Electronic Supplementary Material (ESI) for Materials Horizons.
This journal is © The Royal Society of Chemistry 2024

Supporting Information

Realizing Long-Term Cycling Stability of O3-Type Layered Oxide Cathode for Sodium-Ion Batteries

Guohua Zhang,[1] Yuheng Gao,[2] Ping Zhang,[1] Yuheng Gao,[1] Jingrong Hou,[1] Xuemin Shi,[1] Jiwei Ma,[1] Renyuan Zhang,[1] and Yunhui Huang [2]**

[1]Institute of New Energy for Vehicles, Shanghai Key Laboratory for R&D and Application of Metallic Functional Materials, School of Materials Science and Engineering, Tongji University, Shanghai 201804, China

E-mail: ryzhang@tongji.edu.cn;

[2]State Key Laboratory of Material Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

E-mail: huangyh@hust.edu.cn

* Corresponding author

Table S1. Structural information of NFM, SNFM, LNFM and LSNFM obtained from Rietveld refinements.

NFM

Atom	**Site**	***x***	***y***	***z***	**Occ.**
O	6c	0	0	0.2348	1
Fe	3b	0	0	0.5	0.28
Mn	3b	0	0	0.5	0.5
Ni	3b	0	0	0.5	0.22
Na	3a	0	0	0	0.95

Space group $R\overline{3}m$. $a = b = 2.94863(1)$ Å, $c = 16.32531(7)$ Å, $V = 122.923$ Å^3. $R_p = 2.51\%$, $R_{wp} = 3.32\%$, $R_{exp} = 2.56\%$, $\chi^2 = 1.67$.

SNFM

Atom	**Site**	***x***	***y***	***z***	**Occ.**
O	6c	0	0	0.2348	1
Fe	3b	0	0	0.5	0.27
Mn	3b	0	0	0.5	0.5
Ni	3b	0	0	0.5	0.22
Na	3a	0	0	0	0.95
Sn	3b	0	0	0.5	0.01

Space group $R\overline{3}m$. $a = b = 2.95216(8)$ Å, $c = 16.35792(2)$ Å, $V = 123.464$ Å^3. $R_p = 2.83\%$, $R_{wp} = 3.79\%$, $R_{exp} = 2.85\%$, $\chi^2 = 1.77$.

LNFM

Atom	**Site**	***x***	***y***	***z***	**Occ.**
O	6c	0	0	0.2348	1
Fe	3b	0	0	0.5	0.21
Mn	3b	0	0	0.5	0.5
Ni	3b	0	0	0.5	0.22
Na	3a	0	0	0	0.95
Li	3b	0	0	0.5	0.07

Space group $R\overline{3}m$. $a = b = 2.94553(5)$ Å, $c = 16.20275(1)$ Å, $V = 121.744$ Å^3. $R_p = 2.62\%$, $R_{wp} = 3.53\%$, $R_{exp} = 2.61\%$, $\chi^2 = 1.83$.

LSNFM

Atom	**Site**	***x***	***y***	***z***	**Occ.**
O	6c	0	0	0.2348	1
Fe	3b	0	0	0.5	0.2
Mn	3b	0	0	0.5	0.5
Ni	3b	0	0	0.5	0.22
Na	3a	0	0	0	0.95
Li	3b	0	0	0.5	0.07
Sn	3b	0	0	0.5	0.01

Space group $R\overline{3}m$. $a = b = 2.95058(6)$ Å, $c = 16.21883(2)$ Å, $V = 122.283$ Å^3. $R_p = 2.69\%$, $R_{wp} = 3.60\%$, $R_{exp} = 2.65\%$, $\chi^2 = 1.85$.

Table S2. Comparisons of the lattice parameters among NFM, SNFM, LNFM and LSNFM samples.

Samples	a=b (Å)	c (Å)	V (Å^3)
NFM	2.9486	16.3253	122.923
SNFM	2.9522	16.3579	123.464
LNFM	2.9455	16.2028	121.744
LSNFM	2.9506	16.2188	122.283

Table S3. The lengths of Mn–O bonds and distances of Na^+ layers from Rietveld refinement results for as-prepared samples.

Samples	NFM	SNFM	LNFM	LSNFM
$d_{Mn–O}$ (Å)	2.0336	2.0365	2.0275	2.0305
$d_{O–Na–O}$ (Å)	3.2172	3.2236	3.1930	3.1962

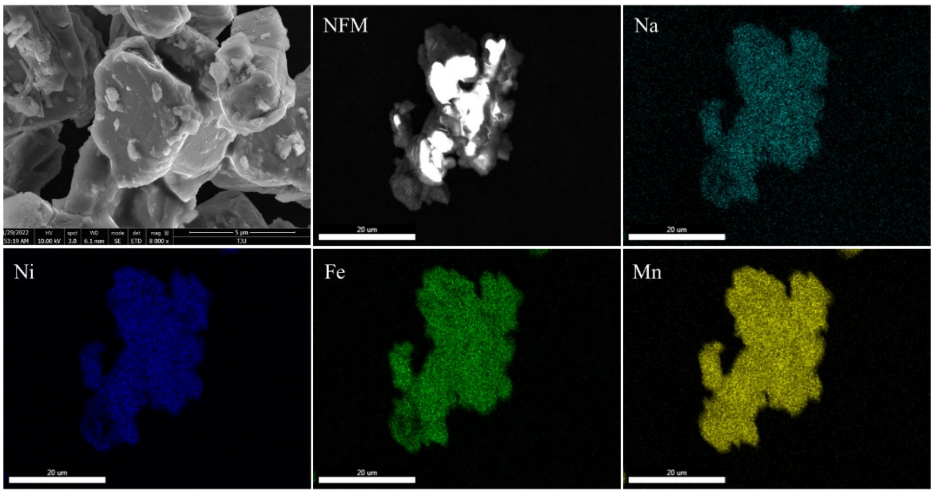

Figure S1. SEM-EDS mapping images of NFM

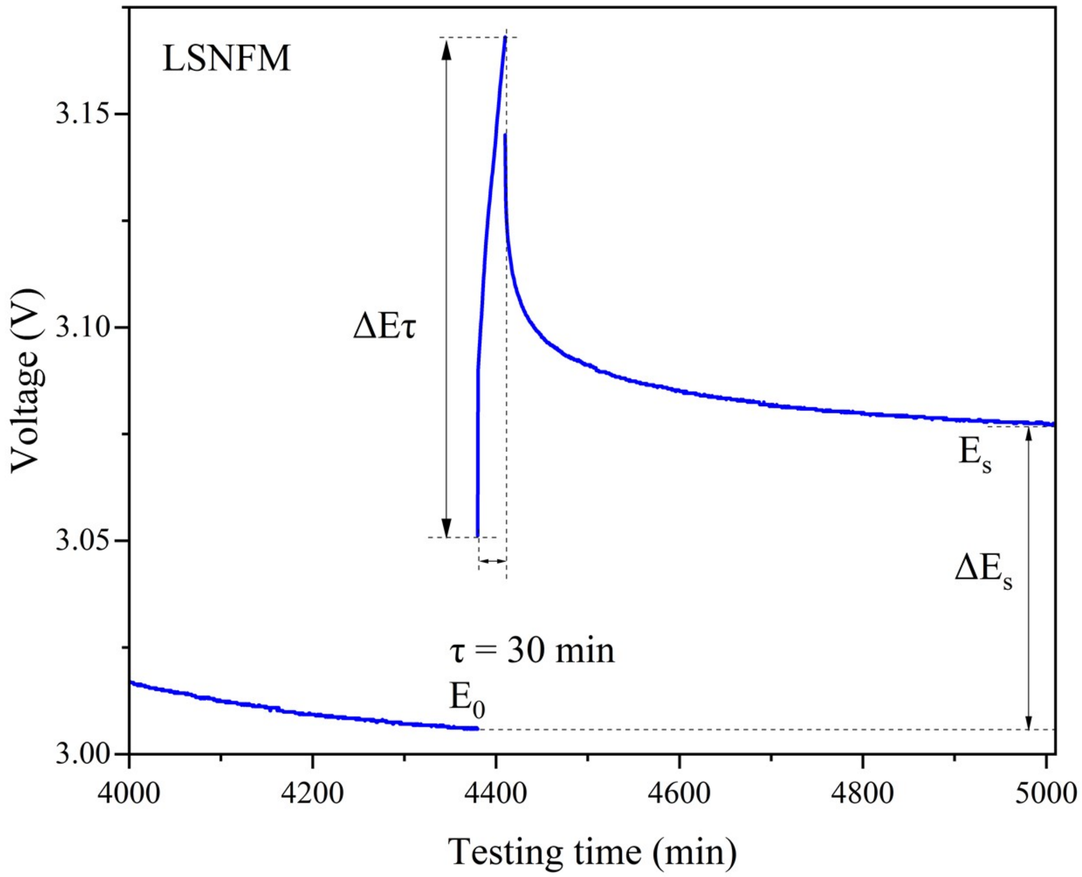

Figure S2. Votage *vs* time profiles for a single titration of a GITT experiment of LSNFM.

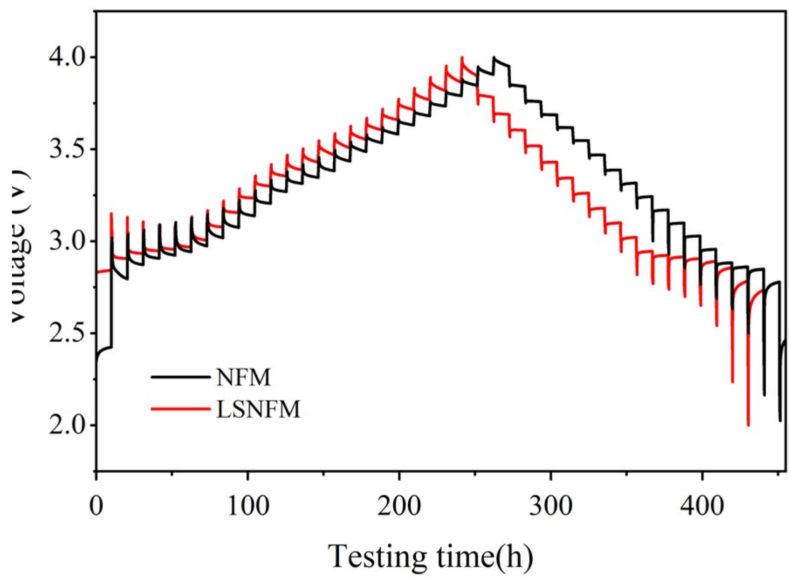

Figure S3. Charge–discharge GITT profiles in the first cycle at 0.1 C.

Figure S4. The calculated Na^+ diffusion coefficients (D_{Na+}) from GITT tests.

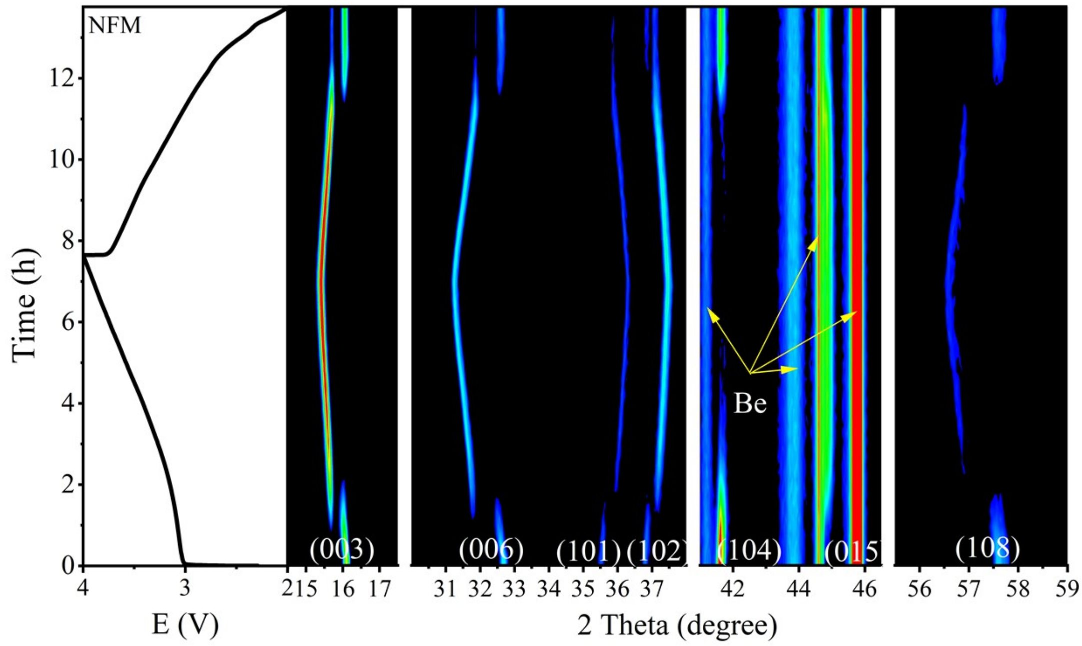

Figure S5. Contour plots of *in-situ* XRD for the NFM material during the first charge/discharge process at 0.1 C in the voltage range of 2.0–4.0 V.

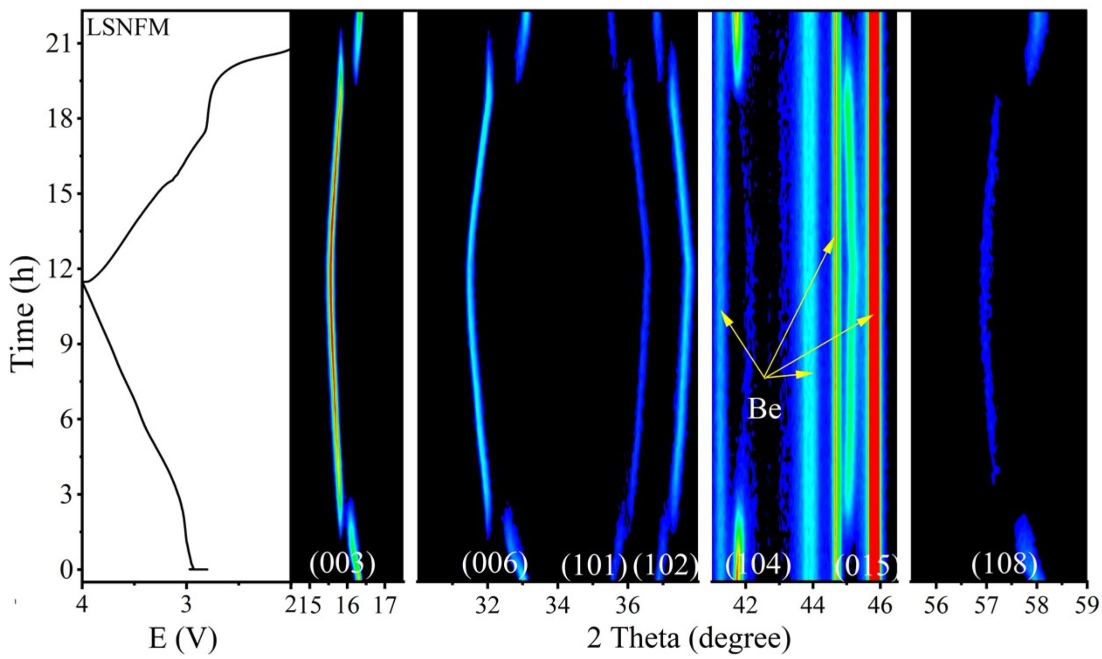

Figure S6. Contour plots of *in-situ* XRD for the LSNFM material during the first charge/discharge process at 0.1 C in the voltage range of 2.0–4.0 V.

Table S4. Cycling performance of the representative and important layered oxide cathode materials

Cathode material	Voltage range	Initial capacity	Cycle retention ratio	Synthesis	Ref.
O3-$NaMn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Ti_{0.2}O_2$	1.5-4.2 V	180 mAh g^{-1}	93.1% after 100 cycles (0.1 C)	Solid-state	[1]
O3-$NaNi_{0.12}Cu_{0.12}Mg_{0.12}Fe_{0.15}Co_{0.15}Mn_{0.1}Ti_{0.1}Sn_{0.1}Sb_{0.04}O_2$	2.0-3.9 V	110 mAh g^{-1}	79% after 200 cycles (1 C), 83% after 500 cycles (3 C)	Solid-state	[2]
O3-$Na_{0.89}Li_{0.05}Cu_{0.11}Ni_{0.11}Fe_{0.3}Mn_{0.43}O_{1.97}F_{0.03}$	1.5-4.0 V	138.6 mAh g^{-1}	80% after 300 cycles (1 C)	Solid-state	[3]
O3-$Na_{0.93}Li_{0.12}Ni_{0.25}Fe_{0.15}Mn_{0.48}O_2$	2.0-4.2 V	130.1 mAh g^{-1}	82.8% after 200 cycles (1600 mA g^{-1})	Solid-state	[4]
O3-$NaLi_{1/9}Ni_{2/9}Fe_{2/9}Mn_{4/9}B_{1/50}O_2$	2.0-4.3 V	160.5 mAh g^{-1}	82.8% after 200 cycles (250 mA g^{-1}/1C)	Solid-state	[5]
O3-$NaFe_{0.2}Co_{0.2}Ni_{0.2}Ti_{0.2}Sn_{0.1}Li_{0.1}O_2$	2.0-4.1 V	112.7 mAh g^{-1}	72% after 100 cycles (0.1 C) 67% after 200 cycles (0.5 C)	Solid-state	[6]
O3-$NaNi_{0.1}Mn_{0.15}Co_{0.2}Cu_{0.1}Fe_{0.1}Li_{0.1}Ti_{0.15}Sn_{0.1}O_2$	2.0-4.1 V	115 mAh g^{-1}	82.7% after 1000 cycles (160 mA g^{-1})	Solid-state	[7]
P2-$Na_{2/3}Li_{1/6}Fe_{1/6}Co_{1/6}Ni_{1/6}Mn_{1/3}O_2$	2.0-4.5 V	171.2 mAh g^{-1}	89.3% after 90 cycles (1C) 63.7% after 300 cycles (5 C)	Solid-state	[8]
P2/O3- $Na_{0.85}Li_{0.05}Ni_{0.25}Cu_{0.025}Mg_{0.025}Fe_{0.05}Al_{0.05}Mn_{0.5}Ti_{0.05}O_2$	2.0-4.2 V	122 mAh g^{-1}	88% after 300 cycles (2C), 90% after 1000 cycles (10 C)	Solid-state	[9]
O3-$NaCu_{0.1}Ni_{0.3}Fe_{0.2}Mn_{0.2}Ti_{0.2}O_2$	2.0-3.9 V	130 mAh g^{-1}	87% after 100 cycles (0.1C) 71% after 500 cycles (0.5C)	Solid-state	[10]
$Na_{3-3x}Al_xPO_4$ coating O3-$NaNi_{0.4}Fe_{0.2}Mn_{0.4}O_2$	2.0-4.0 V 2.0-4.2 V	147.6 mAh g^{-1}	80% after 200 cycles (1 C)	Coprecipitation	[11]
O3-$NaLi_{0.05}Mn_{0.50}Ni_{0.30}Cu_{0.10}Mg_{0.05}O_2$	2.0-4.0 V	172 mAh g^{-1}	63.1% after 1000 cycles (0.5C) 81.6% after 400 cycles (1C)	Coprecipitation	[12]

$NaMgPO_4$@$NaNi_{0.4}Cu_{0.1}Mn_{0.4}Ti_{0.1}O_2$-X	2.4-4.3 V	160 mAh g^{-1}	65% after 100 cycles (0.25 C)	Solid-state	[13]
O3-$NaNi_{0.25}Mg_{0.05}Cu_{0.1}Fe_{0.2}Mn_{0.2}Ti_{0.1}Sn_{0.1}O_2$	2.0-4.0 V	130.8 mAh g^{-1}	75% after 500 cycles (1 C)	Solid-state	[14]
$Na_{0.95}Li_{0.07}Sn_{0.01}Ni_{0.22}Fe_{0.2}Mn_{0.5}O_2$	2.0-4.0 V	108.5 mAh g^{-1}	84% after 500 cycles (1 C) 84.7% after 2000 cycles (5 C)	Solid-state	This work

[1] K. Walczak, A. Plewa, C. Ghica, W. Zając, A. Trenczek-Zając, M. Zając, J. Toboła, J. Molenda, *Energy Storage Mater.,* **2022**, 47, 500.

[2] C. Zhao, F. Ding, Y. Lu, L. Chen, Y. S. Hu, *Angew. Chem. Int. Ed.,* **2020**, 59, 264.

[3] F. Ding, H. Wang, Q. Zhang, L. Zheng, H. Guo, P. Yu, N. Zhang, Q. Guo, F. Xie, R. Dang, X. Rong, Y. Lu, R. Xiao, L. Chen, Y. S. Hu, *J. Am. Chem. Soc.,* **2023**, 145, 13592.

[4] X. G. Yuan, Y. J. Guo, L. Gan, X. A. Yang, W. H. He, X. S. Zhang, Y. X. Yin, S. Xin, H. R. Yao, Z. Huang, Y. G. Guo, *Adv. Funct. Mater.,* **2022**, 32, 2111466.

[5] Y. J. Guo, P. F. Wang, Y. B. Niu, X. D. Zhang, Q. Li, X. Yu, M. Fan, W. P. Chen, Y. Yu, X. Liu, Q. Meng, S. Xin, Y. X. Yin, Y. G. Guo, *Nat. Commun.,* **2021**, 12, 5267.

[6] K. Tian, H. He, X. Li, D. Wang, Z. Wang, R. Zheng, H. Sun, Y. Liu, Q. Wang, *J. Mater. Chem. A,* **2022**, 10, 14943.

[7] X.-Y. Du, Y. Meng, H. Yuan, D. Xiao, *Energy Storage Mater.,* **2023**, 56, 132.

[8] L. Yao, P. Zou, C. Wang, J. Jiang, L. Ma, S. Tan, K. A. Beyer, F. Xu, E. Hu, H. L. Xin, *Adv. Energy Mater.,* **2022**, 12.

[9] J. Mu, T. Cai, W. Dong, C. Zhou, Z. Han, F. Huang, *Chem. Eng. J.,* **2023**, 471.

[10] C.-C. Lin, H.-Y. Liu, J.-W. Kang, C.-C. Yang, C.-H. Li, H.-Y. T. Chen, S.-C. Huang, C.-S. Ni, Y.-C. Chuang, B.-H. Chen, C.-K. Chang, H.-Y. Chen, *Energy Storage Mater.,* **2022**, 51, 159.

[11] H. Wang, F. Ding, Y. Wang, Z. Han, R. Dang, H. Yu, Y. Yang, Z. Chen, Y. Li, F. Xie, S. Zhang, H. Zhang, D. Song, X. Rong, L. Zhang, J. Xu, W. Yin, Y. Lu, R. Xiao, D. Su, L. Chen, Y.-S. Hu, *ACS Energy Lett.,* **2023**, 8, 1434.

[12] J. Deng, W. B. Luo, X. Lu, Q. Yao, Z. Wang, H. K. Liu, H. Zhou, S. X. Dou, *Adv. Energy Mater.,* **2017**, 8, 1701610.

[13] W. Xu, R. Dang, L. Zhou, Y. Yang, T. Lin, Q. Guo, F. Xie, Z. Hu, F. Ding, Y. Liu, Y. Liu, H. Mao, J. Hong, Z. Zuo, X. Wang, R. Yang, X. Jin, X. Hou, Y. Lu, X. Rong, N. Xu, Y. S. Hu, *Adv. Mater.,* **2023**, 35, e2301314.

[14] F. Ding, C. Zhao, D. Xiao, X. Rong, H. Wang, Y. Li, Y. Yang, Y. Lu, Y. S. Hu, *J. Am. Chem. Soc.,* **2022**, 144, 8286.