

## Supporting Information

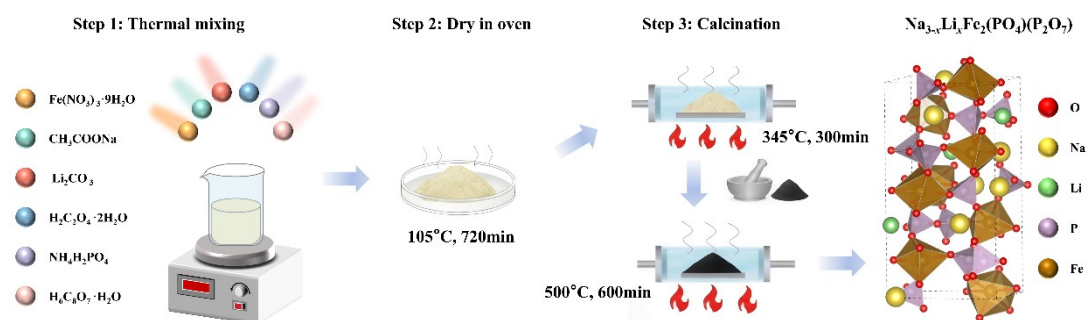
### **Alkali-Site Lithium Doping Enables a High-Performance $\text{Na}_3\text{Fe}_2(\text{PO}_4)(\text{P}_2\text{O}_7)$ Cathode for Sodium-Ion Batteries**

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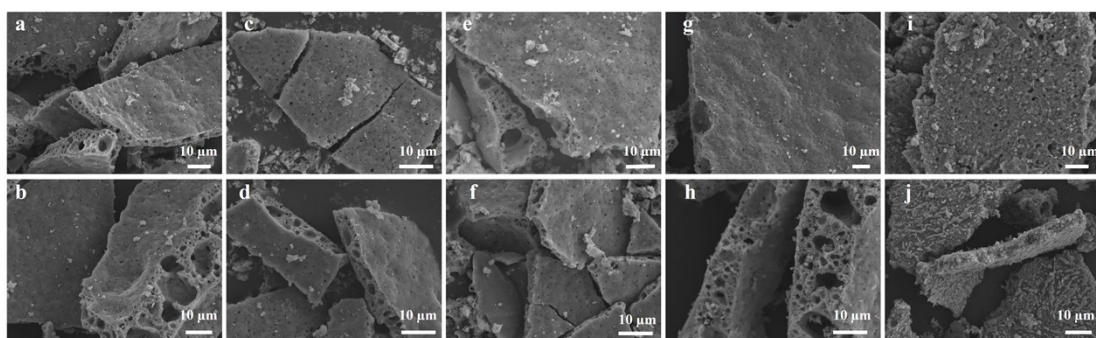
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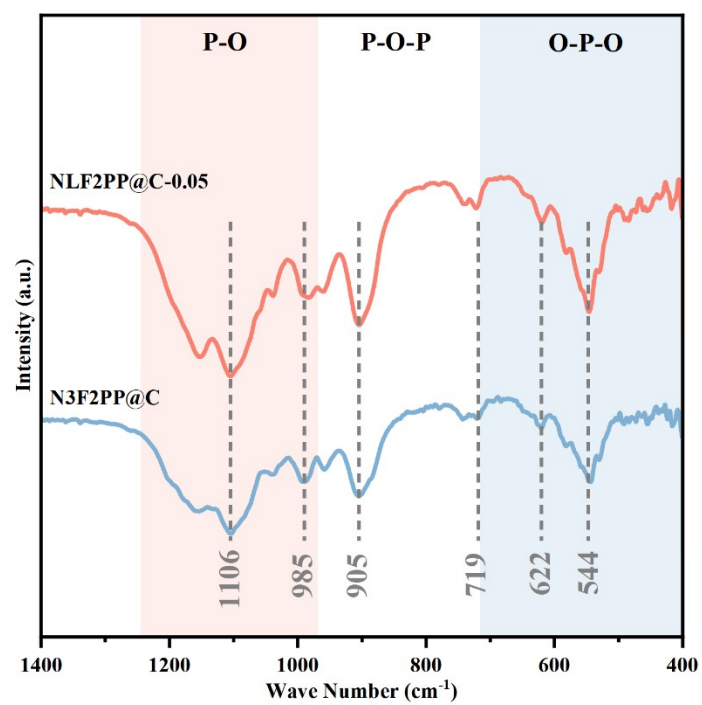
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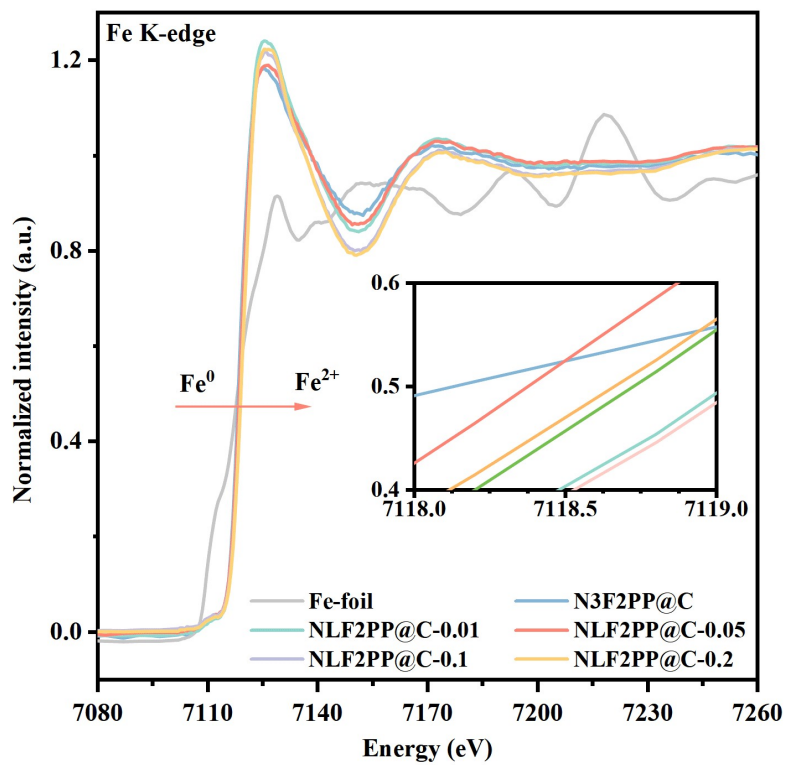
**Figure S1.** Schematic illustration of the synthesis process of the as-prepared samples.



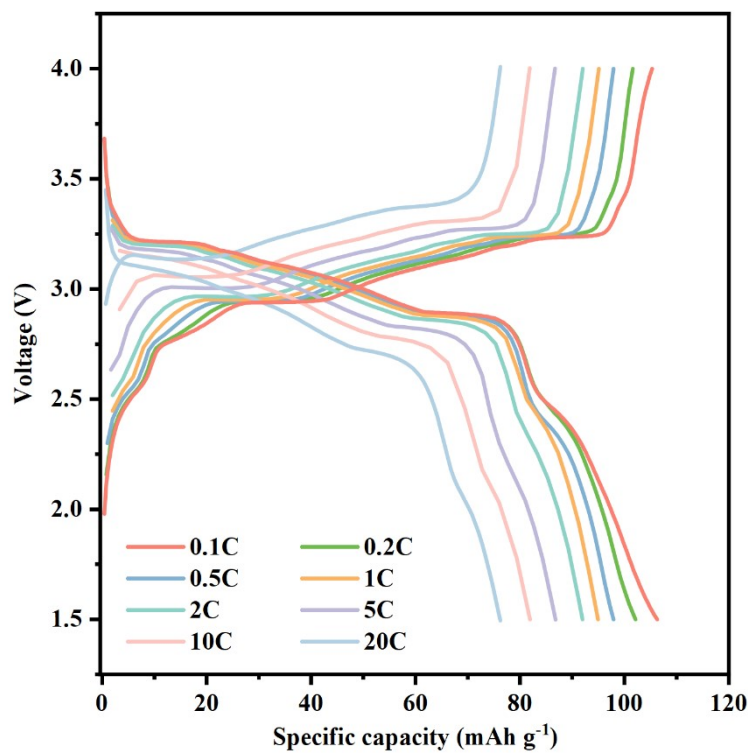
**Figure S2.** SEM images of  $\text{Na}_{3-x}\text{Li}_x\text{Fe}_2(\text{PO}_4)(\text{P}_2\text{O}_7)\text{@C}$  material. Among them, (a and b)  $\text{N3F2PP@C}$ , (c and d)  $\text{NLF2PP@C-0.01}$ , (e and f)  $\text{NLF2PP@C-0.05}$ , (g and h)  $\text{NLF2PP@C-0.1}$ , (i and j)  $\text{NLF2PP@C-0.2}$ .



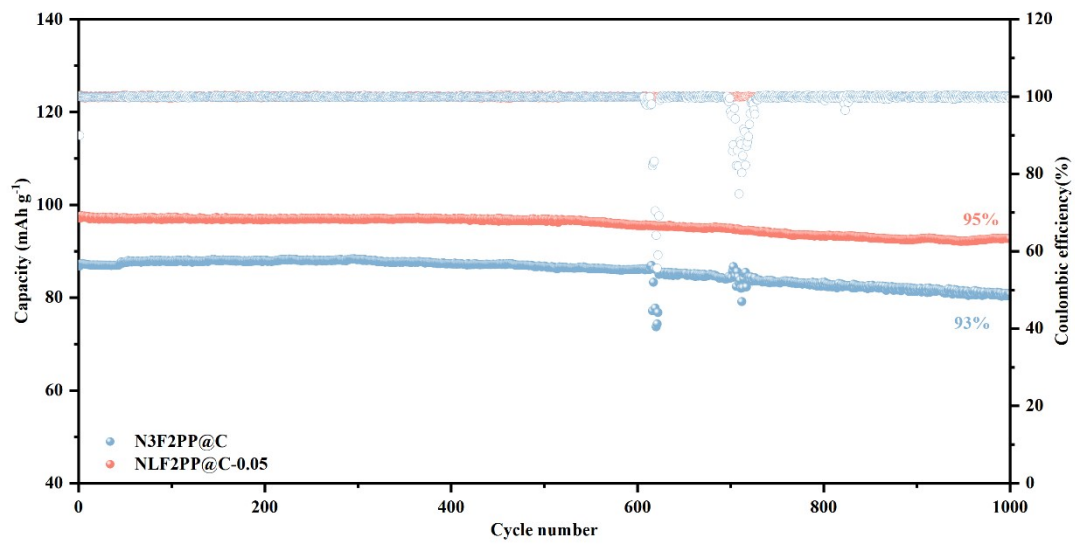
**Figure S3.** Fourier transform infrared (FT-IR) spectra of N3F2PP@C and NLF2PP@C-0.05.



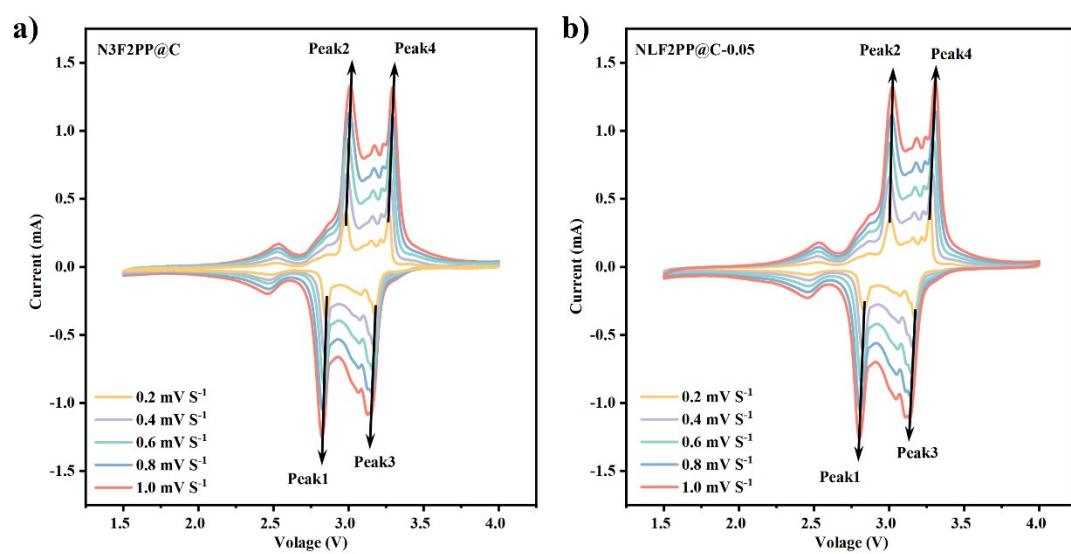
**Figure S4.** Fe K-edge XAS spectra of all cathodes.



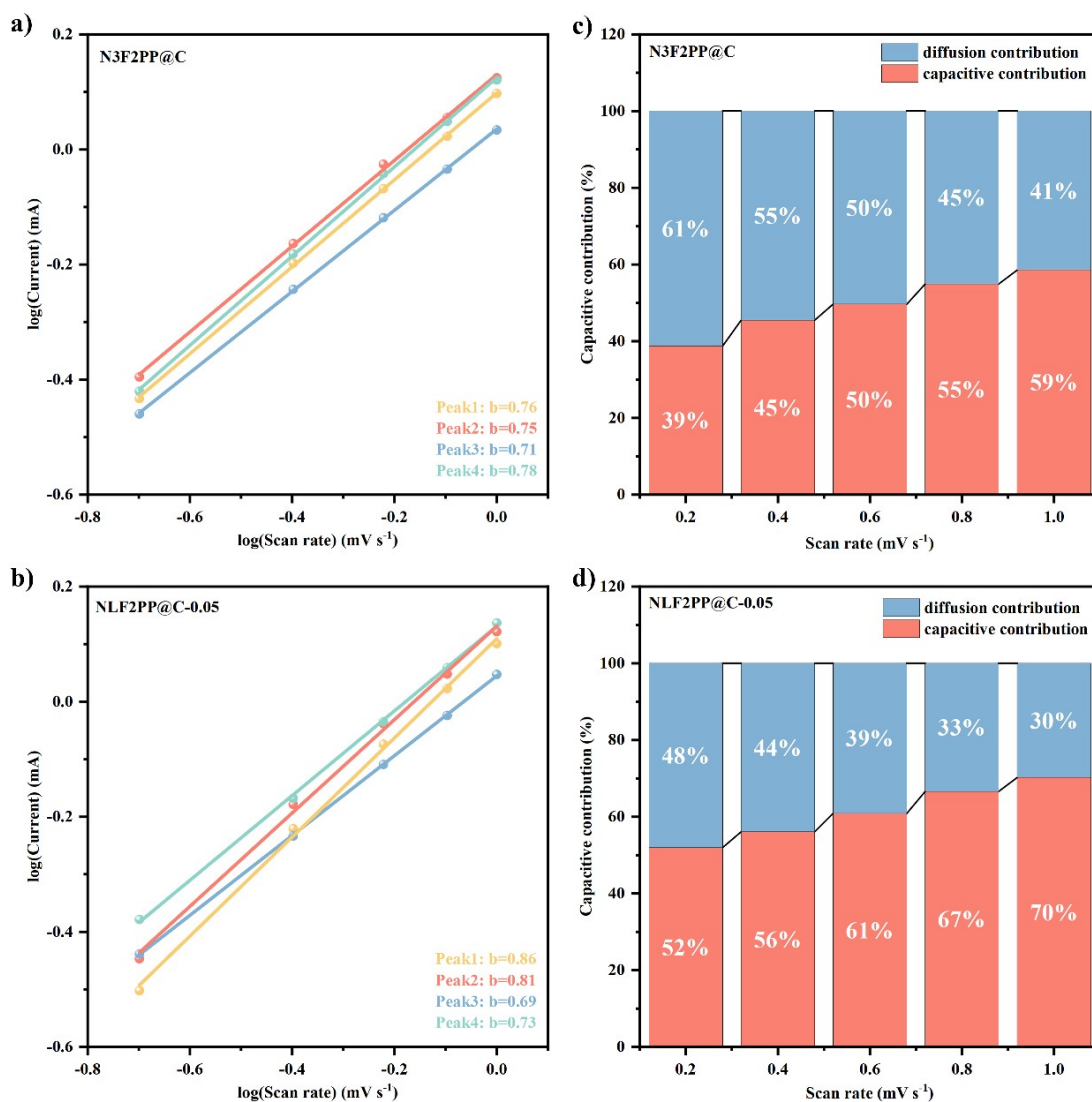
**Figure S5.** The GCD curves of N3F2PP@C at current rates from 0.1 to 20 C.



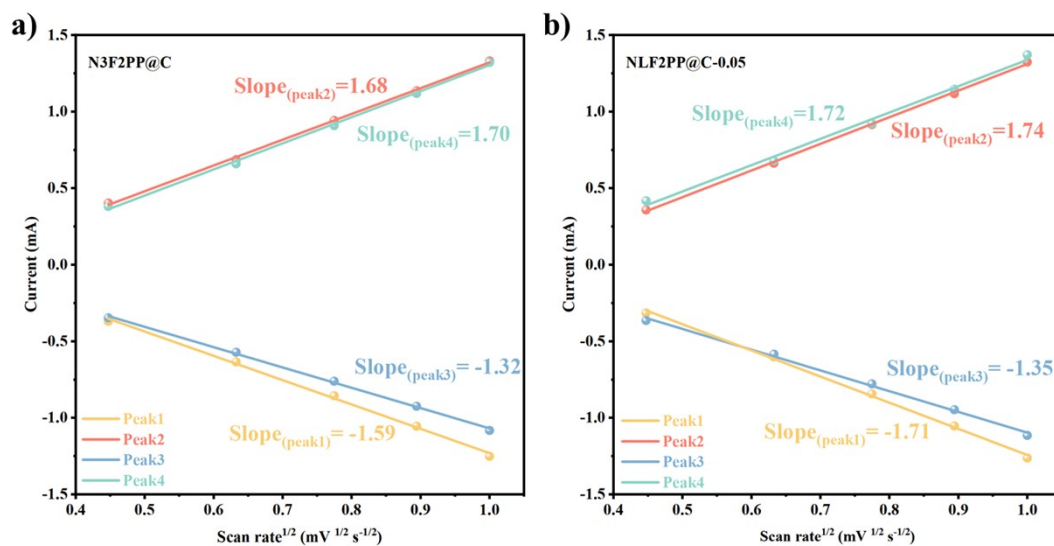
**Figure S6.** Long-term cycling performance of N3F2PP@C and NLF2PP@C-0.05 at 5 C.



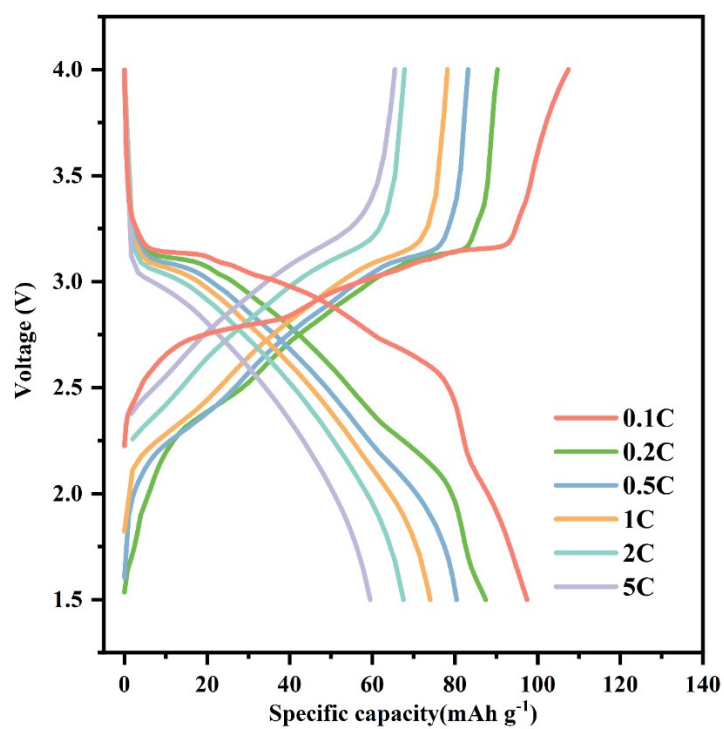
**Figure S7.** CV curves of (a) N3F2PP@C and (b) NLF2PP@-0.05 cathode at different sweep rates.



**Figure S8.** Electrochemical kinetics analysis of (a and c) N3F2PP@C and (b and d) NLF2PP@C-0.05. (a and b) The relationship between peak current ( $I_p$ ) and scan rate ( $v$ ). (c and d) Percentage of pseudo-capacitance control at different scan rates.



**Figure S9.** The relationship between the peak current ( $I_p$ ) of the (a) N3F2PP@C and (b) NLF2PP@C-0.05 cathode and the square root of the scan rate ( $v^{1/2}$ ).



**Figure S10.** The GCD curves of N3F2PP@C||HC at current rates from 0.1 to 5 C.

Table S1. Specific discharge capacities and the corresponding capacity recovery rates of NLF2PP@C-*x* electrodes. The recovery rate is calculated by comparing the discharge capacity at 1 C after high-rate cycling (up to 20 C) with the initial capacity at 1 C.

Sample	Initial Capacity (1 C, mAh/g)	Restored Capacity (1 C, mAh/g)	Capacity Recovery Rate (%)
N3F2PP@C	95.2	95.5	100.3%
NLF2PP@C-0.01	95.8	96.7	100.9%
NLF2PP@C-0.05	102.4	103.5	101.1%
NLF2PP@C-0.1	96.2	97.3	101.1%
NLF2PP@C-0.2	88.2	88.2	100.0%