

Supporting Information

Utilizing Autogenously Protective Atmosphere to Synthesize Ultrahigh Capacity-Retention Prussian White Cathode for Potassium-Ion Batteries

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Experimental

Materials: All chemical materials and electrolytes were purchased from Sigma Aldrich.

Materials synthesis: Prussian white samples (PWs) were synthesized by a simple solution precipitation method without extra inert gas introduced. Typically, 0.4 mmol $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 4 g potassium citrate, 1 g citric acid and 50 mg Fe powder were added into 80 ml deionized water under stirring, with H_2 gas generation. Then, 80 mL potassium ferrocyanide solution (3 mmol) was dropwise added into the above mixed solution under continuously stirring. A milky uniform mixture was obtained at room temperature. After 12 hours of aging, the samples were collected by centrifugation (8000 rpm, 5 min), rinsed with distilled water for several times. The product was then collected and dried at 110°C in a vacuum oven for 12 h.

Characterization: X-ray diffraction (XRD) patterns was obtained on diffractometer (Rigaku D/max 2500/PC) in which Cu-K α ($\lambda = 0.154$ nm) was used as the radiation source. The patterns were refined by the rietveld method with the software TOPAS. The water content of the synthesized powders (sample weight, 6 mg) was tested by TGA (Shimadzu DTG-60, Japan). The surface composition of PW and the valence state of Fe were detected by X-ray photoelectron spectroscopy (XPS) on a PHI 5000 VersaProbe II measurements with monochromatic Al K α radiation. The elemental content of C/N and K/Fe was confirmed by chemical analysis through Elemental Analysis (CHNS/O) and Inductive Coupled Plasma Emission Spectroscopy (ICP), respectively. The morphology and selected

area electron diffraction (SADE) of samples were obtained by High-resolution Transmission Electron Microscopy (FEI Tecnai G2 F30). ^1H Nuclear Magnetic Resonance (NMR) spectrums were collected by a Bruker AVANCE III 400 instrument. The valence change of cyanide ligands of K-PW during charge/discharge process was obtained by Raman spectras using a Raman spectrometer (Horiba LabRAM HR800).

Electrochemistry: The cathodes consisted of PW samples, super P, and polyvinylidene fluoride (PVDF) at a mass ratio of 70:20:10, coated on Al foil. The anodes consisted of graphite powder, super P and polyvinylidene fluoride (PVDF) at a mass ratio of 80:10:10, coated on Cu foil. Both electrode samples were dried at 110°C under vacuum for 24 h. Then the electrodes pieces were cut into circular disks with diameter of 12mm. The loading mass of PW and graphite is $\sim 1 \text{ mg/cm}^2$, $\sim 2 \text{ mg/cm}^2$ respectively. Potassium metal (Sigma-aldrich Industrial corporation) was used as anodes in potassium half-cells. The electrolytes were 0.5M KPF_6 dissolved in ethylene carbonate (EC, purity 98%) and diethyl carbonate (DEC, purity >99%) with volume radio 1:1 or propylene carbonate (PC purity 98%). Fluoroethylene carbonate (FEC, purity 99%) was selected as an additive in EC/DEC electrolyte. Dimethyl carbonate (DMC, purity 99%) was used as the cleaning solvent. The water content in the above solvent was below 10 ppm by Karl Fischer titration (Metrohm 831). The separator was the glass fiber filter (Grade GF/A, Whatman). R2032-type coin cells were assembled in a Braun glove box under Ar atmosphere. The galvanostatic discharge/charge tests were performed on Land 2001A battery testing system at 298 K. The voltage range for electrochemical tests is 2.5 ~ 4.5 V (vs. K^+/K). The Cyclic

Voltammetry tests were conducted on a VMP-3 multi-channel workstation, with a scan rate of 0.2 mV s^{-1} . The Electrochemical Impedance Spectroscopy were also conducted from VMP-3multi-channel workstation, with frequency from 0.01 to 100k HZ.

List of Supporting Figures and Tables

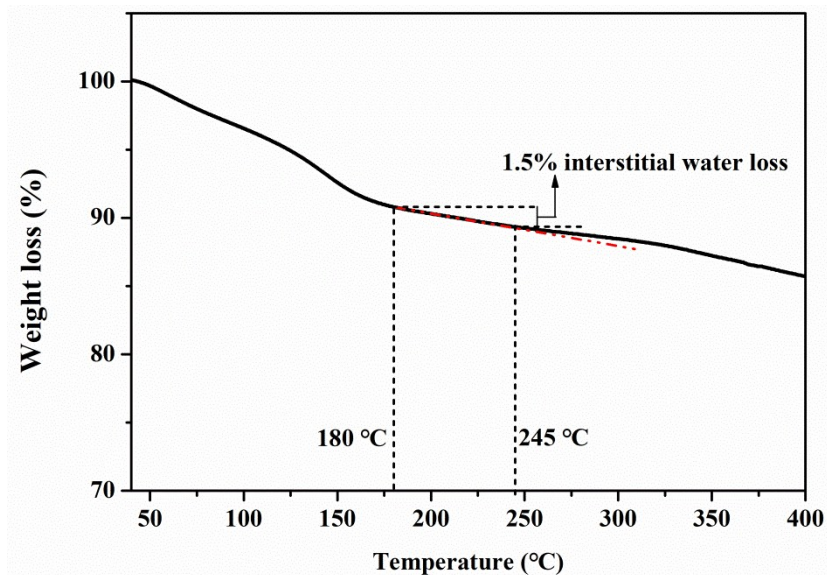


Fig. S1 TG curves of as-prepared K-PW samples at a heating rate of 5 °C / min under Ar gas. Before 180 °C, the weight loss of PW samples came from adsorbed water. The mass percentage of interstitial water is about 1.5 by calculated in interval 180 < T < 245 °C.¹

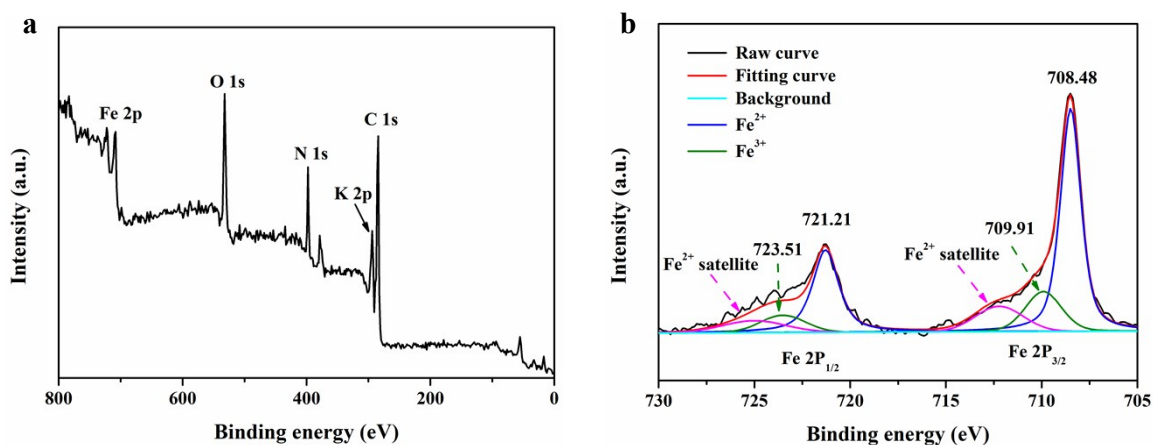


Fig. S2 The XPS spectra of as-prepared K-PW. (a) full range spectrum, and (b) Fe 2P spectra.¹⁻³ In the Fe 2p spectrum (Fig. S2b), it can be seen that the content of Fe²⁺ (at 708.48 and 721.21 eV) is far higher than that of Fe³⁺ (at 709.91 and 723.51 eV).

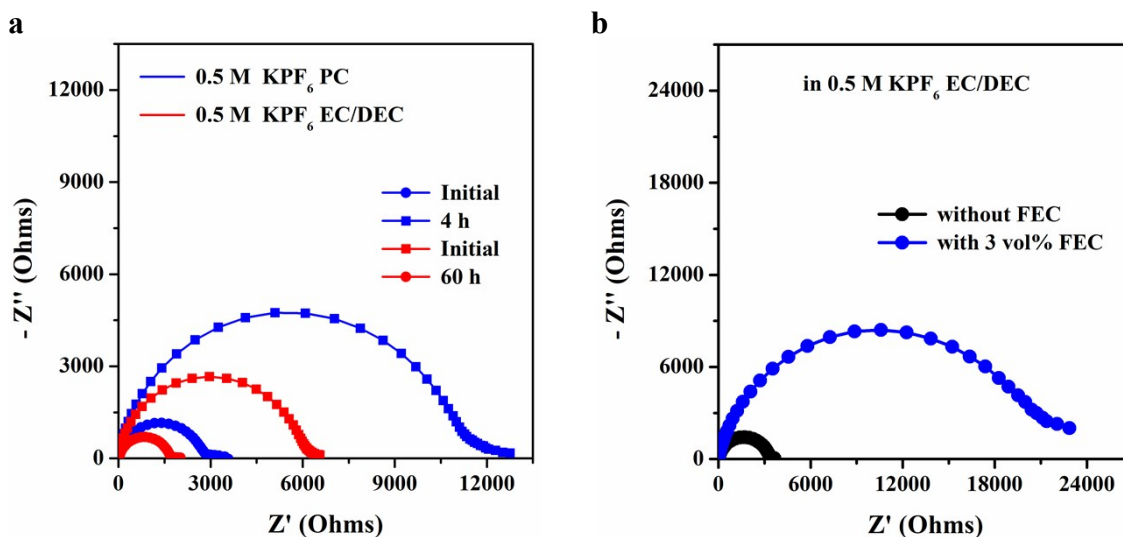


Fig. S3 The comparison of EIS spectra of K/K cells in different KPF₆-containing carbonate-based electrolytes. (a) Filled with two different solvents at different rest time, (b) With/without FEC additive in EC/DEC electrolyte after resting for 4 hours.

In Fig. S3a the charge transfer resistance of K/K cells which corresponds to the diameter of the semicircle in the high-frequency region, was similar just after assembling in PC and EC/DEC electrolytes. With the increasing of rest time, the impedance in PC increased significantly compared with that in EC/DEC.

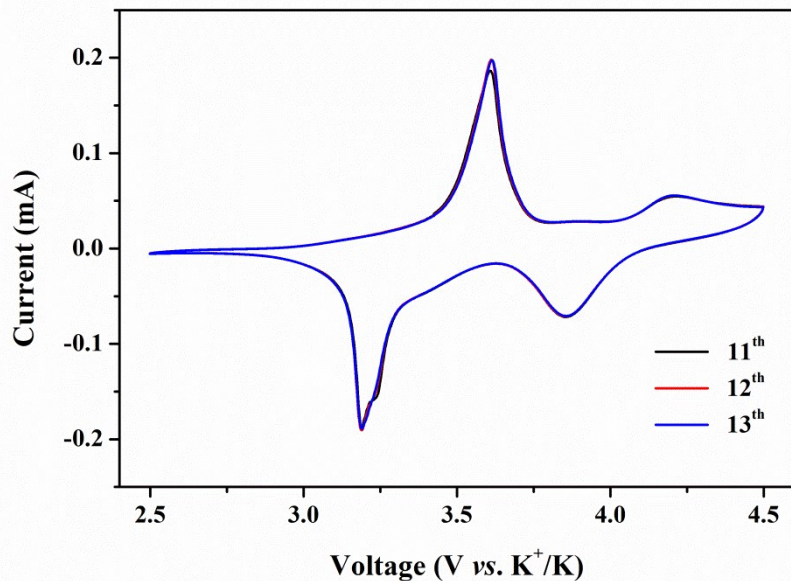


Fig. S4 The cyclic voltammetry (CV) curves of K/K-PW cell after 10 cycles at 50 mA g⁻¹ with the 0.5 M KPF₆ EC/DEC, obtained at the scan rate of 0.2 mV s⁻¹.

The CV profiles of K/K-PW cells (Fig. S4) show two redox couples at 3.6/3.2 V and 4.2/3.85 V (vs. K⁺/K), corresponding to the N-coordinated Fe³⁺/Fe²⁺ with a high-spin configuration and the C-coordinated Fe³⁺/Fe²⁺ with a low-spin configuration, respectively.

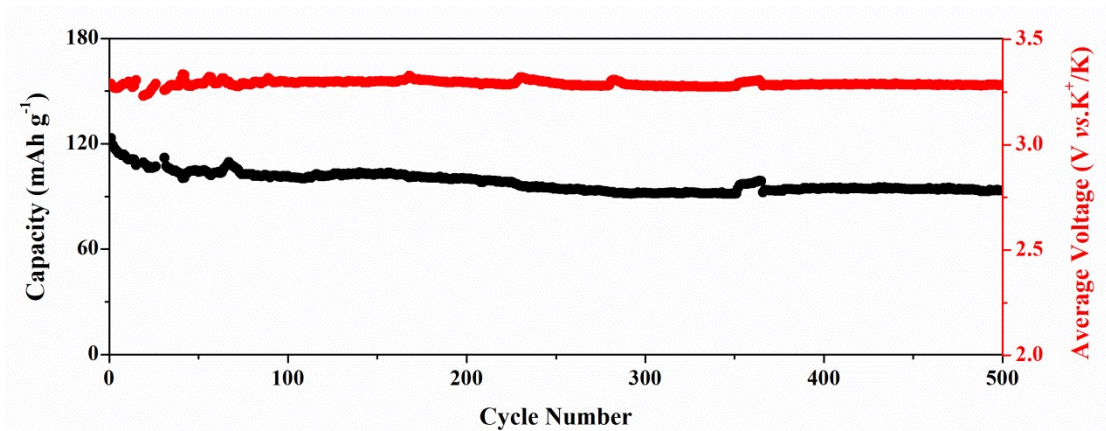


Fig. S5 The cyclic profiles of K/K-PW cell in 0.5 M KPF₆ EC/DEC at a current density of 100 mA g⁻¹.

From Fig. S5, the as-prepared K-PW electrode shows outstanding cycling stability with a capacity of 93.3 mAh g⁻¹ after 500 cycles. The capacity decay in the early cycles could be mainly related to structural water decomposition in K-PW at high current.⁴⁻⁶

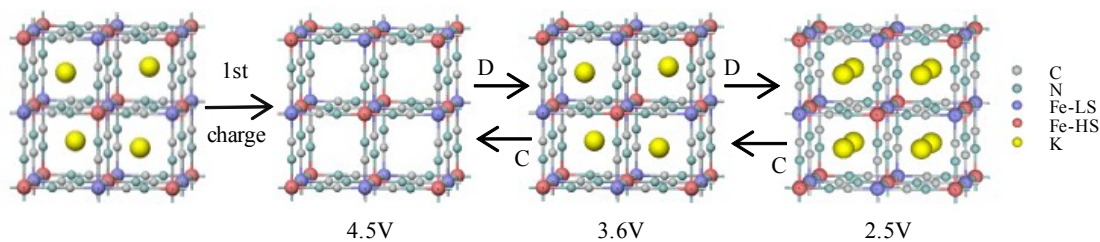


Fig. S6 Schematic view of the potassiation/depotassiation mechanism during the cyclic tests for the Prussian white electrode.

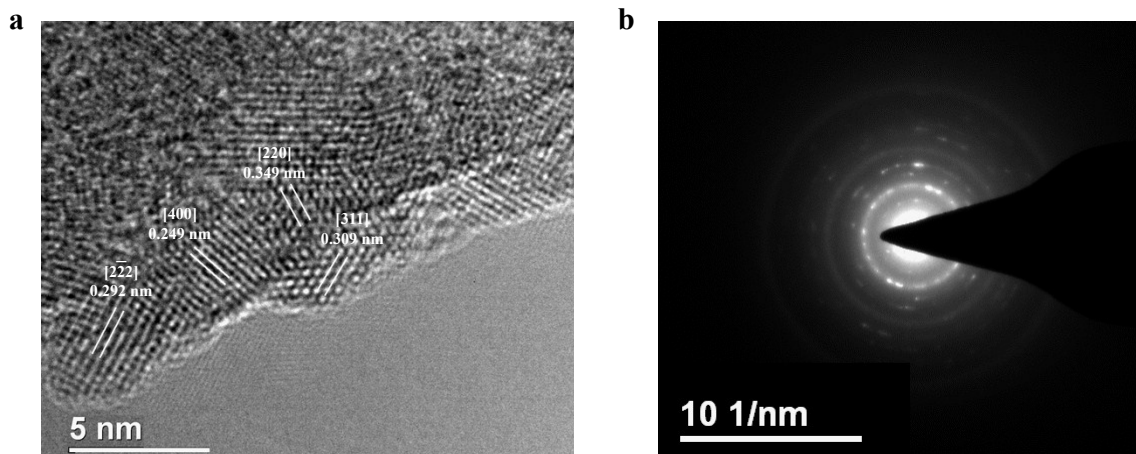


Fig. S7 The TEM and SADE images of K-PW electrode after 10 cycles in half-cell with 0.5 M KPF_6 EC/DEC. The electrode was washed by DMC solvent.

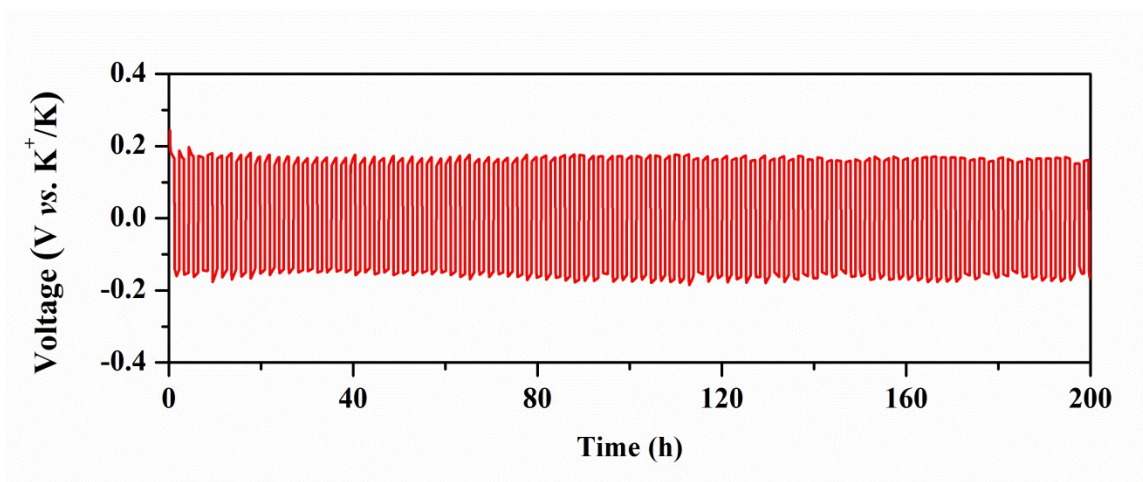


Fig. S8 Voltage profile of K plating/stripping in K/K cell with 0.5 M KPF_6 EC/DEC.

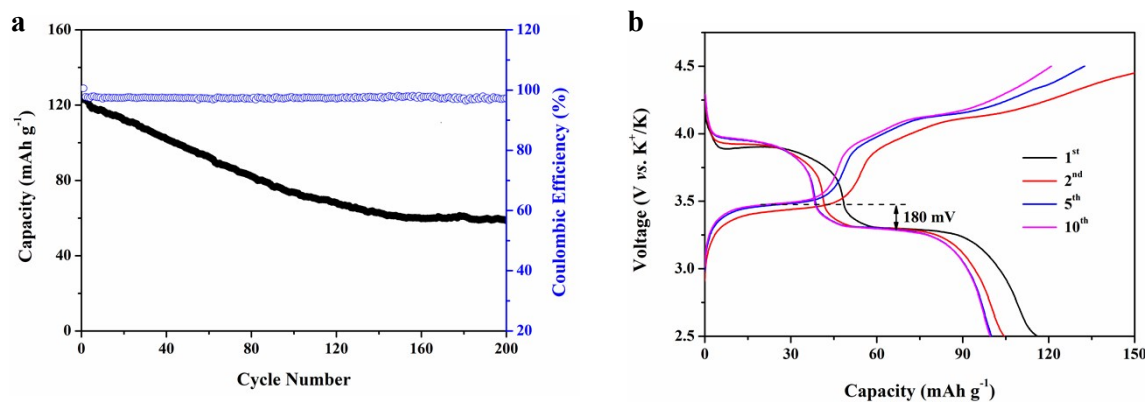


Fig. S9 (a) The cycling behavior of K-PW/K cell with 3 vol% FEC, at a current density of 50 mA g^{-1} . (b) The galvanostatic profiles of the cell using the cycled K-PW cathode, fresh potassium anode and 0.5 M KPF_6 EC/DEC without FEC.

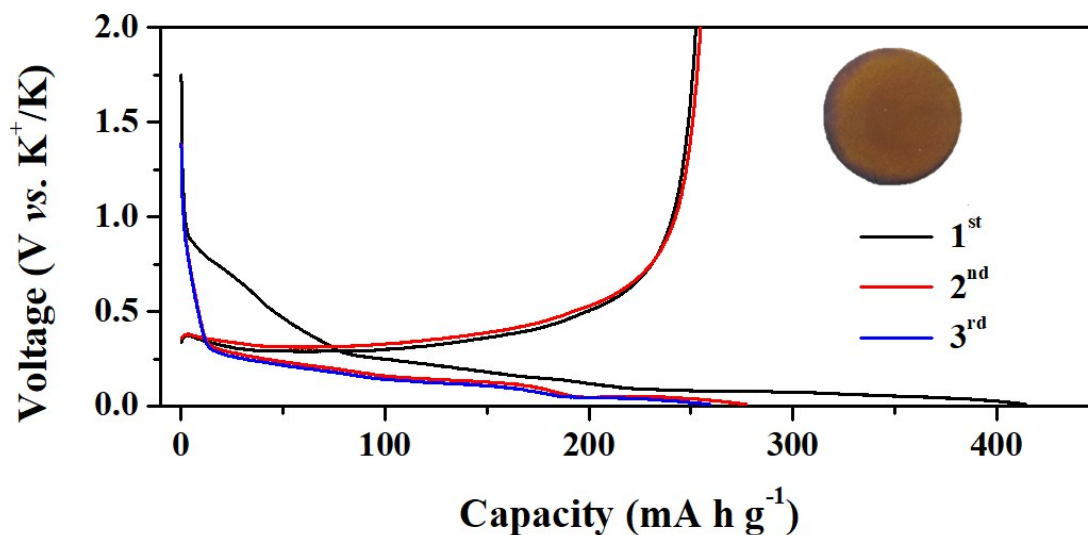


Fig. S10 The charge-discharge profiles of natural graphite electrode in half-cell with 0.5 M KPF_6 in EC/DEC electrolyte.

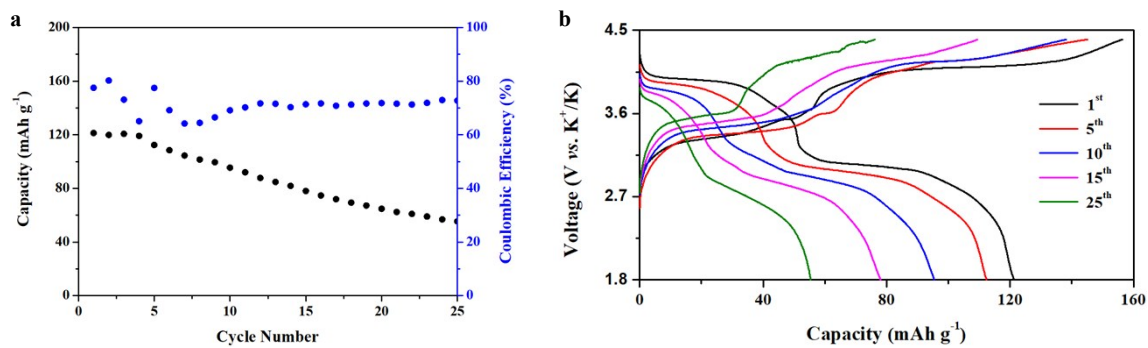


Fig. S11 The cycling behavior (a) and the selected charge-discharge profiles (b) of full-cell with 3 vol% FEC, at a current density of 50 mA g⁻¹.

Table S1. TG, ICP and CHNS/O results of PW samples

Element	K	Fe	C	N	H ₂ O
Mole ratio	0.846	1	2.906	2.876	0.173

The derivation process of K_xFe[Fe(CN)₆]_y·zH₂O is as follows :

The mole ratio of cyanide in K-PW samples is based on the mole ratio of N.⁷

$$\begin{aligned}
 1) \quad & \frac{x}{1+y} = 0.846 \\
 2) \quad & \frac{6y}{1+y} = 2.876 \\
 3) \quad & \frac{z}{1+y} = 0.173
 \end{aligned}$$

Calculated : x = 1.62 ; y = 0.92 ; z = 0.33

Table S2. Electrochemical cycling performance of as-prepared K-PW compared to $K_xFe[Fe(CN)_6]$ cathodes in the previous reports

Half-cell	Capacity (mAh g ⁻¹)	Current density (mA g ⁻¹)	Retention	Reference
$K_{1.68}Fe_{1.09}Fe(CN)_6 \cdot 2.1H_2O$	110.5	20	81.8% after 100 cycles	8
$KFe[Fe(CN)_6]_{0.82} \cdot 2.87H_2O$	118.7	10	95.4% after 100 cycles	2
$K_{1.69}Fe[Fe(CN)_6]_{0.90} \cdot 0.4H_2O$	120	100	72% after 300 cycles	9
$K_{1.92}Fe[Fe(CN)_6]_{0.94} \cdot 0.4H_2O$	133	13	92.8% after 200 cycles	10
$K_{1.64}Fe[Fe(CN)_6]_{0.89} \cdot 0.15H_2O$	130	30	84.6% after 100 cycles	11
$K_{1.62}Fe[Fe(CN)_6]_{0.92} \cdot 0.33H_2O$	120.9	50	98.2% after 100 cycles	this work

REFERENCES

1. Biesinger, M. C., Payne, B. P., Grosvenor, A. P., Lau, L. W. M., Gerson, A. R., & Smart, R. S. C, *Applied Surface Science*, 2011, **257**, 2717-2730.;
2. S. Chong, Y. Chen, Y. Zheng, Q. Tan, C. Shu, Y. Liu and Z. Guo, *Journal of Materials Chemistry A*, 2017, **5**, 22465-22471.
3. W. Ren, M. Qin, Z. Zhu, M. Yan, Q. Li, L. Zhang, D. Liu and L. Mai, *Nano Lett.*, 2017, **17**, 4713-4718.
4. L. Wang, J. Song, R. Qiao, L. A. Wray, M. A. Hossain, Y.-D. Chuang, W. Yang, Y. Lu, D. Evans, J.-J. Lee, et al, *J. Am. Chem. Soc.*, 2015, **137**, 2548-2554.
5. X. Wu, W. Deng, J. Qian, Y. Cao, X. Ai and H. Yang, *J. Mater. Chem. A*, 2013, **1**, 10130-10134.
6. Y. Lu, L. Wang, J. Cheng and J. B. Goodenough, *Chem. Commun.*, 2012, **48**, 6544-6546.
7. Y.-H. Zhu, X. Yang, D. Bao, X.-F. Bie, T. Sun, S. Wang, Y.-S. Jiang, X.-B. Zhang, J.-M. Yan and Q. Jiang, *Joule*, 2018, **2**, 736-746.
8. X. Wu, Z. Jian, Z. Li and X. Ji, *Electrochemistry Communications*, 2017, **77**, 54-57.
9. G. He and L. F. Nazar, *ACS Energy Letters*, 2017, **2**, 1122-1127.
10. J. Liao, Q. Hu, Y. Yu, H. Wang, Z. Tang, Z. Wen and C. Chen, *Journal of Materials Chemistry A*, 2017, **5**, 19017-19024.
11. X. Bie, K. Kubota, T. Hosaka, K. Chihara and S. Komaba, *Journal of Materials Chemistry A*, 2017, **5**, 4325-4330.

