

Electronic Supplementary Information (ESI)

Self-doped polypyrrole with ionizable sodium sulfonate as a renewable cathode Material for sodium ion batteries

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1. Experimental Section

The PP-PS copolymer was synthesized by two-step reaction as shown in Scheme 1. Firstly, sodium 3-(Pyrrol-1-yl) propanesulfonate (1) was made by adding pyrrole (1.34 g, 20 mmol) and 1, 3-propane sultone (2.44 g, 20 mmol) separately in NaH (20 mmol, 60% suspension in paraffin oil) in dry dimethyl sulfoxide solution (10 mL) under constant stirring at 60 °C in a nitrogen atmosphere and then keep this reaction mixture for 2 hours at the same condition to ensure the displacement reaction. After then, adding acetone into the reaction mixture precipitated a solid product, which was filtered, washed with hot tetrahydrofuran to remove residual sultone, and dried in a vacuum oven at 60 °C for 24 h to give a white powder. Secondly, the as-prepared sodium 3-(pyrrol-1-yl) propanesulfonate (1 mmol) was used to copolymerize with pyrrole (1 mmol) in H₂O (8 mL) at room temperature under nitrogen atmosphere using FeCl₃ (1.3 g, 8 mmol) as an oxidant.

Chemical structure of the PP-PS polymer was characterized by FT-IR spectroscopy using a NICOLET AVATAR360 FT-IR spectrometer with KBr pellets. The particle morphology of the PP-PS powder was examined by scanning electron microscopy (SEM) on a Sirion2000 machine (Holland). CV response of the PP-PS polymer was measured with a powder microelectrode in a two-electrode cell using a larger Na sheet as both counter electrode and reference electrode. The preparation method for powder microelectrode has been described in detail in Ref.[1]. The CVs were

recorded using a CHI 660A electrochemical workstation (Shanghai, China). The charge–discharge measurements were carried out using 2016 type coin cells. The cells were assembled in an argon-filled glove box, using a Na metal disc as the negative electrode and a Whatman GF/D borosilicate glass fiber sheet saturated with 1M $\text{NaPF}_6 + \text{EC}$ /DEC (v/v = 1:1) as the electrolyte. The PP-PS electrode film was consisted of 60% PP-PS powder, 30% vapor grown carbon nanofiber (VGCF, Showa Denko Co.), 10% polytetrafluoroethylene (PTFE) (wt.%) and prepared by roll-pressing the mixture into a ca.~0.1mm thick electrode film and then pressing the film onto an Al collector. The PP-PS electrodes are 1 cm^2 with $\sim 2\text{ mg}$ electrode-active material. The charge–discharge experiments were executed using a programmable computer-controlled battery charger (LAND CT2001A, Wuhan, China) in the potential range of 2.0 - 4.0 V versus Na/Na^+ for the PP-PS electrode at constant currents of 40 mA g^{-1} . The Na contents in the PP-PS cathodes at different states of charge and discharge were determined by ICP analysis. The electrode samples for the ICP analysis were taken from the disassembled coin cells after full charge and discharge and then rinsed with pure diethyl carbonate solvent for several times. Then the electrode samples were burnt in air at $600\text{ }^\circ\text{C}$ for 8 h to give a residue of sodium oxides. The Na residues were dissolved in a 0.8 mol L^{-1} HCl (10 mL)solution directly for ICP analysis using IRIS Intrepid III XSP spectrometer.

2. Cycling performance of the PP-PS electrode

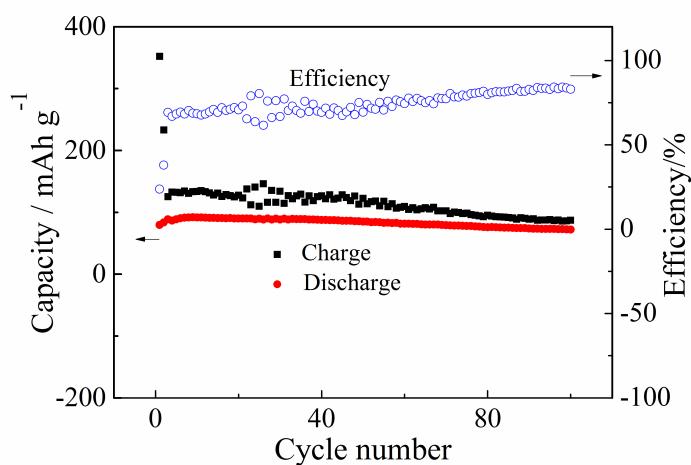


Fig. S1 Cycling performance of coin-type Na/PP-PS cells .

3. Charge-discharge capacities of the VGCF carbon in the Na⁺ electrolyte.

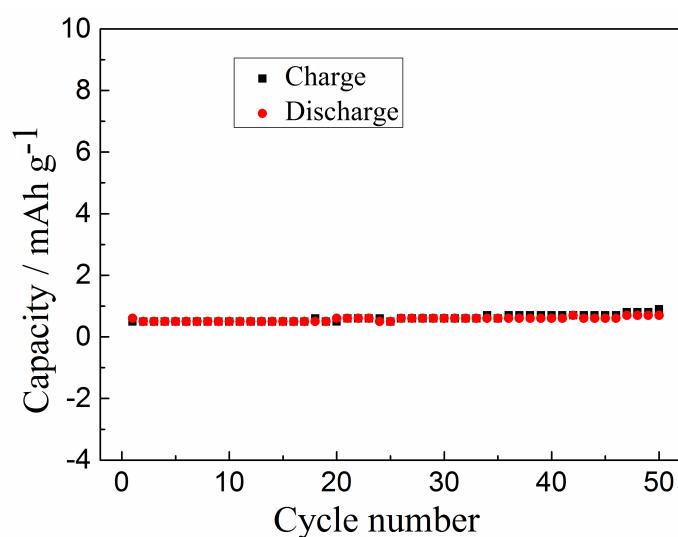


Fig. S2 The reversible capacities with cycle numbers of coin-type Na/VGCF cell using $1.0 \text{ mol L}^{-1} \text{ NaPF}_6 + \text{EC/DEC (v/v = 1:1)}$ electrolyte.

[1] C.S. Cha, C.M. Li, H.X. Yang, P.F. Liu, J. Electroanal. Chem. 368 (1994) 47.