Supplementary Information (SI) for Journal of Materials Chemistry A.
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Supporting Information

Ultrastable LiF/Carbon Nanocomposites as Sacrificial Additives for Enhancing the Lifespan of Anode-Free Lithium Metal Batteries

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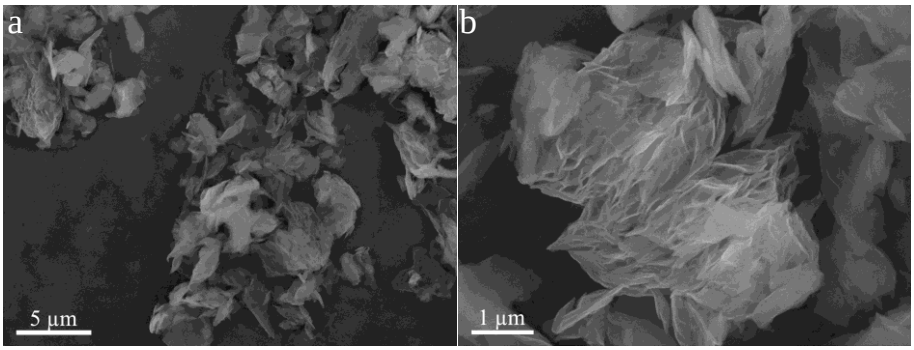

Figure S1 (a) The SEM image of the CF material. (b) Magnified area of the particle showing the porous structure.

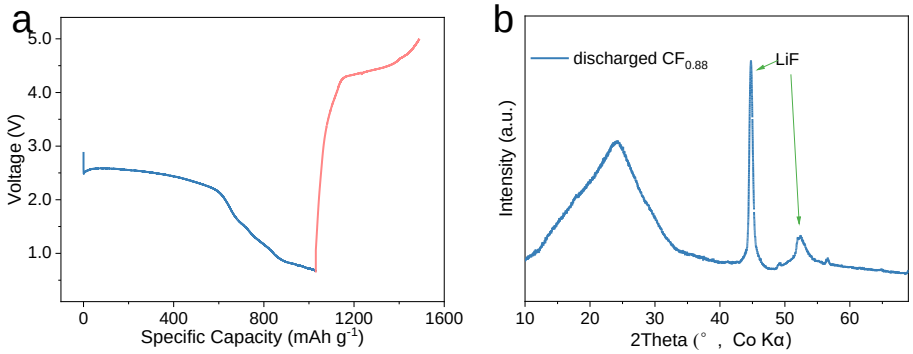

Figure S2 (a) The discharge/charge curve of carbon fluoride. (b) The XRD pattern of the carbon fluoride after discharge.

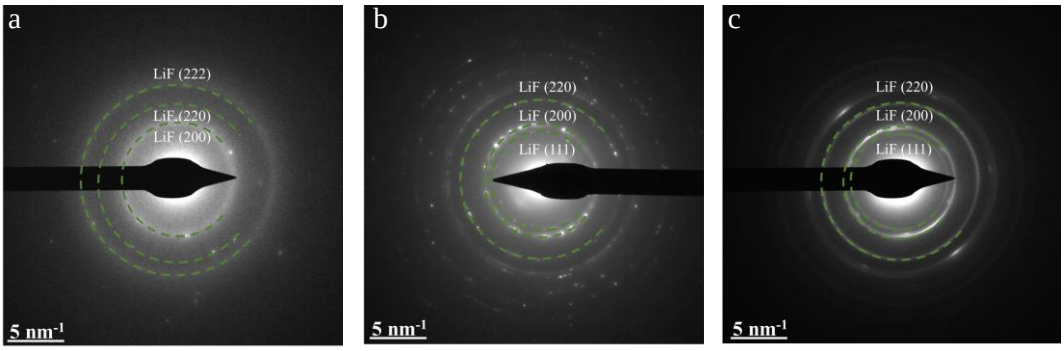

Figure S3 The SAED patterns corresponding to (a) Figure 1c, (b) Figure 1g and (c) Figure 1k.

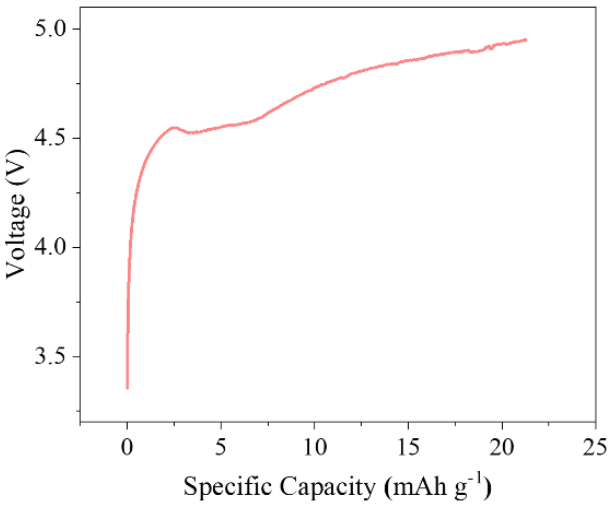

Figure S4 The charge curve of carbon black material with a current density of 25 mA g^{-1}.

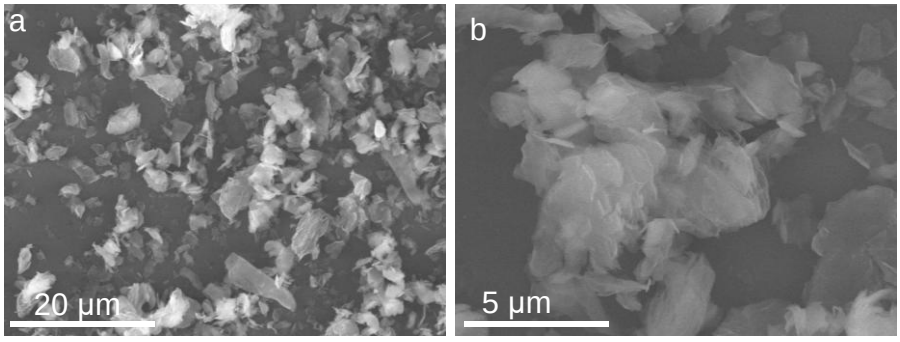

Figure S5 (a) The SEM image of LiF-NDs/C. (b) The magnified image.

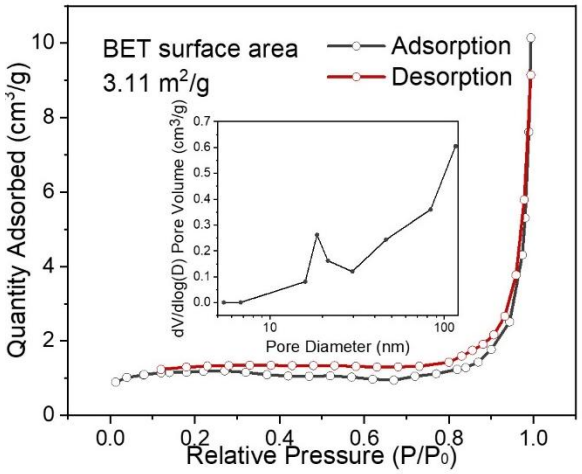

Figure S6 N_2 adsorption-desorption isotherms of LiF-NDs/C. Inset figure is the corresponding pore volume distribution.

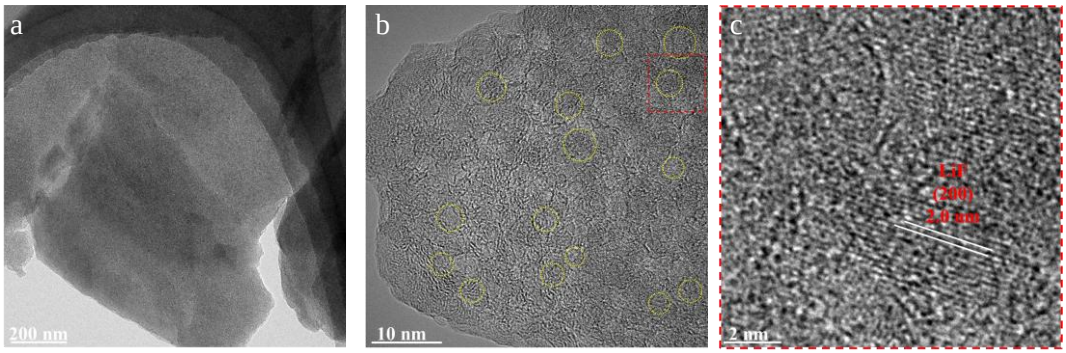

Figure S7 (a) The bright-field image of LiF/C NDs. (b) The HRTEM image of of LiF/C NDs. (c) The enlarged view of the marked region in Figure S7b by the red rectangle.

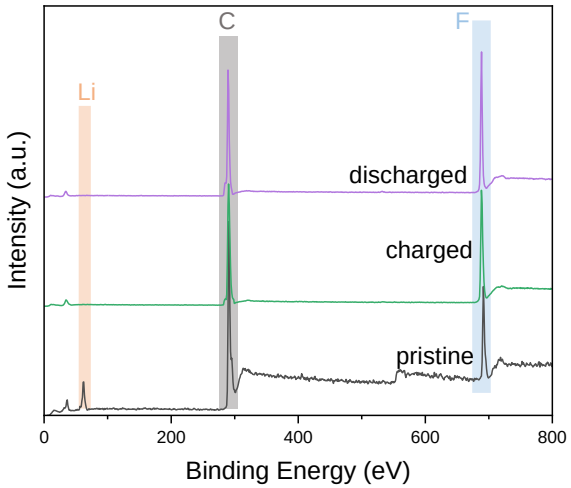

Figure S8 XPS spectra of LiF-NDs/C at different cycle state.

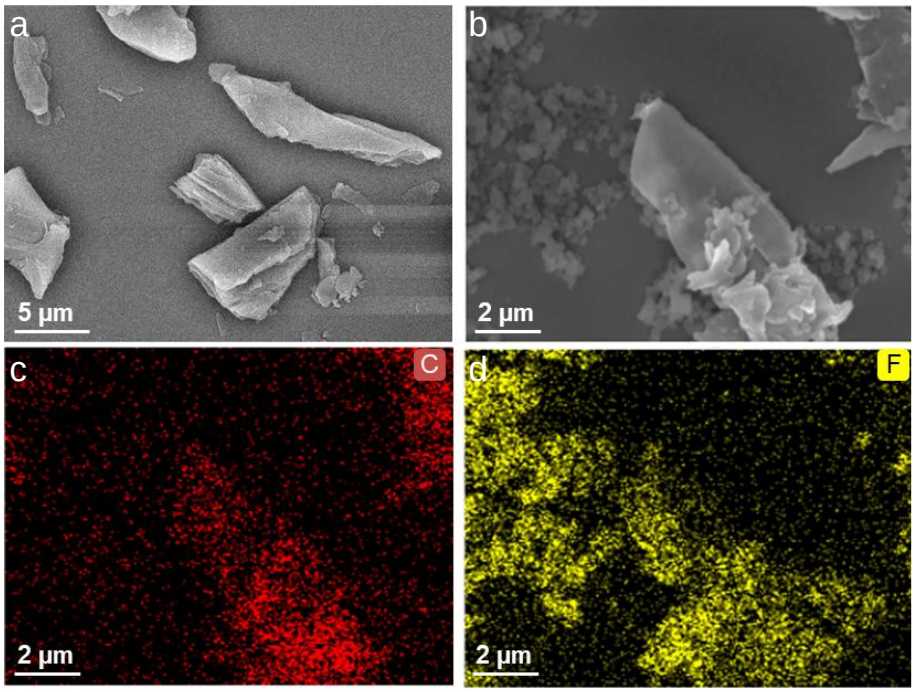

Figure S9 (a) The SEM image of carbon fluoride bulk material. (b) The SEM image of carbon fluoride bulk after lithiation of 1 M Li/Bp and the corresponding energy dispersive X-ray spectra with the elemental maps of (c) C and (d) F.

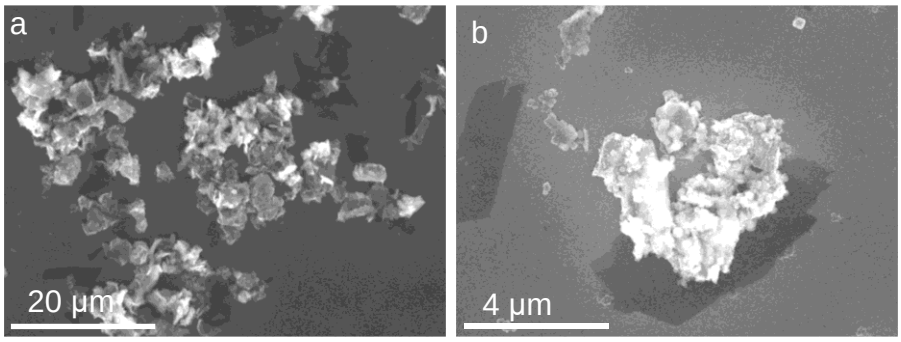

Figure S10 (a) The SEM image of LiF-NDs/C after heating to 400 °C. (b) The magnified image of the agglomerated LiF particles.

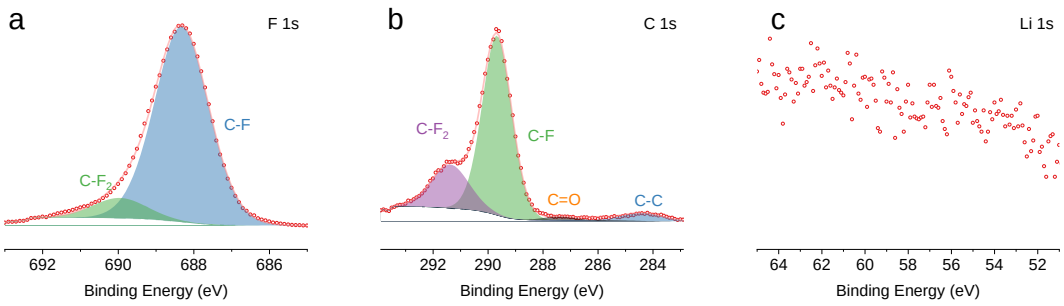

Figure S11 High-resolution core-level XPS spectrum of the (a) F 1s, (b) C 1s and (c) Li 1s regions for the carbon fluoride.

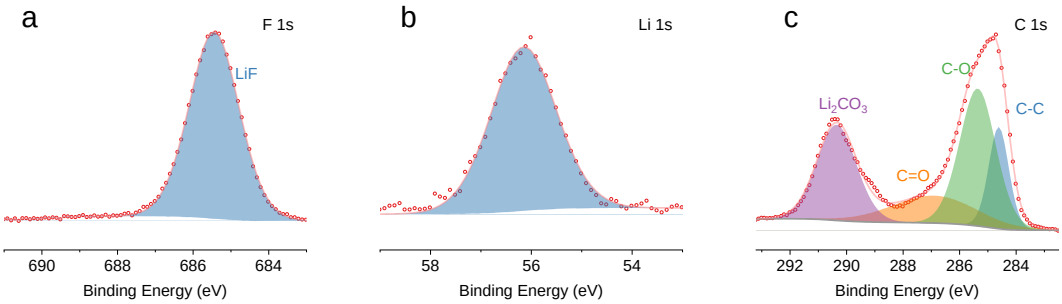

Figure S12 High-resolution core-level XPS spectrum of the (a) F 1s, (b) C 1s and (c) Li 1s regions for the LiF-NDs/C.

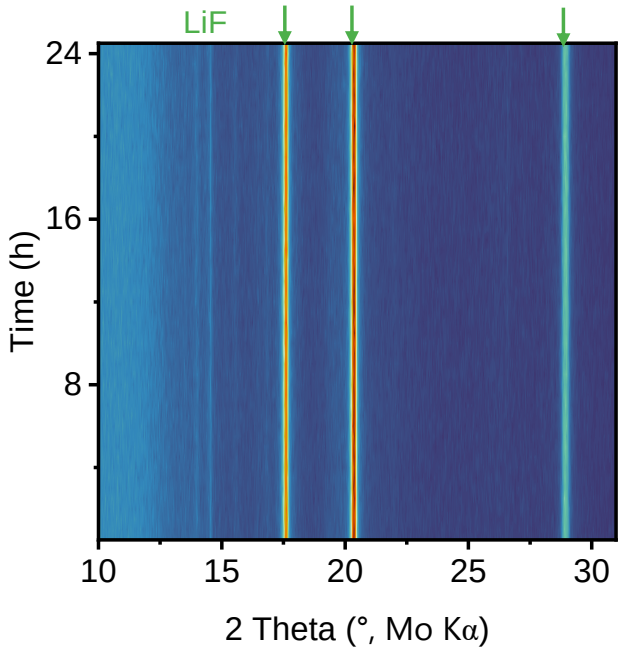

Figure S13 The *in-situ* XRD pattern of LiF-NDs/C upon the air exposure durations with 30% relative humidity.

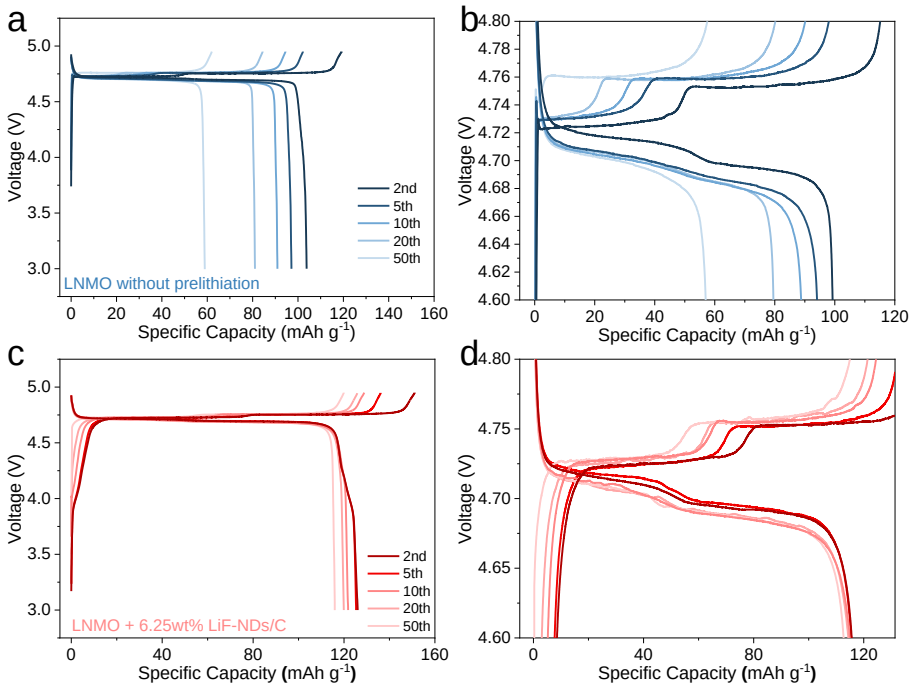

Figure S14 Voltage profiles of (a) LNMO without prelithiation cell and (b) the corresponding enlarged view. Voltage profiles of (c) LNMO with 6.25 wt% LiF-NDs/C cell and (d) the corresponding enlarged view.

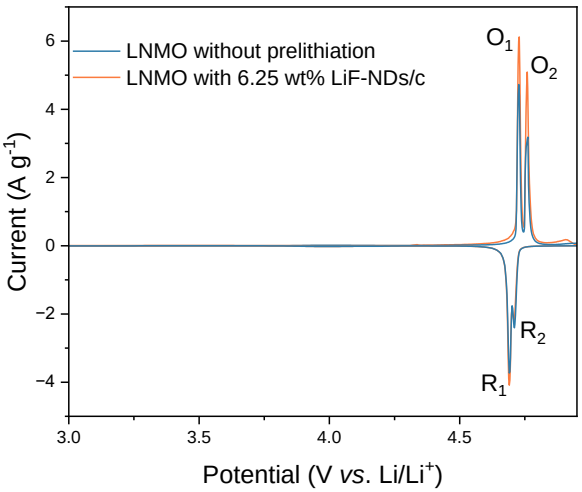

Figure S15 The CV curves of LNMO electrodes in anode-free Li cells with and without LiF-NDs/C additive.

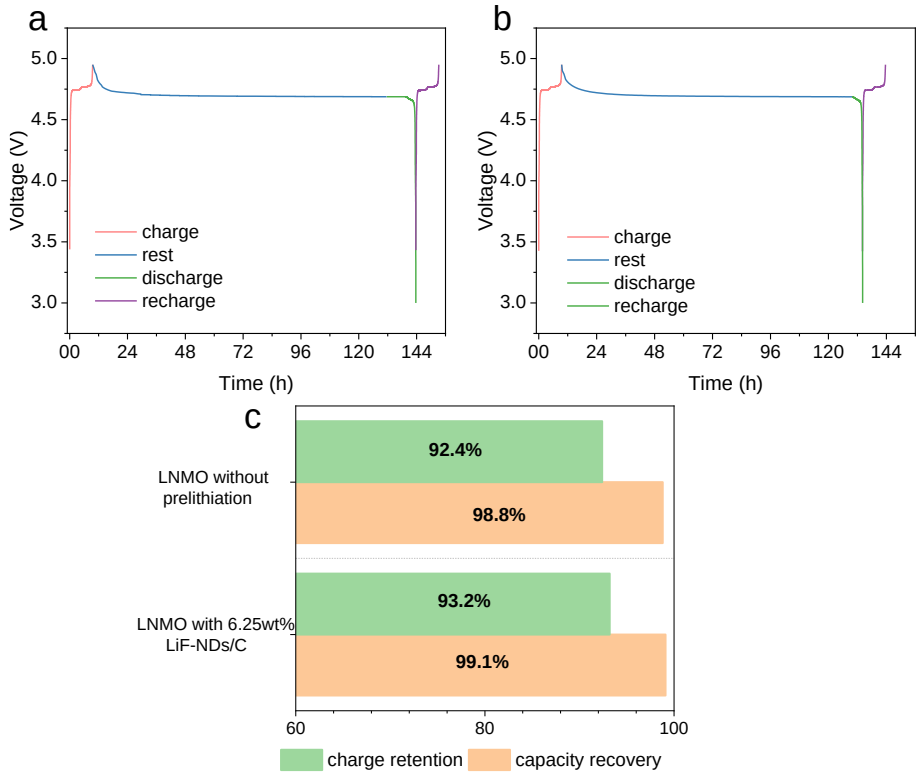

Figure S16 (a) Voltage evolution during self-discharge test of LNMO without prelithiation. (b) Voltage evolution during self-discharge test of LNMO with 6.25 wt% LiF-NDs/C. (c) The charge retention and capacity recovery values

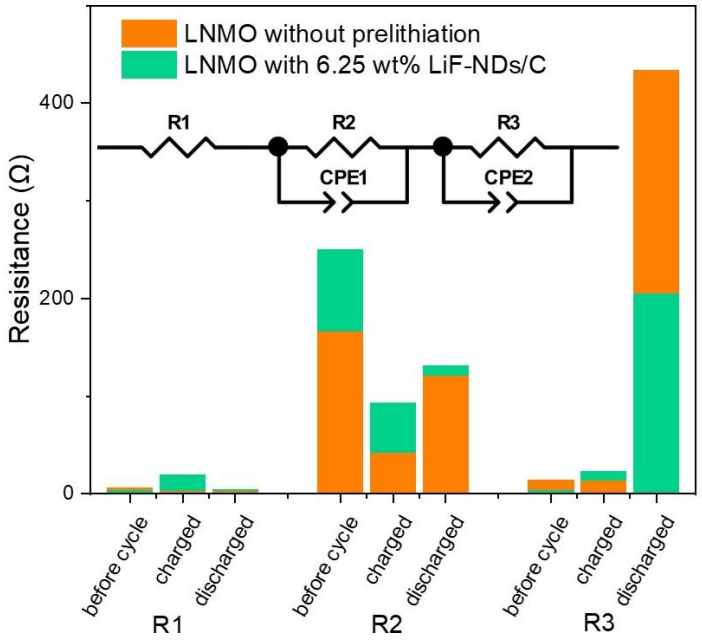

Figure S17 The fitted resistance for NCM811| |Li with PE and Li2S@C|PE. Inset figure is the equivalent circuits for EIS fitting.

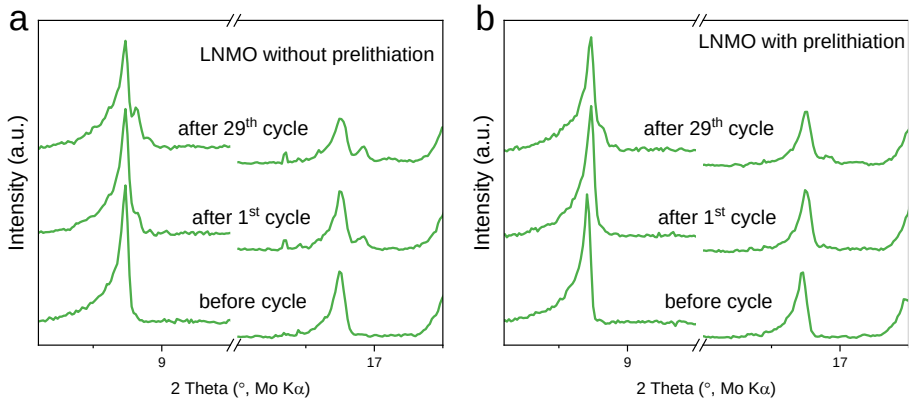

Figure S18 The detailed *in-situ* XRD patterns of LNMO (a) without and (b) with prelithiation corresponding to Figure 7.

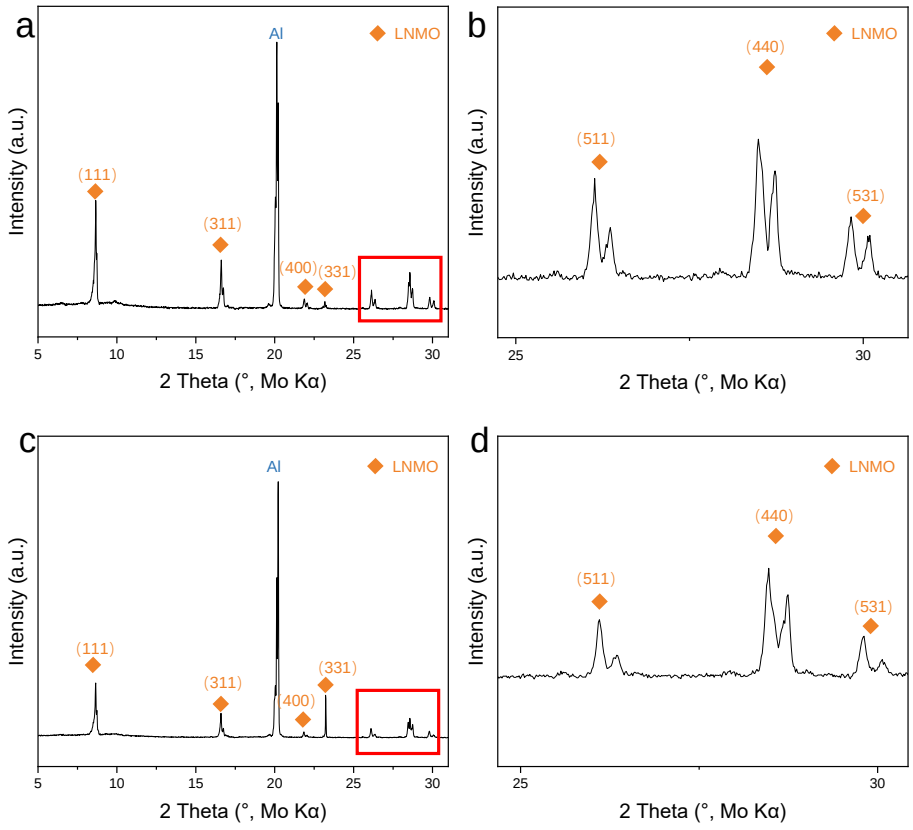

Figure S19 (a) The XRD spectrum of discharged LNMO after 29 cycles within anode-free configuration corresponding to Figure 7d. (b) The enlarged view of the red rectangle in Figure S19a. (c) The XRD spectrum of discharged LNMO after 30 cycles within anode-free configuration corresponding to Figure 7d. (d) The enlarged view of the red rectangle in Figure S19c

Table S1 Parameters for the anode-free cell with and without prelithiation additive.

Parameters （LNMO）	**Without Prelithiation**	**Prelithiation**
Cathode Specific Capacity (mAh g^{-1})	108.2	126.0
Cathode Mass (g)	8	8
LiF-NDs/C Mass (g)	0	0.5
Carbon Mass (g)	0.5	0.5
Binder Mass (g)	0.5	0.5
Output Voltage (V)	4.69	4.69
Energy Density Based on Active Materials (Wh kg^{-1})	507.46	590.94
Energy Density of Cathode (Wh kg^{-1})	451.08	497.63
Energy Density of Cathode After 50 Cycles(Wh kg^{-1})	231.45	352.25

Table S2 Parameters for the LNMO||graphite cell in theory and LNMO||Cu pouch cell with prelithiation additive.

Parameters （LNMO）	**LNMO||graphite (Theoretically)**	**LNMO||Cu**
Capacity (Ah)	1	1
Cathode Specific Capacity (mAh g^{-1})	125	/
Cathode Mass (g)	9	/
Anode Mass (g)	3.3	/
N/P ratio	1.1	/
Output Voltage (V)	4.59	/
Cathode Loading Mass (Double Side Coating) (mg cm^{-2})	18.75	20
Active Area (6*4*20) (cm^2)	480	480
Areal capacity (mAh/cm^2)	2.08	2.08
Al Foil (g)	1	/
Cu Foil (g)	2.17	/
E/C Ratio (g Ah^{-1})	2.5	2.5
Electrolyte (g)	2.5	2.5
Separator (g)	0.71	/
Package + Tabs (g)	0.82	/
Total Mass (g)	18.67	16.7
Energy Density (Wh kg^{-1})	235.5	278.2