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Supporting Information

$Na_4Fe(CN)_6$/NaCl solid solution cathode material with enhanced electrochemical performances for sodium ion batteries

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S1 Synthesis of $Na_4Fe(CN)_6$/NaCl solid solution

The $Na_4Fe(CN)_6$/NaCl solid solution was synthesized through ethanol extraction method at room temperature. Since $Na_4Fe(CN)_6$ and NaCl were soluble in aqueous solution but insoluble in ethanol, when 10mL aqueous solution containing 1mol/L $Na_4Fe(CN)_6$ (Aldrich) and 1mol NaCl (Aldrich) was slowly dropped into 400mL stirred ethanol by peristaltic pump, the yellowish precipitate was formed in ethanol. After centrifugation and dried under vacuum at 100℃ for 8h, the final obtained $Na_4Fe(CN)_6$/NaCl solid solution product was preserved in glove box. The NaCl sample and the $Na_4Fe(CN)_6$ sample were also reprocessed by ethanol extraction method before applied to sodium ion battery.

S2 Characterization

The structural characteristic of the as-prepared material was determined by X-ray diffraction (XRD, D/max-2200/PC, Rigaku Co., Ltd.) with filtered Cu Kα radiation. The transmission electron microscopy (TEM, JEM-2010, JEOL Ltd.) was adopted to analyze the morphology and the selected-area electron diffraction (SAED) of the as-prepared material. X-ray photoelectron spectroscopy (XPS, KRATOS AXIS Ultra-DLD, Kratos Analytical) was obtained with a monochromatic Al Kαradiation source. The binding energies of all elements were calibrated to that of carbon (284.6 eV) .

The $Na_4Fe(CN)_6$/NaCl cathodes for electrochemical testing were prepared by slurrying 80wt.% $Na_4Fe(CN)_6$/NaCl powder, 10wt.% super P, and 10wt.% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP), and then casting the mixture onto an aluminum foil. After vacuum drying at 80^{o}C for about 4h, the electrode disks (14 mm) were punched and weighed. The cathode active material loading was 3-4 mg cm^{-2}. After further drying under vacuum at 120 °C for 12 h, the $Na_4Fe(CN)_6/NaCl$ cathodes were incorporated into coin cells (R2016) with sodium metal foil and 1.0M $NaClO_4$/EC+DMC (1:1, v/v) electrolyte. The cells were assembled in an argon filled glove box. The Na|NaCl cell and The Na|$Na_4Fe(CN)_6$ cell were also assembled in the same way. The galvanostatic charge-discharge test was conducted using a battery test system (Land CT2001A model, Wuhan Jinnuo Electronics Co., Ltd.). All cyclic voltammetric experiments were performed on CHI electrochemical workstation (CHI 670D, CHI Instrument Co.). Electrochemical impedance spectroscopy (EIS) was performed using a solartron equipment (SI 1287+ SI 1260, Solartron Analytical Ltd.) within a frequency range of 0.1 Hz-100K Hz at open circuit potential (2.3V). The amplitude of the alternating voltage was 5mV. All electrochemical experiments were carried out at 25℃.

S3 The selected-area electron diffraction (SAED) analysis of NaCl and $Na_4Fe(CN)_6$

Figure S1 shows the selected-area electron diffraction (SAED) patterns of NaCl (a) and $Na_4Fe(CN)_6$ (b). It is clear that both NaCl and $Na_4Fe(CN)_6$ samples exhibit only one type of lattice distance, while for the $Na_4Fe(CN)_6/NaCl$ solid solution, two types of lattice distances are observed. These results indicate that the structure of $Na_4Fe(CN)_6/NaCl$ solid solution is different to NaCl and $Na_4Fe(CN)_6$, which mainly due to the formation of the interconnected cages in its framework.

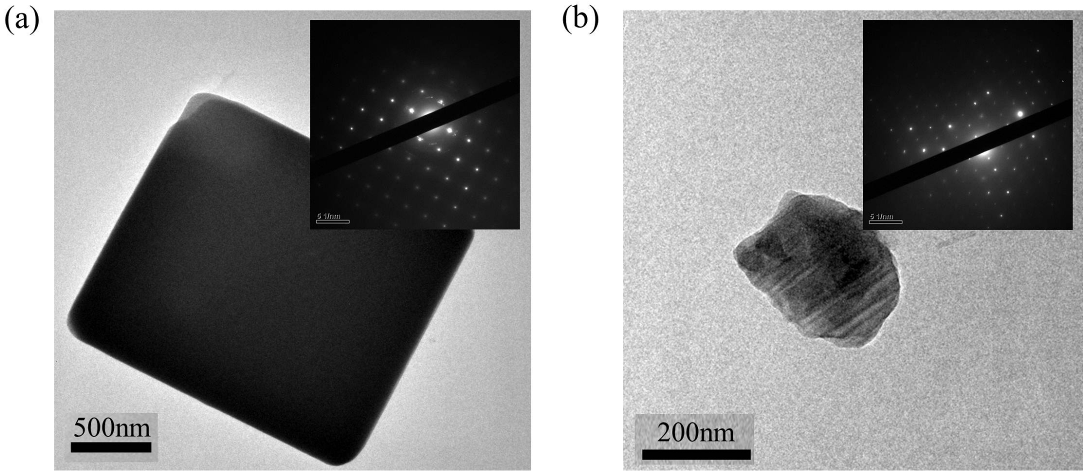

Figure S1. The selected-area electron diffraction (SAED) patterns of (a) NaCl and (b) $Na_4Fe(CN)_6$.

S4 The electrochemical impedance spectroscopy

Figure S2 shows the typical Nyquist plots of the Na|$Na_4Fe(CN)_6$/NaCl cell, Na|NaCl cell and Na| $Na_4Fe(CN)_6$ cell after three charge-discharge cycles. It is obvious that the charge-transfer resistance of the Na|$Na_4Fe(CN)_6$/NaCl cell is much lower than those of Na|NaCl cell and Na| $Na_4Fe(CN)_6$ cell. These results indicate an easier Na^+ intercalation/deintercalation process on the $Na_4Fe(CN)_6$/NaCl electrode compared with the pure $Na_4Fe(CN)_6$ and NaCl electrodes.

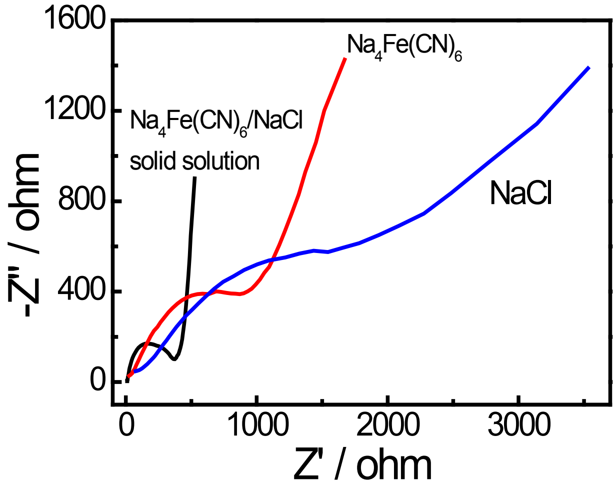

Figure S2. The Nyquist plots of the solid state solution-Na cell, NaCl-Na cell and $Na_4Fe(CN)_6$-Na cell charge/ discharged after 3 cycles.