

Supplementary information

Fe^{HS} Vacancies in Prussian White Cathode Leads to Enhanced Fe^{LS} Activity and Electrode Kinetics Towards Boosted K⁺ Storage

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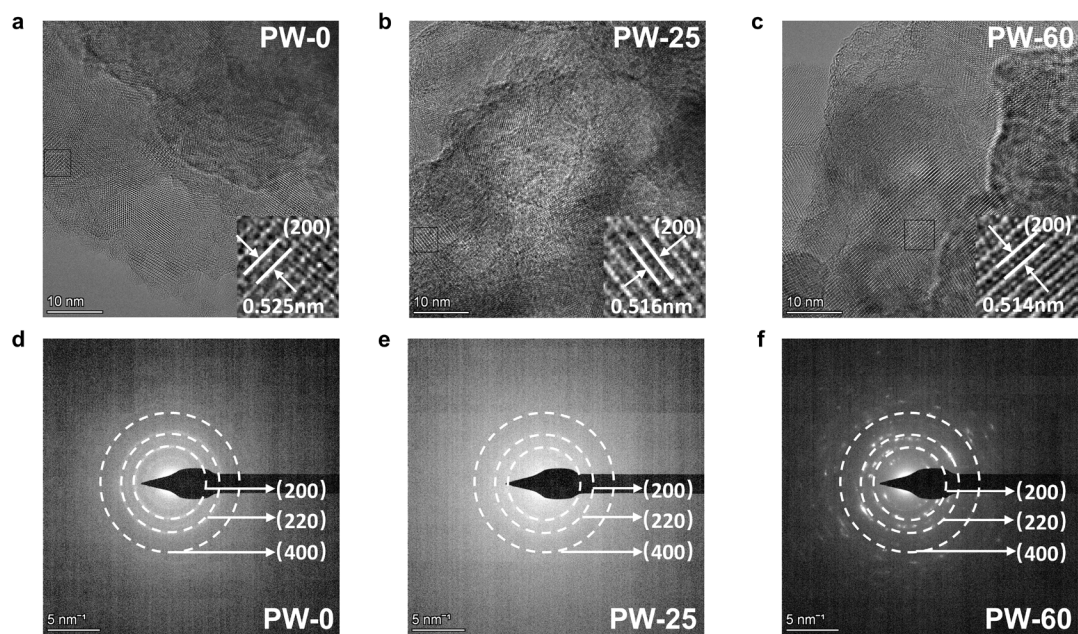


Figure S1. (a-c) HRTEM images, and (d-f) selected area electron diffractions of as-prepared three samples.

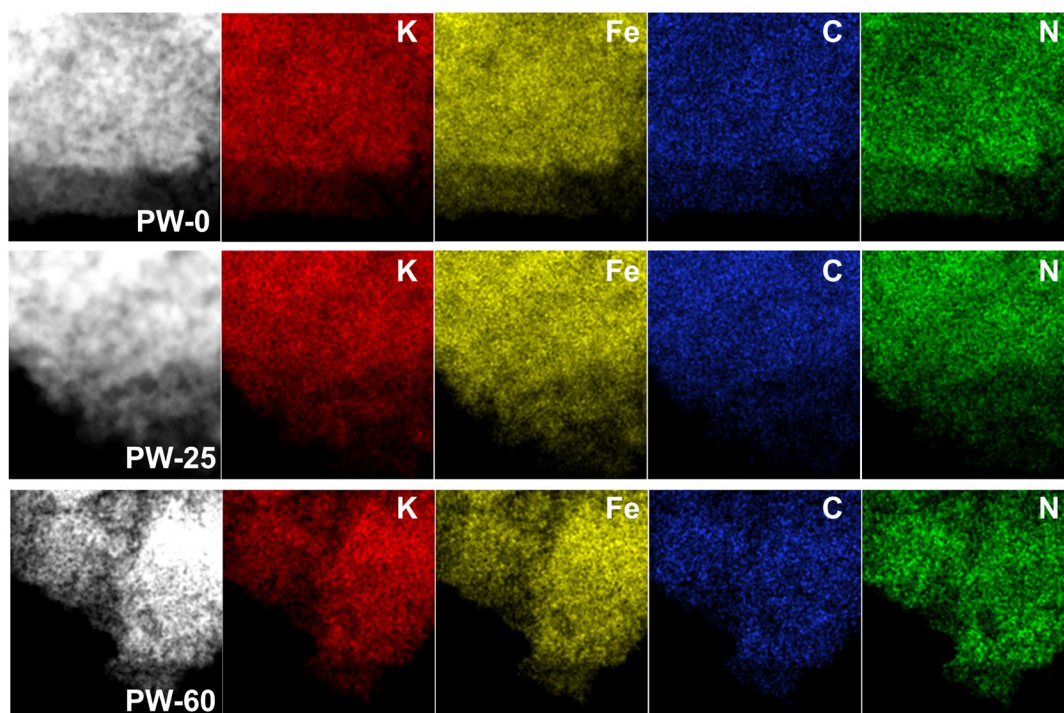


Figure S2. EDS elemental mapping images of as-prepared three samples.

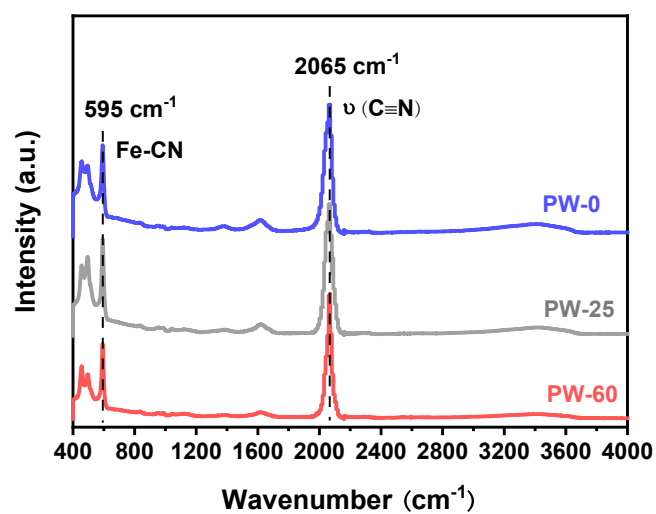


Figure S3. FTIR spectrum of PW-0, PW-25 and PW-60.

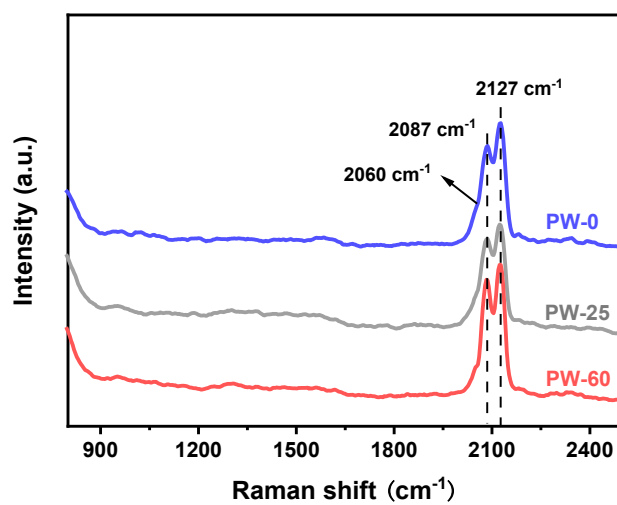


Figure S4. Raman spectrum of PW-0, PW-25 and PW-60.

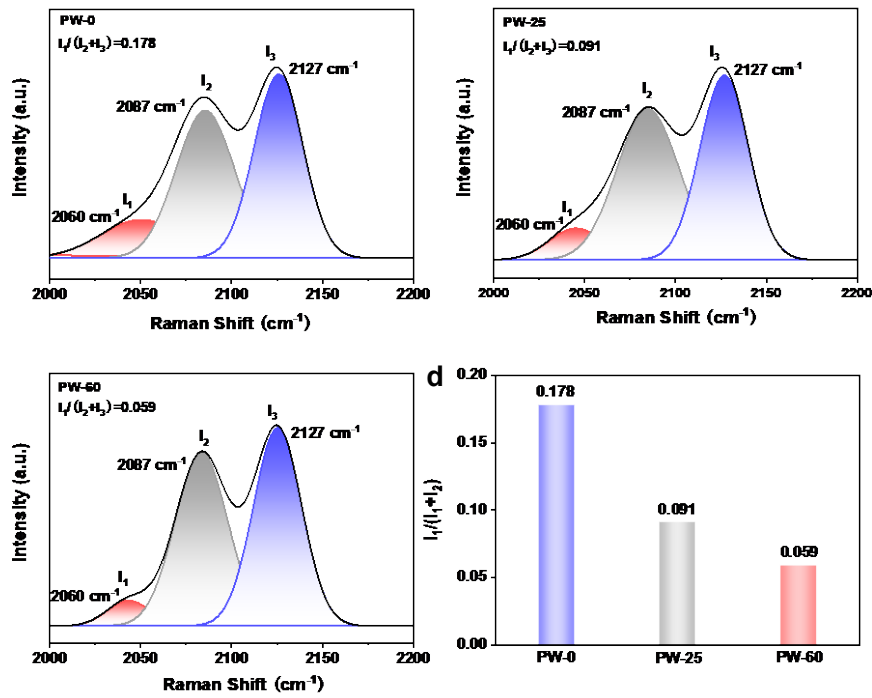


Figure S5. Raman spectra of (a) PW-0, (b) PW-25 and (c) PW-60, (d) peak area ratios (I_1/I_2+I_3) comparison.

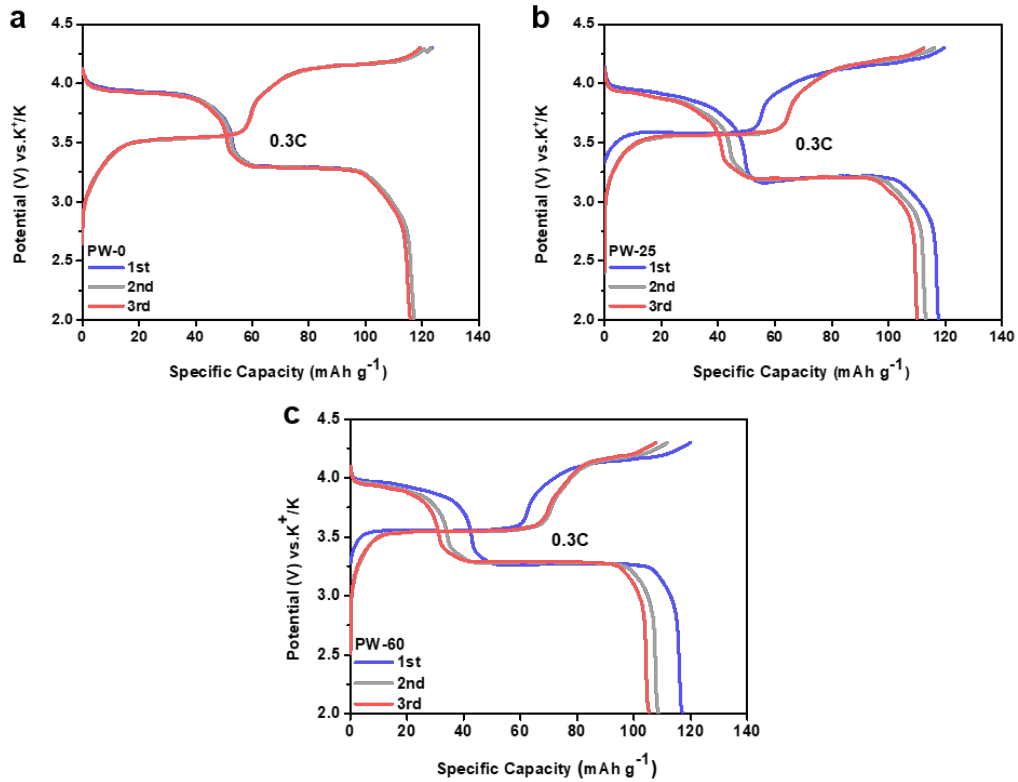


Figure S6. The first three cycles GCD curves at 0.3C of (a) PW-0, (b) PW-25 and (c) PW-60. (1C = 100 mA g⁻¹)

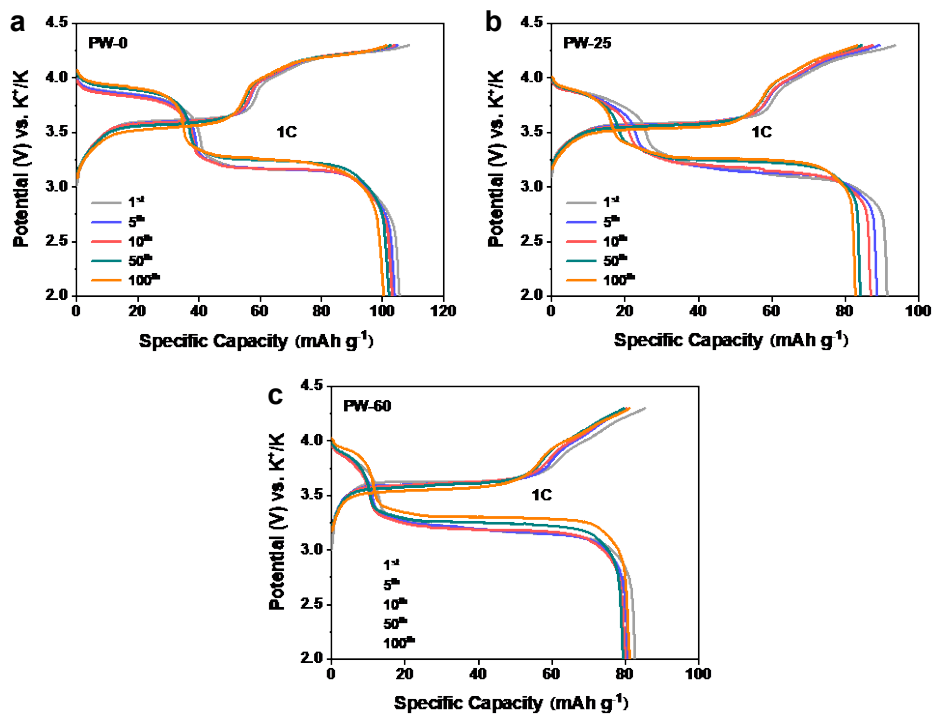


Figure S7. The 1st, 5th, 10th, 50th and 100th GCD curves at 1C of (a) PW-0, (b) PW-25 and (c) PW-60, following three cycles at 0.3C. (1C = 100 mA g⁻¹)

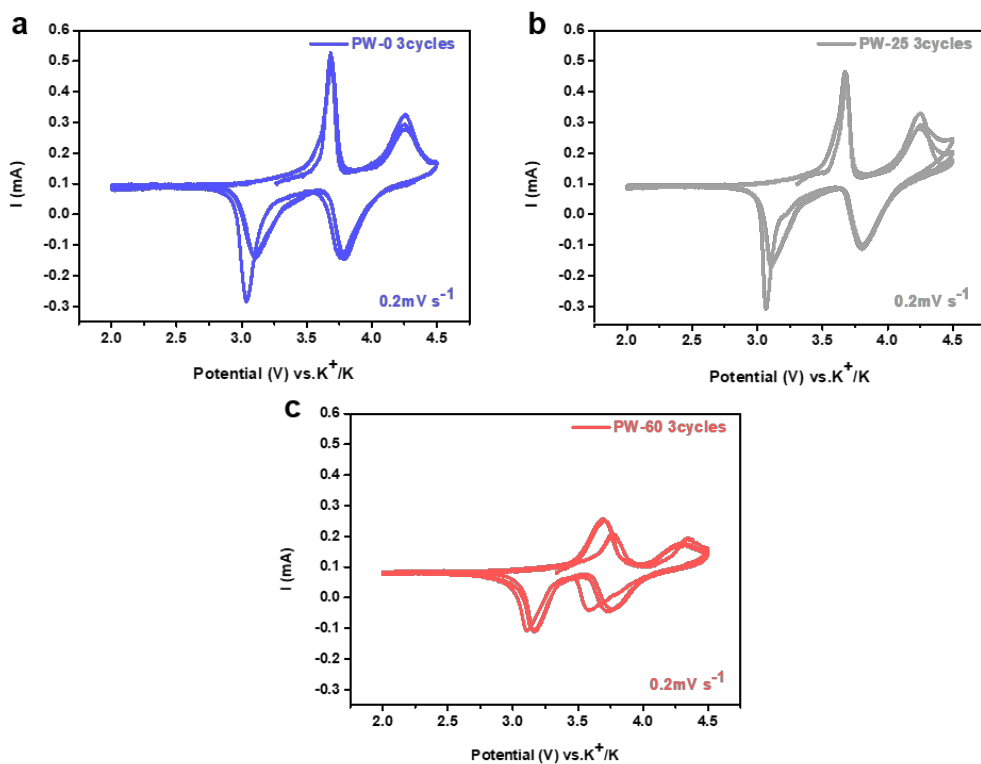


Figure S8. The first 3 cycles cyclic voltammetry curves of (a) PW-0, (b) PW-25 and (c) PW-60 at a scan rate of 0.2 mV s⁻¹ within the voltage range of 2.0-4.3V (vs. K⁺/K).

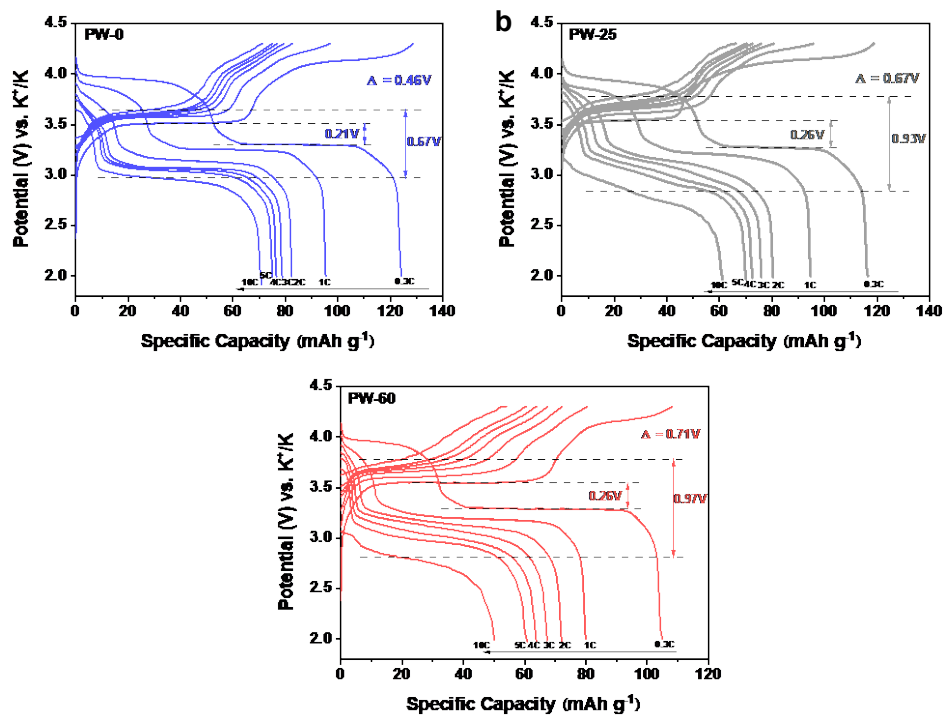


Figure S9. The GCD curves at different current densities of (a) PW-0, (b) PW-25 and (c) PW-60. (1C = 100 mA g⁻¹)

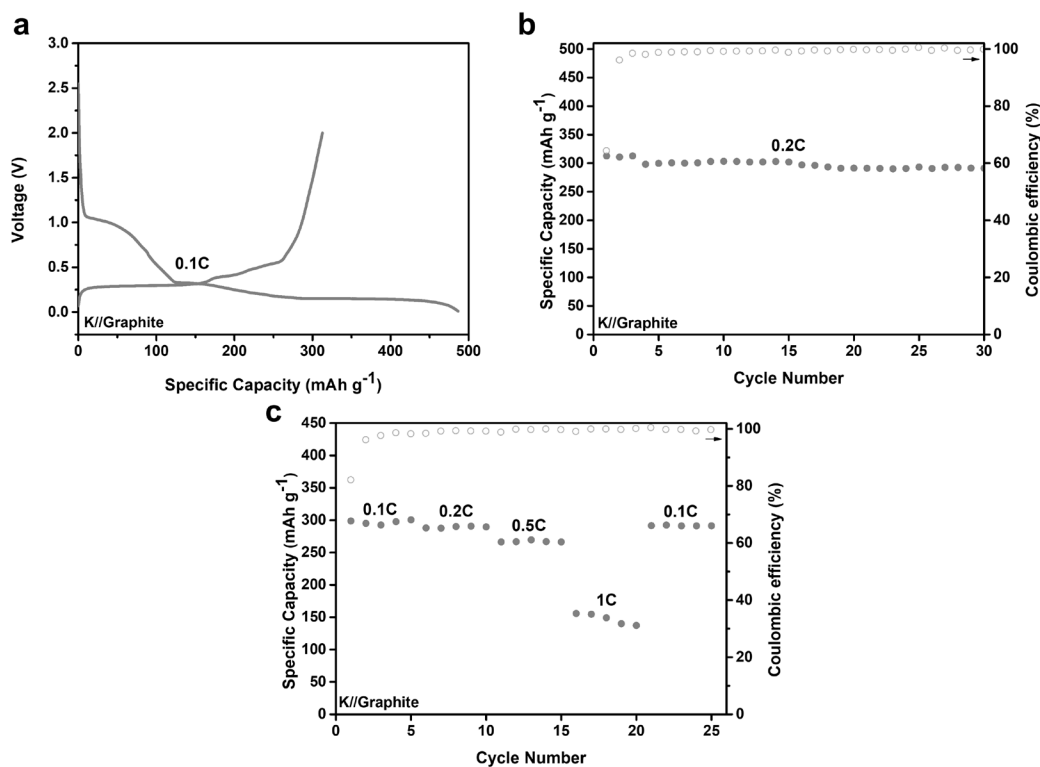


Figure S10. (a) The first galvanostatic charge-discharge profile of the K//Graphite

half-cell at 0.1C, (b) The cycle performance of K//Graphite half-cell at 0.2C, (c) The rate performance of K//Graphite half-cell. (1C = 280 mA g⁻¹)

Table S1. Certain parameters of full cell for PW-0.

Parameters of full cell	
N/P ratio	0.87
electrolyte amount	140 ul

Table S2. Comparison of potassium storage properties between the PW-0 and previously reported Prussian blue analogs.

Cathode material	Initial discharge capacity (mAh g ⁻¹ /mA g ⁻¹)	Capacity retention/cycle	Rate performance (mAh g ⁻¹ /mA g ⁻¹)	Reference
PW-0	93.1/100	93.1%/300	70.2/1000	This work
KMF-40	120.5/100	69.4%/100	73.2/500	1
KMF-EDTA	154.7/15	92.3%/300	74/500	2
KNiHCF	62.8/100	88.6%/100	51.1/1000	3
KNHCF	57.0/10	87.3%/1000	13.1/500	4
KFeHCF-E	77.0/25	87.6%/3200	42/1000	5
PW-HQ	113.1/50	93.0%/1000	60.4/1000	6
PB-PPY	108.6/50	~48.7%/900	35.5/500	7
KFeHCF-V	77.6/25	81.2%/50	32/200	8
KHCF@PPY	88.9/50	86.8%/500	60/1000	9
PBN _{0.4} C _{0.6}	86.0/20	96.9%/150	~45/200	10

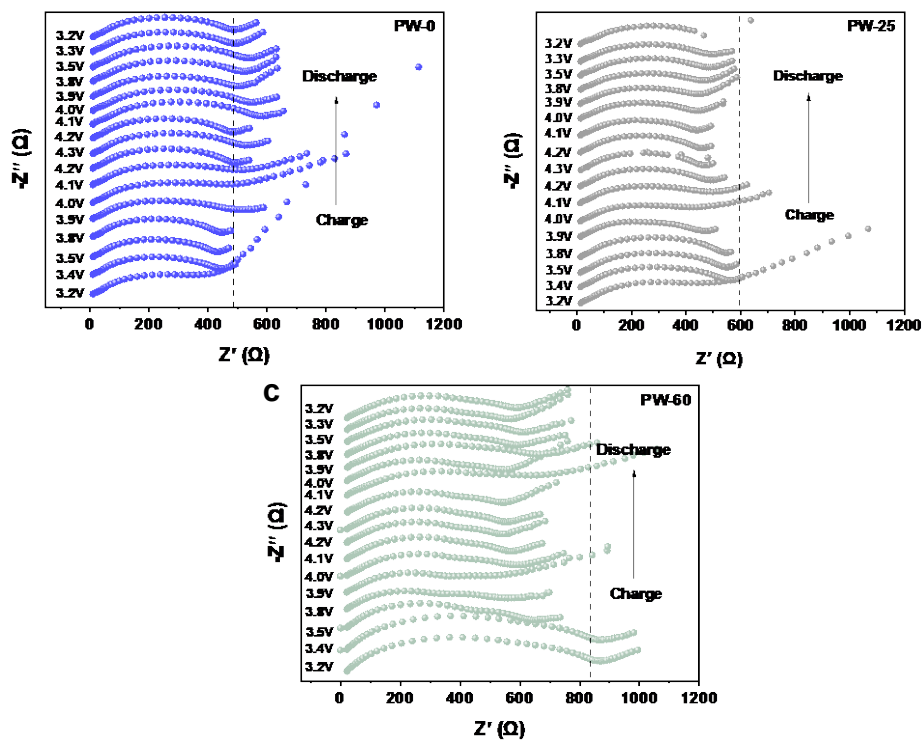


Figure S11. In-situ EIS Nyquist plots of (a) PW-0, (b) PW-25 and (c) PW-60.

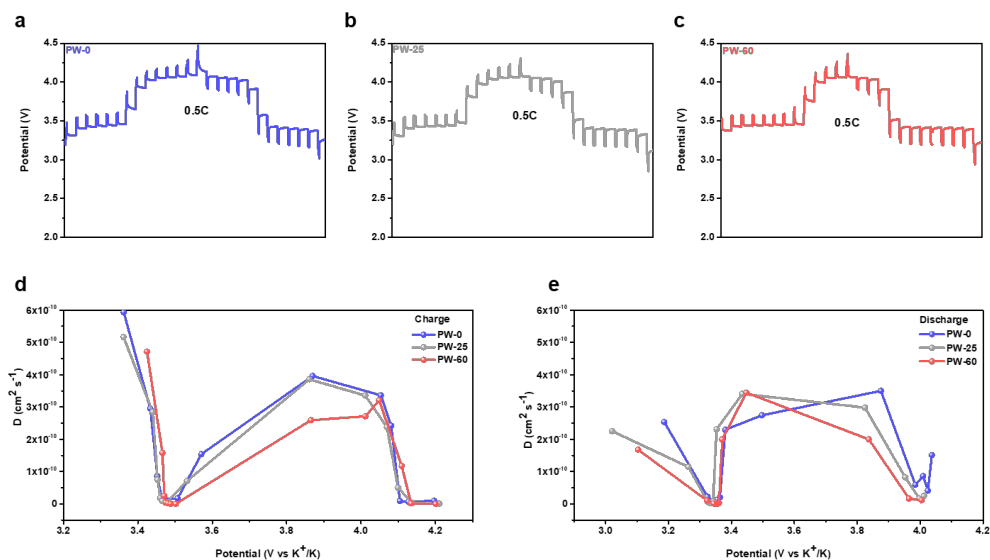


Figure S12. (a-c) The GITT curves obtained at a current density of 0.5C within the voltage range of 2.0-4.3V (vs. K^+/K), and (d-e) the calculated diffusion coefficients of PW-0, PW-25 and PW-60. ($1C = 100 \text{ mA g}^{-1}$)

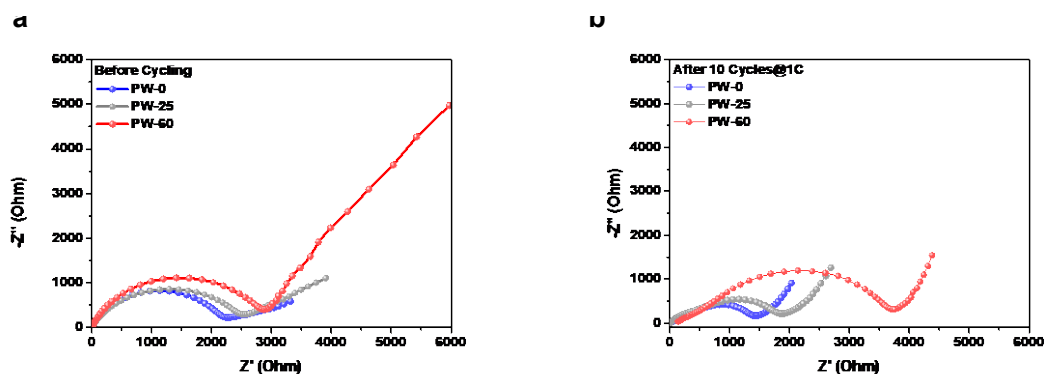


Figure S13. The Nyquist plots of (a) pristine electrodes without cycling and (b) the electrodes after ten cycles at 1C. (1C = 100 mA g⁻¹)

Reference

1. W. Chen, Z. Jian, H. Li, Y. Qi, W. Jin, Y. Xia, *Chinese Chemical Letters*, 2021, **32**, 2433-2437.
2. L. Deng, J. Qu, X. Liu, J. Zhang, Y. Hong, M. Feng, J. Wang, M. Hu, L. Zeng, Q. Zhang, L. Guo, Y. Zhu, *Nature. Communication*, 2021, **12**, 2167.
3. L. Li, Z. Hu, C. Wang, Q. Zhang, S. Zhao, J. Peng, K. Zhang, S.-L. Chou, J. Chen, *Angew. Chem., Int. Ed*, 2021, **60**, 13050-13056.
4. S. Chong, Y. Wu, S. Guo, Y. Cao, *Energy Storage Mater*, 2019, **22**, 120-127.
5. W. Shu, M. Huang, L. Geng, F. Qiao, X. Wang, *Small*, 2023, **19**, 2207080.
6. R. Ma, Z. Wang, Q. Fu, W. Zhou, Y. Mo, J. Tu, Z. Wang, P. Gao, C. Fan, J. Liu, J. *Energy Chem*, 2023, **83**, 16-23.
7. M. Zhou, X. Tian, Y. Sun, X. He, H. Li, T. Ma, Q. Zhao, J. Qiu, *Nano Res*, 2023, **16**, 6326-6333.
8. Z. Wang, W. Zhuo, J. Li, L. Ma, S. Tan, G. Zhang, H. Yin, W. Qin, H. Wang, L. Pan, A. Qin, W. Mai, *Nano Energy*, 2022, **98**, 107243.
9. Q. Xue, L. Li, Y. Huang, R. Huang, F. Wu, R. Chen, *ACS Appl. Mater. Interfaces* 2019, **11**, 22339-22345.
10. B. Huang, Y. Shao, Y. Liu, Z. Lu, X. Lu, S. Liao, *ACS Appl. Energy Mater*, 2019, **2**, 6528-6535.