Supporting Information

In Situ Dual-Modification Strategy for O3-$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ towards High-Performance Sodium-Ion Batteries

Ningyun Hong[a], Jianwei Li[e], Shihong Guo[a], Huawei Han[a], Haoji Wang[b], Xinyu Hu[b], Jiangnan Huang[b], Baichao Zhang[b], Fang Hua[a], Bai Song[f], Nesrin Bugday[c], Sedat Yasar[c], Serdar Altin[d], Wentao Deng[b,*], Guoqiang Zou[b], Hongshuai Hou[b], Zhen Long[a,*], Xiaobo Ji[b,*]

[a] Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, College of Material Science and Engineering, Tianjin University of Technology, Tianjin, China

[b] State Key Laboratory of Powder Metallurgy, College of Chemistry and Chemical Engineering, Central South University, Changsha, China

[c] Department of Chemistry, Inonu University, Malatya, Turkey

[d] Department of Physics, Inonu University, Malatya, Turkey

[e] Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences (CAS), Xining, China

[f] Dongying Cospowers Technology Limited Company, China

Supplementary Note:

The Na^+ chemical diffusion coefficients for GITT results can be calculated by the Weppner and Huggins equation:

$$D_{GITT} = \frac{4}{\pi\tau}\left(\frac{m_B V_m}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \qquad (\tau \ll L^2/D) \qquad (1)$$

Where m_B, M_B, S, and V_M are the molecular weight, mass and molar volume of the cathode electrode, respectively. S and L represent the surface area and average radius of the active material particles. ΔE_s and ΔE_τ are steady-state voltage and the total change of the cell voltage during the current pulse process.

For CV results, the apparent Na^+ diffusion coefficients D_{Na+} can be calculated based on the Randles-Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{Na+}^{1/2} v^{1/2} \Delta C_0 \qquad (2)$$

Where I_p is the peak current, n denotes the electron transfer number of the reaction, A represents the electrode area of the cathode, v represents the scan rate, and ΔC_0 is the concentration of Na^+ in the lattice.

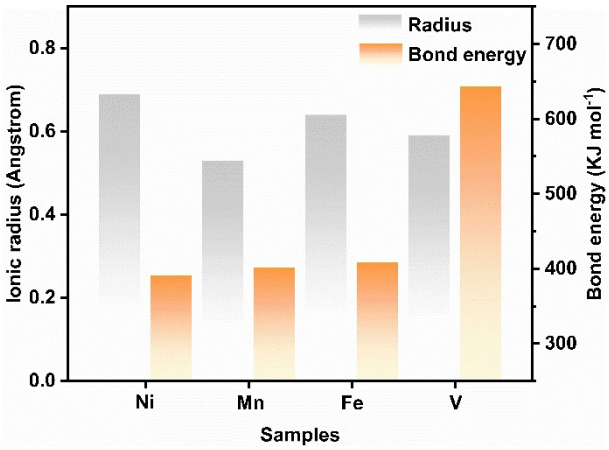

Fig. S1. The comparison of ionic radius and bonding energy with different elements.

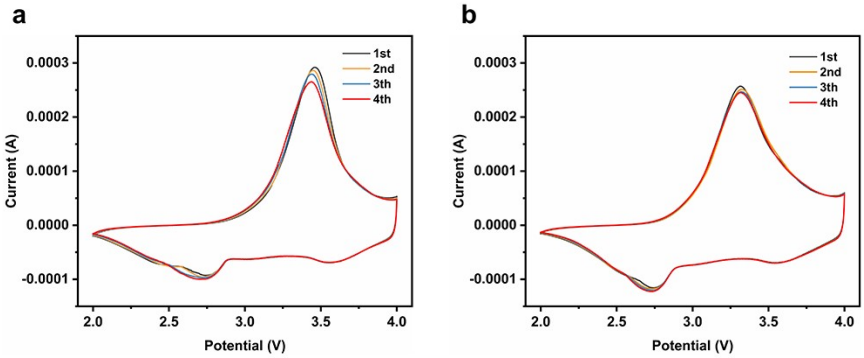

Fig. S2. (a-b) The initial four CV curves at a scanning rate of 0.1 mV s^{-1} for NFM and NFMV-1.

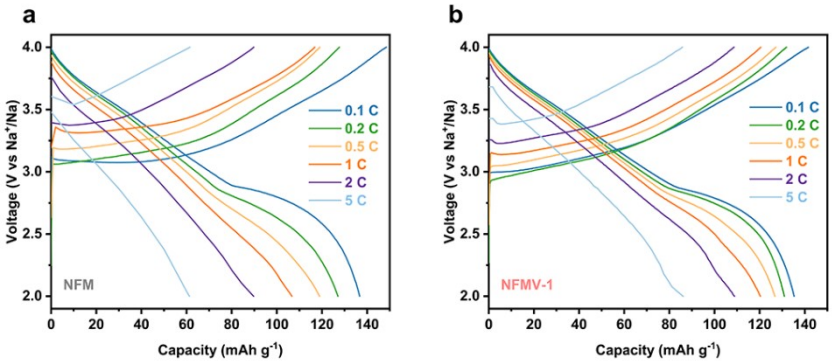

Fig. S3. (a-b) GCD curves at different current rate for NFM and NFMV-1.

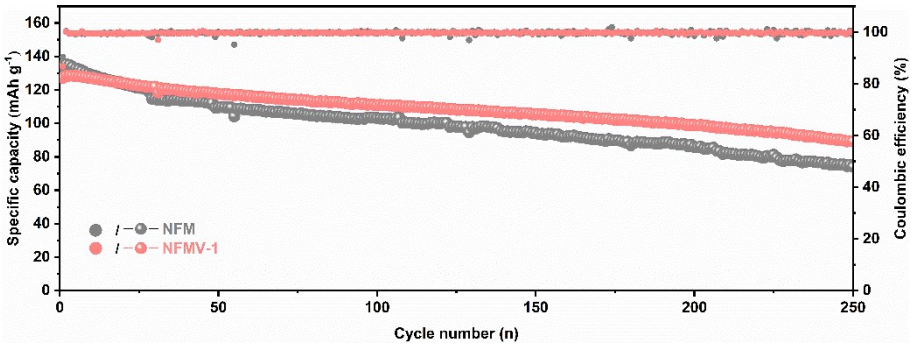

Fig. S4. Long-term cycling performance of NFM and NFMV-1 at 1 C at the voltage from 2.0-4.2 V

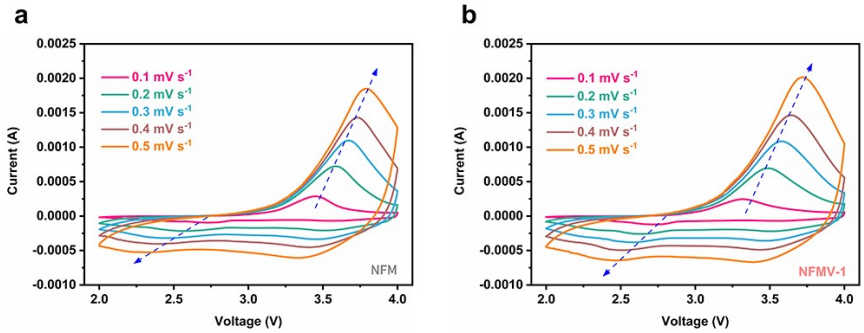

Fig. S5. (a-b) GCD curves at different scan rate for NFM and NFMV-1.

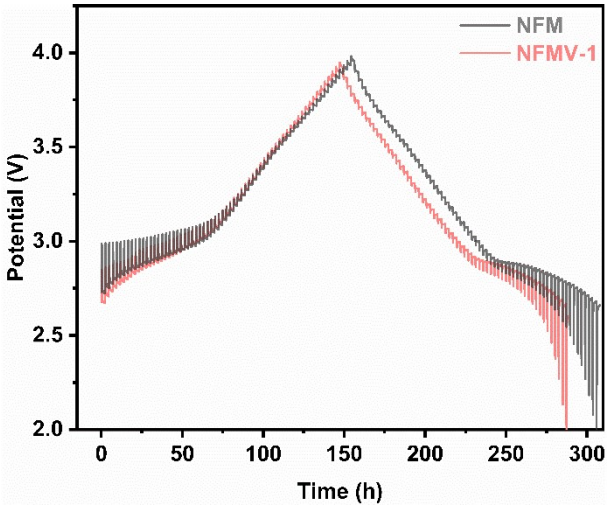

Fig. S6. Transient voltage-time profile obtained from GITT test for the obtained Samples.

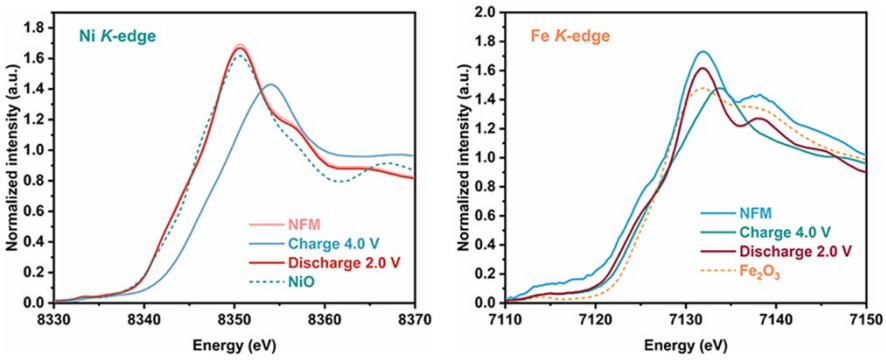

Fig. S7. Ni/Fe K-edge of NFM under different charging state.

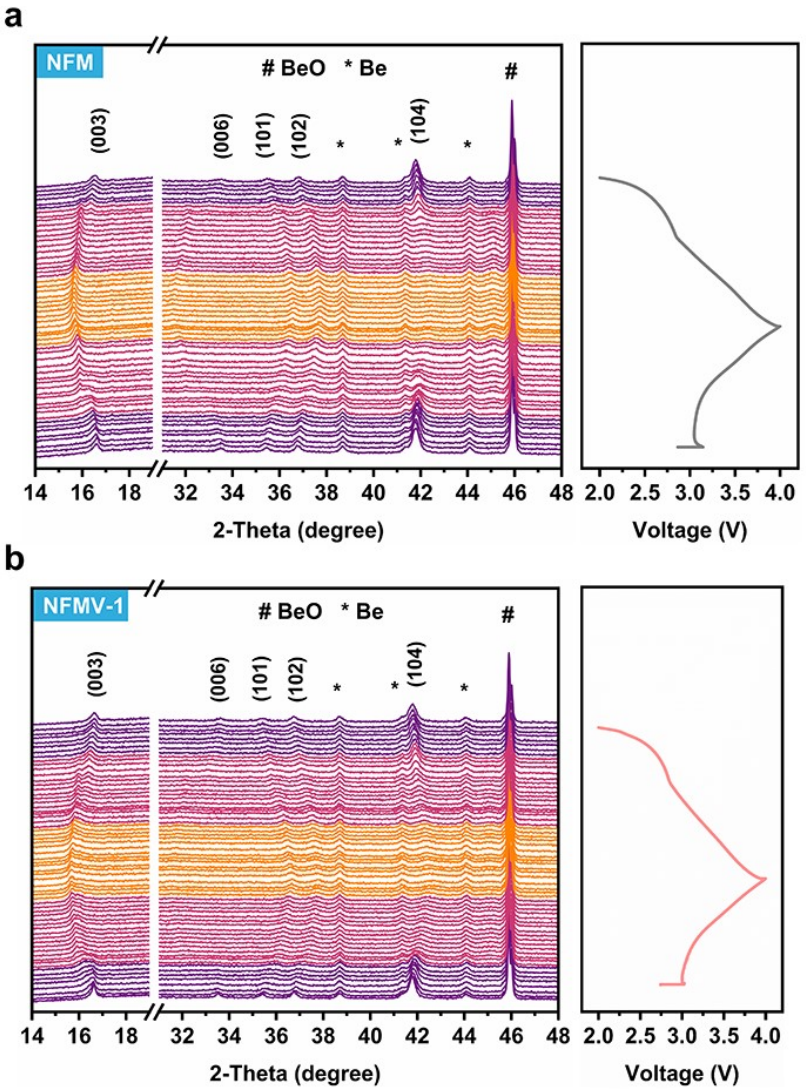

Fig. S8. In situ XRD patterns collected during the first charge/discharge of NFM and NFMV-1 over a voltage range of 2.0-4.0 V.

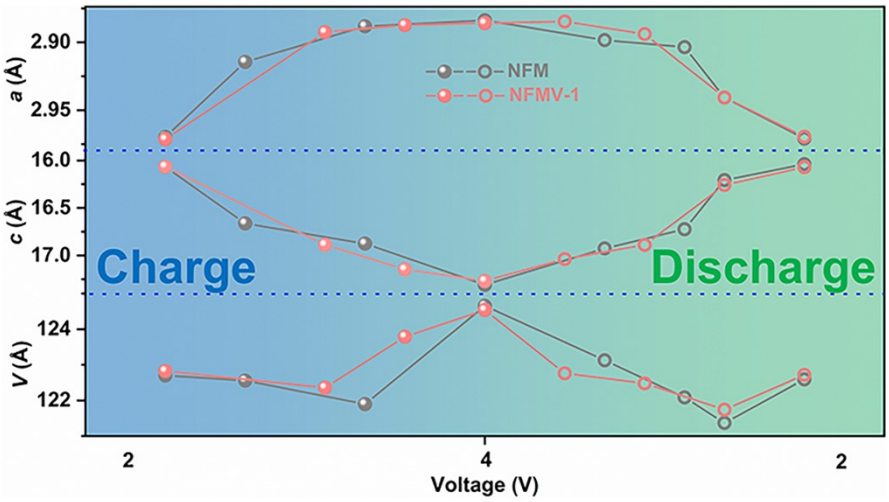

Fig. S9. The detailed change of lattice parameters of selected electrodes during the cycling process.

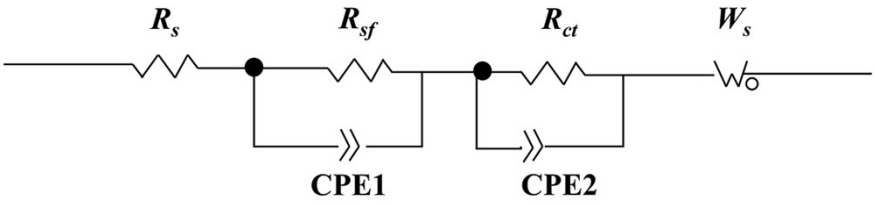

Fig. S10. equivalent circuit of EIS.

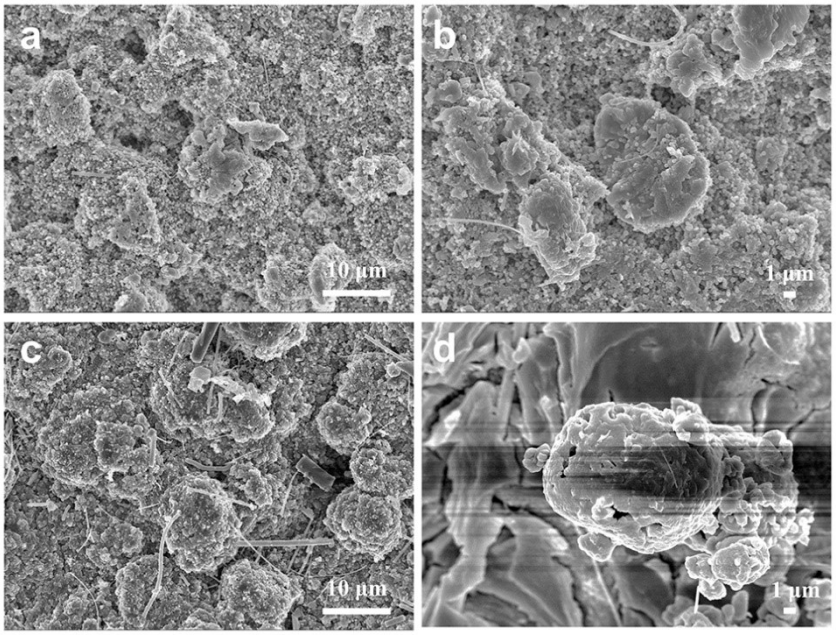

Fig. S11. SEM image of the of cycled cathodes for (a-b) NFM, (c-d)NFMV-1.

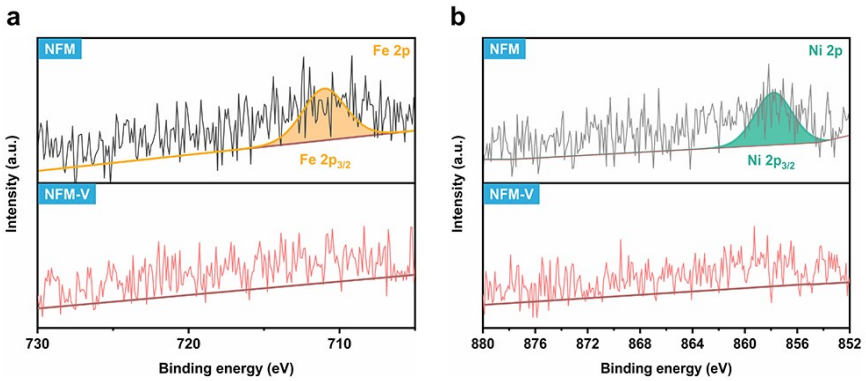

Fig. S12. XPS results of cycled cathodes for selected elements.

Table S1. ICP-OES results of all the samples.

Theoretical chemical formula	Measured atomic ratio				
	Na	Ni	Mn	Fe	V
$NaNi_{0.333}Mn_{0.333}Fe_{0.333}O_2$	1.003	0.337	0.335	0.333	0
$NaNi_{0.331}Mn_{0.331}Fe_{0.331}V_{0.005}O_2$	1.001	0.333	0.332	0.331	0.0048
$NaNi_{0.330}Mn_{0.330}Fe_{0.330}V_{0.010}O_2$	1.006	0.328	0.330	0.329	0.0106
$NaNi_{0.328}Mn_{0.328}Fe_{0.328}V_{0.015}O_2$	0.997	0.325	0.329	0.323	0.0140

Table S2. Crystallographic data and refinement parameters of all the samples.

Samples	NFM	NFMV-0.5	NFMV-1	NFMV-1.5
a, b [Å]	2.9788	2.9775	2.9742	2.9722
c [Å]	16.0304	16.0375	16.0518	16.0578
α, β [°]	90	90	90	90
γ [°]	120	120	120	120
V [Å^3]	123.189	123.134	122.972	122.85
R_p [%]	1.75	4.35	1.31	1.51
R_{wp} [%]	2.47	5.58	1.86	2.05

Table S3. Atomic distances, slab thickness and d-spacing of the Na layer for NFM and NFMV-1 from XRD refinement.

Samples	NFM	NFMV-1
TM-O [Å]	2.089	2.076
Na-O [Å]	2.272	2.284
TMO_2 [Å]	2.372	2.336
Na-spacing [Å]	2.970	3.014
Interlayer [Å]	5.342	5.350

Table S4. The calculated diffusion coefficients by GITT test for (a) NFM, (b) NFMV-1.

Samples	Charge D_{Na+} [10^{-11} cm^2 s^{-1}]	Discharge D_{Na+} [10^{-11} cm^2 s^{-1}]
NFM	6.80	3.95
NFMV-1	12.32	5.94

Table S5. EIS test results for (a) NFM, (b) NFMV after different cycled.

Samples	R_s (Ω)	R_{sf} (Ω)	R_{ct} (Ω)
NFM-uncycled	5.4	0	257.0
NFMV-uncycled	5.4	0	153.2
NFM-after 2 cycled	5.4	0	274.1
NFMV-after 2 cycled	5.6	0	164.8
NFM-after 500 cycled	7.2	469.7	734.2
NFMV-after 500 cycled	7.0	218.0	587.4

Table S6. Comparison of cycling performances of V-NFM with other modified NFM cathodes.

Cathode	Voltage window (V)	Cycling stability	Ref.
NVO-NFM	2.0-4.0 V	75.8%, 500, 2 C 96.4%, 150, 0.5 C	This work
NFM	2.0-4.0 V	50.7%, 500, 2 C 74.2%, 150, 0.5 C	This work
Zn-NFM	2.0-4.0 V	86.53%, 200, 1C	1
F-NFM	2.0-4.0 V	90%, 70, 1C	2
ZrO2-NFM	1.5-4.0 V	86%,100, 1 C	3
MoF-NFM	2.0-4.0 V	91.97%, 100, 1C	4
NTP-NFM	1.5-4.2 V	77.5%, 100, 1C	5
Sn-NFM	2.0-4.1 V	75%, 150, 0.5C	6

Table S7. Crystallographic and Rietveld refinement data of the NFM cathode.

Atom	Wyckoff position	x	y	z	Occ.
Na	3b	0	0	0	1
Ni	3a	0	0	0.5	0.333
Mn	3a	0	0	0	0.333
Fe	3a	0	0	0	0.333
O	6c	0	0	0.25933(14)	1

Table S8. Crystallographic and Rietveld refinement data of the NFMV-1 cathode.

Atom	Wyckoff position	x	y	z	Occ.
Na	3b	0	0	0	1
Ni	3a	0	0	0.5	0.330
Mn	3a	0	0	0	0.330
Fe	3a	0	0	0	0.330
V	3a	0	0	0	0.010
O	6c	0	0	0.26055(10)	1

Table S9. EXAFS fitting results for Fourier transformed $k^3 \chi(k)$ Ni K-edges structural parameters of samples.

Samples	Atom	X-Y pair	CN	R (Å)	σ2 /(10^{-2} Å²)	ΔE_0 (eV)	R-factor
NFM	Ni-O	Ni-O	6	2.06929	0.779	-5.558	0.006
	Ni-TM	Ni-TM	6	2.95681	0.720		
NFMV-1	Ni-O	Ni-O	6	2.09134	0.983	-2.752	0.014
	Ni-TM	Ni-TM	6	2.99016	0.719		

CN: coordination number; R: bond length; σ^2 : Debye-Waller factor (disorder); ΔE_0: energy parameter.

Table S10 Transition metal ion dissolution results of cycled batteries.

Sample	Concentration (ug/L)		
	Ni	Fe	Mn
NFM	276.34	650.53	16.93
NFMV-1	154.35	443.78	15.89

Reference

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2. Q. Zhang, Y. Huang, Y. Liu, S. Sun, K. Wang, Y. Li, X. Li, J. Han and Y. Huang, *Science China Materials*, 2017, **60**, 629-636.
3. Y. Yu, D. Ning, Q. Li, A. Franz, L. Zheng, N. Zhang, G. Ren, G. Schumacher and X. Liu, *Energy Storage Materials*, 2021, **38**, 130-140.
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