

Supplementary Materials

NH₄BF₄-assisted conversion of alkaline surface species enables air-stable Li₅FeO₄ cathode prelithiation additives

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Optimization of the NH_4BF_4 treatment condition

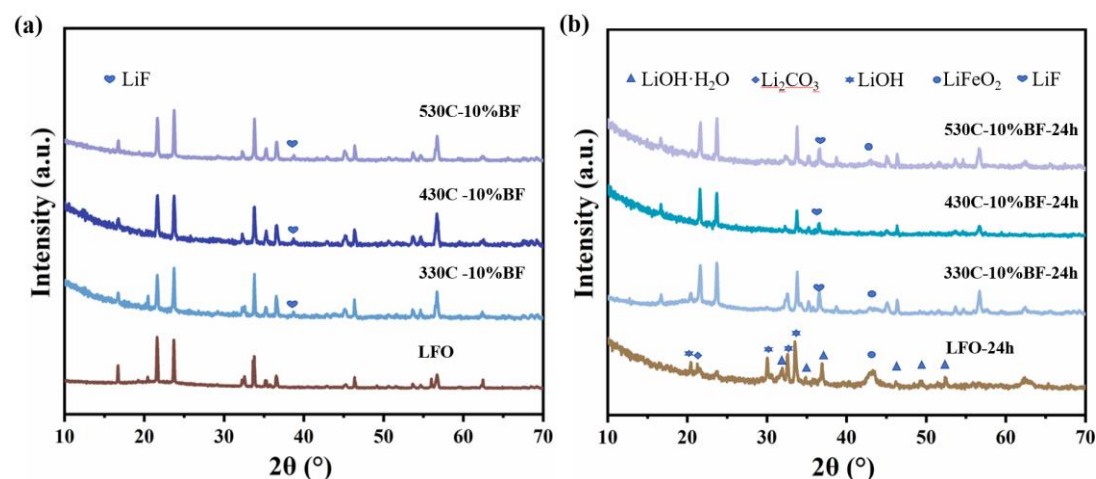
The NH_4BF_4 -assisted treatment condition was optimized by varying the calcination temperature and NH_4BF_4 content. The temperature was first screened at a fixed NH_4BF_4 content of 10 wt%. As shown in Figure S1a, the main diffraction peaks of LFO are largely retained after treatment at 330, 430, and 530 °C. A weak LiF signal can be observed in the treated samples, indicating the occurrence of fluorination during calcination. After humid-air exposure for 24 h, pristine LFO shows obvious impurity peaks assigned to $\text{LiOH}\cdot\text{H}_2\text{O}$, Li_2CO_3 , LiOH , and LiFeO_2 , while these impurity features are much weaker in the BF-treated samples (Figure S1b). The XRD patterns of the three treated samples are broadly similar, suggesting that XRD alone cannot clearly distinguish the optimal treatment temperature.

The electrochemical profiles provide a more direct comparison of the lithium-donating capability. Before exposure, the samples treated at different temperatures show typical irreversible delithiation behavior of LFO-based prelithiation additives (Figure S2a). After humid-air exposure, however, their retained charge capacities differ clearly (Figure S2b). Among them, the sample treated at 430 °C delivers the most favorable charge capacity after exposure while maintaining the characteristic delithiation profile. Therefore, 430 °C was selected as the optimized calcination temperature.

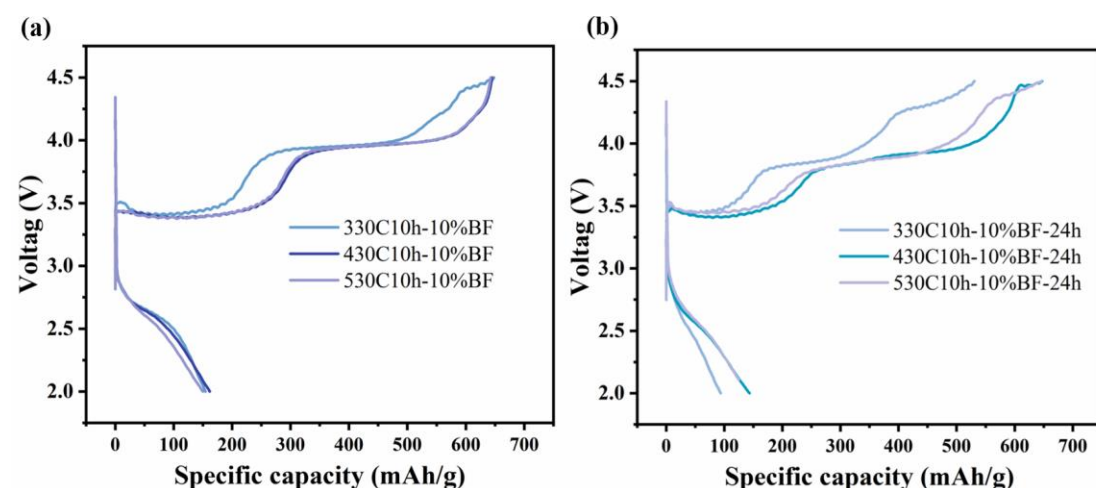
The NH_4BF_4 content was then optimized at 430 °C. As shown in Figure S3a, the main LFO phase is retained for the samples treated with 5, 10, and 15 wt% NH_4BF_4 . After humid-air exposure, all BF-treated samples show suppressed impurity formation compared with LFO-24h (Figure S3b). Similar to the temperature series, the XRD difference among the samples with different NH_4BF_4 contents is not pronounced. The electrochemical profiles show a clearer difference. Before exposure, the three samples exhibit comparable delithiation profiles (Figure S4a). After exposure, the 10 wt% sample retains a higher charge capacity than the 5 and 15 wt% samples (Figure S4b). This result indicates that 10 wt% NH_4BF_4 gives the best balance between humid-air

stability and lithium-donating capacity under the present treatment condition.

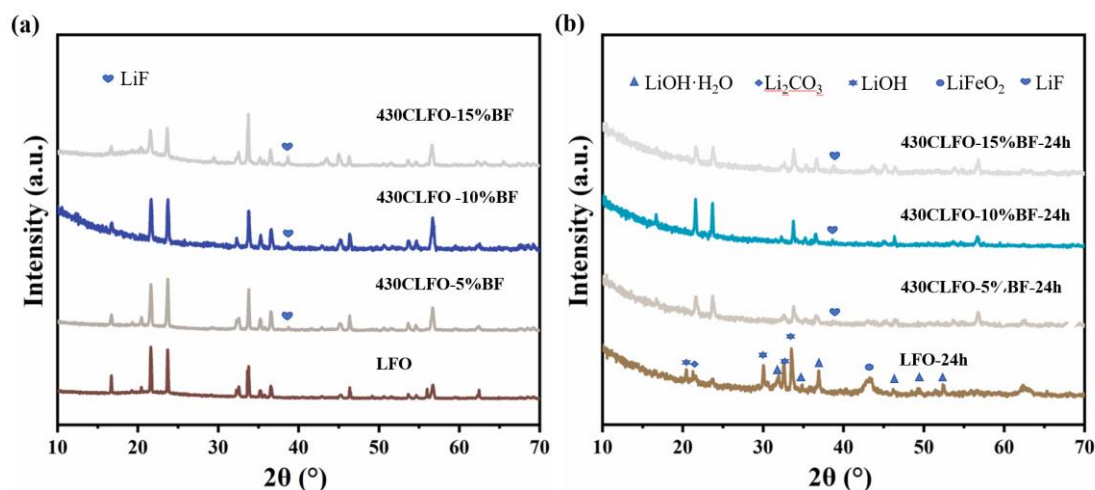
Based on these results, LFO treated with 10 wt% NH_4BF_4 at 430 °C for 10 h was selected as the optimized sample and is denoted as LFO-BF in the main text.



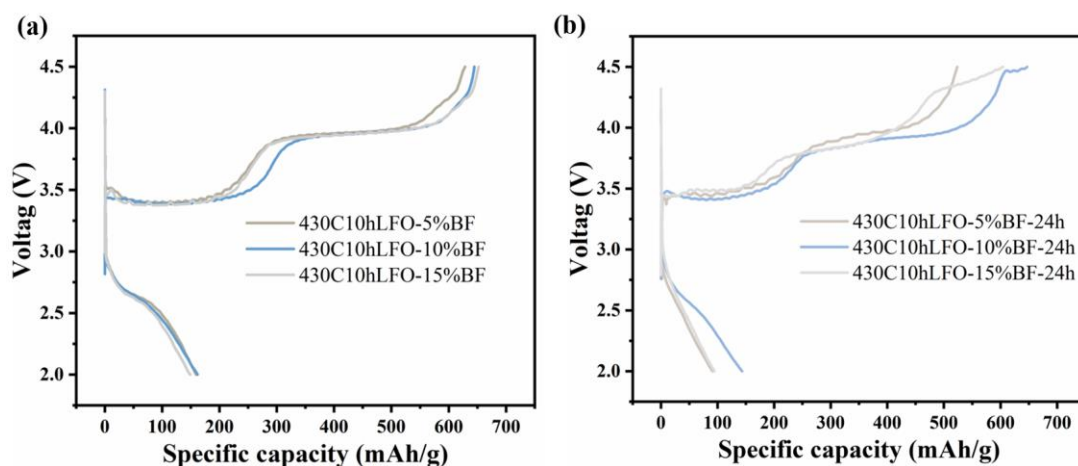
Supplementary Figure 1. (a) XRD patterns of pristine LFO and LFO treated with 10 wt% NH_4BF_4 at 330, 430, and 530 °C for 10 h. (b) XRD patterns of the corresponding samples after humid-air exposure for 24 h. The reference impurity peaks of $\text{LiOH}\cdot\text{H}_2\text{O}$, Li_2CO_3 , LiOH, LiFeO_2 , and LiF are marked.



Supplementary Figure 2. (a) Initial voltage profiles of samples treated with 10 wt% NH_4BF_4 at 330, 430, and 530 °C for 10 h. (b) Initial voltage profiles of the corresponding samples after humid-air exposure for 24 h.



Supplementary Figure 3. (a) XRD patterns of pristine LFO and LFO treated with 5, 10, and 15 wt% NH_4BF_4 at 430 °C for 10 h. (b) XRD patterns of the corresponding samples after humid-air exposure for 24 h. The reference impurity peaks of $\text{LiOH}\cdot\text{H}_2\text{O}$, Li_2CO_3 , LiOH , LiFeO_2 , and LiF are marked.

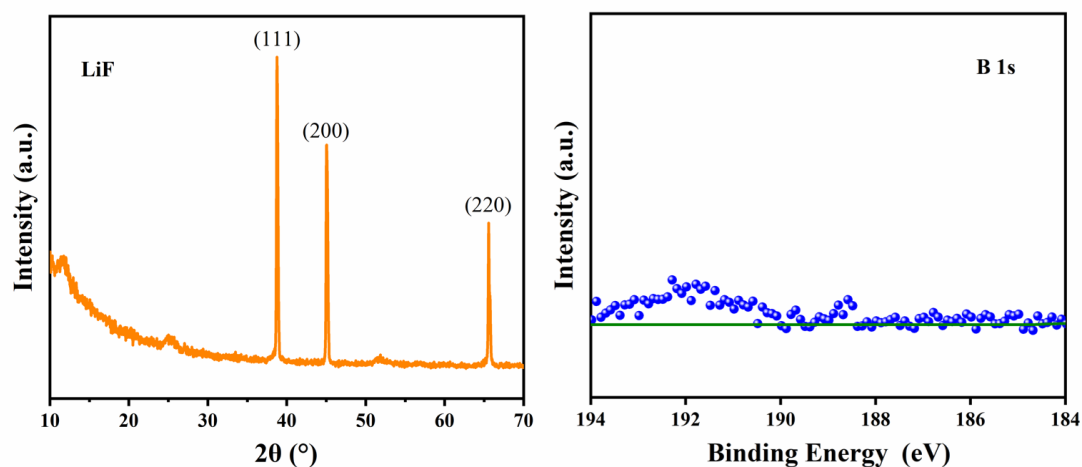


Supplementary Figure 4. (a) Initial voltage profiles of samples treated with 5, 10, and 15 wt% NH_4BF_4 at 430 °C for 10 h. (b) Initial voltage profiles of the corresponding samples after humid-air exposure for 24 h.

Model reaction between NH_4BF_4 and LiOH

To examine the reaction between NH_4BF_4 -derived species and alkaline Li species, an equimolar $\text{NH}_4\text{BF}_4/\text{LiOH}$ mixture was heated at 430 °C for 10 h under Ar. The resulting solid product exhibits characteristic LiF reflections in XRD, whereas only a weak B 1s signal is detected by XPS (Figure S5). These results support LiF formation

accompanied by limited retention of B-containing solid species under the treatment conditions.

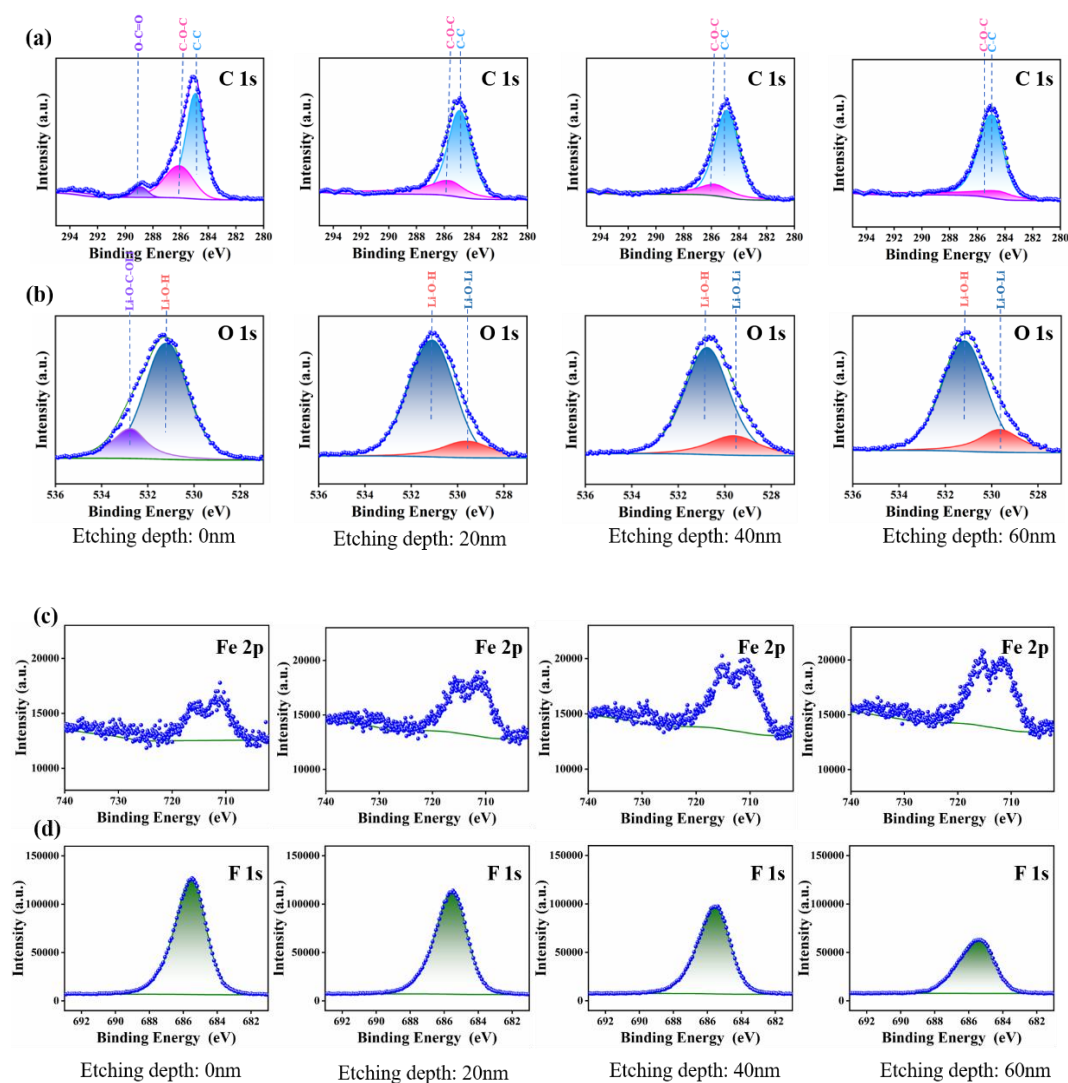


Supplementary Figure 5. (a) XRD pattern and (b) B 1s XPS spectrum of the solid product obtained by heating an equimolar $\text{NH}_4\text{BF}_4/\text{LiOH}$ mixture at 430 °C under Ar. The characteristic reflections of LiF are marked in (a), while only a weak B 1s signal close to the background is observed in (b).

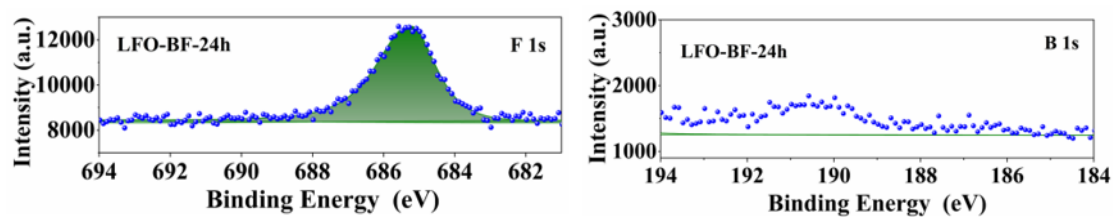
XPS depth profiling of LFO-BF

To further examine the depth distribution of the surface-modified species, XPS spectra were collected after Ar-ion etching to estimated depths of 0, 20, 40, and 60 nm. As shown in Figure S6, the F 1s intensity gradually decreases with increasing etching depth, while the Fe 2p signal becomes more prominent toward the particle interior. The C 1s spectra show a progressive reduction in surface carbonate/oxygen-containing carbon species, and corresponding changes are observed in the O 1s spectra. These depth-dependent changes indicate that the fluorinated species are preferentially concentrated near the particle surface rather than uniformly distributed throughout the bulk. It should be noted that the approximately 25 nm surface-modified region observed by HRTEM represents a locally distinguishable region at the examined particle edge rather than a sharp compositional boundary. The persistence of the F signal at greater estimated etching depths therefore does not contradict the TEM observation, but instead indicates a gradual decrease in fluorine

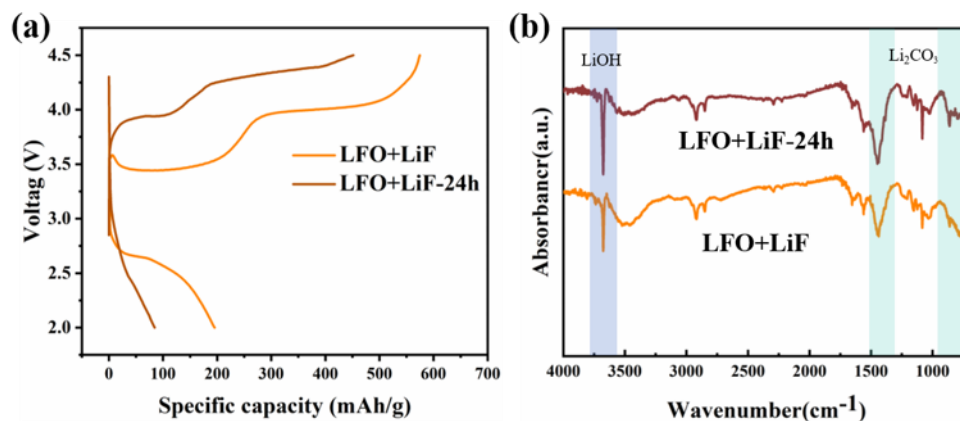
concentration from the outer surface toward the interior.



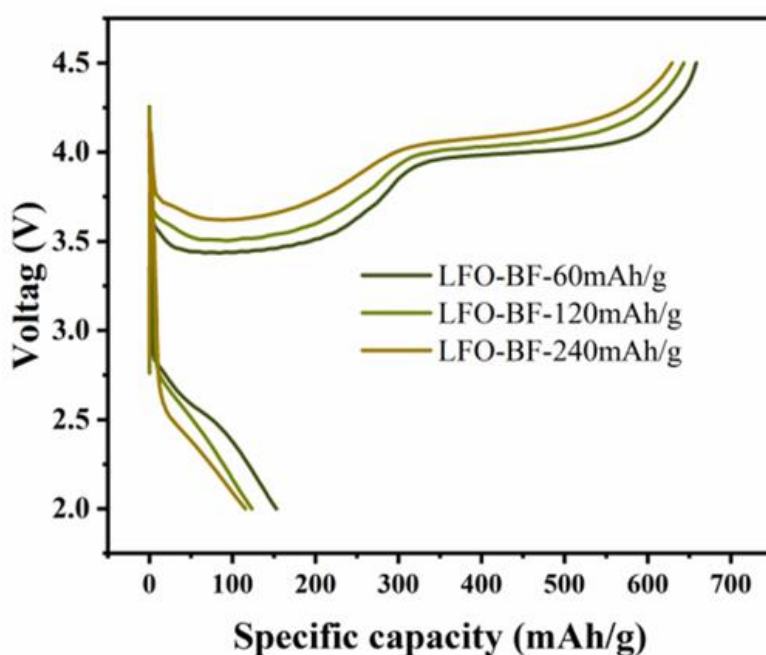
Supplementary Figure 6. (a) C 1s, (b) O 1s, (c) Fe 2p, and (d) F 1s XPS spectra of LFO-BF collected at estimated etching depths of 0, 20, 40, and 60 nm.



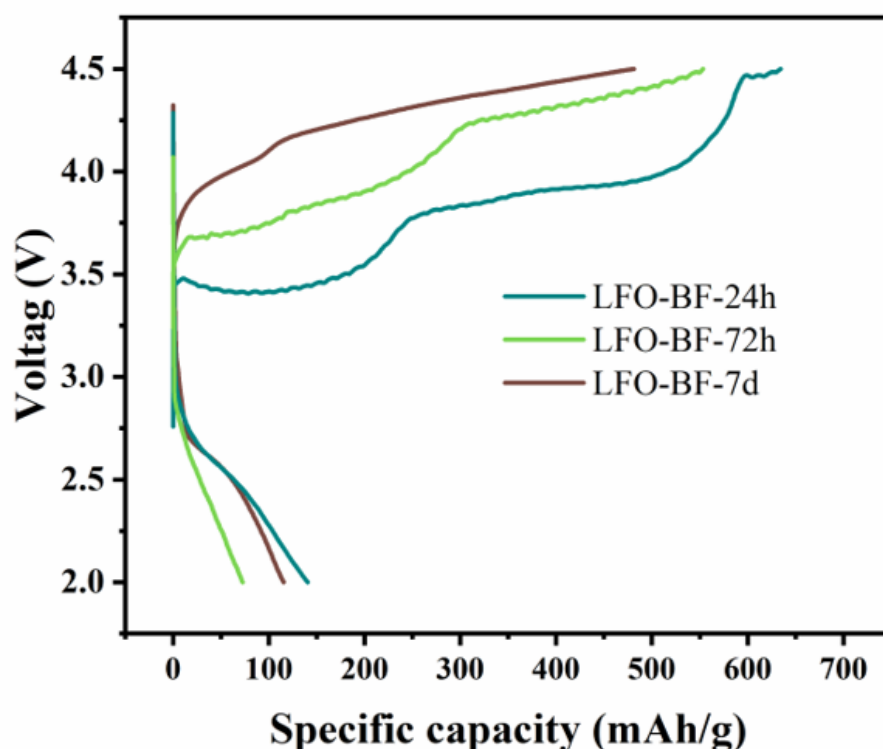
Supplementary Figure 7. F 1s and B 1s XPS spectra of LFO-BF after humid-air exposure for 24 h.



Supplementary Figure 8. Physical LiF-mixing control. (a) Initial charge-discharge profiles of LFO physically mixed with LiF before and after humid-air exposure at 25 °C and 60% RH for 24 h. (b) Corresponding FTIR spectra before and after exposure, showing enhanced hydroxyl- and carbonate-related absorption bands after humid-air exposure.

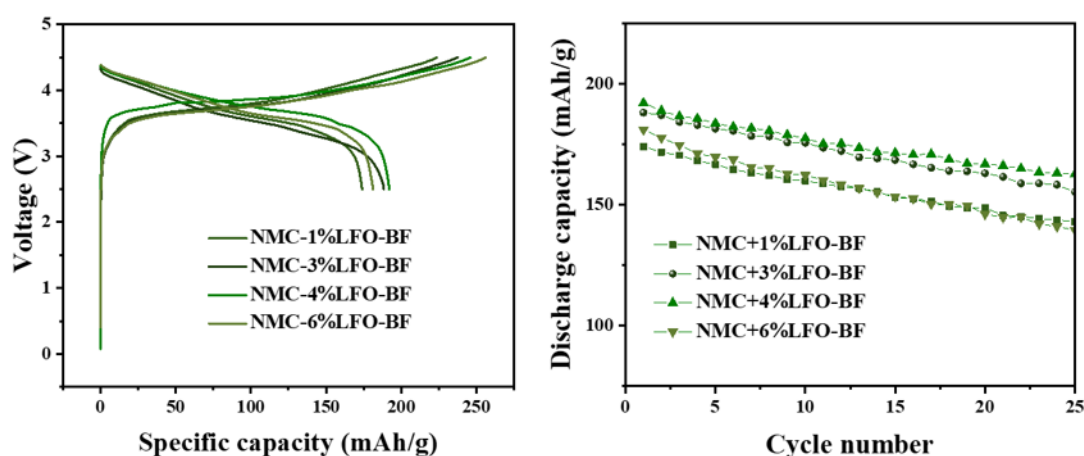


Supplementary Figure 9. Initial charge-discharge profiles of LFO-BF at current densities of 60, 120, and 240 mA g⁻¹.



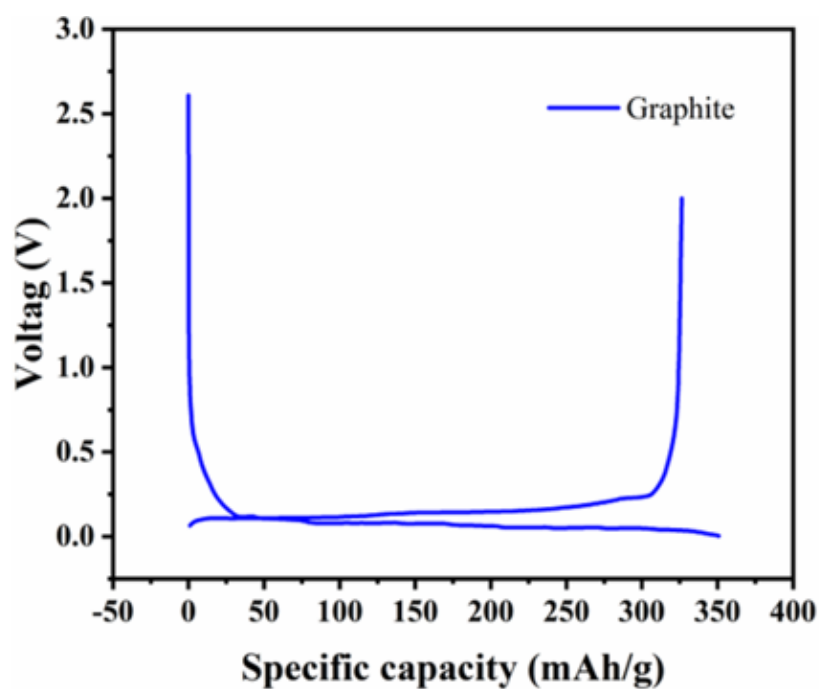
Supplementary Figure 10. Initial voltage profiles of LFO-BF after exposure to humid air at 60% RH for 24 h, 72 h, and 7 days, showing the gradual capacity loss and increased polarization with prolonged exposure.

The long-term humid-air stability of LFO-BF was further evaluated by extending the exposure time at 25 °C and 60% RH to 72 h and 7 days. The charge capacity decreases progressively to 553.3 mAh g⁻¹ after 72 h and 481.1 mAh g⁻¹ after 7 days. Meanwhile, the voltage profiles exhibit increasingly pronounced polarization, with the originally distinct delithiation plateaus becoming progressively less defined and evolving toward a sloping profile. This evolution suggests that, although the NH₄BF₄-derived surface modification markedly retards the loss of accessible lithium, prolonged exposure still induces surface/interfacial degradation and increasingly sluggish delithiation kinetics.



Supplementary Figure 11. Initial charge-discharge profiles and cycling performance of NMC//graphite full cells containing 1, 3, 4, and 6 wt% LFO-BF.

The influence of LFO-BF loading on the full-cell performance was evaluated using 1, 3, 4, and 6 wt% additive contents (Figure S11). Increasing the additive content generally increases the first-charge capacity because more sacrificial lithium is available. However, the increase in charge capacity at higher LFO-BF contents is not accompanied by a proportional increase in reversible discharge capacity. Among the tested compositions, the cell containing 4 wt% LFO-BF shows the most favorable balance between lithium compensation and reversible capacity, and this loading was therefore selected for the full-cell cycling measurements.



Supplementary Figure 12. First-cycle lithiation/delithiation profile of the graphite electrode measured in a Li half cell. The graphite electrode delivers lithiation and delithiation capacities of approximately 350 and 325 mAh g⁻¹, respectively, corresponding to an initial Coulombic efficiency of approximately 93%.