

Supplementary Information

Phase Engineering and Ion Diffusion Kinetics for High Power and Long Lifespan Potassium-Ion Batteries

Xuan-Wen Gao^{¶, ‡}, Qi Li[¶], Rui Yang[¶], Yingying Song[§], Zhao-Meng Liu^{¶, ‡}, Qinfen Gu[£], Wen-Bin Luo^{¶}*

[¶]Institute for Energy Electrochemistry and Urban Mines Metallurgy, School of Metallurgy, Northeastern University, Shen yang, Liaoning 110819, China.

[‡] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China

[£]Australian Synchrotron (ANSTO), 800 Blackburn Rd, Clayton, Victoria 3168, Australia.

[§]School of Science and Engineering, University of Dundee, Nethergate, Dundee, DD1 4HN, Scotland, UK

Corresponding Authors

E-mail: luowenbin@smm.neu.edu.cn

KEYWORDS

Potassium ion battery, ion exchange, cathode material, phase interface, ion diffusion kinetics

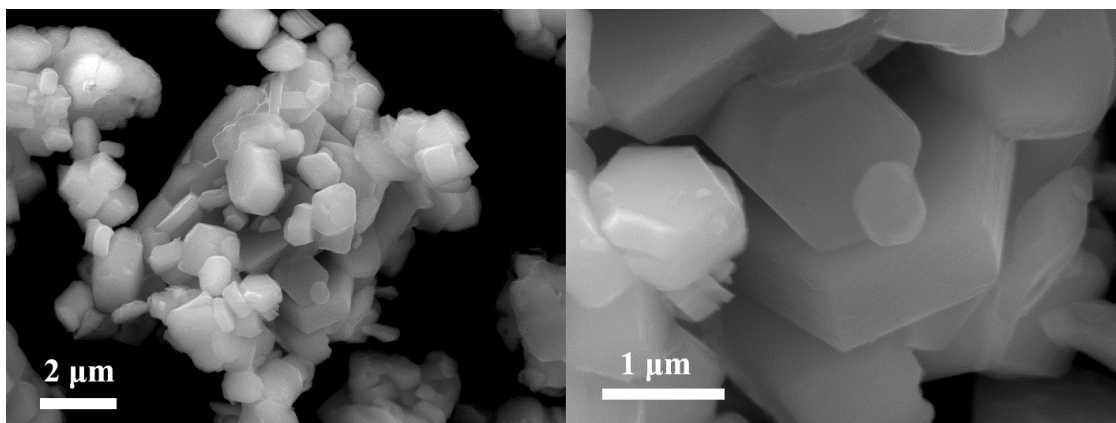


Figure S1. Scanning Electron Microscope (SEM) image of P2-NMCT, showing agglomerates with diameters of approximately 10 microns, where each individual agglomerate spans a few microns.

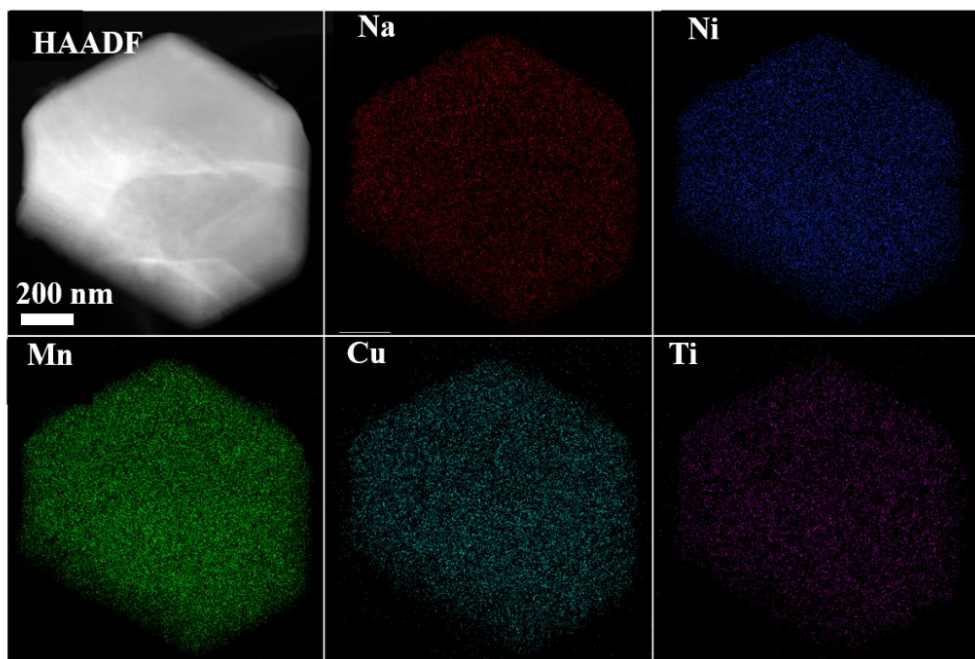


Figure S2. Energy Dispersive X-ray Spectroscopy (EDS) mapping of P2-NMCT, demonstrating the uniform distribution of Na, Ni, Mn, Cu, and Ti within the particle.

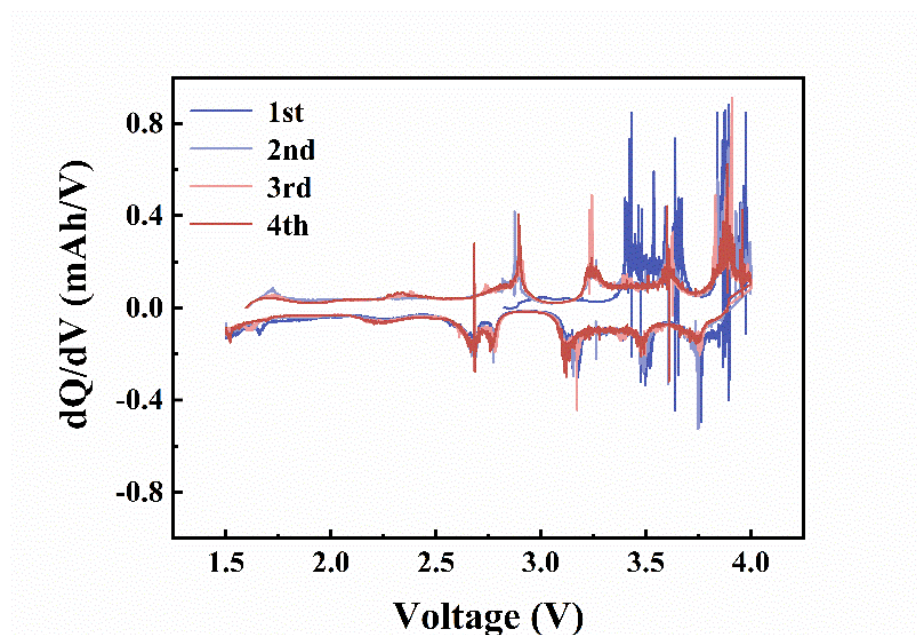


Figure S3. dQ/dV curves of P2-NMCT at 15 mA g^{-1} in the voltage range of 1.5-4.0 V during the fourth cycle, validating the observed changes in the oxidation-reduction peaks during the afore mentioned processes.

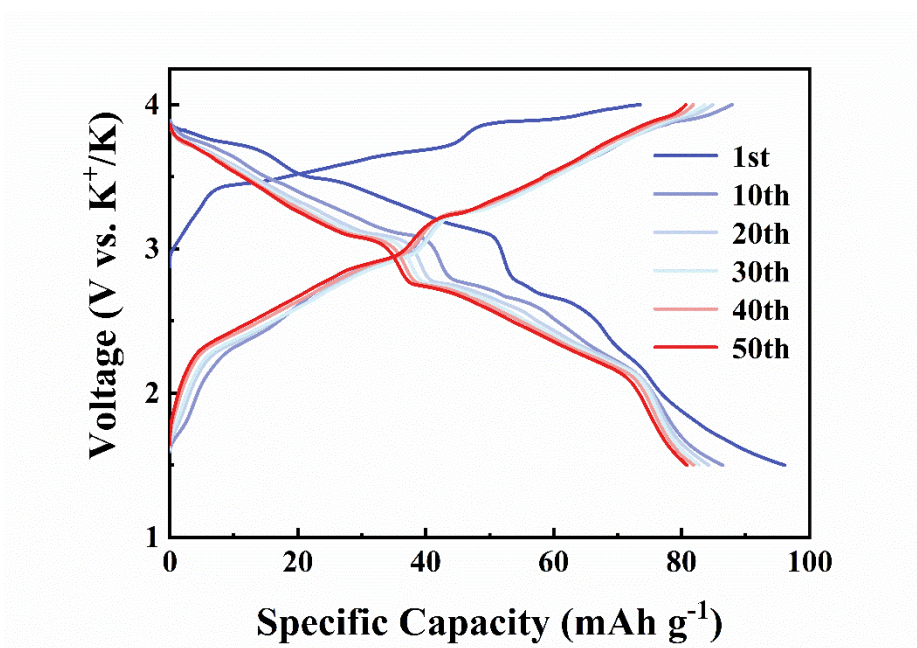


Figure S4 Electrochemical charge-discharge profiles of P2-NMCT for the 1st, 10th, 20th, 30th, 40th, 50th cycles at a current density of 15 mA g^{-1} , respectively.

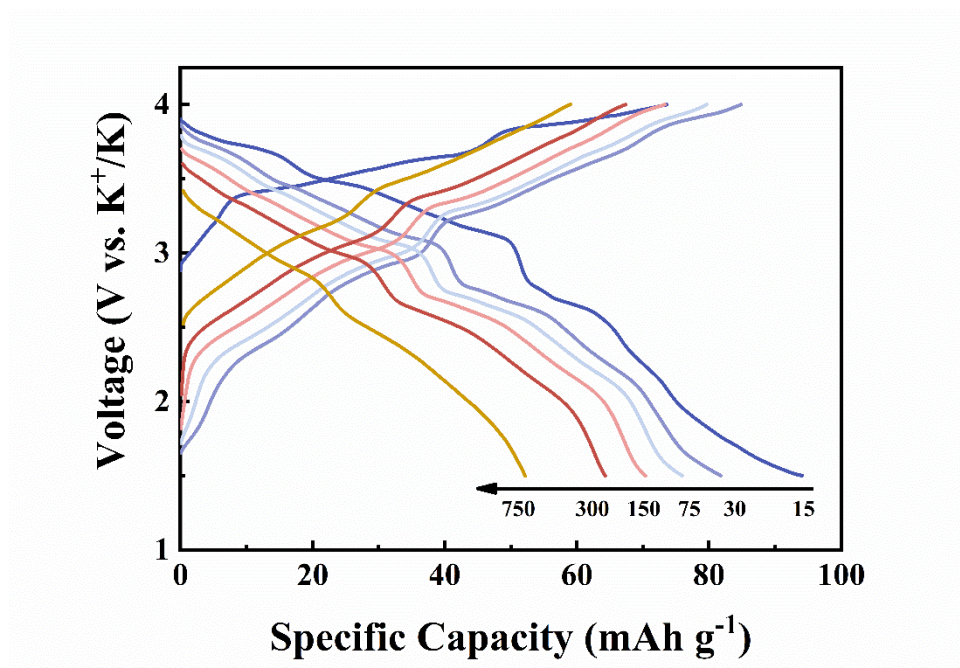


Figure S5 Comparative charge-discharge profiles of the sixth cycles at different current rates, indicating that P2-NMCT exhibits excellent dynamic performance and structural stability.

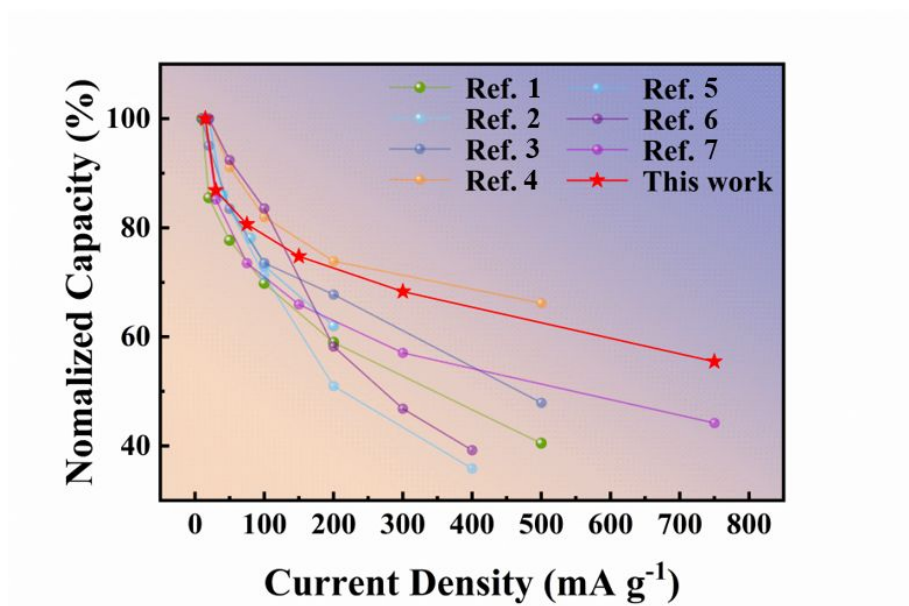


Figure S6. Comparison of rate capability between P2-NMCT and various reported cathode materials from the literature ^[1-7]

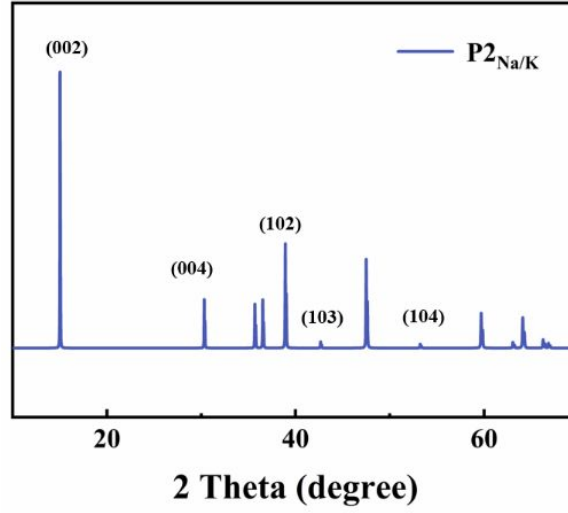


Figure S7. Power Diffraction Pattern Calculation of VESTA of P2-NMCT, corresponding to P2 phase (P2Na/K) with a mixed distribution of K^+/Na^+ in the alkali metal layer.

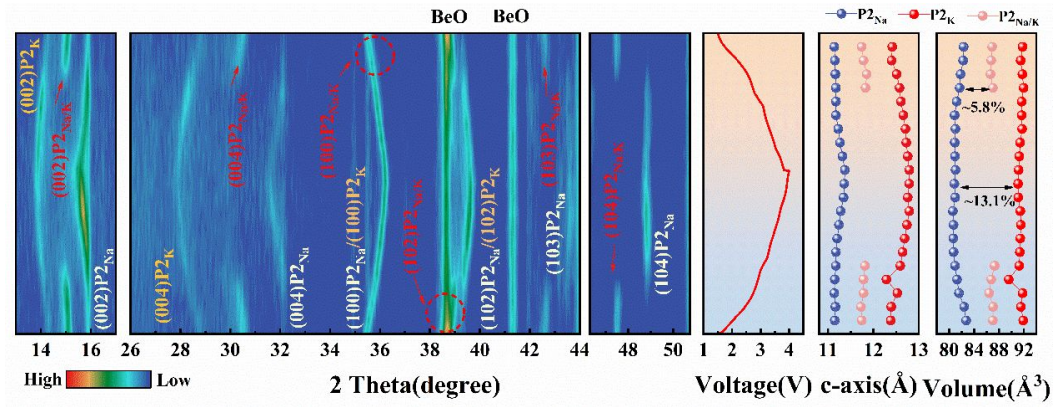


Figure S8 The *in-situ* XRD spectra collected at 75 mA g^{-1} in the voltage range of 1.5-4.0 V, showing the trends in c-axis length and unit cell volume changes during the fifth cycle of P2-NMCT.

Table S1. Results of XRD Rietveld refinements of the pristine P2-NMCT samples

P2-NMCT	
Space group	P63/mmc
a/b	2.89819
c	11.13638
Density/ g cm^{-3}	4.6692
Rwp	5.81

Table S2. Elemental orbits, peak positions of fitting peaks, position constraints, and ratios of elements with different valence states in P2-NMCT, confirming the Ti doping.

Elemental orbits	Peak position of the fitting peak (eV)	Position constraint (eV)	Ratio of elements with different valence states
Mn $2p_{3/2}$	641.94, 643.94	$\Delta_{\text{Mn}}=11.2$	$\text{Mn}^{3+}: \text{Mn}^{4+} \approx 3.4$
Mn $2p_{1/2}$	653.14, 655.14		
Ni $2p_{3/2}$	854.44, 856.24	$\Delta_{\text{Ni}}=17.3$	$\text{Ni}^{2+}: \text{Ni}^{3+} \approx 3.8$
Ni $2p_{1/2}$	871.74, 873.54		
Cu $2p_{3/2}$	933.14	$\Delta_{\text{Cu}}=19.8$	/
Cu $2p_{1/2}$	952.94		
Ti $2p_{3/2}$	457.94	$\Delta_{\text{Ti}}=5.7$	/
Ti $2p_{1/2}$	463.64		

Table S3 Calculation results of the average diffusion coefficient (D) during different charge and discharge stages, indicating that the D value in region I exceeds those in regions II, III, and the single-phase states.

Number of cycles	State	Average D value
1st	Charge	2.80615×10^{-11}
	Discharge	1.27884×10^{-10}
2nd	Charge	5.04668×10^{-11}
	Discharge	5.1199×10^{-11}
	I	9.5411×10^{-11}
	II	3.40655×10^{-11}
	III	5.0876×10^{-11}
3rd	Charge	5.23382×10^{-11}
	Discharge	5.76041×10^{-11}
	I	7.97918×10^{-11}
	II	4.2161×10^{-11}
	III	3.79118×10^{-11}

References

- [1] Y. S. Xu, Y. N. Zhou, Q. H. Zhang, M. Y. Qi, S. J. Guo, J. M. Luo, Y. G. Sun, L. Gu, A. M. Cao, L. J. Wan, Chem. Eng. J. 2021, 412, 128735.
- [2] C. Liu, S. Luo, H. Huang, X. Liu, Y. Zhai, Z. Wang, Chem. Eng. J. 2019, 378, 122167
- [3] X. Zhang, Y. Yang, X. Qu, Z. Wei, G. Sun, K. Zheng, H. Yu, F. Du, Adv. Funct.

- Mater. 2019, 29, 1905679.
- [4] S. Li, L. Wu, H. Fu, A. M. Rao, L. Cha, J. Zhou, B. Lu, Small Methods 2023, 7, 2300893.
 - [5] Z. Zhang, Q. Hu, J. Liao, Y. Xu, L. Duan, R. Tian, Y. Du, J. Shen, X. Zhou, Nano Letters 2023, 23, 694.
 - [6] N. P. N. Puneeth, S.D. Kaushik, R. K. Selvan, Mater. Letters, 2022, 316, 131997.
 - [7] Z. D. Liu, X. W. Gao, J. J. Mu, H. Chen, G. Gao, Q. S. Lai, D. R. Yang, Q. F. Gu, W. B. Luo, Adv. Funct. Mater. 2024, 2315006.