

Electronic Supplementary Information for

Collaborative manipulation strategy to enhance sodium ion storage capability of Prussian white cathodes

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This file contains **Experimental section, Fig. S1-S9 and Table.S1-3.**

Experimental Section

Materials Synthesis: The co-precipitation method was employed to synthesize the PW materials required for the experiments. Specifically, for the PW materials used in the experiment, 3.039 g of $\text{Na}_4\text{Fe}(\text{CN})_6$ with 23.376 g of NaCl were first dissolved in 100 mL of ultrapure water to obtain solution A. Then 2.969 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 9.927 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and 5.161 g of sodium citrate were dissolved in 100 ml of water with 2 g PVP in 100ml of water to obtain solution B. Solution A was stirred under the condition of oil bath at 80°C , and then solution B was added drop by drop into solution A. Stirring was continuously carried out at a stirring speed of 1000 r/min, and stirring was stopped after stirring for 14 h, and the solution was subjected to heat preservation and aging at 80°C for 8 h. The products of the reaction were collected by filtration and the obtained products were washed with $\text{Na}_2\text{S}_2\text{O}_3$ solution (4% concentration). The obtained PW was vacuum dried at 120°C for 20 h in a vacuum drying oven to further remove the water of crystallization in the PW to obtain a PW material with very low water content.

The synthesized and dried PW material was subjected to high-temperature treatment by heating at a rate of 5°C min^{-1} under the condition of N_2 ventilation and holding for 8 h after heating to 180°C to obtain the material of PW-180.

Electrolyte Preparation: 5 mL of FEC, 15 mL of DEC and 5 mL of HFE are mixed to serve as solvents. 4.199 g of NaPF_6 is then introduced into above mixed solvents to prepare HFE-electrolyte (1.0 M NaPF_6 in FEC, DEC, and HFE with a volume ratio of 1:3:1).

Material Characterization: X-ray diffraction data for observation of sample cells, lattice parameters, and ex-situ XRD tests were measured using a SmartLab9KW X-ray diffractometer with a $\text{Cu K}\alpha$ radiation source from 10° to 80° (2θ). SEM images for observation of sample morphology were taken using a Hitachi S4800 instrument (Japan) scanning electron microscope. Thermogravimetric (TG) tests were carried out on a STA449F5 Jupiter synchronized thermogravimetric-differential scanning calorimeter, which was used to increase the temperature from 25°C to 400°C at a rate of 5°C min^{-1} under N_2 atmosphere. For Raman spectroscopic analysis, a Qontor Renishaw micro-laser Raman spectrometer was used with an Ar^+ laser using a wavelength of 532 nm. Electrolyte wettability of electrodes is measured using Biolin Theta Flex optical contact angle measuring instrument. The ionic conductivity of the electrolyte is tested with METTLER TOLEDO FE38-standard conductivity meter. The sodium ion mobility number was calculated by assembling a Na//Na cell and performing the EIS(electrochemical

impedance)-CA(chronoamperometry)-EIS test via Equation $t_{\text{Na}^+} = \frac{I_{ss}[\Delta V - I_0 R_0]}{I_0[\Delta V - I_{ss} R_f]}$ (R_0 is the starting resistance of the sodium interface; R_f is the stabilising resistance; I_{ss} is the measured stabilisation; I_0 is the starting current; ΔV is the test voltage of 5mV) (EIS testing was performed using Biologic SP-150 electrochemical workstation in the frequency range of 7 MHz to 100 mHz; CA testing were carried out by Biologic SP-150 electrochemical workstation at 5mV for 1 h 40 min). The electrolyte was tested for viscosity at 25°C using an ARES-G2 rheometer from TA, USA.

Electrochemical Measurements: the working positive electrode was prepared by coating a slurry containing 50

wt% active substance (PW, PW-100, PW-160, PW-180, PW-200, PW-300), 30 wt% carbon black (Super P), and 20 wt% polyvinylidene fluoride (PVDF) onto an aluminum foil collector. The electrolytes were commercial NaClO₄ electrolyte (1.0M NaClO₄ in EC (Ethylene carbonate): DMC (Dimethyl carbonate): EMC (Methyl ethyl carbonate) =1:1:1 Vol% with 2.0% FEC) and home-made HFE electrolyte (1.0 M NaPF₆ in FEC (Fluoroethylene carbonate): DEC (Diethyl carbonate): HFE=1: 3: 1 Vol%), and a CR2032 type coin half-cell with sodium flake as the negative electrode for the electrochemical tests. The batteries were assembled in an argon-filled glove box. The assembled batteries were activated in the voltage range of 2-4 V at 0.1C and then cycled at 0.5C using the LAND CT2001A battery test system (Wuhan, China) at 25°C. Cyclic voltammetry (CV) testing was performed using a CHI 600E electrochemical workstation at a scan rate of 0.1 mV s⁻¹ at 2-4 V.

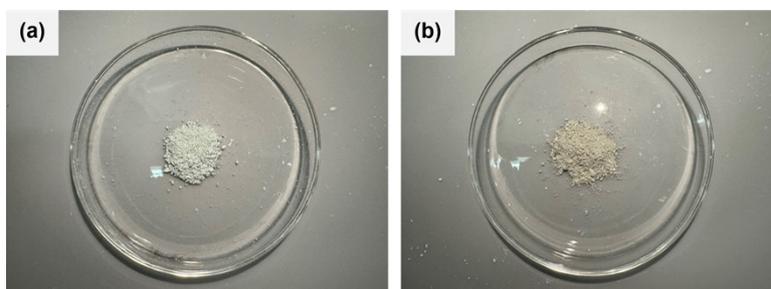


Fig. S1 Photo images of PW (a) and PW-180 (b).

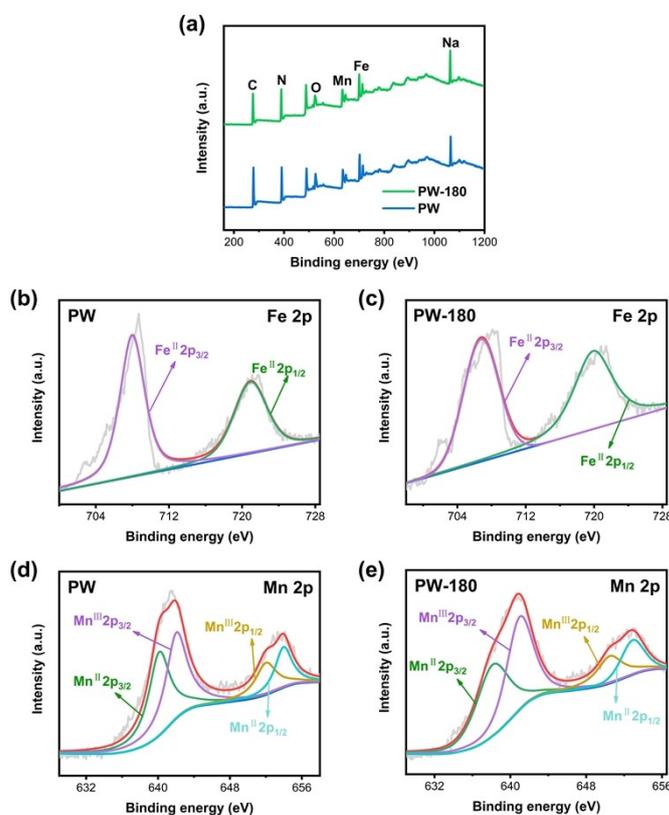


Fig. S2 (a) XPS survey spectra of PW and PW-180. Fe 2p XPS spectra of PW (b) and PW-180 (c). Mn 2p XPS spectra of PW (d) and PW-180 (e).

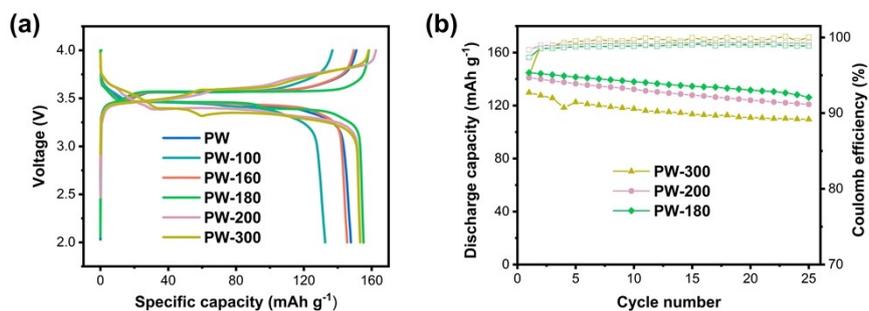


Fig. S3 (a) Initial charge-discharge profiles of materials after heat treatment at different temperatures. (b) The corresponding cycle performances of PW-180, PW-200 and PW-300 at 0.5C.

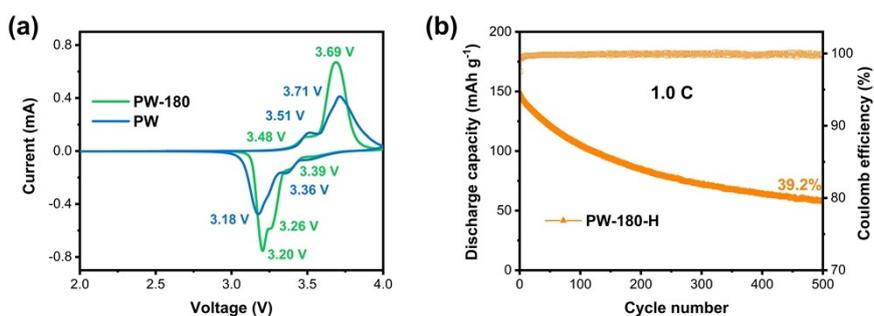


Fig. S4 (a) CV curves of PW and PW-180 at 0.1 mV s^{-1} . (b) Long term cycle performance of PW-180-H at 1.0 C.

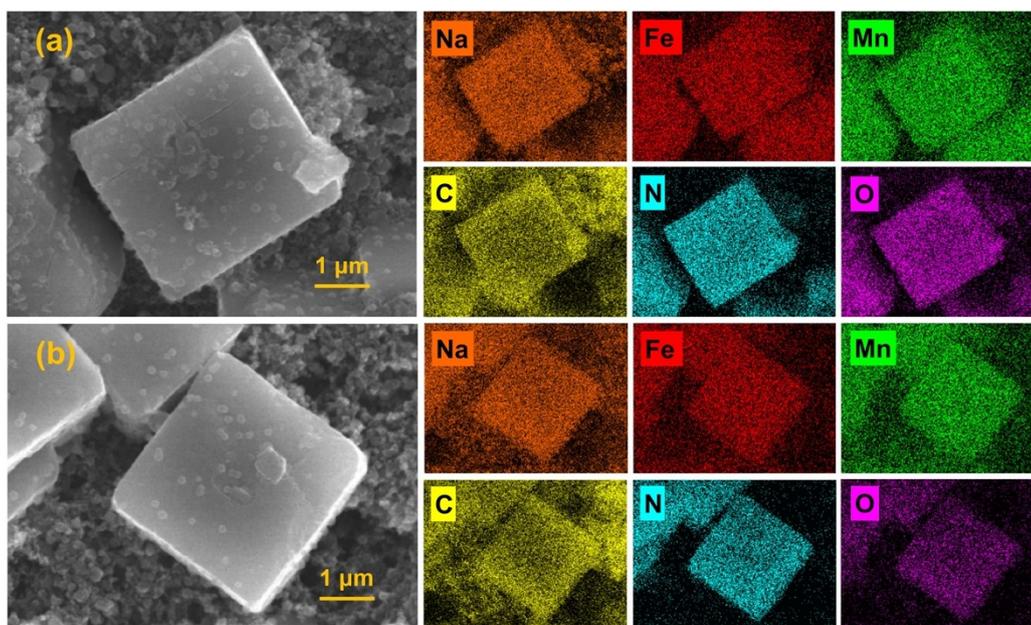


Fig. S5 SEM images and corresponding EDS-mapping images of PW (a) and PW-180 (b) after cycling.

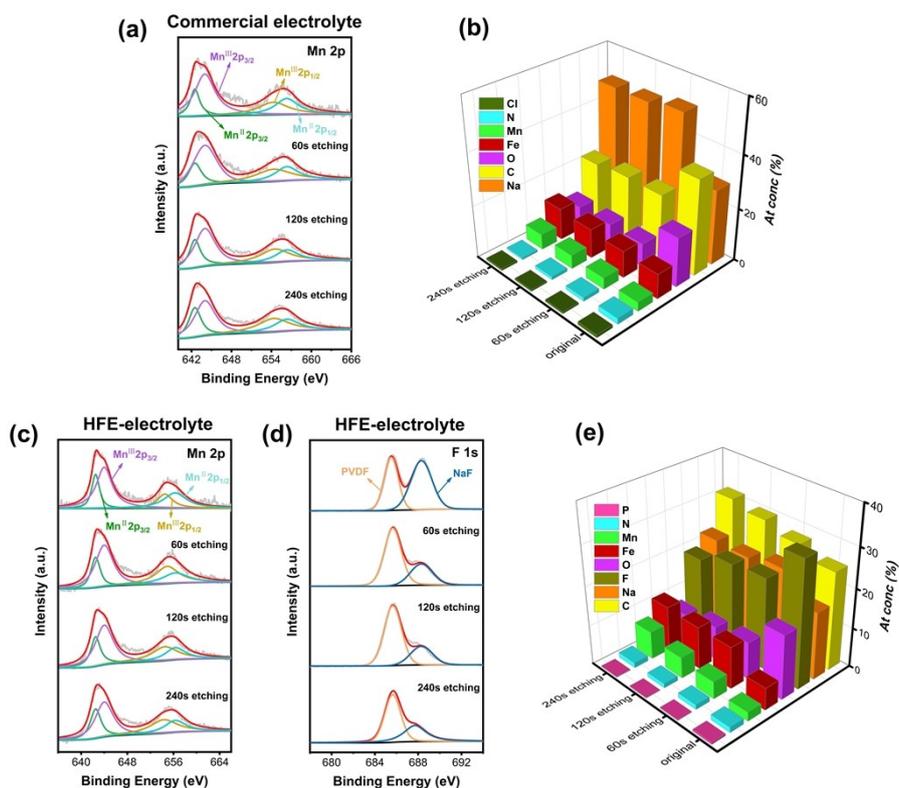


Fig. S6 Mn 2P XPS analyses (a) on PW after cycling in commercial electrolyte. Elemental ratio (b) on cycled PW electrodes in commercial electrolyte. Mn 2P XPS analyses (c) on PW after cycling in HFE-electrolyte. F 1s XPS analyses (d) on PW after cycling in HFE-electrolyte. Elemental ratio (e) on cycled PW electrodes HFE-electrolyte.

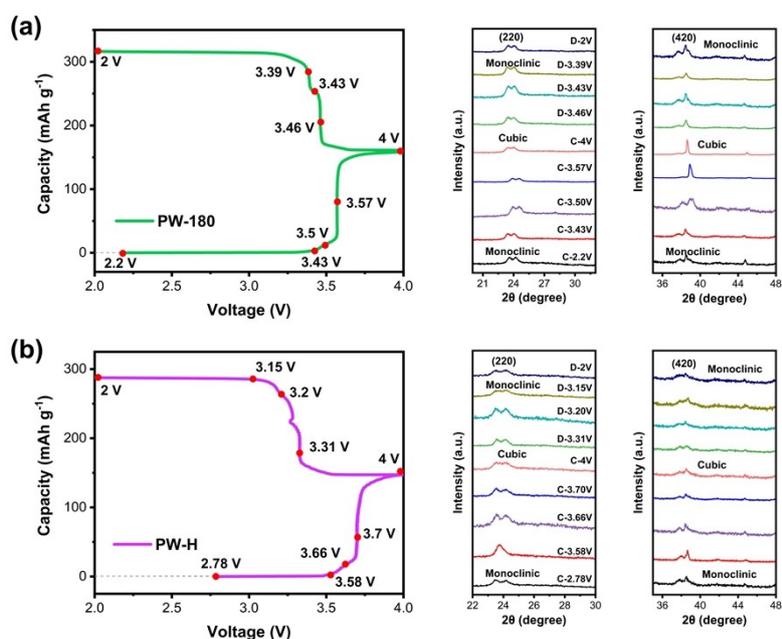


Fig. S7 Ex-situ XRD patterns of (a) PW-180 and (b) PW-H at different states along with Na⁺ extraction and insertion at 0.1 C.

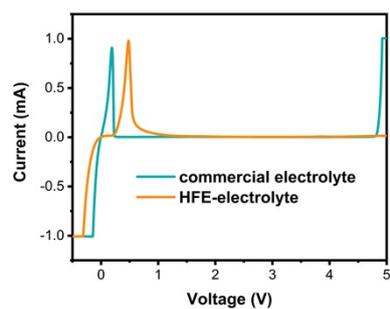


Fig. S8 LSV curves of commercial electrolyte and HFE-electrolyte at 1 mV s^{-1} .

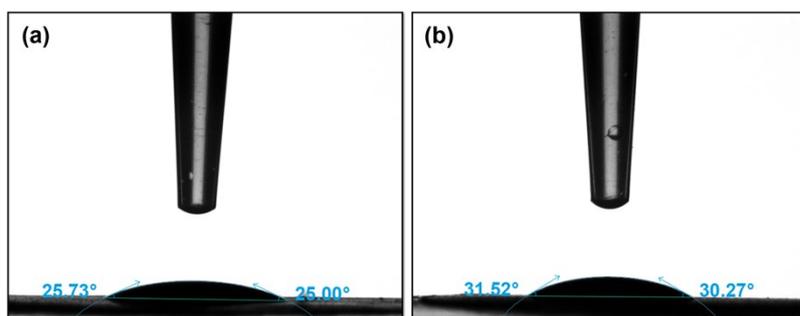


Fig. S9 Wettability images of commercial electrolyte (a) and HFE-electrolyte (b).

Table S1 Ionic conductivity of different electrolytes

electrolyte	ionic conductivity (mS cm^{-1})
commercial electrolyte	7.9
HFE-electrolyte	4.0

Table S2 Ionic transfer number of different electrolytes

electrolyte	ionic transfer number
commercial electrolyte	0.46
HFE-electrolyte	0.21

Table S3 Viscosity of different electrolytes

electrolyte	viscosity (mPa s)
commercial electrolyte	3.15
HFE-electrolyte	0.91