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Supplementary Material

Entropy modulation strategy of P2-type layered transition-metal oxide cathodes for sodium-ion batteries with a high performance

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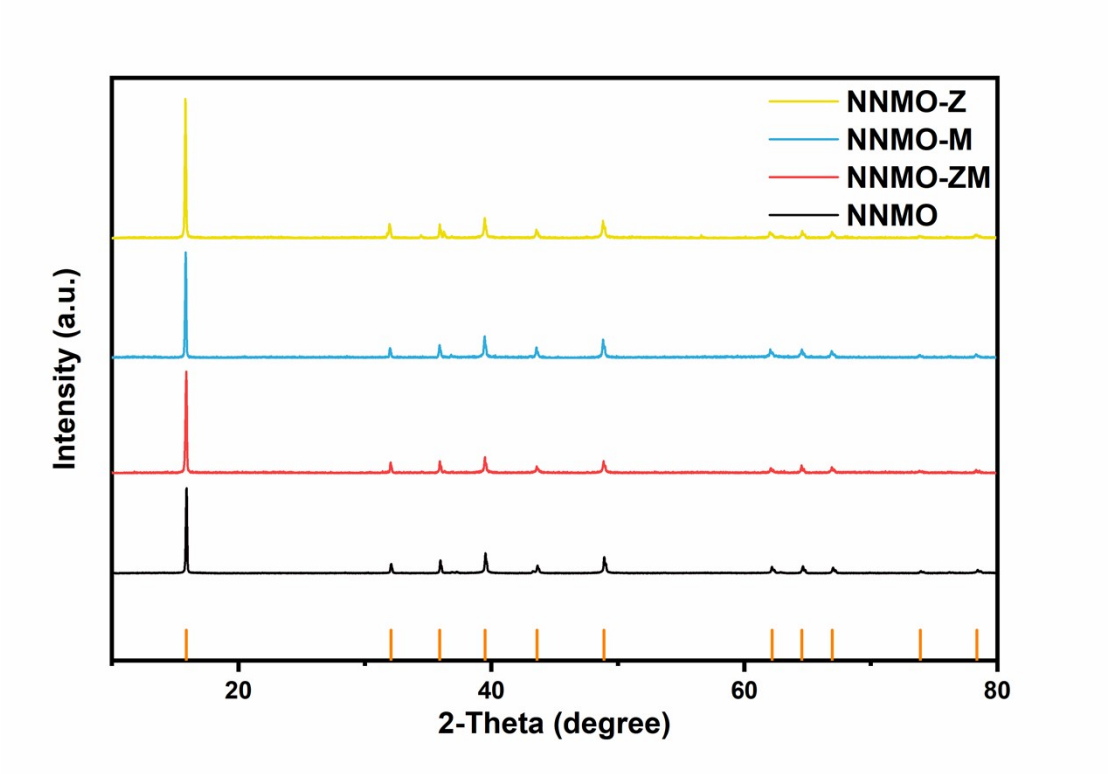

Fig. S1: Powder XRD patterns of NNMO-ZM, NNMO-M, NNMO-Z and NNMO.

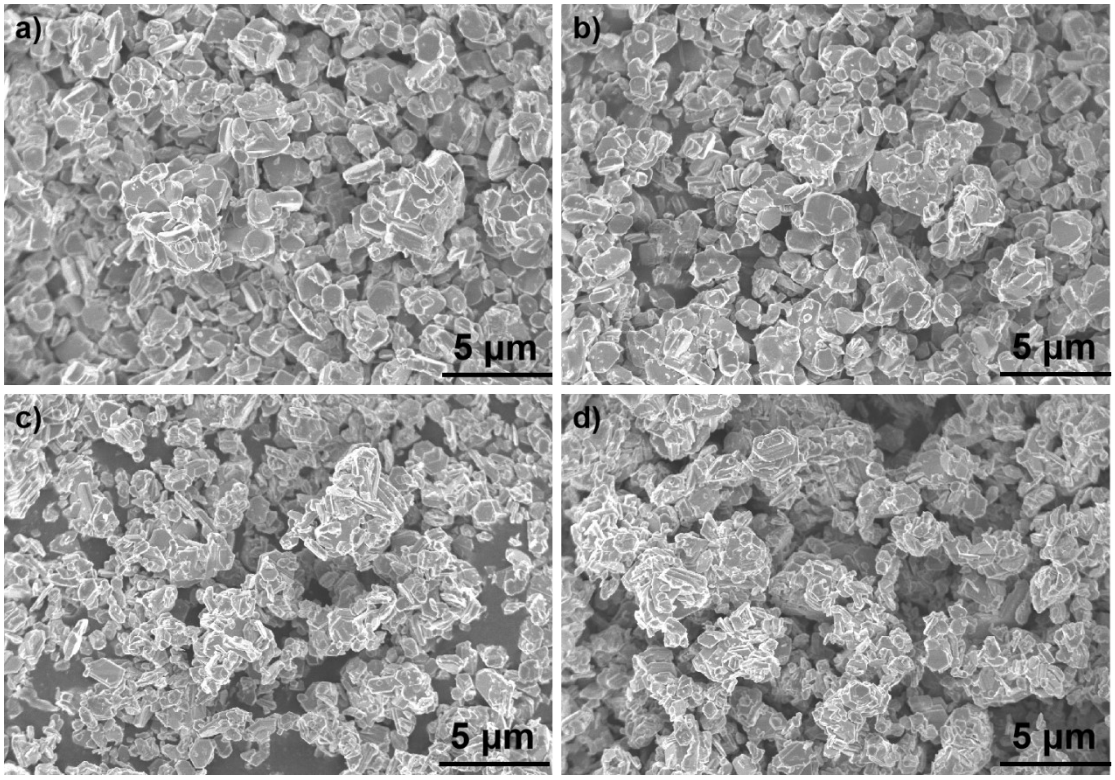

Fig. S2: SEM images of four samples. (a) NNMO-ZM; (b) NNMO-M; (c) NNMO-Z; (d) NNMO.

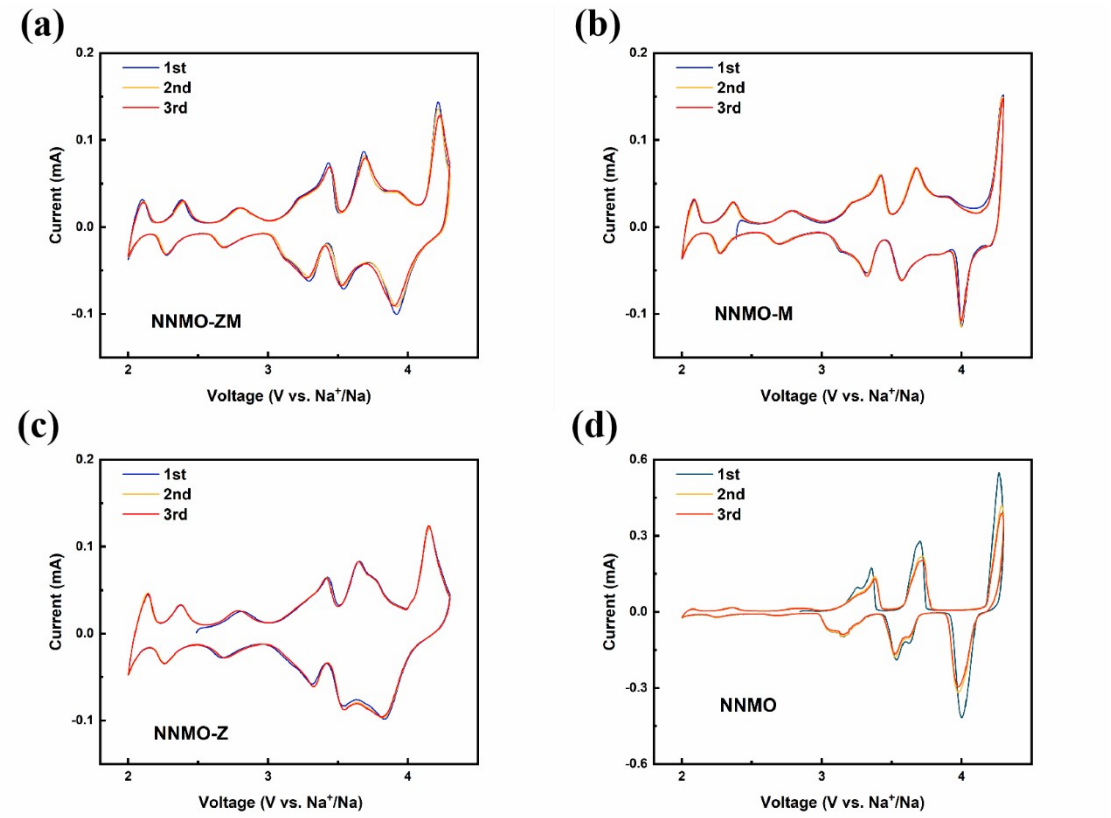

Fig. S3: CV curves of (a) NNMO-ZM，(b) NNMO-M， (c) NNMO-Z and (d) NNMO electrodes between 2.0 and 4.3 V at 0.1 mV s^{-1} scan rate.

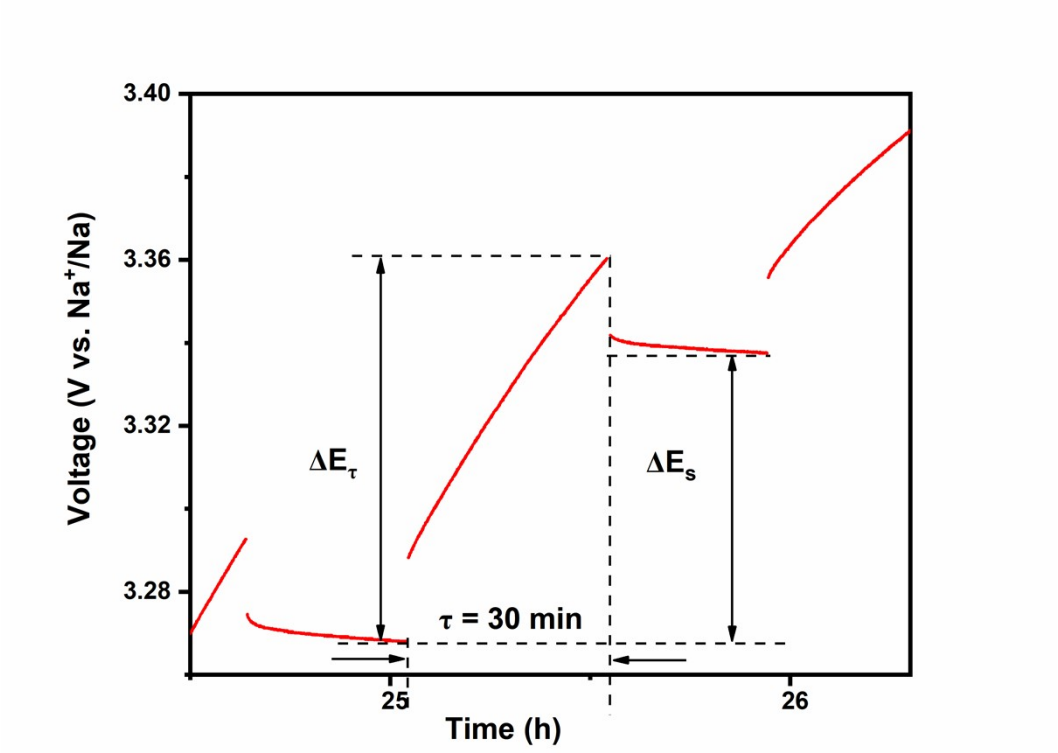

Fig. S4: Schematic illustration of selected steps of GITT test for NNMO-ZM with a charge/discharge time of 30 min.

Based on the GITT measurement, the Na^+ diffusion coefficient can be calculated by Equation S1:

$$D_{Na+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left[\frac{\Delta E_s}{\Delta E_t}\right]^2 \quad \text{S1}$$

where D_{Na+} ($cm^2\ s^{-1}$) represents the Na^+ diffusion coefficient, V_M ($cm^3\ mol^{-1}$), m_B, and M_B are the molar volume, weight, and molar weight of the active materials, respectively, S and τ(s) denote the surface area of the electrode and the testing time in each step, and ΔE_s and ΔE_t are the quasi-equilibrium potential and the change in cell voltage E during the current pulse, respectively.[1-4]

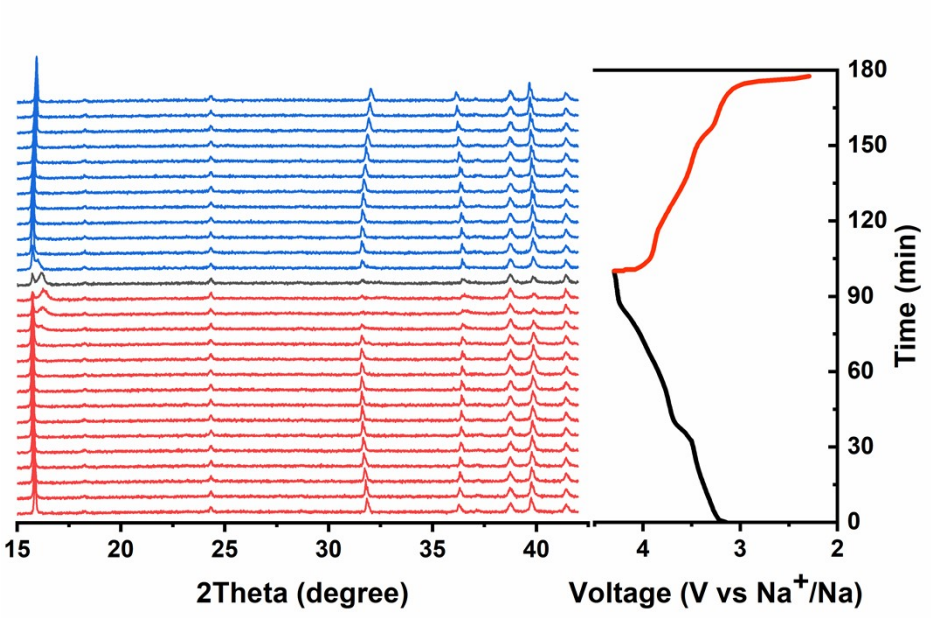

Fig. S5: Contour maps of in situ XRD patterns from NNMO-ZM.

Table S1: Summary of refined structural parameters of $Na_{0.67}Mn_{0.67}Ni_{0.21}Mg_{0.12-x}Zn_xO_2$

sample	a[Å]	c[Å]	V[Å^3]	Rwp(%)	Rp(%)	GOF
NNMO-ZM	2.88348	11.19062	80.578	4.43	2.88	1.41
NNMO-M	2.88312	11.18777	80.537	5.505	3.72	1.57
NNMO-Z	2.88285	11.18284	80.420	5.056	3.93	1.48
NNMO	2.88278	11.15952	80.316	4.609	3.61	1.64

Table S2: Crystallographic parameters of NNMO-ZM refined by the Rietveld method.

Space group P63/mmc						
Lattice	a[Å]	c[Å]	V[Å^3]	Rwp(%)	Rp(%)	GOF
Hexagonal	2.8835 (±0.0002)	11.1906 (±0.0009)	80.58 (±0.01)	5.489	3.69	1.41
Atom	Site	x	y	z	Occ.	U_{iso}
Na_c	2d	0.6667	0.3333	0.25	0.425	0.43552
Na_f	2b	0	0	0.25	0.286	0.12242
Mn	2a	0	0	0	0.667	0
O	4f	0.6667	0.3333	0.07645	0.975	0.03096
Ni	2a	0	0	0	0.213	0
Zn	2a	0	0	0	0.06	0
Mg	2a	0	0	0	0.06	0

Table S3: The result of $Mn2p_{3/2}$ multiple splitting peaks from NNMO-ZM.

$Mn2p_{3/2}$ (Multiple splitting peaks)					
Peak	Binding energy/eV	Chemical state	Atomic percent %	Atomic percent %	
$Mn2p_{3/2}$	641.8		38.07		
$Mn2p_{3/2}$	642.66		24.38		
$Mn2p_{3/2}$	643.36		14.11		
$Mn2p_{3/2}$	644.11	Mn(IV)	8.39	91.82	100
$Mn2p_{3/2}$	644.96		4.58		
$Mn2p_{3/2}$	645.96		2.29		
$Mn2p_{3/2}$	641.23	Mn(III)	8.18	8.18	

Reference

1. Y. Wang, Q. Wang, X. Ding, M. Wang, Y. Xin and H. Gao, *Applied Surface Science*, 2022, **601**, 154218.
2. Q. Wang, X. Ding, J. Li, H. Jin and H. Gao, *Chemical Engineering Journal*, 2022, **448**, 137740.
3. M. Wang, Q. Wang, X. Ding, Y. Wang, Y. Xin, P. Singh, F. Wu and H. Gao, *Interdisciplinary Materials*, 2022, **1**, 373-395.
4. Q. Wang, C. Ling, J. Li, H. Gao, Z. Wang and H. Jin, *Chemical Engineering Journal*, 2021, **425**, 130680.