Supplementary Material (ESI) for Energy & Environmental Science

MS Title: $Fe(CN)_6^{-4}$-doped Polypyrrole: A High Capacity and High Rate Cathode Material for Sodium-ion Batteries

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Electronic supplementary information:

1. Experimental details:

Materials preparation. The PPy/FC powders were synthesized by chemical oxidative polymerization of pyrrole monomers in $Na_4Fe(CN)_6$–saturated aqueous solution as described in detail in the previous work [15]. The polymerization was carried out at 0-5 °C for 30 min. The polymeric precipitate was washed several times with deionized water and ethanol alternately and finally dried at 60 °C in vacuum box for 24h.

Structural Characterization. The morphologies of the PPy/FC particles were observed by Scanning Electron Microscope (Sirion 2000, FEI). Powder X-ray diffraction (XRD) was used to characterize the crystalline structures of the PPy/FC samples using a Shimadzu XRD-6000 diffractometer equipped with Cu Kα radiation. The XRD spectra were collected in a range of 2θ values from 10° to 80° at a scanning rate of 2° min^{-1} and a step size of 0.02°**.** Elemental analysis of the polymer products were carried out on VarioEL Ⅲ(German). To determine the amount of $Fe(CN)_6^{4-}$ incorporated into the polypyrrole，the polymer was destroyed by heating in air at 550°C for 10 h, the iron oxides obtained was then dissolved in HCl for the atomic emission analysis using IRIS Intrepid □ XSP spectrometer. FT-IR spectra were recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets. XPS tests was carried out on a KRATOS XSAM800 Instrument with the magnesium source Mg Kα 1253.6 eV operated at 12.5 kV and 16mA. To characterize the structural changes of the doped polymer during cycling, the electrode samples at different depths of charge and discharge (1.5-3.8V) were taken out from the disassembled cells and rinsed with pure diethyl carbonate solvent in an Ar-filled glove box and then immediately sent for ex situ FT-IR analysis and ex situ XPS analysis.

To quantify the amount of the sodium ions inserted and extrated during charge and discharge, the coin cells were divided to three sets (one set was stayed without cycling, one set was cycled for 5 times and left at fully charged state (3.8V), and another set was cycled for 5 times and left at discharged states (1.5V))and then disassembled in a glove box. The electrode samples were taken from the cells and rinsed with pure diethyl carbonate solvent for 3 times. Then the electrode samples was burnt in air at 550°C for 10 h to give the iron and sodium oxides. The Fe and Na residues were dissolved in HCl for the atomic emission analysis using IRIS Intrepid □ XSP spectrometer.

Electrochemical Measurements. Electrochemical performance characterization of the doped and undoped polymers was carried out using 2016-type coin cells. The working electrodes were made by pressing a 0.8 cm^2 thin film, (3.8g/cm^2) (containing 80 wt % the as-prepared polymer materials, 10 wt % acetylene black, and 10wt % polytetrafluoroethylene) onto an Al mesh. The counter electrode was a disk of sodium metal foil and the electrolyte with water content lower than 1ppm was a 1 mol L^{-1} $NaPF_6$ (Alfa Aesar) dissolved in a mixture of ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (EC:DEC = 1:1 by vol., Shinestar battery materials co. Ltd, China). The Na disks were made by rolling sodium lumps into thin pieces and then cut into circulated plates. The test cells were assembled in an argon-filled glove box with water/oxygen content lower than 1ppm and the galvanostatic charging-discharging experiments were conducted by on LAND cycler (Wuhan Kingnuo Electronic Co., China) at various rates from1.5V to 3.8V at room temperature. The cyclic voltammetry (CV) was carried out with coin cell at a scan rate of 0.1mV s^{-1} using a CHI 660a electrochemical workstation (ChenHua Instruments Co., China) in the voltage range 2.0 – 3.9V

2. XRD patterns of the as-prepared PPy/FC

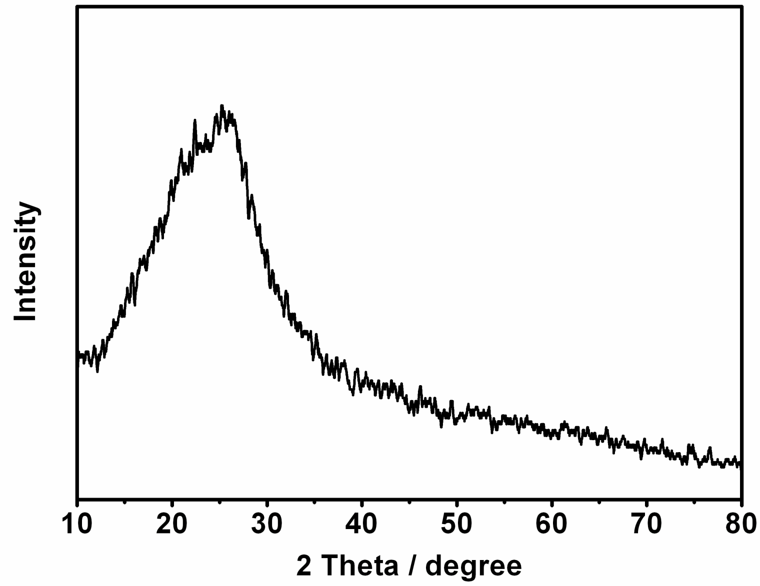

Figure S1. XRD patterns of the as-prepared PPy/FC

2. A comparison of FTIR spectra of $Na_4Fe(CN)_6$ salt and the $Fe(CN)_6{}^{4-}$-doped PPy

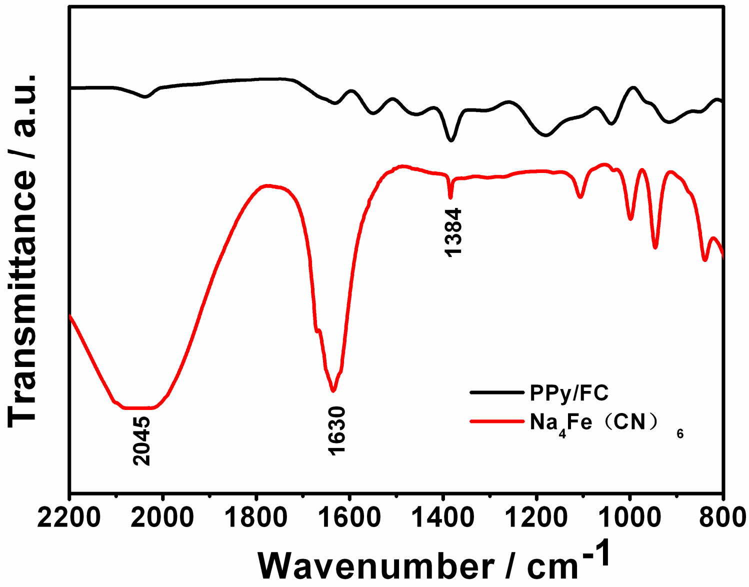

Figure S2. A comparison of FTIR spectra of $Na_4Fe(CN)_6$ salt and the $Fe(CN)_6{}^{4-}$ doped PPy

3. X-ray photoelectron spectra of the Fe 2p3/2 electrons measured from the PPy/FC electrode at different depths of charge or discharge.

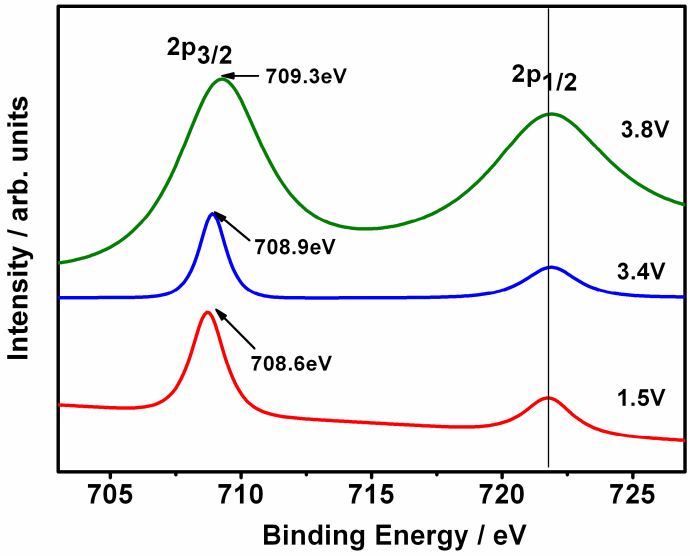

Figure S3. X-ray photoelectron spectra of the PPy/FC electrode at different discharged and charged states. a. discharged to +1.5V, b.charged to +3.4V and c. fully charged to

+3.8V

4. The experimental values of Na, Fe and their molar ratio of the doped PPy cycled at different states of charge and discharge.

Table 1 the average amounts of Na, Fe and their ratios of the doped PPy cycled at different states of charge and discharge, measured from ICP analysis

	Fe % wt.	Na % wt	Molar ratio of Na/Fe	Corresponding Numbers of Na^+ ions
Uncycled	2.672	1.19	1.0845	
Fully discharged to 1.5V	2.670	4.65	4.2408	3.84
Fully discharged to 3.8V	2.659	1.31	1.1994	3.67

* Theoretical numbers of the Na^+ ions according to Equation 1 is 4.

It is found from table 1 (ESI) that even without cycling, the electrode still contained considerable amount of Na and showed a molar ratio of Na/Fe of 1.0845, obviously due to incomplete removal of the Na content though the electrodes were rinsed for 3 times using pure diethyl carbonate solvent. Nevertheless, the electrode samples taken from a fully discharged state (1.5V) at 5th cycles of the cells showed a high Na/Fe ratio of 4.2408, corresponding to 3.84 Na inserted into the polymer. When recharged to 3.8 V, the electrode samples gave a Na/Fe molar ratio of 1.1994, demonstrating an extraction of the inserted Na ions from the polymer chains.