Supplementary Information

Nanostructured potassium and sodium ions incorporated Prussian blue framework as cathode materials for sodium-ion batteries

Yang Liu,[*a] Dandan He,[a] Ruimin Han,[a,b] Gangya Wei[a] and Yun Qiao[*a,b]

[a] School of Chemistry and Chemical Engineering, Henan Normal University. Xinxiang 453007, China

[b] National and Local Joint Engineering Laboratory of Motive Power and Key Materials, Henan Normal University, Xinxiang 453007, China

* Corresponding author

E-mail: liuy986@163.com; qyvec@163.com

Experimental Section

Synthesis: The analytical grade chemicals were directly used without any modification or treatment. Deionized water as solvent was selected in the experiment. In a typical preparation, 1.69 g $K_4Fe(CN)_6 \cdot 3H_2O$ was dissolved in 200 mL deionized water to form a transparent solution. 0.76 g $MnCl_2$ and a certain amount of sodium citrate were dissolved in 200 mL deionized water under stirring. The above two precursor solutions were then mixed and maintained for 12 h at room temperature. A precipitate was obtained and collected by centrifugation, and washed with deionized water and ethanol thoroughly and then dried in oven at 80 °C. The as-prepared PB were denoted as KNMF-0 (without sodium citrate), KNMF-1 (1.0 g sodium citrate), KNMF-2 (2.0 g sodium citrate), KNMF-3 (3.0 g sodium citrate), respectively.

Characterizations: The X-ray diffraction (XRD) pattern was collected to character the crystalline phase using an X' pert PRO X-ray diffractometer with Cu Kα radiation. The fine morphology and microstructure information were observed on a JEM-2010 electron microscope. Thermogravimetric analysis (TGA) was conducted on a Discovery TGA from 50 to 500 ^oC in flowing air at a rate of 10 °C min^{-1}. The molar ration of the sample was analyzed by direct-reading inductively coupled plasma emission spectrometer (ICP-OES, Optima 4300DV, USA).

Electrochemical Measurements: The Electrochemical performance and kinetic were evaluated in a typical CR2032 coin cell. The working electrode was prepared by mixing active material (70 wt.%), super P (20 wt.%), and polyvinylidene fluoride (PVDF, 10 wt.%) in N-methylpyrrolidinone (NMP) and then coated on aluminum foil and dried at 80 °C in vacuum. Sodium-ion cell was assembled in an argon-filled glove box using sodium metallic foil as counter electrode, glass fiber (purchased form Whatman) as separator, and 1 mol L^{-1} $NaClO_4$ in a mixed solvent of ethylene carbonate (EC) and diethylene carbonate (DEC) (v/v=1:1) as the electrolyte. Cyclic voltammetry (CV) and chronopotentiometry measurements were test using the CHI760E electrochemical workstation. Galvanostatic charge and discharge of the cell was carried out on Land testing system in a voltage range of 2.0 and 4.2 V.

Table S1. The element content of K, Na, Mn, and Fe in the four samples.

Sample	K(wt%)	Na(wt%)	Mn (wt%)	Fe(wt%)
KNMF-0	19.71	0.00	16.69	15.46
KNMF-1	19.52	0.14	16.51	15.47
KNMF-2	19.29	1.47	16.59	15.47
KNMF-3	18.83	1.77	16.67	15.09

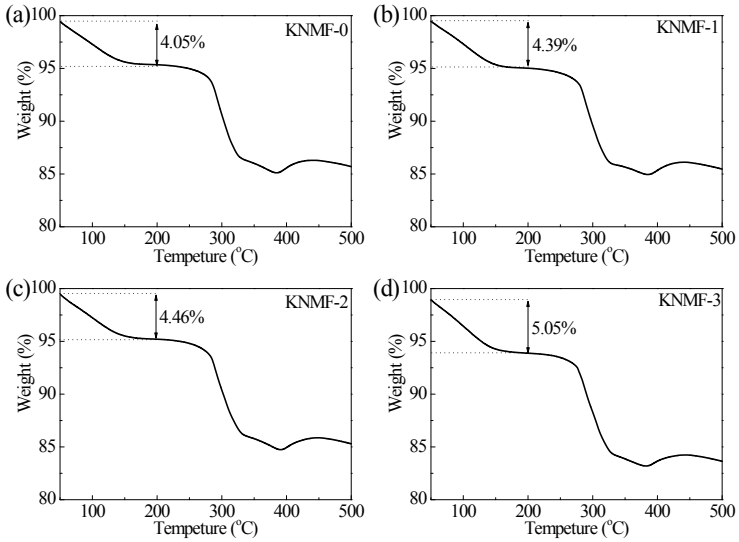

Figure S1. TG curves of the four samples.

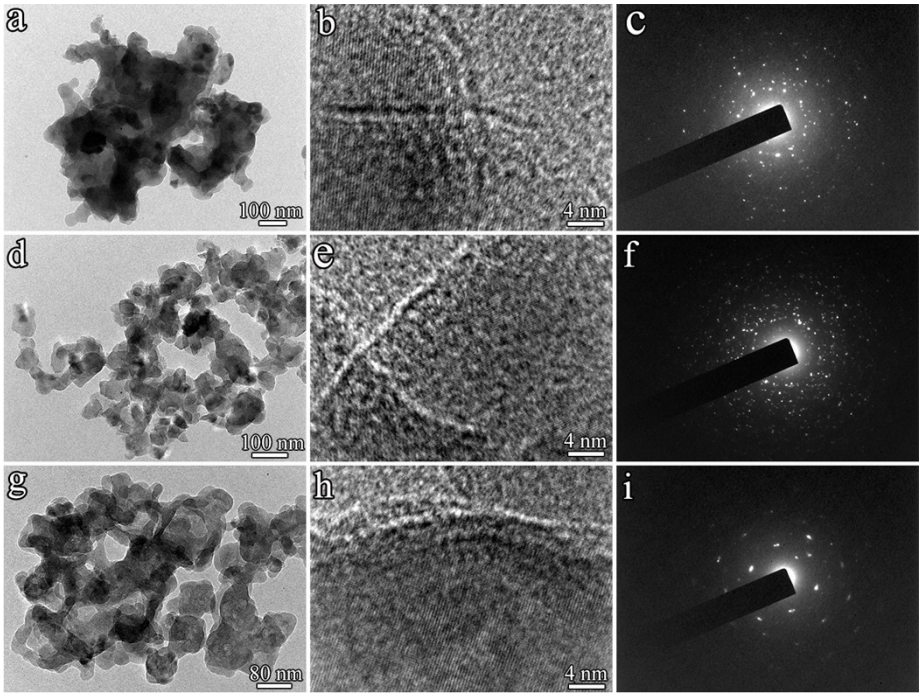

Figure S2. TEM (a, d, g), HRTEM (b, e, h) images and SAED pattern (c, f, i) of KNMF-0, KNMF-1 and KNMF-2, respectively.

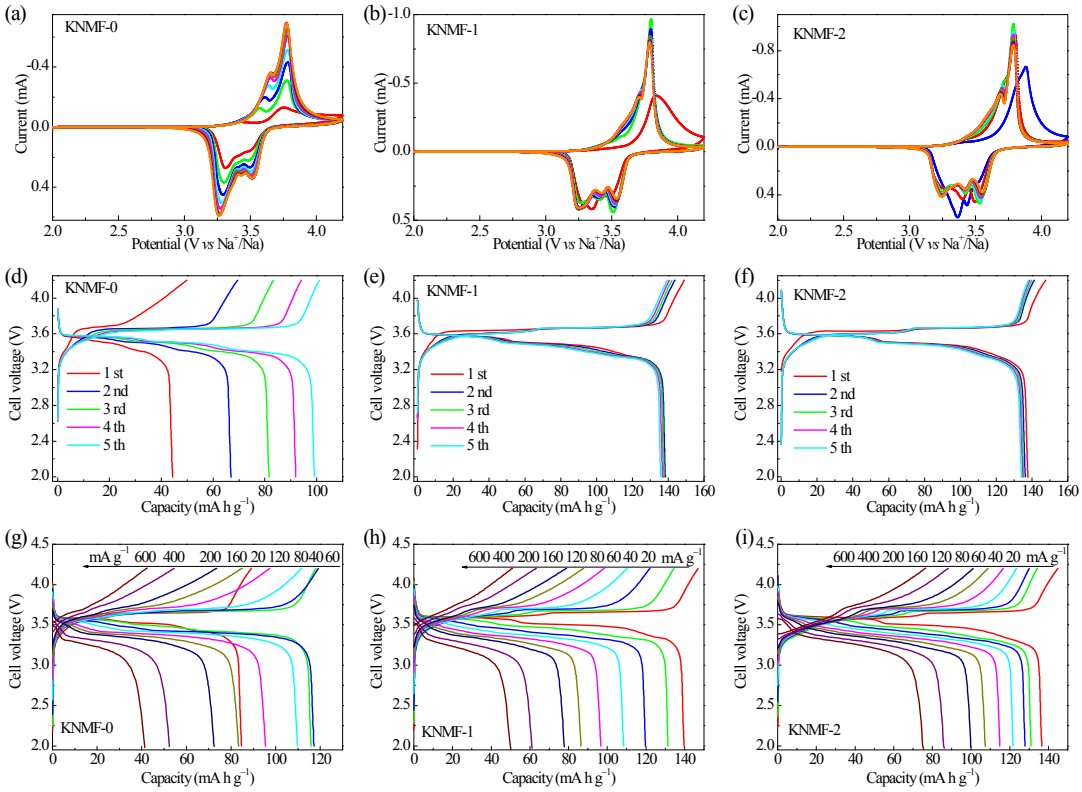

Figure S3. (a, b, c) CV curves at a scan rate of 0.2 mV s^{-1}, (d, e, f) charge-discharge curves at a current density of 40 mA g^{-1}, and (g, h, i) charge and discharge curves at various current densities for KNMF-0, KNMF-1, and KNMF-2, respectively.

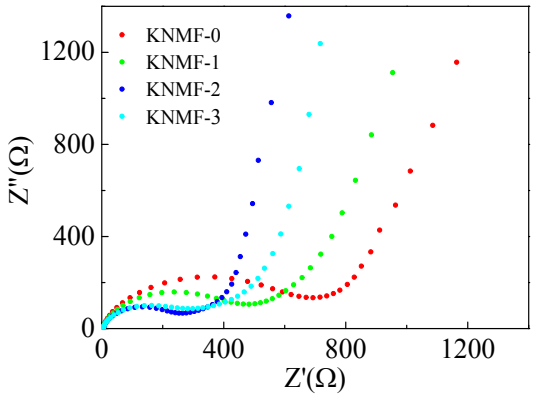

Figure S4. Nyquist plots of the electrodes after the first charge/discharge cycle.

The electrochemical impedance spectra (EIS) was conducted to further understand the ion diffusion kinetic and charge transfer in various electrodes, as shown in Figure S4. Two overlapped semicircles at high and middle frequency, and a sloped line at low frequency can be found in the Nyquist plots. The semicircle for KNMF-3 electrode in high-medium frequency is much smaller than other electrodes, thus indicating that the KNMF-3 possesses a low contact impedance between the electrode interface and electrolyte, and also a low charge-transfer impedance. In addition, the low-frequency slope line is considered as the Warburg diffusion process of Na^+ or/and K^+ ions in the electrode. It can be seen that the slope angle for KNMF-3 is steeper than that in other electrodes, manifesting excellent Na^+ ions diffusivity. These results demonstrate that KNMF-3 enable a rapid electrochemical kinetics for electronic and ionic transport.