

Supporting Information

Structure, Electrochemical, and Transport Properties of Li- and F-Modified P2- $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ Cathode Materials for Na-Ion Batteries

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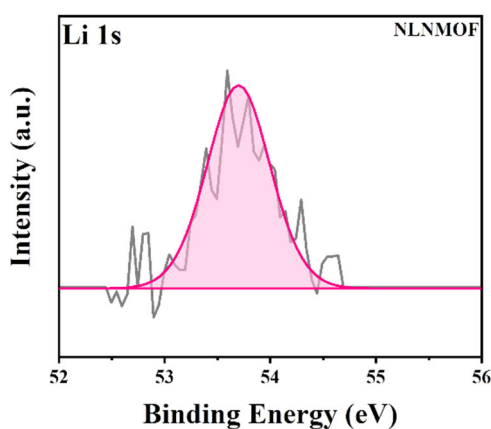


Figure S1. XPS spectra of (a) Li 1s and (b) F 1s of NLNMOF.

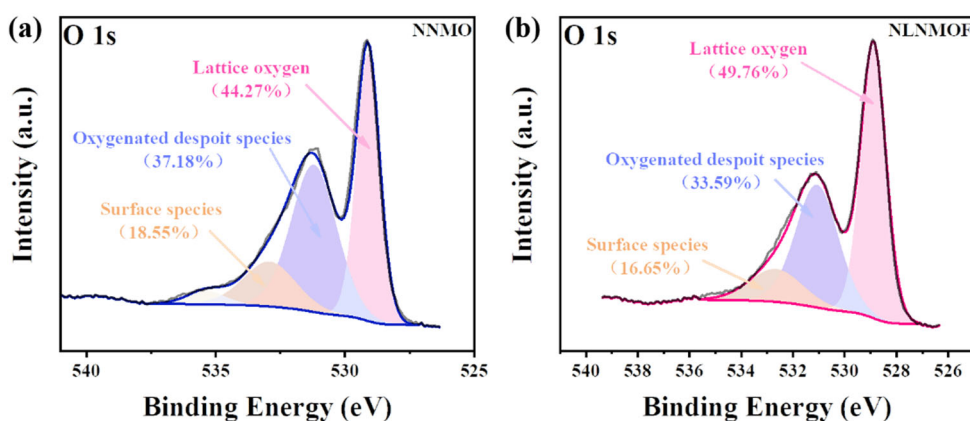


Figure S2. XPS O 1S spectra of (a) NNMO and (b) NLNMOF.

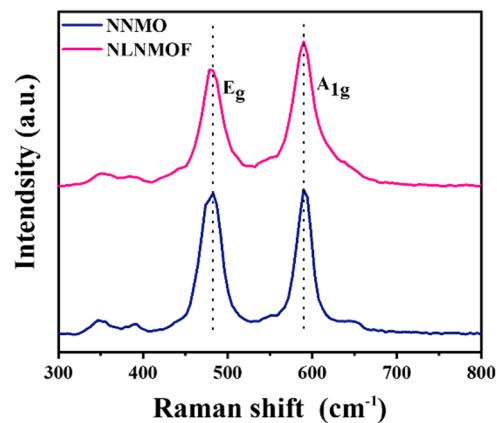


Figure S3. Raman spectra of NNMO and NLNMOF.

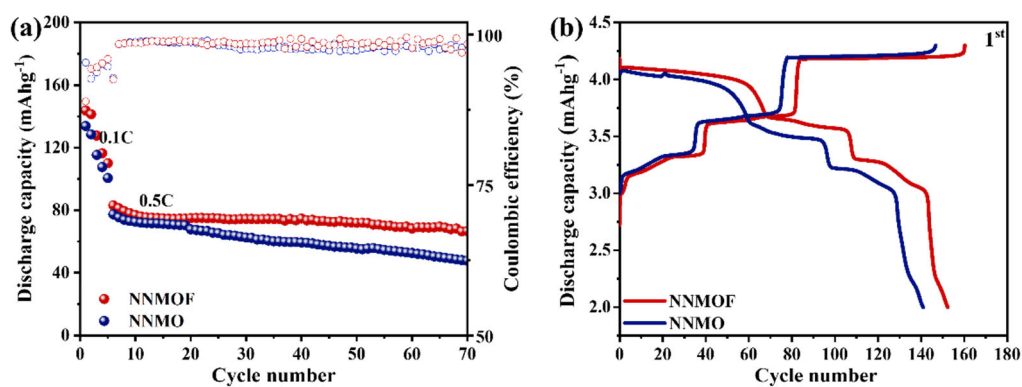


Figure S4. (a) The cycling performances of NNMO and NNMOF between 2.0 V and 4.3 V. (b) The initial charge-discharge curves of NNMO and NNMOF.

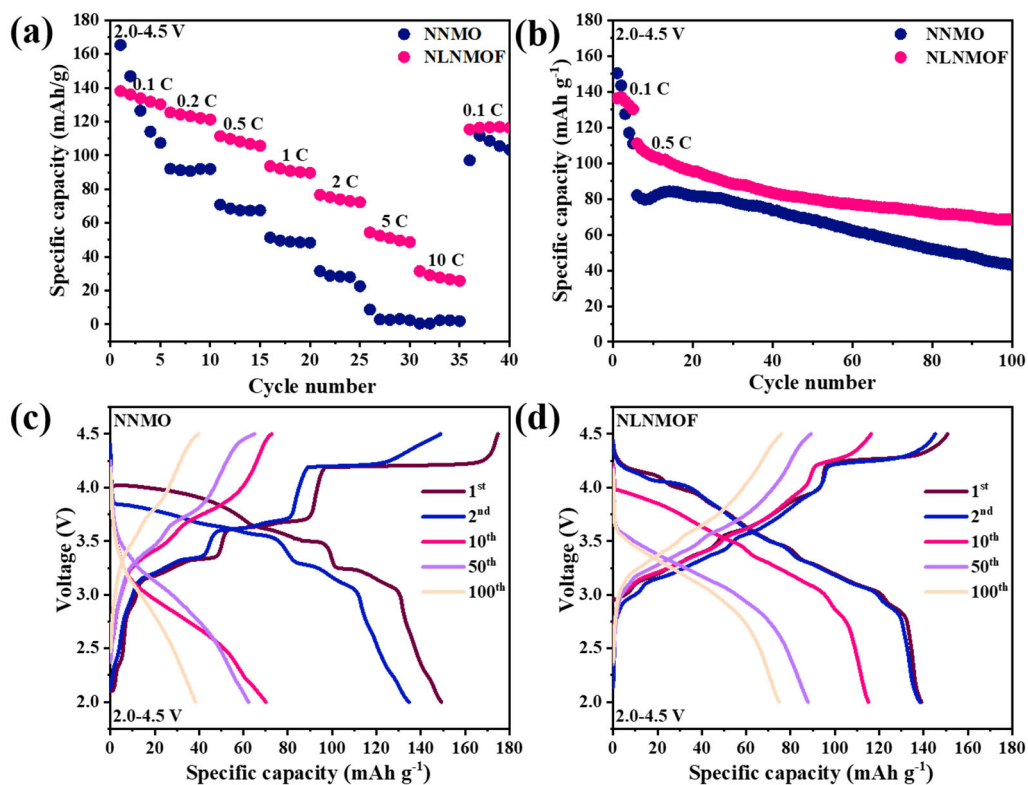


Figure S5. (a) Rate and (b) cycling performances of NNMO and NLNMOF electrodes between 2.0-4.5 V. The charge-discharge profiles of (c) NNMO and (d) NLNMOF for the 1st, 2nd, 10th, 50th and 100th cycle.

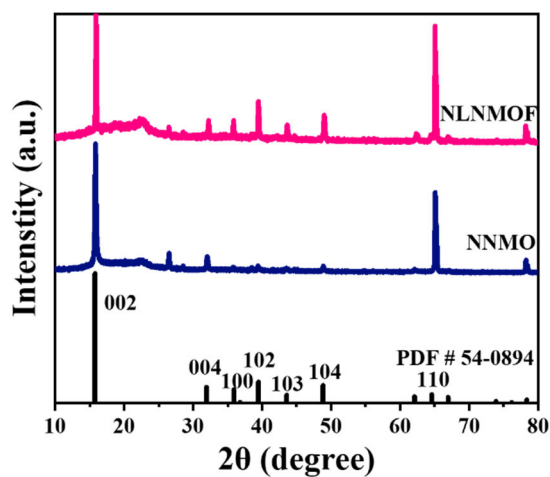


Figure S6. XRD patterns acquired on NNMO and NLNMOF electrodes after 100 cycles at 0.5 C.

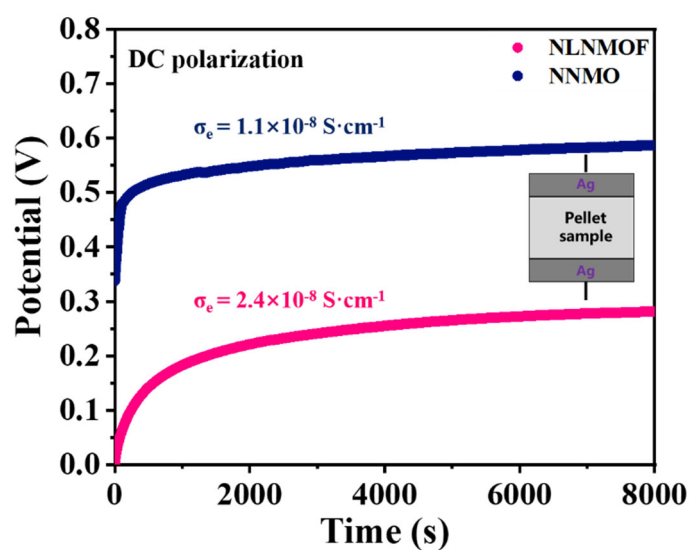


Figure S7. DC polarization profiles acquired on NNMO and NLNMOF pellets. The inset illustrates the measurement set-up.

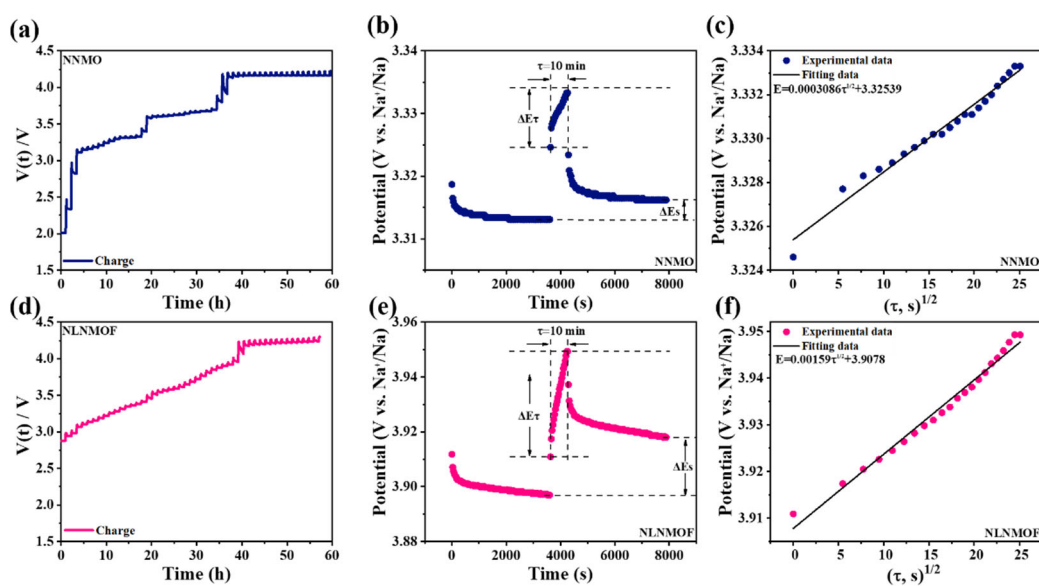


Figure S8. GITT curves (cell voltage vs. time) measured for (a) NNMO and (d) NLNMOF electrodes. A single titration step for (b) NNMO and (e) NLNMOF. The linear fit of the cell voltage as a function of the square root of time for (c) NNMO and (f) NLNMOF.

Supplementary Tables [65]

Table S1. Recipes used for the preparation of NNMO and NLNMOF samples in a 3 g batch

Mass (g)	NaNO ₃	Ni(NO ₃) ₂ ·6H ₂ O	Mn(NO ₃) ₂ ·4H ₂ O	C ₆ H ₈ O ₇ ·H ₂ O	LiNO ₃	NaF
NLNMOF	1.815	2.622	4.596	5.742	0.209	0.064
NNMO	1.732	2.779	4.871	5.565	-	-

Table S2. The proportions of Ni²⁺ and Ni³⁺ estimated from XPS results before and after cycling

Samples	Before cycling		After cycling	
	Ni ²⁺	Ni ³⁺	Ni ²⁺	Ni ³⁺
NNMO	63.67%	36.33%	48.43%	51.57%
NLNMOF	74.65%	25.35%	68.60%	31.40%

Table S3. Raman peak assignments for NNMO and NLNMOF (Unit: cm⁻¹)

Samples	Ni ³⁺	E _g	O–Ni–O stretching vibration	Mn ⁴⁺ (δ -MnO ₂ type)	A _{1g}	Spinel phase ¹	Mn ⁴⁺ (β -MnO ₂ or λ -MnO ₂ type)
NNMO	436; 513	476	517	574	580; 584	619	-
NLNMOF	446; 526	480	535	-	589	624	657

Table S4. R_o, R_{SEI}, and R_{ct} estimated for NNMO and LNNMO electrodes

Sample	Before cycling			After 10 cycles			After 100 cycles		
	R _o (Ω)	R _{SEI} (Ω)	R _{SEI} (Ω)	R _o (Ω)	R _{SEI} (Ω)	R _{ct} (Ω)	R _o (Ω)	R _{SEI} (Ω)	R _{ct} (Ω)
NNMO	6.6	26.1	37.6	4.3	35.3		4.7	45.7	35.8
NLNMOF	3.9	57.3		4.2	41.7		5.8	41.7	

REFERENCE

65 Talyosef, Y.; Markovsky, B.; Salitra, G.; Aurbach, D.; Kim, H. J.; Choi, S., The study of LiNi_{0.5}Mn_{1.5}O₄ 5-V cathodes for Li-ion batteries. *Journal of Power Sources* **2005**, 146 (1-2), 664-669.