Supporting Information

Non-topotactic Transformation Pathway in Electrochemical Li^+/Na^+ Ion-Exchanged Na-Mn-Fe Phosphates for Sodium-ion Batteries

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1. Experimental section

1.1. Electrochemical Li^+/Na^+ Ion-Exchange Synthesis of $NaMn_{0.6}Fe_{0.4}PO_4$

The starting material, $LiMn_{0.6}Fe_{0.4}PO_4$, was synthesized by a solvothermal method. First, 0.002 mol $LiOH{\cdot}H_2O$ was dissolved in 30 mL of ethylene glycol. After complete dissolution, 0.015 mol H_3PO_4 was added to obtain Solution A. Next, 0.006 mol $MnSO_4{\cdot}H_2O$ was dissolved in 10 mL of deionized water. After dissolution, 0.004 mol $FeSO_4{\cdot}7H_2O$ and 0.01 mol ascorbic acid were sequentially added. After complete dissolution, 20 mL of ethylene glycol was added to obtain Solution B. Solution B was slowly poured into Solution A and mixed to form a light green suspension. After stirring for 30 min, the suspension was transferred to a 100 mL PTFE-lined autoclave and reacted at 180 °C for 5 h. Upon completion of the reaction, the precipitate was washed several times by centrifugation with deionized water and ethanol. The product was dried at 60 °C for 12 h to obtain the $LiMn_{0.6}Fe_{0.4}PO_4$ precursor powder. Then, the precursor was ball-milled with glucose at a mass ratio of 5:1 at 300 r/min for 4 h. Subsequently, the mixture was sintered in a tube furnace under an argon atmosphere at a heating rate of 5 °C/min to 700 °C for 6 h, yielding black $LiMn_{0.6}Fe_{0.4}PO_4$/C powder.

To prepare $NaMn_{0.6}Fe_{0.4}PO_4$/C, the $LiMn_{0.6}Fe_{0.4}PO_4$/C powder was first made into a working electrode and assembled into a coin-type half-cell with a lithium metal counter electrode. The cell was charged to 4.5 V to extract all Li^+ ions. The delithiated cathode sheet was then taken out from the cell, rinsed with dimethyl carbonate (DMC) to remove residual lithium salts and organic species, and dried. Next, it was assembled into a new half-cell with a sodium metal counter electrode and discharged to 1.7 V to insert Na^+ ions, yielding $NaMn_{0.6}Fe_{0.4}PO_4$/C. Finally, the electrode was cycled three times between 1.7 and 4.3 V to reach a stable structural state. See Section 1.3 for details on half-cell assembly.

1.2. Material characterization

The crystal structure of the samples was characterized by X-ray diffraction (XRD, PANalytical Empyrean, Cu Kα radiation, λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was used to analyze the elemental composition and chemical states. The morphology of the samples was observed using a scanning electron microscope (SEM, TESCAN). Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDX) data were collected using a Thermo Scientific Talos F200X microscope. Fourier-transform infrared (FTIR) spectra were recorded using a Thermo Scientific iS50 spectrometer.

1.3. Electrochemical measurements

CR2032-type coin cells were assembled to evaluate the electrochemical performance. All cell assembly processes were conducted in an argon-filled glovebox with moisture and oxygen levels maintained below 0.1 ppm. To prepare the cathode electrode, the active material (80 wt%), Super P (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) were thoroughly mixed in N-methyl-2-pyrrolidone (NMP) solvent to form a uniform black slurry. The slurry was then coated onto aluminum foil. After drying at 110°C, the electrodes were punched into 12 mm diameter circular discs. The electrolyte used for lithium-ion coin cells was 1 M $LiPF_6$ dissolved in a mixture of EC and DMC (1:1 by volume), containing 5 wt% FEC. The electrolyte used for sodium-ion coin cells was 1 M $NaClO_4$ dissolved in propylene carbonate (PC) with 2 wt% fluoroethylene carbonate (FEC) as an additive. Galvanostatic charge/discharge tests were conducted on a Land battery testing system (Wuhan Land Electronics Co., Ltd). For galvanostatic intermittent titration technique (GITT) measurements, all electrodes were subjected to 5 minutes of charging or discharging at 0.1 C followed by a 60-minute rest to allow the system to reach a quasi-equilibrium state. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were carried out using a Bio-Logic SP-300 electrochemical workstation.

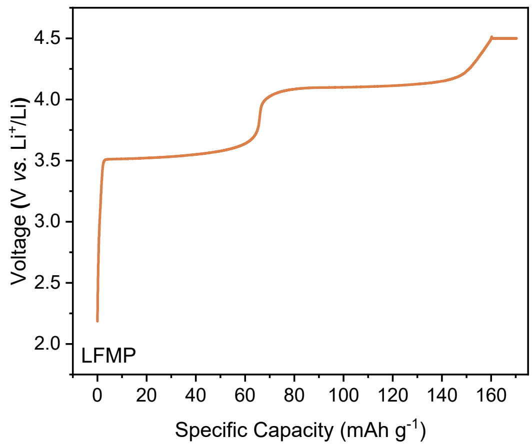

Figure S1. Capacitance-voltage curve of LFMP electrode charging.

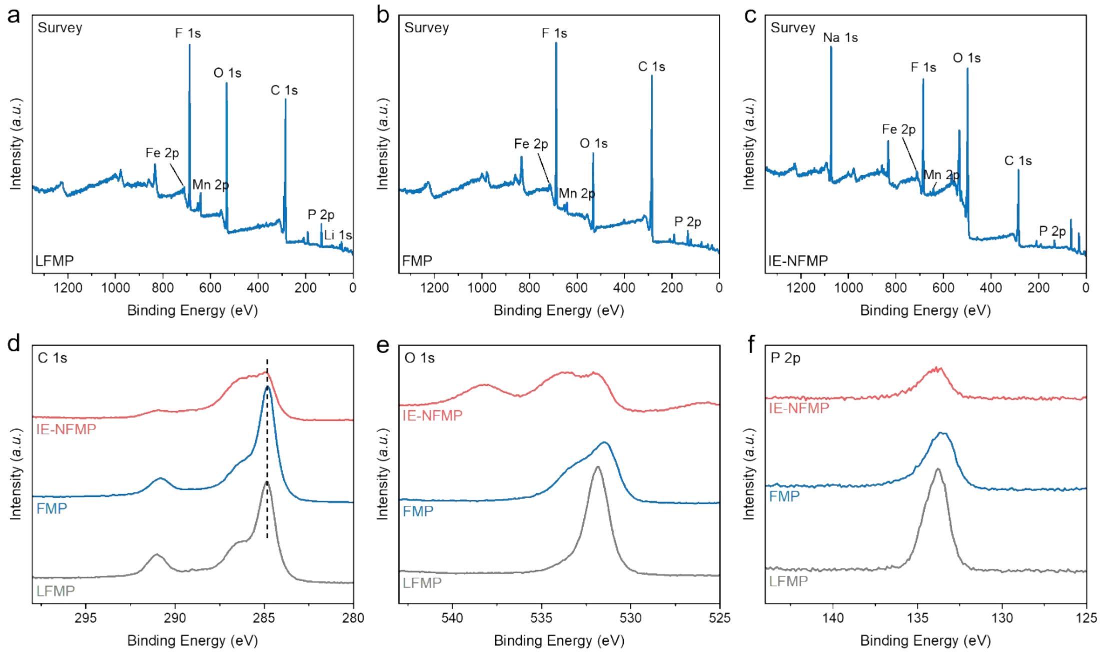

Figure S2. XPS spectra of the samples. (a)-(c) Survey; (d) C 1s; (e) O 1s; (f) P 2p.

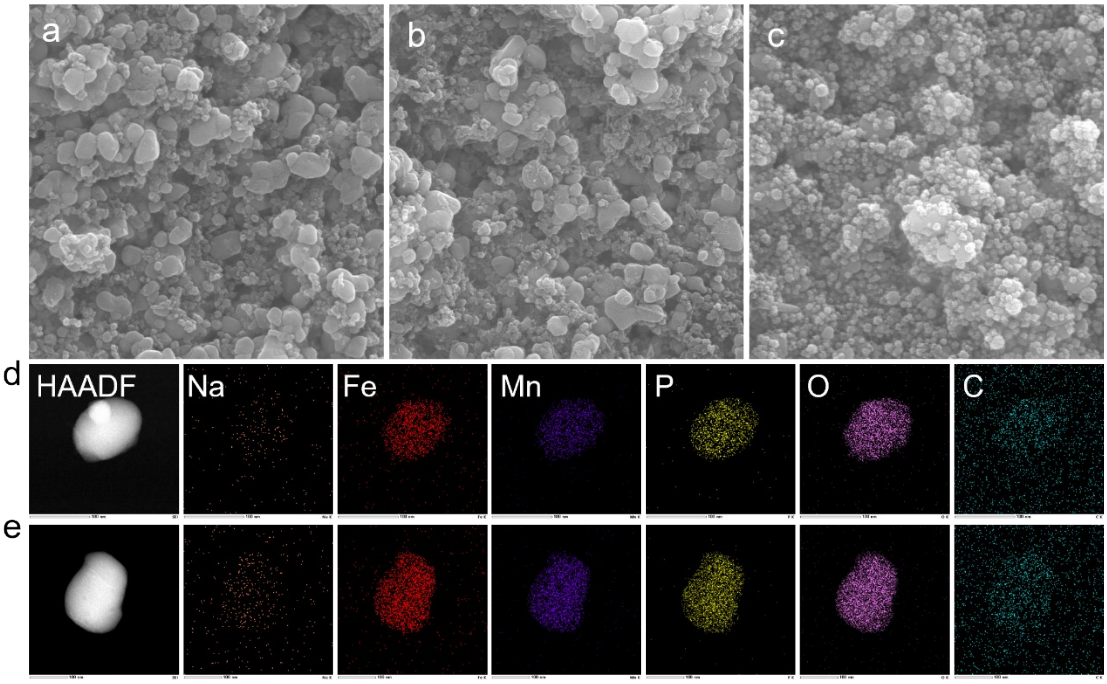

Figure S3. (a)-(c) High-magnification SEM images of the samples. (d) TEM-EDS mapping of LFMP and (e) FMP.

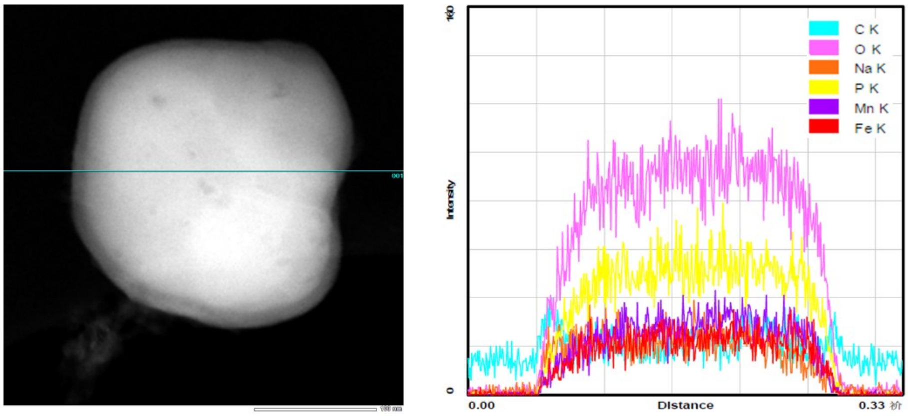

Figure S4. TEM-EDS line scan results for IE-NFMP.

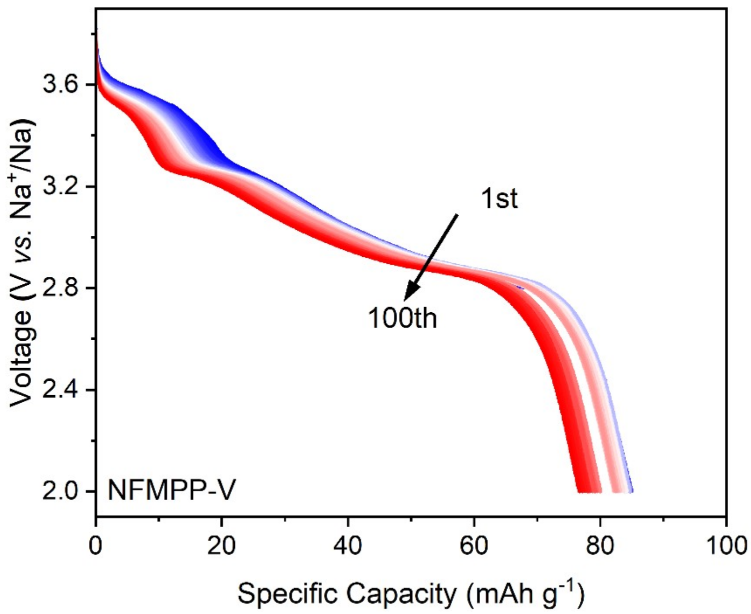

Figure S5. Discharge curves for the first 100 cycles.

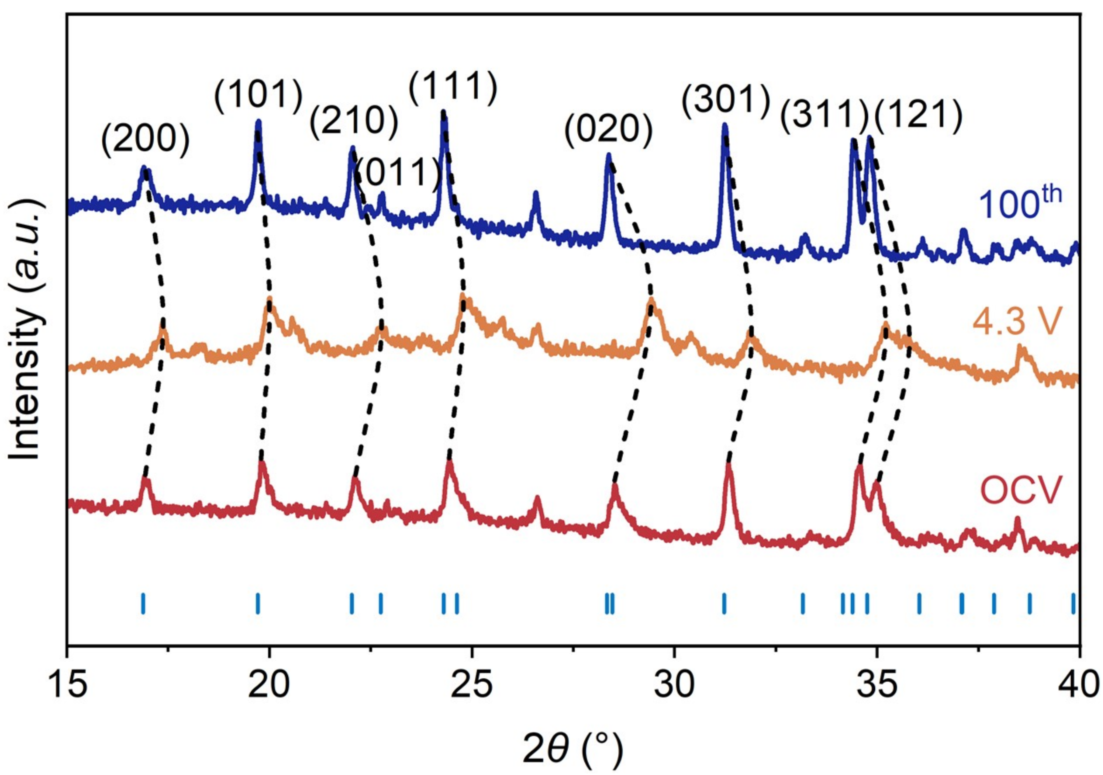

Figure S6. XRD patterns at different voltages and cycling states of IE-NFMP.

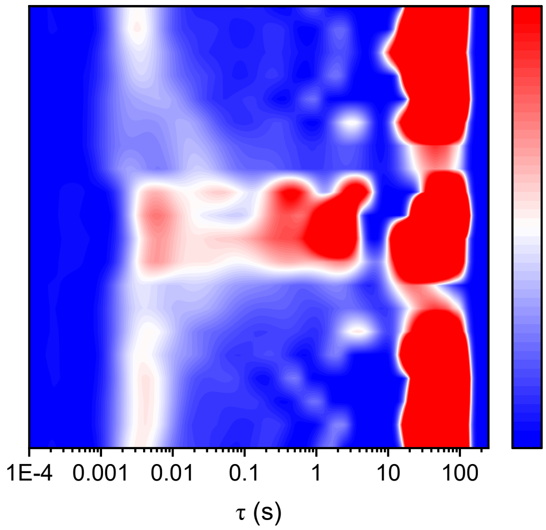

Figure S7. Two-dimensional contour map of DRT analysis from *in-situ* EIS of IE-NFMP electrode.

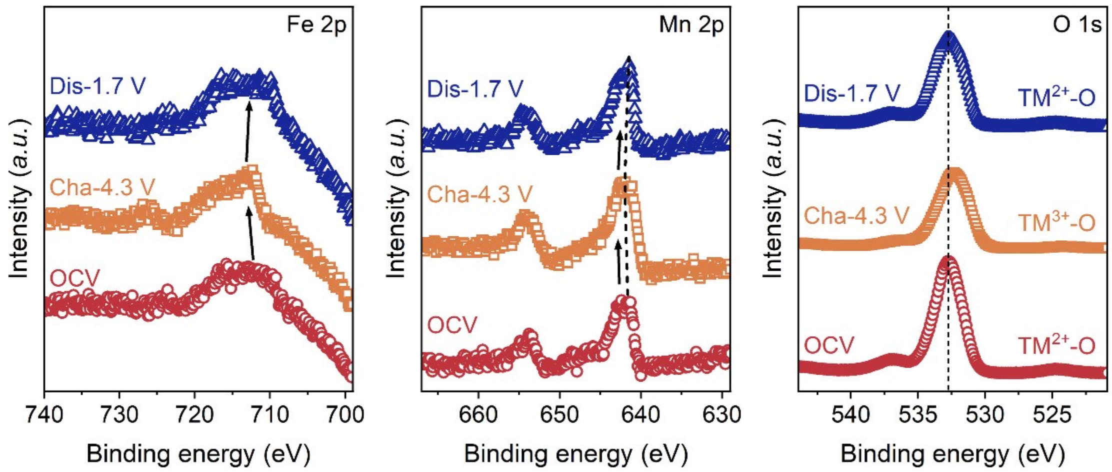

Figure S8. *Ex situ* Fe 2p, Mn 2p and O 1s XPS at different states.

Table S1. Process feasibility analysis table

No.	Materials	Process	Capacity	Rate	Cycling
1	triphylite-$NaFePO_4$ (*Vacuum* **2023**, 210 111853)[1]	Using a CR2032 coin cell to remove lithium in $LiFePO_4$, followed by sodiation to form $NaFePO_4$.	140 mAh g^{-1} (0.1C)	60 mAh g^{-1} at 1C	50% retention after 100 cycles
2	triphylite-$NaFePO_4$ (*Chemical Physics Letters* **2024**, 834 140983)[2]	$LiFePO_4$ is oxidized in an aqueous $Na_2S_2O_8$ solution to remove lithium, and the resulting $FePO_4$ is then sodiation by reacting with NaOH in anhydrous ethanol.	125.4 mAh g^{-1} (0.1C)	54.63 mAh g^{-1} at 2C	91.4% retention after 100 cycles at 0.1C
3	triphylite-$NaFePO_4$ (*ACS Appl. Mater. Interfaces* **2015**, 7, 17977−17984)[3]	Electrochemical delithiation of $LiFePO_4$ electrodes was performed using a three-electrode system in 1 mol L^{-1} Li_2SO_4 aqueous solution, followed by transfer to 1 mol L^{-1} Na_2SO_4 aqueous solution for sodium intercalation.	111 mAh g^{-1} (0.1C)	46 mAh g^{-1} at 2C	90% retention after 240 cycles at 0.1C
4	triphylite-$NaFePO_4$ (*J Mater Sci: Mater Electron* **2023**, 34:469)[4]	Same as 1	138.8 mAh g^{-1} (0.1C)	/	96% retention after 50 cycles at 0.1C
5	triphylite-$NaFePO_4$ *(J. Mater. Chem. A* **2016**, 4, 4882–4892)[5]	Same as 3	142 mAh g^{-1} (0.1C)	38 mAh g^{-1} at 20C	92% retention after 200 cycles at 0.1C
6	triphylite-$NaFePO_4$@AlF_3 *(Journal of Alloys and Compounds* **2019**, 784 720e726)[6]	Except for using AlF_3-coated $LiFePO_4$ as the starting material, same as 3	83.9 mAh g^{-1} (1C)	/	66.5% retention after 50 cycles at 1C
7	triphylite-$NaMn_{0.6}Fe_{0.4}PO_4$（**This work**）	Using $LiMn_{0.6}Fe_{0.4}PO_4$ as the starting material, same as 1	132.1 mAh g^{-1} (0.06C)	74.2 mAh g^{-1} at 0.18C	97.4% retention after 70 cycles at 0.12C

References

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