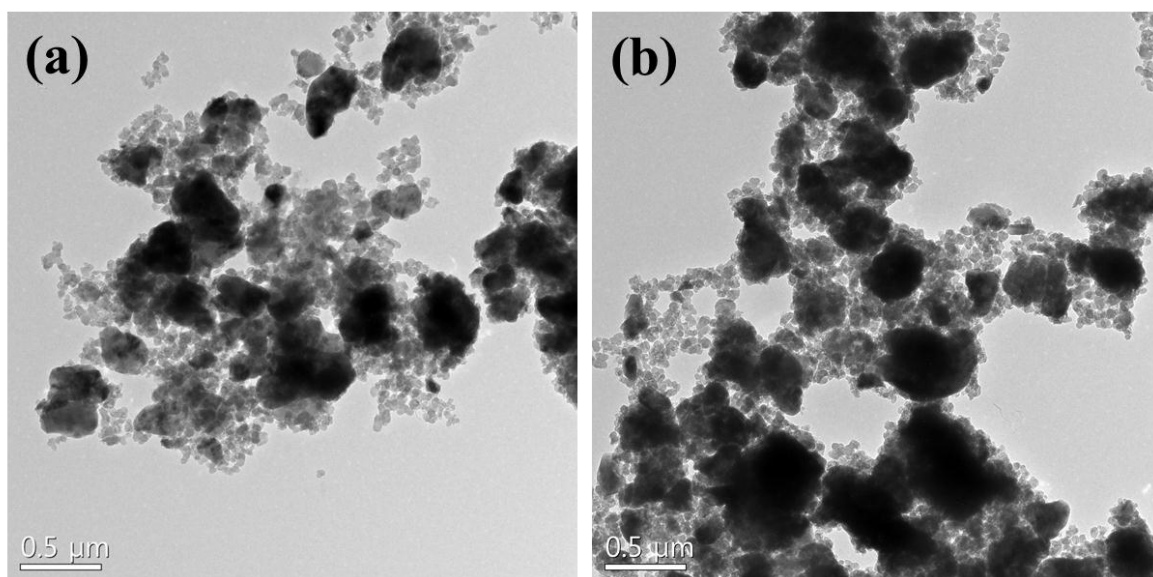


Figure S2. TEM images of samples subjected to ball milling for (a) 10 min and (b) 30 min.

S.3 Figure S3 presents an open-circuit voltage/constant current voltage (OCV/CCV) plot of BM30 obtained from a galvanostatic intermittent titration (GITT) experiment. The degree of difference between OCV and CCV was similar between BM30 and BM10. (Fig. 4) The internal resistance of the BM30 sample induced by oxygen release above 4.5 V was sufficiently lower for BM30, and the difference between OCV and CCV was also decreased at the beginning of positive electrode charging due to facile lithium extraction.

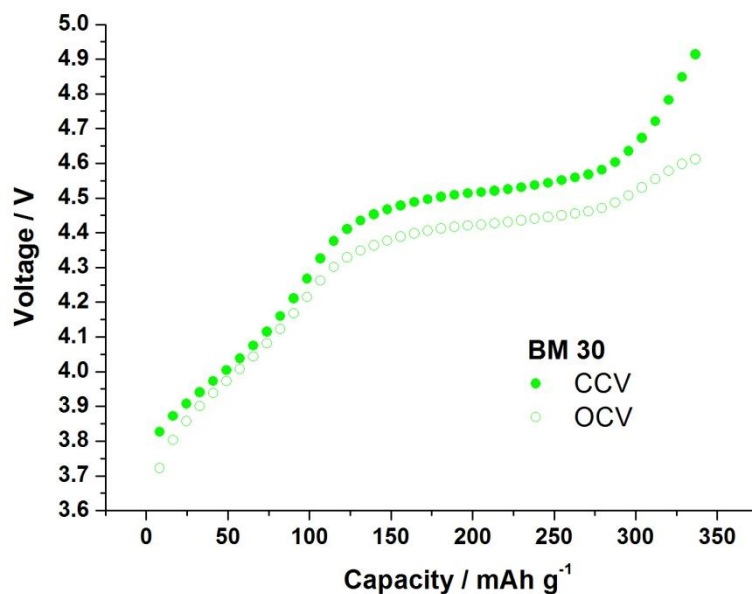


Figure S3. The OCV (open circuit voltage) and CCV (closed circuit voltage) plot of BM30 acquired with a current flux of 15 mA/g for 30 min and a 150-min time interval during the 1st charging.

S.4 To help understand the pre-activation of Li_2MnO_3 after ball milling, the first discharge from OCV to 2 V was performed for each sample “without initial charging”, as shown in Figure S4. In contrast to ANL-NMC, BM30 delivered a discharge capacity of 9 mAh/g, indicating an increase in the electrochemically active component available for reductive lithiation without the 1st charging process. For example, Li^+ can be inserted into the spinel component with the reduction of Mn ions in the structure ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}$) without the 1st charging process.

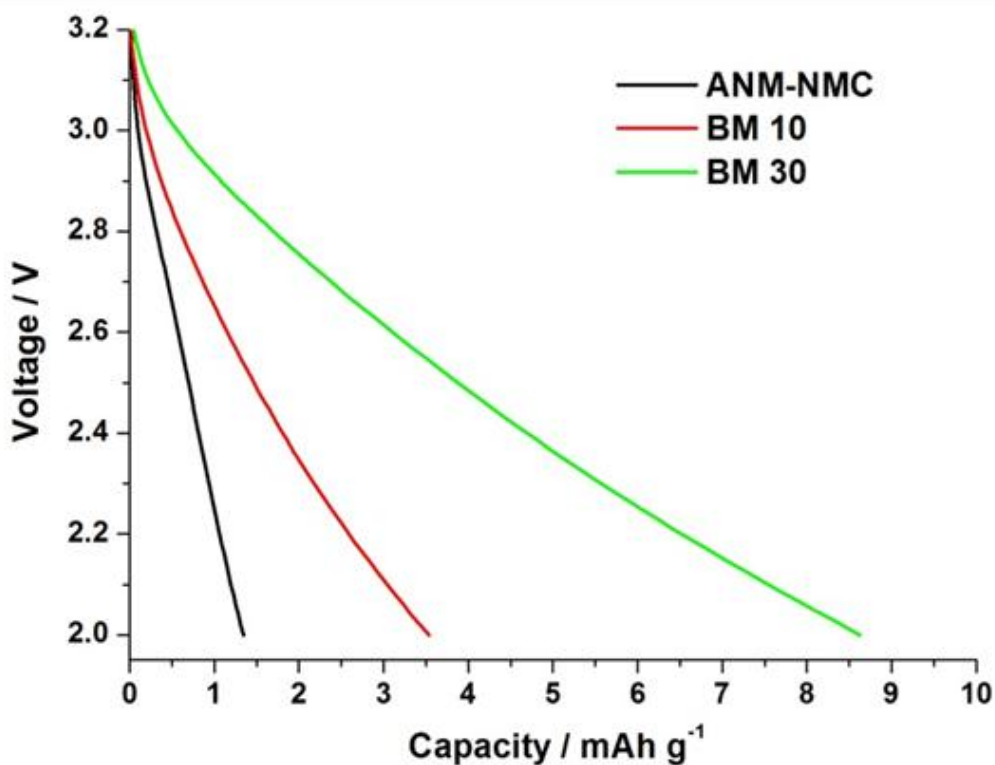


Figure S4. Voltage profiles for the initial discharge of each sample to 2.0 V. The cells were cycled at a constant current with a current density of 15 mA/g.

S.5 The formation of oxygen-containing species, such as lithium carbonate, which accumulated on the electrode surface after cycling. By-products were also confirmed in our experiments, corresponding to the sub-peaks CO_3^{2-} , C-F, and $-\text{CH}_2-$, as shown in Figure S5. However, the peaks disappeared after Ar^+ etching, indicating that the products only formed on the surface.

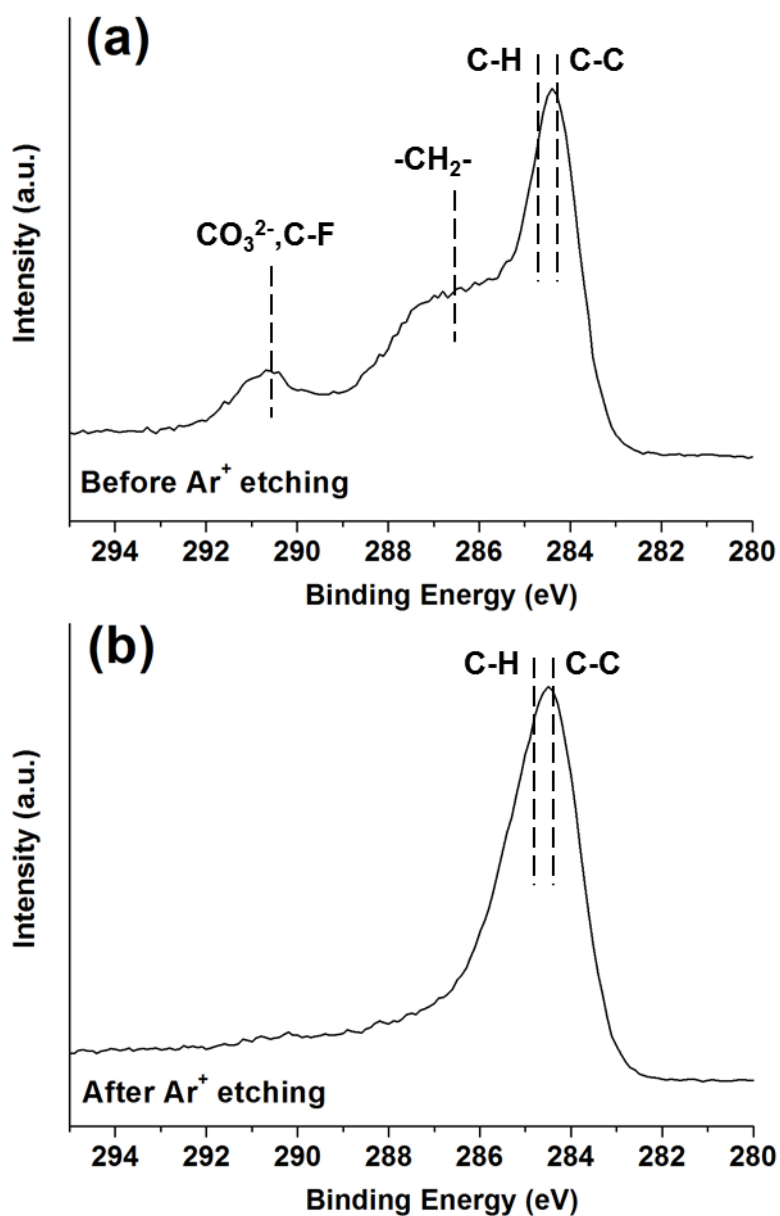


Figure S5. C 1s X-ray photoelectron spectra collected from ANL-NMC electrodes after the 20th cycle, (a) before and (b) after Ar^+ etching.

S.6 Figure S6 shows F 1s X-ray photoelectron spectra collected from ANL-NMC and BM30 electrodes for depth profiles 10 nm from the surface. LiPF_6 salt absorbed from the electrolyte was found on the surface; however, the LiPF_6 peak disappeared from the surface of both samples 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, the LiF peak at 685.8 eV was the only peak that did not shift with increasing etching depth. Therefore, these results indicate that a minimal amount of NiF_2 is formed on the surface of nanosized Li-rich layered oxide during cycling, resulting from the reaction with the electrolyte.

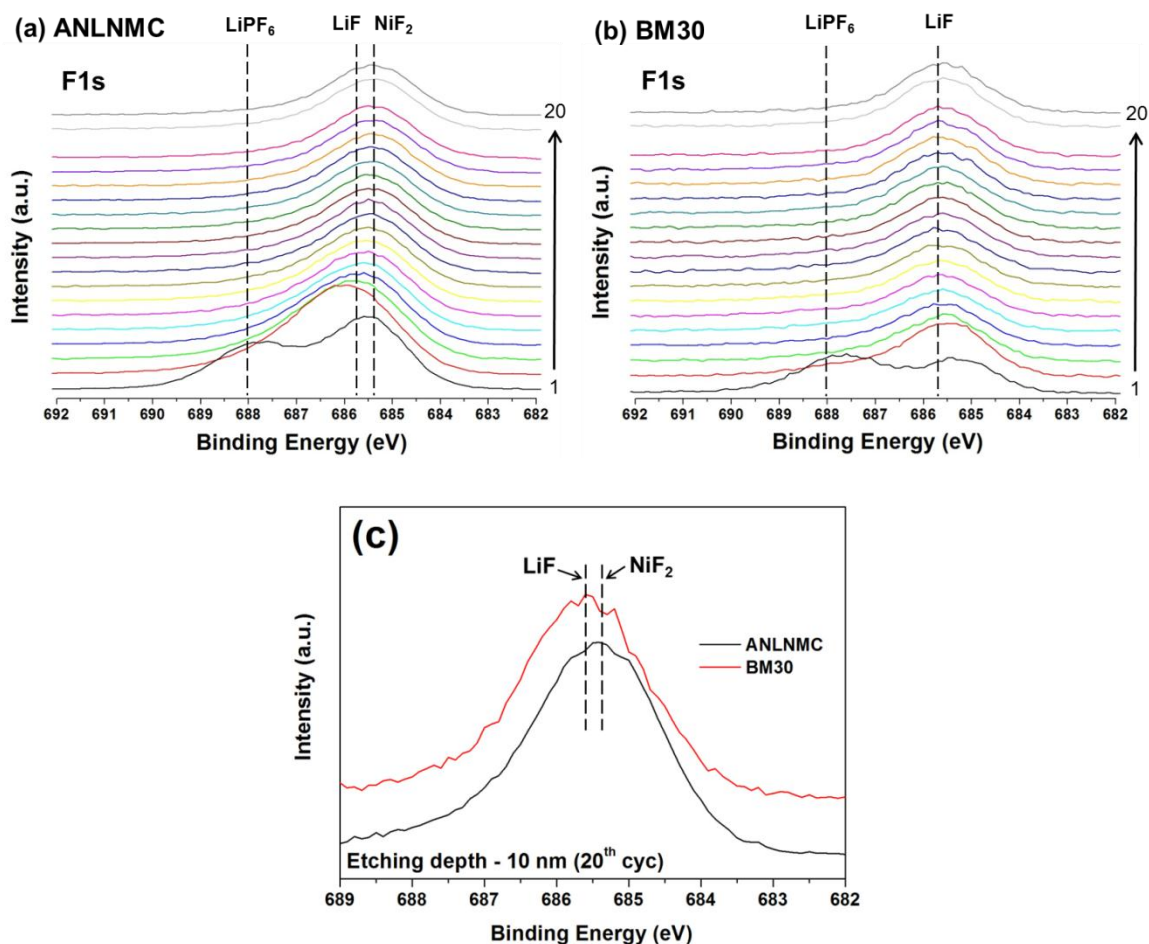


Figure S6. X-ray photoelectron spectra collected in the F 1s region from (a) ANL-NMC and (b) BM30 electrodes, and (c) their extended X-ray photoelectron spectra. All samples were tested after the 20th cycle, and the XPS spectra of the electrodes were collected during a depth profile.

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