Synergistic Bulk and Interface Modification via Lanthanization Enhances Structural Stability and Ion Kinetics in O3-$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ Cathodes

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Supplementary Figures

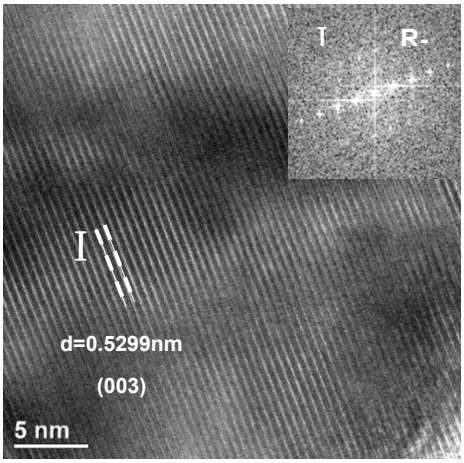

Figure S1. HRTEM image of NFM.

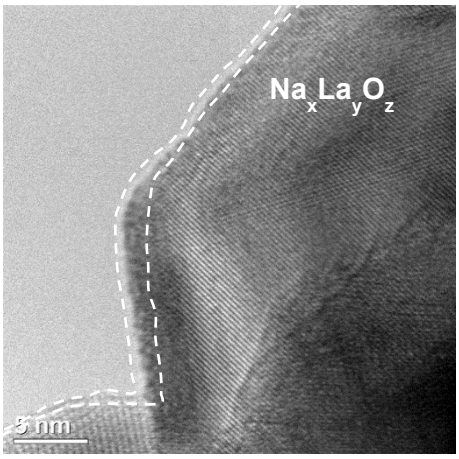

Figure S2. HRTEM image of La-NFM.

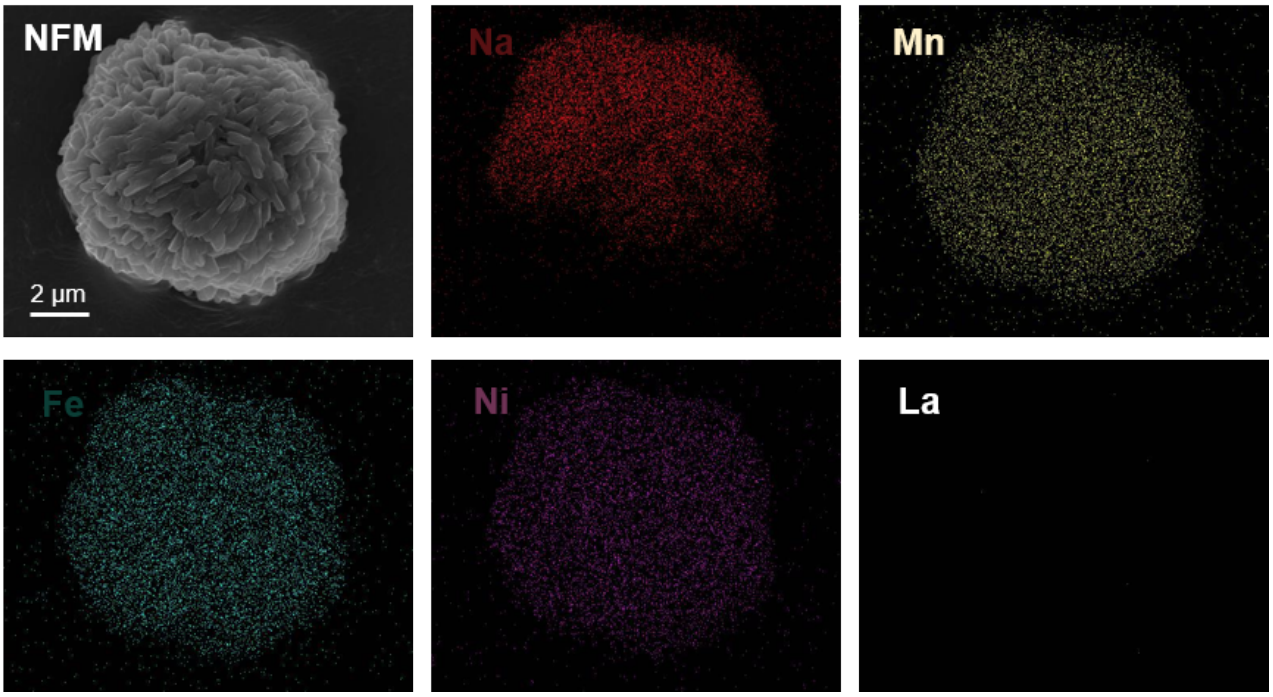

Figure S3. Corresponding EDS mapping images of NFM.

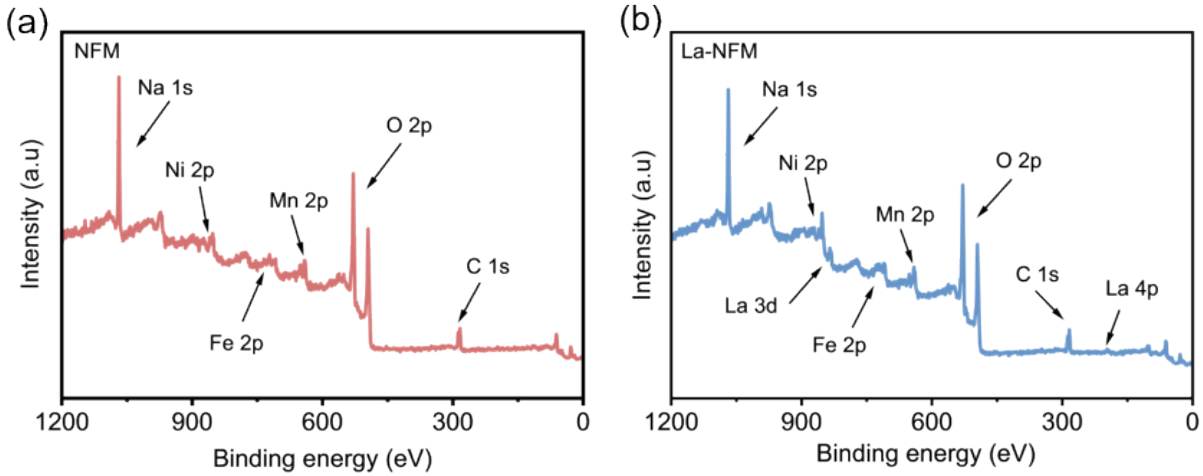

Figure S4. XPS full spectra of (a) NFM and (b) La-NFM.

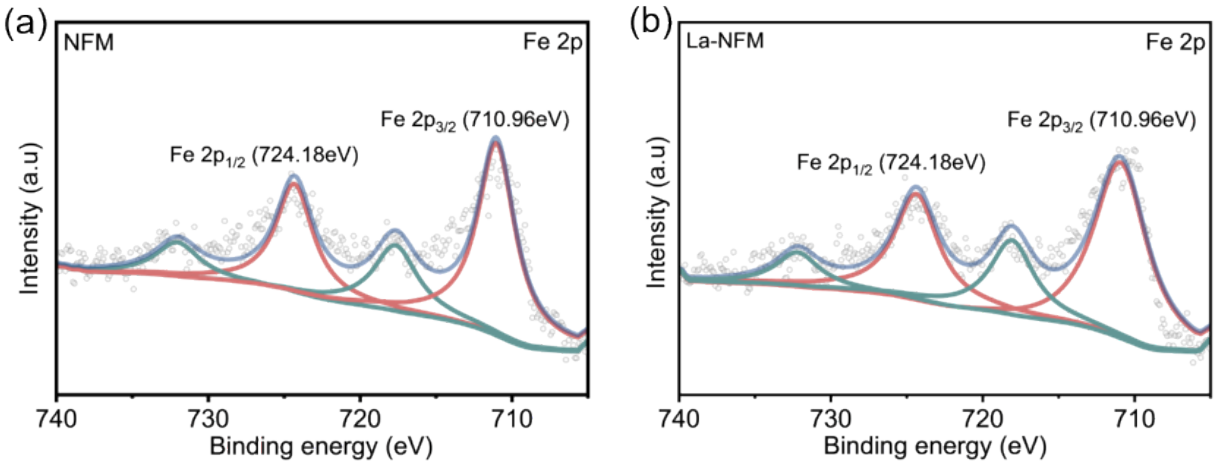

Figure S5. XPS image of Fe 2p in (a) NFM and (b) La-NFM.

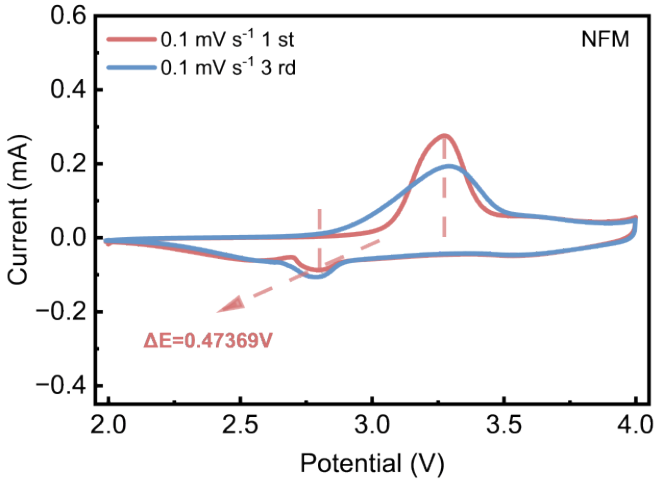

Figure S6. CV curves of NFM at 0.1 mV s^{-1}.

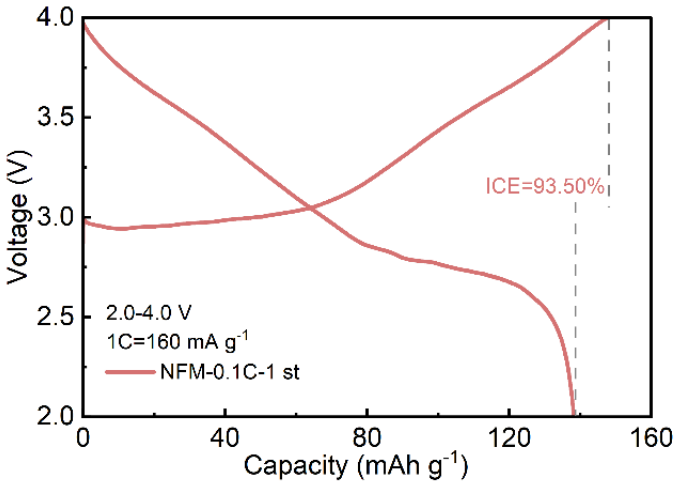

Figure S7. The charge-discharge curves for NFM of the first cycle at 0.1 C.

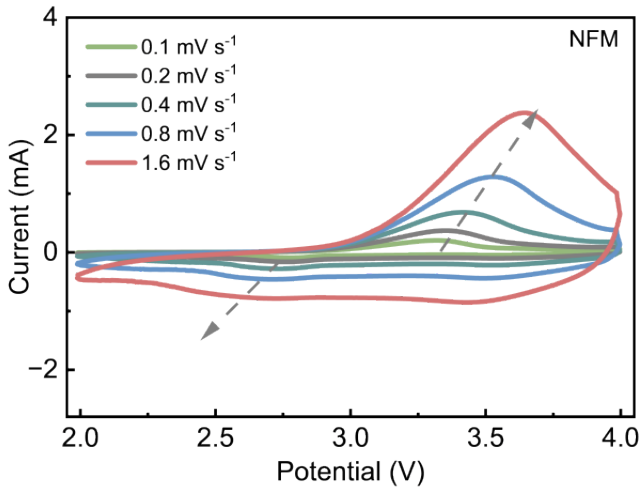

Figure S8. CV curves of NFM at various scan rates.

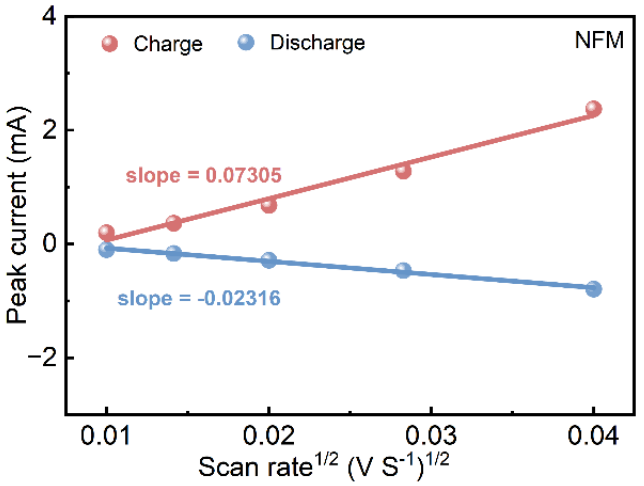

Figure S9. The relationship of the peak current (Ip) and the square root of scan rate ($v^{1/2}$) of NFM.

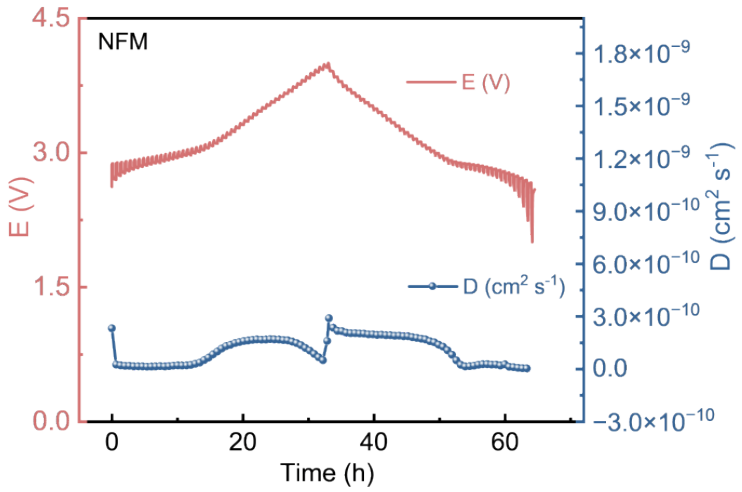

Figure S10. GITT curves and Na^+ diffusion coefficients of NFM.

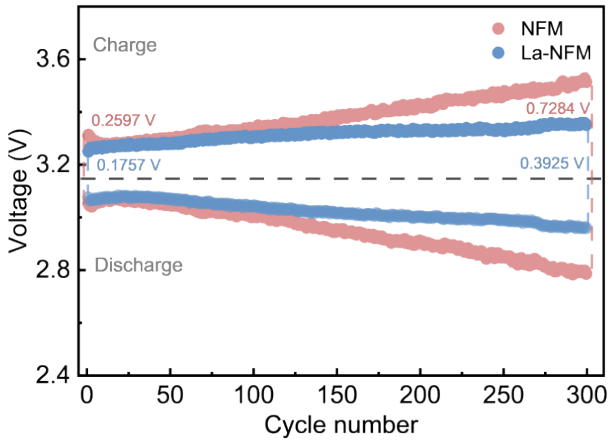

Figure S11. The average charge-discharge voltage of NFM and La-NFM at different cycles during cycling at 1 C (calculated by energy/capacity).

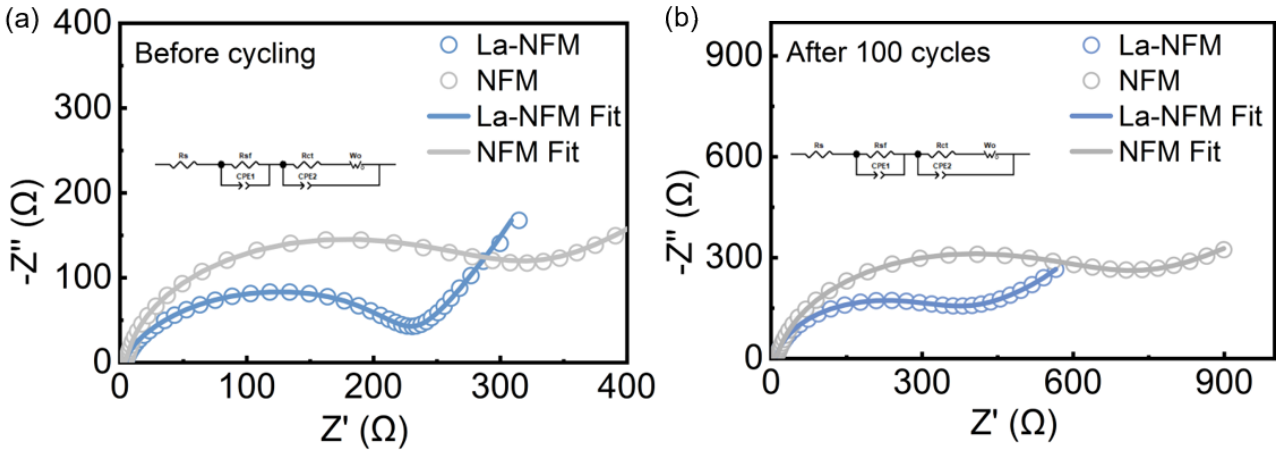

Figure S12. EIS spectra of NFM and La-NFM (a) before cycling and (b) after 100 cycles at 1 C.

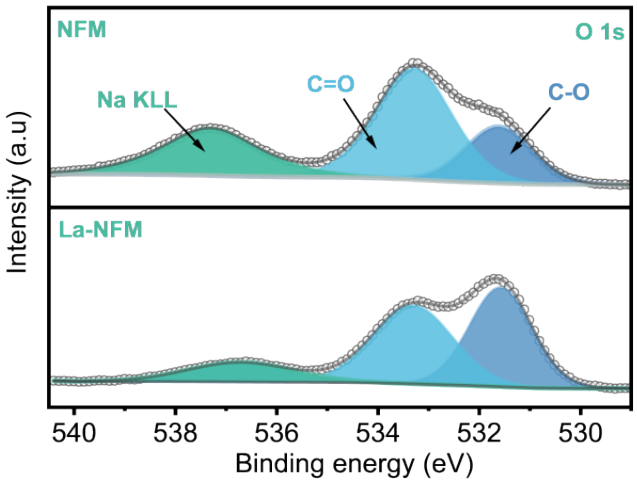

Figure S13. O 1s for NFM and La-NFM electrodes after 100 cycles at 1C.

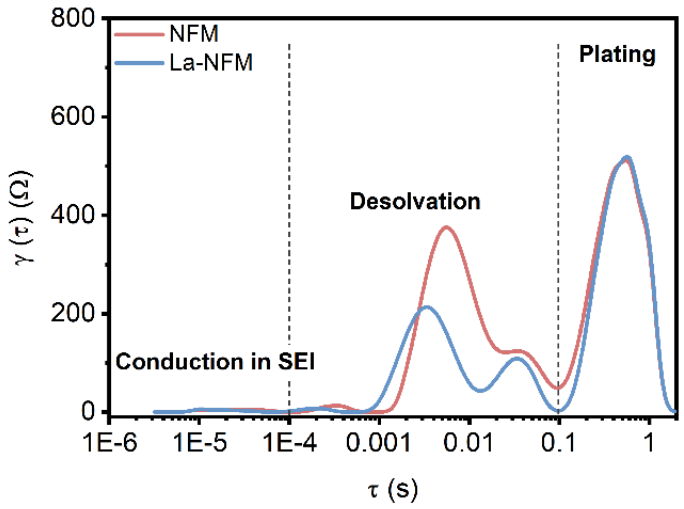

Figure S14. DRT results of NFM and La-NFM after 100 cycles at 1 C.

Supplementary Tables

Table S1. Total energy comparison of NFM and four structures predicted for La-NFM.

Structure	Total energy (eV)
NFM	−626.457201
La-NFM@Na	−632.418478
La-NFM@Ni	−631.412779
La-NFM@Fe	−627.396013
La-NFM@Mn	−626.557262

Table S2. Atomic coordinates and possible occupancies of the unit cell of NFM based on Rietveld refinement.

Atom	Mult.	X	Y	Z	Occ.
Na	3a	0.00000	0.00000	0.00000	1.0000
Ni	3b	0.00000	0.00000	0.50000	0.3330
Fe	3b	0.00000	0.00000	0.50000	0.3330
Mn	3b	0.00000	0.00000	0.50000	0.3330
O	6c	0.00000	0.00000	0.23396	1.0000

Table S3. Atomic coordinates and possible occupancies of the unit cell of La-NFM based on Rietveld refinement.

Atom	Mult.	X	Y	Z	Occ.
Na	3a	0.00000	0.00000	0.00000	0.9900
Ni	3b	0.00000	0.00000	0.50000	0.3300
Fe	3b	0.00000	0.00000	0.50000	0.3300
Mn	3b	0.00000	0.00000	0.50000	0.3300
La	3a	0.00000	0.00000	0.50000	0.0100
O	6c	0.00000	0.00000	0.5000	1.0000

Table S4. Crystallographic data and refinement parameters of NFM and La-NFM.

Samples	a[Å]	b[Å]	c[Å]	V[Å^3]	R_p[%]	R_{wp}[%]
NFM	2.97787	2.97787	15.99950	122.871	4.62	3.67
La-NFM	2.97732	2.97732	16.03950	123.132	4.54	6.73

Table S5. Atomic distances, slab thickness, and d-spacing of the Na layer for NFM and La-NFM.

Samples	NFM	La-NFM
TM-O [Å]	2.02857	2.02788
Na-O [Å]	2.34174	2.34157
TMO_2 [Å]	1.89862	1.90188
Na-spacing [Å]	3.43643	3.44462
Interlayer [Å]	5.33505	5.34650

Table S6. Comparison between our results and reported results on the electrochemical performance of NFM at 4.0 V.

Modified strategy	Current density (mA g^{-1})	Cycle number	Residual capacity (mAh g^{-1})	Capacity retention (%)	Ref
Mg doping	120	50	~80	77	[1]
F doping	150	70	110	85	[2]
Ta doping	150	200	103.8	80.15	[3]
$Na_{3-3x}Al_xPO_4$ coating and Al doping	140	200	112	80	[4]
Co_xB coating	130	300	~95	79.6	[5]
Ti/Mg doping	----	100	~96	88.4	[6]
Al/Cu doping	130	200	~101	81	[7]
Zn doping	130	200	~103	86.53	[8]
ZrO_2 coating	----	100	~95	86	[9]
Nb doping	120	200	~101	83.81	[10]
This work	160	100	120	92.44	
		200	110	86.04	
		300	103.7	79.95	

Table S7. EIS plots and fitted curves of NFM and La-NFM.

Samples	Rs (Ω)	Rct (Ω)
NFM	4.626	292.8
La-NFM	4.512	190.4
NFM after 100 cycles	7.74	635.2
La-NFM after 100 cycles	6.62	420.5

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