Supplementary Information

A Universal Strategy for Bridging Prussian Blue Analogues and Sodium Layered Oxide Cathodes: Direct Fast Conversion, Dynamic Structural Evolution, and

Sodium Storage Mechanisms

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Materials Synthesis

Preparation of ternary PBAs-NFM: 4 mmol Na₄Fe(CN)₆ was dispersed in 200 ml DI water as solution A. 2 mmol MnSO₄·H₂O, 2 mmol NiSO₄·6H₂O and 8 mmol Na₃C₆H₅O₇ were dissolved in 200 ml DI water as solution B. Solution B was added dropwise to solution A by a peristaltic pump with continuous stirring for 6 h and aged for 24 h at room temperature. Finally, the PBAs-NFM can be obtained after washing the precipitate and drying it overnight at 120 °C in a vacuum oven.

Preparation of binary PBAs-FM: The preparation process is the same as for the PBAs-NFM, except that solution B is prepared from 4 mmol $MnSO_4$ ·H₂O and 8 mmol $Na_3C_6H_5O_7$ in 200 ml DI water.

Preparation of quaternary PBAs-NFMM: The preparation process is the same as for the PBAs-NFM, except that solution B is prepared from 2 mmol $MnSO_4$ ·H₂O, 1.33 mmol $NiSO_4$ ·6H₂O, 0.67 mmol MgSO₄·7H₂O, and 8 mmol Na₃C₆H₅O₇ in 200 ml DI water.

Preparation of layered oxides with fast sintering method: The PBAs precursors are placed in a ceramic boat and heated at 950 °C for 10 min at a heating rate of 3 °C min⁻¹ in an air atmosphere. Then, the product is taken out of the muffle furnace and quenched in air to obtain the desired materials.

Preparation of layered oxides with long period sintering method: The PBAs precursors are placed in a ceramic boat and heated at 950 °C for 12 h at a heating rate of 3 °C min⁻¹ in an air atmosphere and cooled naturally to room temperature to obtain the desired materials.

Materials Characterization.

The powder XRD test experiment was supported by a D8 Advance (Bruker) diffractometer with a range of 10-80° and a scan rate of 5°/min, and the in situ XRD pattern was obtained by a special Swagelok cell. The composition of the prepared layer oxides was calculated by the proportion of each element in the ICP test result. The composition of the layered oxide by long period sintering PBAs-FM, PBAs-NFM and PBAs-NFMM are $Na_{0.5}Fe_{0.5}Mn_{0.5}O_2$, $Na_{0.8}Ni_{0.2}Fe_{0.5}Mn_{0.3}O_2$ and $Na_{0.8}Ni_{0.15}Fe_{0.5}Mg_{0.05}Mn_{0.3}O_2$, respectively. The composition of the layered oxide by fast sintering PBAs-FM, PBAs-NFM and PBAs-NFMM $Na_{0.55}Fe_{0.5}Mn_{0.5}O_2$, $Na_{0.85}Ni_{0.2}Fe_{0.5}Mn_{0.3}O_2$ are and Na_{0.85}Ni_{0.15}Fe_{0.5}Mg_{0.05}Mn_{0.3}O₂, respectively. The *in situ* high-temperature XRD patterns at room temperatures were collected using a Panalytical Empyrean goniometer equipped with an Anton-Paar HTK 16N high temperature stage. XPS was performed on a Kratos Axis Supra photoelectron spectrometer with Al K α radiation, and the C 1s peak at 284.8 eV was used to calibrate all binding energies. The Ni/Fe/Mn-K edge X-ray absorption fine structure (XAFS) spectra were obtained in transmission mode on Table XAFS-500A (Specreation Instruments Co., Ltd.). The morphological and structural peculiarities, as well as the atomic images, were characterized by SEM (S4800), HR-TEM (JEM 2100F), and advanced spherical-arbitration-corrected STEM (JEMARM200CF), respectively.

Electrochemical Measurements.

The electrochemical performance of the materials was evaluated in coin cells (CR2032) with a Na foli as the counter electrode and porous glass fiber as the separator. The electrolyte was a solution of 1 M NaClO₄ (propylene carbonate (PC): fluoroethylene carbonate (FEC) = 95:5, vol %). The cathode film was fabricated by a well-dispersed slurry (active material : Super P : polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone

(NMP) = 7:2:1), casting the slurry onto a clean Al foil, and drying at 80 °C in a vacuum oven for about 12 h. Electrochemical measurements were performed on a Neware battery test equipment (MIHW-200-160CH, Shenzhen, China) over the voltage range of 2–4 V and 2-4.3 V vs Na⁺/Na (1 C = 120 mA g⁻¹).



Figure S1. XRD patterns of PBAs. (a) PBAs-FM, (b) PBAs-NFM, and (c) PBAs-NFMM.



Figure S2. XRD patterns of (a) NaFM, (b) NaNFM, and (c) NaNFMM.



Figure S3. (a) SEM image of NaNFM and corresponding EDS mapping of (b) Na, (c) Ni, (d) Fe, (e) Mn, and (f) O.



Figure S4. (a) SEM image of NaNFMM and corresponding EDS mapping of (b) Na, (c) Ni, (d) Fe, (e) Mn, (f) Mg, and (g) O.



Figure S5. (a)TEM and (b) HR-TEM image of NaNFM, (c) The Linear fitting diagram of crystal plane spacing of NaNFM.



Figure S6. XPS spectra of NaNFM: (a) Fe 2p, (b) Mn 2p, (c) Ni 2p, and (d) O1s.



Figure S7. XPS spectra of NaNFMM: (a) Ni 2p, (b) Fe 2p, (c) Mn 2p, (d) O1s.



Figure S8. The structure transformation of PBAs-NFM in different calcination temperature range: (a) 25-200 °C, (b) 300-460 °C, (c) 480-580 °C, (d) 620-700 °C, (e) 760-950 °C, (f) cooling to 25 °C.



Figure S9. Intensity contour maps of structure transformation during calcination of PBAs-NFM.



Figure S10. In situ HTXRD patterns of the process from PBAs-NFMM to NaNFMM.



Figure S11. The corresponding main characteristic diffraction peak intensity contour maps (bird's eye view) of the process from PBAs-NFMM to NaNFMM.



Figure S12. The structure transformation of PBAs-FM in different calcination temperature range: (a) 25-200 °C, (b) 300-460 °C, (c) 480-580 °C, and (d) 600-950 °C.



Figure S13. Intensity contour maps of structure transformation during calcination of PBAs-FM.



Figure S14. The electrochemical performance of electrodes in the voltage range of 2-4 V. (a) The specific energy of NaNFM comparison with PBAs-NFM at 0.1 C. (b) The charge and discharge curves of PBAs-NFM at different current density.



Figure S15. The charge and discharge curves of long cycle at 1 C in the voltage range of 2-4 V. (a) NaNFM. (b) PBAs-NFM.



Figure S16. The electrochemical performance of electrodes in the voltage range of 2-4 V. (a) The specific energy of NaNFMM comparison with PBAs-NFMM at 0.1 C. (b) The charge and discharge curves of PBAs-NFMM at different current density.



Figure S17. The charge and discharge curves of long cycle at 1 C in the voltage range of 2-4 V. (a) NaNFMM. (b) PBAs-NFMM.



Figure S18. The charge and discharge curves at 0.1 C of NaFM and PBAs-FM in the voltage range of 2-4 V.



Figure S19. XRD patterns of (a) NaFM-F, (b) NaNFM-F, and (c) NaNFMM-F.



Figure S20. Structure of NaFM-F. (a) XRD with Rietveld refinement. (b) SEM image. (c) TEM and (d) HRTEM images.



Figure S21. The linear fitting diagram of crystal plane spacing of NaFM-F.



Figure S22. (a) TEM image of NaFM-F and corresponding EDS mapping of (b) Na, (c) Mn, (d) Fe and (e) O.



Figure S23. XPS spectra of NaFM-F of (a) Fe 2p, (b) Mn 2p, and (c) O 1s.



Figure S24. (a) TEM image of NaNFM-F and corresponding EDS mapping of (b) Na, (c)

Ni, (d) Fe, (e) Mn.



Figure S25. HRXPS spectra of NaNFM-F of (a) Ni 2p, (b) Fe 2p, (c) Mn 2p, and (d) O 1s. HRXPS spectra of NaNFMM-F of (e) Ni 1s, (f) Fe 2p, (g) Mn 2p, and (h) O 1s.



Figure S26. (a) SEM image of NaNFMM-F and corresponding EDS mapping of (b) Na, (c) Ni, (d) Fe, (e) Mg, (f) Mn, and (g) O.



Figure S27. The electrochemical performance of NaFM-F in the voltage range of 2-4 V. (a) The comparison of specific energy with PBAs-FM at 0.1 C. (b) Charge and discharge curves at 0.1 C. (c) Rate performance. (d) Charge and discharge curves at different current density.



Figure S28. The cycle performance for NaNFM-F.



Figure S29. The WT-EXAFS spectra of (a) Fe, (b) Mn, and (c) Ni foil.



Figure S30. Intensity contour maps concerning the evolution of all characteristic diffraction peaks during the charge and discharge process of NaNFM-F in the voltage range of 2-4.3 V.

Sample	Space group	a/Å	b/ Å	c/ Å	V/Å ³	R _{wp}	R _p
PBAs-FM	P 21/n	10.55326	7.51315	7.40841	587.218(0.000)	14.2	10.0
PBAs-NFM	P 21/n	10.46002	7.48944	7.30163	571.7(0.179)	12.0	7.66
PBAs-NFMM	P 21/n	10.48927	7.50527	7.32612	576.482(0.125)	12.7	7.98

Table S1. Crystallographic parameters of PBAs-FM, PBAs-NFM and PBAs-NFMMcathode material refined by the Rietveld method.

Sample	Space	a/Å	b/ Å	c/ Å	V/Å ³	R	R
	group					wb	Ч
NaFM	P6 ₃ /mmc	2.91490	2.91490	11.2847	83.036(0.011)	3.32	1.67
NaNFM	R [∃] m	2.97689	2.97689	16.2012	124.338(0.000)	13.0	8.04
NaNFMM	R ³ m	2.96563	2.96563	16.26814	123.909(0.009)	11.6	7.52

 Table S2. Crystallographic parameters of the NaFM, NaNFM and NaNFMM cathode

 material refined by the Rietveld method.

	Space						
Sample	group	a/Å	b/ Å	c/ Å	V/Å ³	R _{wp}	R _p
NaFM-S	P6 ₃ /mmc	2.92608	2.92608	11.2746	83.60(0.012)	3.79	2.21
NaNFM-S	R ³ <i>m</i>	2.98260	2.98260	16.1553	124.462(0.010)	9.38	6.18
NaNFMM-S	R ³ m	2.96953	2.96953	16.21018	123.793(0.001)	7.97	5.37

Table S3. Crystallographic parameters of the NaFM-F, NaNFM-F and NaNFMM-Fcathode material refined by the Rietveld method.