Supplementary Material

High-entropy configuration of O3-type layered transition-metal oxide cathode with high-voltage stability for sodium-ion batteries†

Lei Liu [a], Yuhang Xin [a], Yingshuai Wang [a], Xiangyu Ding [a], Qingbo Zhou [a], Ziye Wang [a], Weiqing Huang [b], Hongcai Gao [a,c,d*]*

[a] School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

[b] School of Mechanical Engineering, Beijing Institute of Technology, Beijing 100081, P.R. China

[c] Yangtze Delta Region Academy of Beijing Institute of Technology, Jiaxing, 314019, China

[d] Beijing Institute of Technology Chongqing Innovation Center, Chongqing 401120. P.R. China

† Electronic supplementary information (ESI) available.

Corresponding author: gaohc@bit.edu.cn (Prof. Hongcai Gao) hwq@bit.edu.cn (Prof. Weiqing Huang)

TableS1 Crystallographic data obtained from Rietveld Refinements of NFM, NFMT, NFMS and NFMTS.

	a (Å)	b (Å)	c (Å)	V (Å^3)	Na-O (Å)	TM-O (Å)	$d_{(101)}$
NFM	2.9718	2.9718	16.2428	124.2320	2.37199	2.02171	2.53919
NFMT	2.9729	2.9729	16.0686	122.9965	2.30812	2.05776	2.54225
NFMS	2.9661	2.9661	16.1570	123.1039	2.36365	2.01595	2.53431
NFMTS	2.9716	2.9716	16.2421	124.2091	2.39485	2.00426	2.54167

TableS2 Atom occupancy parameters obtained from Rietveld Refinements of NFM, NFMT, NFMS and NFMTS.

Chemic	Measured atomic						
	Na	Mn	Fe	Ni	Ti	Sb	O
NFM	1.00000	0.3999	0.20005	0.39998	0.0000	0.00000	1.0000
NFMT	1.00000	0.3000	0.20005	0.39998	0.0999	0.00000	1.0000
NFMS	1.00000	0.3999	0.20005	0.35005	0.0000	0.05004	1.0000
NFMTS	1.00000	0.3000	0.20005	0.35005	0.0999	0.05004	1.0000

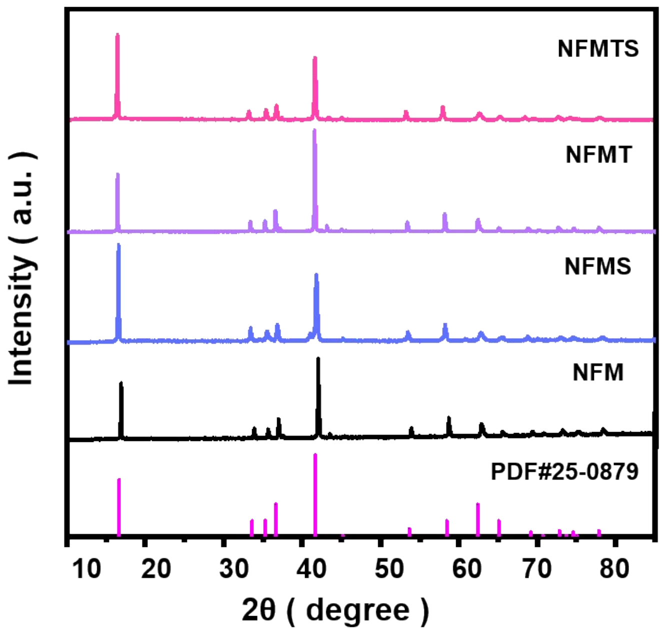

Figure S1 XRD pattern of NFM, NFMS, NFMT and NFMTS

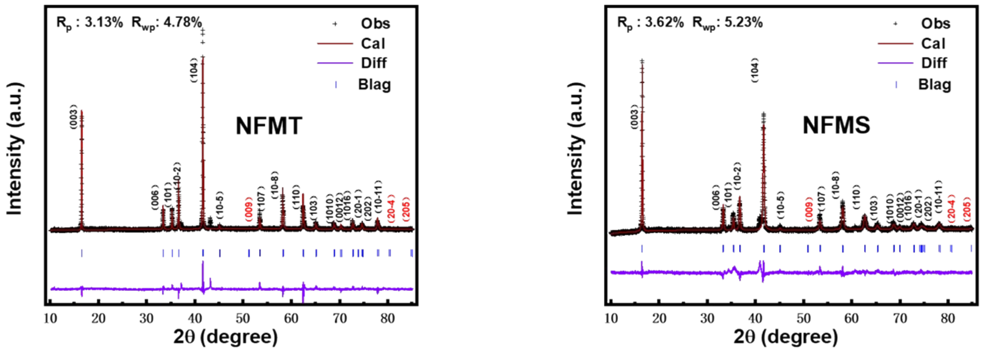

Figure S2 XRD pattern and Rietveld refinement profile of NFMT and NFMS

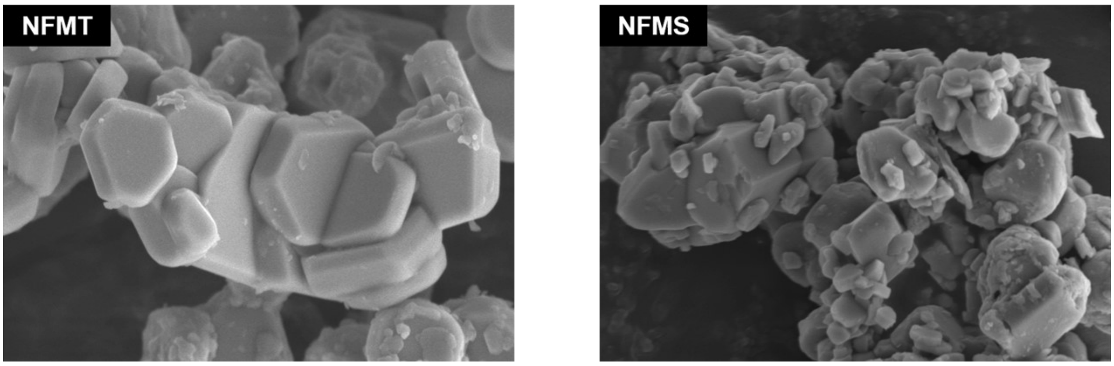

Figure S3 SEM images of NFMT and NFMS

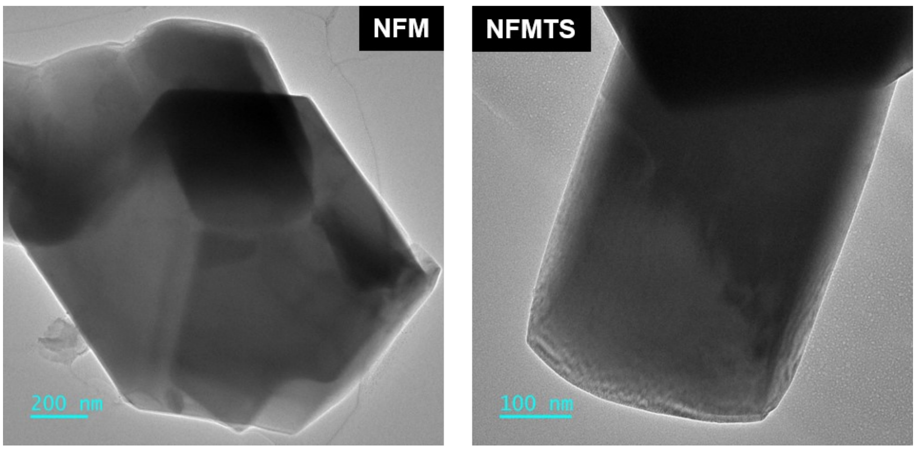

Figure S4. TEM images of NFM and NFMTS

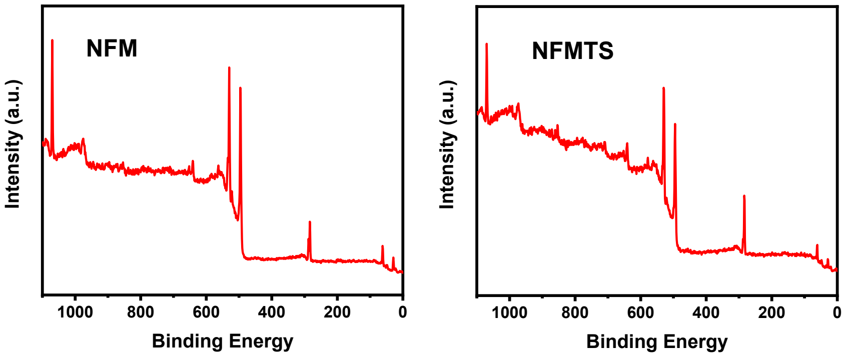

Figure S5. XPS spectrum of NFM and NFMTS

TableS3 Cycle performance of NFM, NFMT, NFMS and NFMTS.

	NFM	NFMT	NFMS	NFMTS
Initial specific capacity ($mAh \cdot g^{-1}$)	134.4	144.4	109.9	122.0
Specific capacity after 200 cycles ($mAh \cdot g^{-1}$)	63.4	71.7	64.2	92.5
Capacity retention (%)	47.2	49.6	58.5	76.0

TableS4 The comparative specific capacity of previously reported various modified NFM electrodes and NFMTS.

	Discharge specific capacity at 0.1C ($mAh \cdot g^{-1}$)	Working Voltage (V)	References
$NaNi_{0.35}Fe_{0.2}Mn_{0.3}Ti_{0.1}Sb_{0.05}O_2$	217.2	1.7-4.3	This work
$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	160	1.9-4.2	44
$NaLi_{0.05}(Ni_{0.25}Fe_{0.5}Mn_{0.25})_{0.95}O_2$	177	1.7-4.4	43
$NaNi_{0.32}Fe_{0.32}Mn_{0.32}Al_{0.02}Cu_{0.02}O_2$	140	2.0-4.0	45
$NaNi_{0.2}Fe_{0.2}Mn_{0.2}Co_{0.2}Ti_{0.2}O_2$	180	1.5-4.2	46
$Na_{0.95}Ni_{1/3}Fe_{1/3}Mn_{1/3}O_2$	133.3	2.0-4.0	44
$NaNi_{0.12}Cu_{0.12}Mg_{0.12}Fe_{0.15}Mn_{0.1}Co_{0.15}Ti_{0.1}Sn_{0.1}Sb_{0.04}O_2$	110	2.0-3.9	31
$NaNi_{0.2}Fe_{0.2}Mn_{0.2}Co_{0.2}O_2$	177	1.9-4.3	47

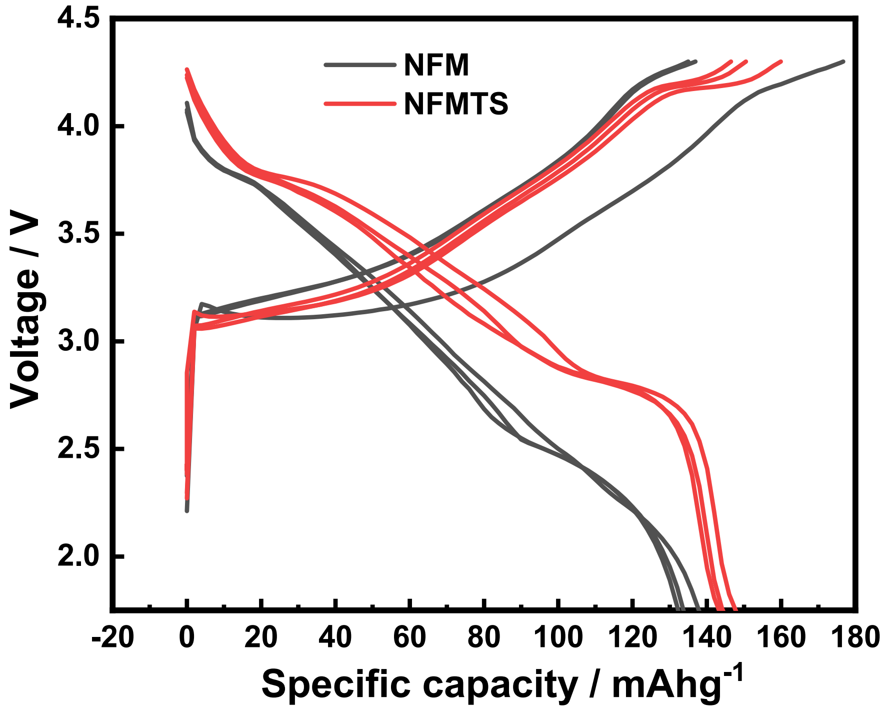

Figure S6. The charge and discharge curves of NFM and NFMTS cathodes at high voltage ranges of 1.7-4.3 V.

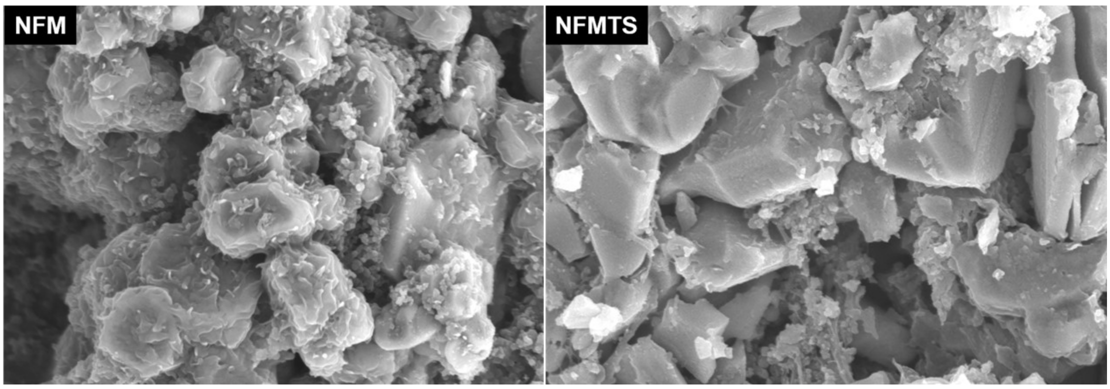

Figure S7. SEM images of NFM and NFMTS cathodes after 20 cycles

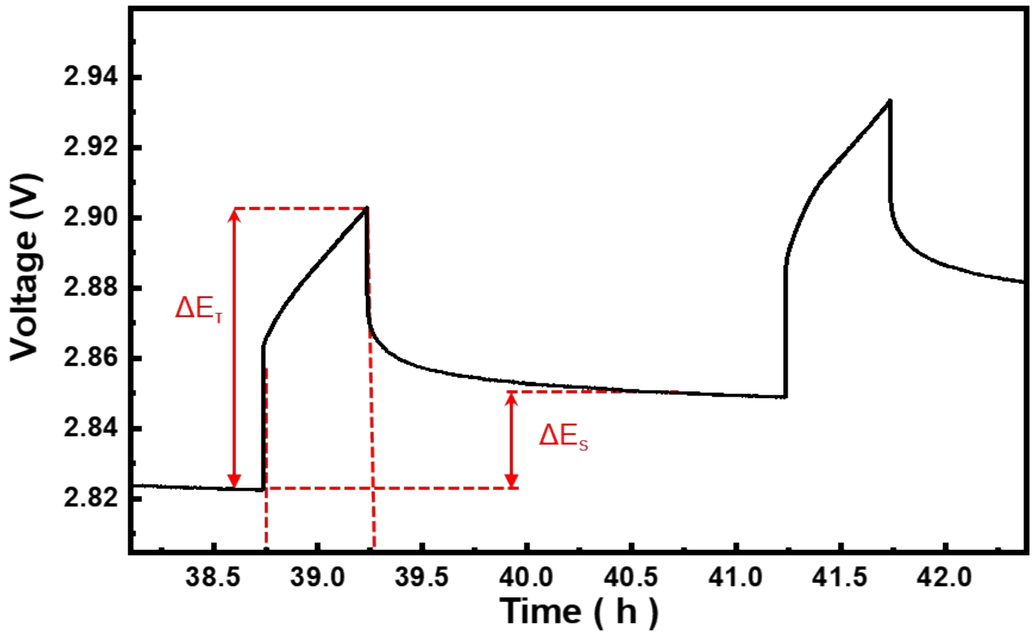

Figure S8. Schematic illustration of selected steps of GITT test for NFM and NFMTS with a charge/discharge time of 30 min and a relaxation time of 2 h.

GITT measurements were performed by charging at a current density of 0.1 C for 30 min following a 120 min open circuit relaxation. D_{Na+} from GITT results is calculated by the following equation:

$$D_{Na+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \qquad (S1)$$

In the above equations, D represents the diffusion coefficient of Na^+ in the cathode, V_M (cm^3 mol^{-1}) denotes the molar volume, m_B and M_B refer to the molecular weight and relative molar weight of the cathode material. S represents the surface area of the electrode. τ represents the time duration of the applied current during galvanostatic intermittent titration. ΔE_S and ΔE_τ represent the steady voltage state and the overall variation in battery voltage *E* during the current pulse, respectively.

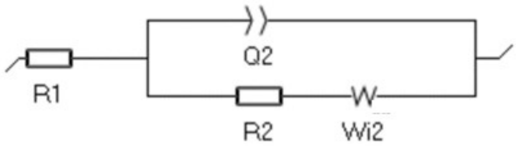

Figure S9. Equivalent circuit diagram in EIS