Enhancing durability of prussian white based sodium batteries through lithium salt-mediated electrode interface

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Experimental section

1. Reagents and materials

All chemicals for the preparation of PW were used directly without further treatment. Sodium ferrocyanide decahydrate ($Na_4Fe(CN)_6 \cdot 10H_2O$, purchased from Aladdin), Manganese sulphate monohydrate ($MnSO_4 \cdot H_2O$, purchased from Aladdin), sodium citrate ($C_6H_5Na_3O_7 \cdot 2\ H_2O$, purchased from Aladdin), DI water, Lithium borate difluorooxalate (LiDFOB, purchased from Duoduo Reagent), Floroethylene carbonate (FEC, purchased from Duoduo Reagent), ethylene carbonate (EC, purchased from Duoduo Reagent), diethyl carbonate (DEC, purchased from Duoduo Reagent), sodium perchlorate ($NaClO_4$, purchased from Duoduo Reagent), N-Methyl-pyrrolidone (NMP, purchased from Macklin Reagent), Poly(1,1-difluoroethylene) (PVDF), Ketjen Black (KB).

2. Synthesis of PW

The solution A was prepared by dissolving 3 mmol of $MnSO_4 \cdot H_2O$ and 3 mmol of $C_6H_5Na_3O_7 \cdot 2H_2O$ in 150 ml of deionized water. Similarly, the solution B was

obtained by dissolving 3 mmol of $Na_4Fe(CN)_6 \cdot 10H_2O$ in 150 ml of deionized water. Subsequently, solution A was introduced into solution B using a peristaltic pump at a flow rate of 0.5 ml/min under an argon atmosphere while maintaining stirring and heating at 60 °C for a duration of 24 hours. After completion, the resulting mixture was cooled to room temperature and allowed to stand for three hours before being subjected to centrifugation. The resulting precipitate underwent multiple washes with deionized water followed by anhydrous ethanol rinse. Finally, the obtained product was vacuum dried at 80 °C for 12 hours, ground into powder form, further dried in a vacuum drying oven at 120 °C for another period of twelve hours, yielding the desired Prussian white powder which was then transferred to an argon glove box for storage.

3. Preparation of electrodes and assembly of cells

A gentle and uniform slurry was formed by thoroughly mixing Prussian White, Ketjen Black, and PVDF in a ratio of 7:2:1, followed by the addition of NMP. The resulting paste was evenly coated onto aluminum foil and subjected to vacuum drying at 80 °C for 12 hours. Subsequently, it was transferred to a vacuum oven at 120 °C for an additional 5 hours of drying. For the half-cells, Prussian white and sodium sheets were utilized as cathode and anode electrodes respectively, enclosed within 2032 cell shells along with GF/D diaphragms. The electrolyte consisted of $NaClO_4$ (1.0 M) dissolved in EC/DEC (1:1, v/v), supplemented with FEC additive (5wt %) and Li-DFOB (0.5wt%, 1wt or 2wt%). All cells were assembled under an argon-filled glove box environment containing less than 0.01 ppm water and oxygen.

4. Electrochemical tests

Long cycle and rate performances was performed on a Wuhan Blue Power system with a voltage window of 2-4.2V. Impedance was tested on a CHI660E electrochemical workstation from 0.01 Hz to 10^6 Hz. Cyclic voltammetry was also performed on a CHI660E electrochemical workstation with a voltage window of 2-4.2 V and a speed of 0.01 mV s^{-1}.

The cathode and anode used in the process of the interface analysis were disassembled after 70 cycles at 1C in the cell.

5. Materials characterization

PW was examined by Powder X-ray diffraction (D8 Advance, Bruker, Germany) with a Cu Kα source. The CEI and SEI of PW||Na were evaluated by X-ray photoelectron spectroscopy (XPS, Themo-Fisher Scientific, America). The morphology was characterized with a field emission scanning electron microscope (FESEM, SU8010, Japan) with an energy dispersive X-ray spectrometer (EDS).

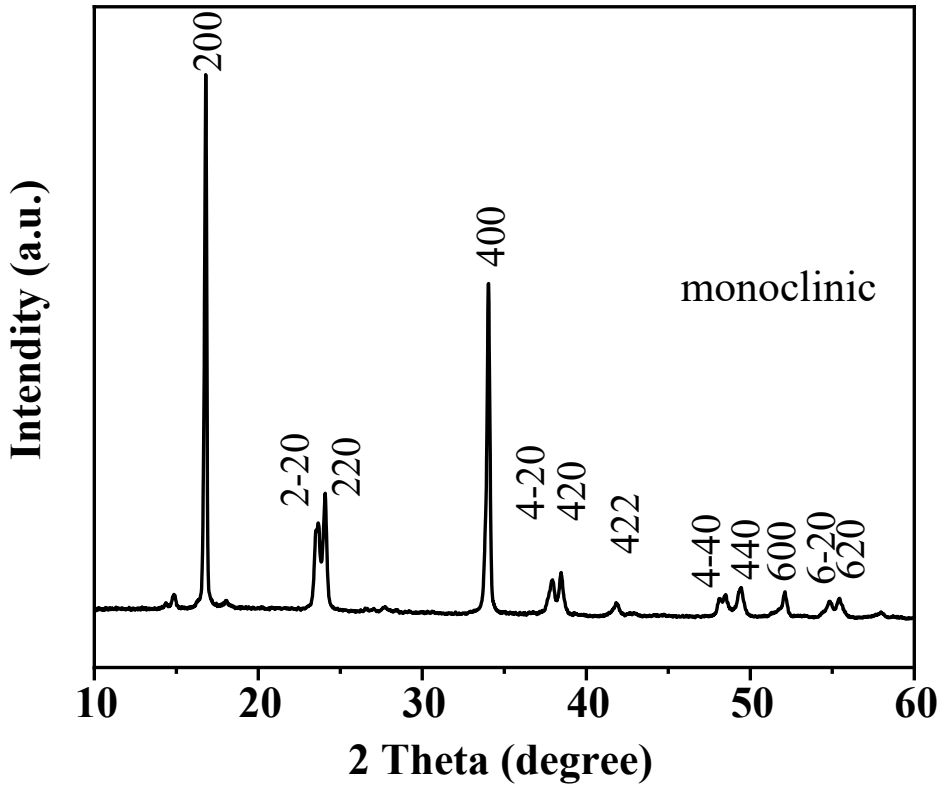

Figure S1.XRD patterns of PW.

Figure S2. High-angle annular dark-field images of PW and the corresponding mapping images of C, N, Na, Fe and Mn elements.

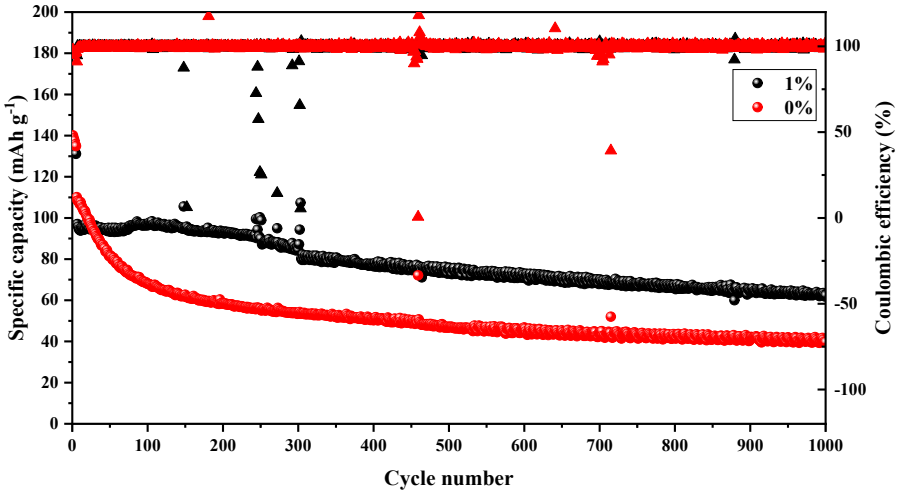

Figure S3. Long-term cycling performances at the current density of 5C.

Figure S4. SEM image of the original PW particles.

Figure S5. SEM image of a) 0% cell PW electrode after cycling and b) 1% cell PW electrode after cycling.

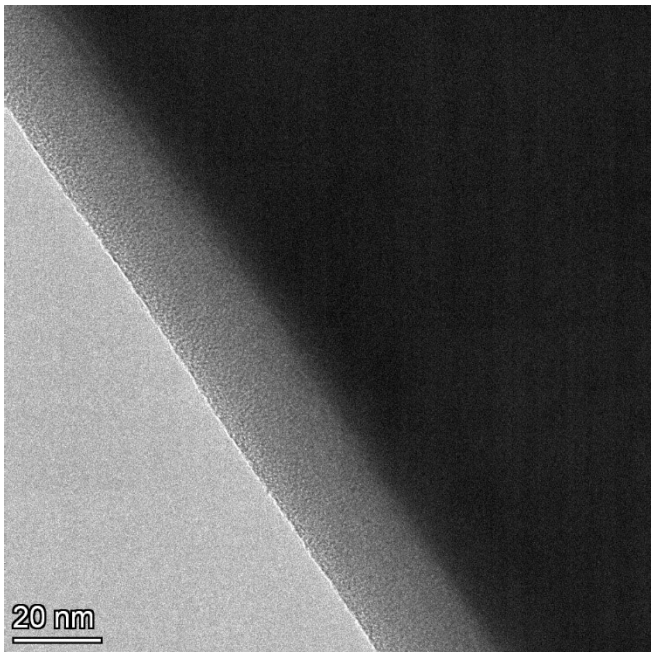

Figure S6. HRTEM of PW of cycled PW/Na in 0% electrolyte.

Figure S7. Cross-section SEM of PW of cycled PW/Na in a) 0% electrolyte and b) 1% electrolyte.

Figure S8. SEM of Sodium of cycled PW/Na in a) 0% electrolyte and b) 1% electrolyte.

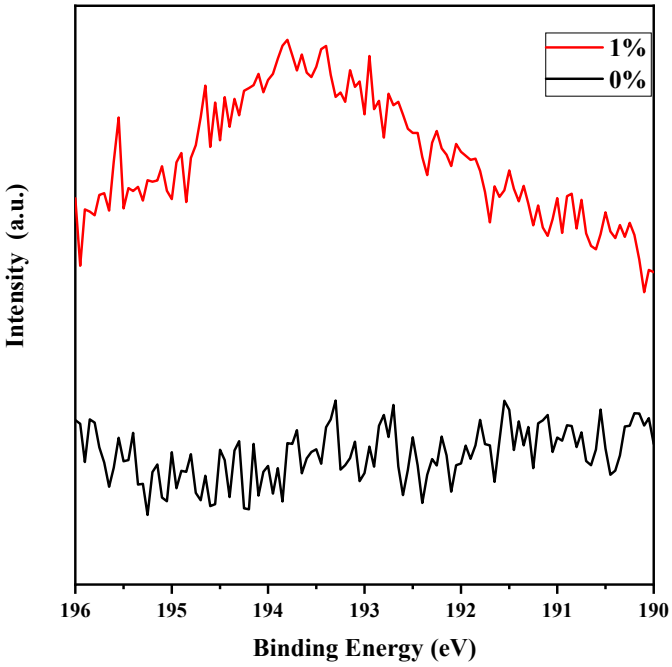

Figure S9. B1s fitted spectra of cycled sodium metal electrode.