Supporting Information

Unlocking Fast and Highly Reversible Sodium Storage in Fe-Based Mixed Polyanion Cathodes for Low-Cost and High-Performance Sodium-Ion Batteries

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Experimental Section

A typical sol-gel method was adopted to synthesize the cathode materials (5 mmol). Specifically, citric acid (99.0%, Aladdin) and Fe(NO₃)₃·9H₂O (99.0%, Aladdin) were dissolved in 30 mL deionized water with a molar ratio of 2: 1 and then 1 g polyvinylpyrrolidone (PVP, 99.0%, Aladdin) were added to obtain solution A. Stoichiometric NaH₂PO₄ (99.0%, Macklin)was added to another 30 ml deionized water to obtain solution B. Afterwards, solution A was added slowly into solution B with constant stirring at 80 °C for 5 h. Then, the sample was transferred to a blast drying oven at 120 °C for 12 h. Finally, the precursor was ground into the powder and was further sintered in a tube furnace at 500°C for 10 h (heating rate: 5° min⁻¹) under a 5 vol.% H₂/ 95 vol.% Ar flow. The Ni-doped Na₃Fe₂- $_x$ Ni_x(PO₄)P₂O₇/C (*x* = 0, 0.05, 0.1 and 0.2) samples were prepared by a same method except the addition of different Ni(NO₃)₂·6H₂O (99.0%, Sinopharm).

Material Characterization.

A powder X-ray diffractometer (XRD) (PANalytical 2Empyrean 2, Cu K_{α} radiation) was used to identify the crystal structures of all samples. Scanning electron microscopy (JSM-7900F) and high-resolution transmission electron microscopy (FEI Tecnai F20)were used to study the surface topography and microstructure of the samples. Raman spectroscopy (inVia) was analyzed for certificate features of carbon (532 nm). Fourier transform infrared spectroscopy (Niolet iN10) was used to study the characteristic functional groups of materials. An X-ray photoelectron spectroscopy (XPS) method (Thermo Scientific Al K_{α}) was used to study the elemental composition and elemental valence states of materials. TGA was conducted on a STA 2500 Regulus with 10 °C min⁻¹ in air atmosphere. The *in-situ* XRD was performed in a PANalytical 2Empyrean 2, Cu K α radiation using an *in-situ* cell with a pure beryllium window.

Electrochemical Measurements

The active material, acetylene black and polyvinylidene fluoride were mixed up in a mass ratio of 7: 2: 1, with N-methyl-2-pyrrolidone as the solvent to form a slurry. Then the slurry was ground and coated on the Al foil and then transferred into a vacuum oven at 80 °C for 12 h. The mass loading of the cathode is ~ 1.5 mg cm⁻². The electrochemical performances were tested in the CR2032 coin cell configuration with the sodium metal as the counter electrode and the glass fiber (Whatman GF/D) as the separator. A solution of 1 M NaClO4 dissolved in ethylene carbonate (EC) / propylene carbonate (PC) (1:1 v/v) with 5 vol.% fluoroethylene carbonate (FEC) was used as the electrolyte. The cell was packaged in an Ar-filled glovebox and aged for 12 h before tests. As for the ex-situ measurements, the electrodes were disassembled in the glove box and rinsed for several times with dimethyl carbonate (DMC). For the assembly of the full cell, the mass ratio of anode active material, acetylene black, and PVDF was 8: 1: 1. The hard carbon electrode was pre-treated by directly contact with sodium metal disk in the above electrolyte solution for 1 h to enhance the initial Coulombic efficiency of the full cell. In this full battery, the mass ratio of NFNPP and hard carbon was controlled at 3 : 1. The full battery is tested within 2.0-4.0 V

Computational Details

We have employed the first-principles to perform density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation. We have chosen the projected augmented wave (PAW) potentials ¹ to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10–5 eV. A geometry optimization was considered convergent when the energy change was smaller than 0.05 eV Å–1. The Brillouin zone integration was performed using 2×2×2 Monkhorst-Pack k-point sampling for a structure.



Fig. S1. Rietveld refined XRD pattern of $Na_3Fe_{1.9}Ni_{0.1}(PO_4)P_2O_7/C$ and $Na_3Fe_2(PO_4)P_2O_7/C$.



Fig. S2. SEM images of $Na_3Fe_2(PO_4)P_2O_7(a)$, $Na_3Fe_{1.95}Ni_{0.05}(PO_4)P_2O_7(b)$ and $Na_3Fe_{1.8}Ni_{0.2}(PO_4)P_2O_7(c)$.



Fig. S3. TEM image of Na₃Fe₂(PO₄)P₂O₇



Fig. S4. TG curves of Na₃Fe_{1.9}Ni_{0.1}(PO₄)P₂O₇/C and Na₃Fe₂(PO₄)P₂O₇/C.



Fig. S5. Raman spectra of $Na_3Fe_2(PO_4)P_2O_7/C$.



Fig. S6 N_2 adsorption-desorption isotherms and pore size distribution curve (inset) of the $Na_3Fe_{1.9}Ni_{0.1}(PO_4)P_2O_7/C$ sample.



Fig. S7. XPS full spectra of $Na_3Fe_{1.9}Ni_{0.1}(PO_4)P_2O_7/C$, inset is the results of ICP.



Fig. S8. High-resolution spectra of Fe 2p for $Na_3Fe_{1.9}Ni_{0.1}(PO_4)P_2O_7/C$.



Fig. S9. (a) Galvanostatic charge/discharge profiles and (b) cycling performance of the pure carbon matrix within the voltage window of 1.5-4.0 V vs. Na⁺/Na.



Fig. S10. Rate performance of Na₃Fe_{2-x}Ni_x(PO₄)P₂O₇/C(x=0, 0.05, 0.1 and 0.2)



Fig. S11. long cycling performances at 1 C of $Na_3Fe_{2-x}Ni_x(PO_4)P_2O_7/C(x=0, 0.05, 0.1 and 0.2)$



Fig. S12. (a) XRD pattern and (b) SEM image of the $Na_3Fe_{1.9}Ni_{0.1}(PO_4)P_2O_7/C$ electrode material after 200 cycles at 1 C



Fig. S13 Voltage decay after cycling of Na₃Fe₂(PO₄)P₂O₇/C and Na₃Fe_{1.9}Ni_{0.1}(PO₄)P₂O₇/C



Fig. S14 Nyquist plots of Na_3Fe_2(PO_4)P_2O_7/C and Na_3Fe_{1.9}Ni_{0.1}(PO_4)P_2O_7/C



Fig. S15 GITT curves and the sodium ions diffusion coefficients for Na₃Fe₂(PO₄)P₂O₇/C.

Kinetic behavior of the electrochemical process has been analyzed in order to analyze in detail the origin of such excellent electrochemical properties. The GITT test was tested for the first cycle at 0.05 C between 1.5 to 4.0 V. For the charging process, first charge for 15 min, and then relax for 60 min, and repeat the same steps until 4.0 V, and vice versa during discharging. According to the Fick's second law, under a sufficient relaxation time ($\tau \ll L^2/D_{Na}^+$) and a simplified condition, D_{Na}^+ could be calculated by the following equation:

$$D_{Na^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

(S1)

where m_B , M_B , V_M , S represent mass, molecular weight, molar volume, and surface area of the cathode material, respectively. ΔE_s is the difference between two consecutive stable voltages after relaxation, and ΔE_t is the transient voltage-change during a single titration step.



Fig. S16 CV curves at various scan rates from 0.1 to 1 mV s⁻¹ of Na₃Fe₂(PO₄)P₂O₇/C.



Fig. S17. XPS spectra of Ni 2p at different COSs for the Na₃Fe_{1.9}Ni_{0.1}(PO₄)P₂O₇/C electrodes.



Fig. S18 Charge/discharge curves of NFNPP at 0.1 C and -10 °C



Fig. S19. Charge/discharge curves of the hard carbon anode.



Fig. S20 Rate performance of the full cell.

Status	R_{ct}/Ω	R _s /Ω
NFPP fresh	1641.0	1570.0
NFPP after cycling	647.4	540.7
NFNPP fresh	1158.0	975.5
NFNPP after cycling	496.4	435.5

Table S1. The impedance values before and after cycling of $Na_3Fe_2(PO_4)P_2O_7/C$ and $Na_3Fe_{1.9}Ni_{0.1}(PO_4)P_2O_7/C$

Table S2. Comparison of the Na storage performances of full cells

Full-cell (cathode//anode)	Capacity	Cycling stability	Ref.
$Na[Ni_{1/3}Fe_{1/3}Mn_{1/3}]O_2//Na_yC$	120 mAh g $^{-1}$ at 75 mA g $^{-1}$	81% after 150 cycles at 75 mA g ⁻¹	2
$Na_3Fe_2(PO_4)_3//Hard carbon$	50.2 mAh g ⁻¹ at 1000 mA g ⁻¹	86.5% after 300 cycles at 100 mA g ⁻¹	3
Na _{0.9} FePO ₄ //HPCFs	52.5 mAh g $^{-1}$ at 400 mA g $^{-1}$	81% after 300 cycles at 20 mA g ⁻¹	4
Na _{1.76} Ni _{0.12} Mn _{0.88} [Fe(CN) ₆] _{0.98} //h ard carbon	90 mAh g ⁻¹ at 100 mA g ⁻¹	77% after 200 cycles at 100 mA g ⁻¹	5
$Na_2FePO_4F@C$ nanofibers//carbon nanofibers	84.5 mAh g ⁻¹ at 0.5 C	84.5% after 200 cycles at 0.5 C	6
Na ₄ Fe ₃ (PO ₄) ₂ P ₂ O ₇ @MCNTs// hard carbon	69.3 mAh g $^{-1}$ at 25 mA g $^{-1}$	74.3% after 100 cycles at 1 C	7
Na ₃ FeMnPO ₄ P ₂ O ₇ /C // hard carbon	105 mAh g 1 at 12 mA g 1	81% after 150 cycles at 2 C	8
	87.3 mAh g $^{-1}$ at 12 mA g $^{-1}$	96.9% after 100 cycles at 120 mA g ⁻¹	This work

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