Electronic Supplementary Information (ESI)

A polyimide anode with high capacity and superior cyclability for aqueous Na-ion batteries

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1. Experimental details

Material Synthesis. PNFE polymer was prepared by a dehydration condensation reaction according to the method previously reported. A typical experimental procedure was to add an equimolar amount of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and ethylenediamine to N-methylpyrrolidone (NMP) solvent, reflux the reaction solution for 6 hours, then filter and wash the precipitate with ethanol for several times. After drying at 120°C in vacuum for 12 hours, the resulting precipitate was heated at 300 °C in nitrogen for 8 hours to give a brown powdered product. The total yield of this synthetic process was ~85%. All the chemicals including 1,4,5,8-naphthalenetetracarboxylicbisimide (NTCDA), ethylene diamine, and N-methylpyrrolidone (NMP) were purchased from Sinopharm Group Co., Ltd. and used without further purification.

Structural Characterization. The crystalline structure of the PNFE was characterized by powder X-ray diffractometry (XRD) 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 70°C at a scanning rate of 4 degree/min and a step size of 0.02°C. The morphologies of the as-synthesized sample were observed by scanning electron microscope (SEM, Sirion 2000, FEI). Fourier Transform Infrared Spectra (FTIR) were recorded on a NICOLET AVATAR 360 spectrometer with KBr pellets.

For IR characterizations, the electrode samples at different charge and discharge states taken out from the disassembled cells were firstly rinsed with pure diethyl carbonate solvent for several times and dried at 80°C in vacuum for 60 min. The dried samples were mixed with KBr (in a mass ratio of 1:200) and pressed into tablets for IR testing. For ICP analysis of Na content, the dried electrode samples were burnt in a tubular furnace at 550 °C for 10 h. The as-obtained sodium oxide residue was then dissolved in HCl for the atomic emission analysis using IRIS Intrepid XPS spectrometer.

Preparation procedure of the ex-situ analysis was carried out in an Ar-filled glove box with water/oxygen content lower than 1 ppm.

Electrochemical Measurements. Electrochemical performances of the as-prepared PNFE electrodes were carried out using three-electrode cells. The working electrodes were made by pressing a 0.8 cm^2 thin film (containing 60% PNFE powder, 30% conductive carbon and 10% polytetrafluroethylene binder) onto a Ti mesh. The counter electrode was a large piece of activated carbon. The electrolyte was a 1 M Na_2SO_4 solution (pH = 7) purged with N_2 for several hours. The galvanostatic charging-discharging experiments were conducted by a Land battery testing system (Wuhan Kingnuo Electronic Co., China)at various rates (1C = 100 mA g^{-1}) in the voltage range -1.0-0 V at room temperature. Cyclic voltammetry (CV) was carried out on a CHI 600c electrochemical workstation (Chen Hua Instruments Co.).

2. Ex situ ICP test of PNFE electrodes at different potential states

Table S1. ICP results for PNFE at different charge/discharge states

Potential states	Tested Na (wt%) in PNFE monomer	Theoretic Na (wt%) in PNFE monomer	Tested n(Na^+) in PNFE monomer
Discharged to -0.55 V	7.38	7.85	0.94
Discharged to – 1.0 V	16.24	15.77	2.06
Charged to 0.0 V	0.24	0	0

3. Charge-discharge curves and cycling performance of the all-organic Na-ion battery

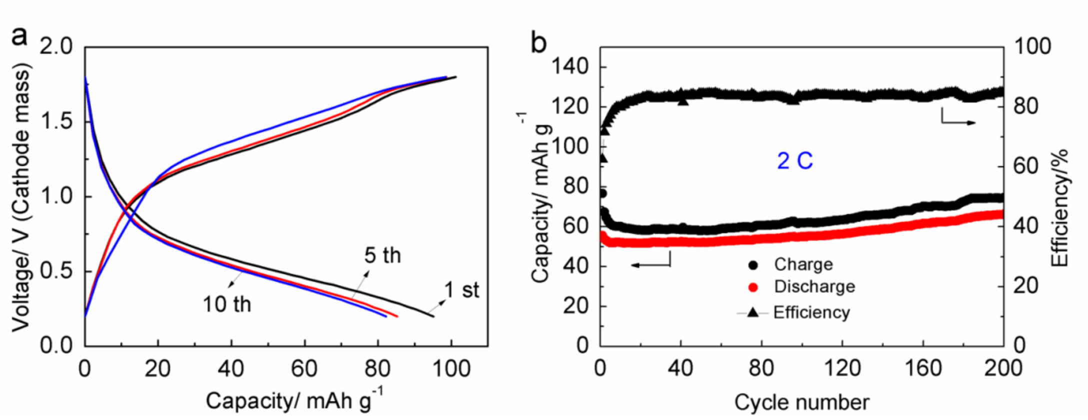

Figure S1 Electrochemical performances of the PNFE/PTVE full cell. a. Charge/discharge profiles in first ten cycles at a current density of 100 mA g^{-1}; b. Long-term cycling stability at a constant current of 2 C (1 C=100 mA g^{-1}).

It should be noticed that the coulombic efficiency of the full cell (Fig.1S b) is quite low, about 85% during cycles. This is because the PTVE cathode can only give a coulombic efficiency of ~90%, though the coulombic efficiency for PNFE was nearly 100%, which leads to a lower coulombic efficiency of the full cell. Therefore, either the cathode and anode plays equally important roles in determining the electrochemical performances of a full cell.