

Supporting Information

Fabrication of conjugated polyimides with porous crosslinked networks and applications as Li-ion battery cathodes

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Experimental section

1. Materials and Preparation.

Phthalic acid dianhydride and naphthalene tetracarboxylic acid dianhydride are purchased from Aladdin Reagent Co., Ltd. Perylene tetracarboxylic dianhydride, methyl pyrobenzoate and imidazole were all purchased from Sigma Chemical Reagent Co., Ltd. Other reagents such as ethanol, dichloromethane, dimethylacetamide (DMAc) and dimethylformamide (DMF) were purchased from Adamas Reagent Company. All the chemicals were of analytical grade and used as received without further treatment.

A 500 mL round-bottomed flask equipped with magnetic stir bar was charged with 5 g of trimethyl-1,3,5-benzene-tricarboxylate (0.02 mol), 100 mL of DMF, and hydrazine hydrate (80%) (120mmol, 7.5g). The mixture was refluxed for 24 h at 120 °C. The white solid was precipitated and filtered. The obtained white sample was washed with DMF and methanol for several times followed by being dried under vacuum (60 °C). The yield of the title compound (1,3,5-benzene-tricarbohydrazide) was 4.5 g (90%). ¹HNMR(400MHz, DMSO, ppm): 9.86 (s, 3H), 8.35 (s, 3H), 4.58 (s, 6H)。

The obtained 1,3,5-benzene-tricarbohydrazide (20 mg, 0.08 mmol) was added into a three-necked flask containing 10 mL of DMF, then a mixture of pyromellitic dianhydride (26 mg, 0.12 mmol) and DMF (10 mL) was added into the flask dropwise. The mixture was stirred for 24 h at 150 °C to finish the condensation reaction and then was cooled to room temperature. The obtained polymer was washed sequentially with DMF and methanol for several times before being dried in vacuum oven at 120 °C for 24 hours to get the target sample named CPPI-1. The CPPI-2 sample was prepared with the similar method to that of CPPI-1 by using naphthalene tetracarboxylic acid dianhydride (32 mg, 0.12 mmol) to instead of pyromellitic acid dianhydride. 1,3,5-benzene-tricarbohydrazide (15 mg, 0.06 mmol, dissolved in DMAc) was added into the mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (35.3 mg, 0.09 mmol) and imidazole (5 g) under the atmosphere of nitrogen. The above mixture was heated at 150 °C for 24 h and then be cooled to 100 °C. A amount of ethanol (20

mL) was added to remove the crystallized imidazole and then stirred for 1 h. Subsequently, the precipitate in the mixed solution was collected by vacuum filtration, washed with DMF and methanol for several times, and dried at 120 °C overnight to yield CPPI-3.

2. Characterization

The scanning electron microscope (SEM) images were obtained on a FEI Sirion-200 (FEI Co., USA) field emission scanning electron microscope. The transmission electron microscopy (TEM) images were taken on JEOL-2100 (JEOL Ltd., Japan) electron microscope at an operating voltage of 200 kV. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2500 X-ray diffractometer with Cu K α radiation ($\lambda=1.54$ Å) at a generator voltage of 40 kV and a generator current of 50 mA with a scanning speed of 5° min⁻¹ from 5° to 60°. The nitrogen adsorption/desorption isotherms were measured *via* an Autosorb-iQA3200-4 sorption analyzer (Quantatech Co., USA). Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. Solid-state ¹³C NMR analysis was conducted on a Bruker AVANCE III 300 Spectrometer. Samples were spun at 5 kHz in a 4 mm zirconium rotor within a magic-angle spinning (MAS) probe. An acquisition time of 20 ms, a contact time of 1 ms, and a 6.5 μ s pre-scan delay were used. The recycle time was 2 s in order to obtain fully relaxed spectra. Fourier transform infrared spectroscopy (FT-IR) was performed using a Spectrum 100 (Perkin Elmer, Inc., USA) spectrometer. Thermogravimetric analysis (TGA) was performed on a Q5000IR (TA Instruments, USA) thermogravimetric analyzer.

3. Electrochemical measurements

The electrochemical characterizations of the composites were performed using 2016 coin-type cells assembled inside an argon-filled glove box with moisture and oxygen contents below 0.1 ppm. The working electrodes were prepared by pasting the slurry of the active material (35 wt.%), conductive carbon black (Super P, 50 wt.%) and polyvinylidene fluoride (PVDF, 15 wt.%) in *N*-methylethyl-2-pyrrolidone (NMP) onto an aluminum foil current collector and then vacuum drying the resulting aluminum foil at 80 °C for 12h. Lithium metal foil was used as the counter electrode.

The area of all the electrode is about 1 cm^2 . The composites loading in the electrode was about 1 mg cm^{-2} . The electrolyte was composed of 1 M LiPF_6 in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 w/w). The galvanostatic charge/discharge tests were performed using Land CA2001A testing system in the voltage range of 1.5 to 4.0 V (vs. Li/Li⁺). Cyclic voltammogram (CV) measurements were performed on CHI760D electrochemical workstation using a voltage range of 1.5 to 4.0 V (vs. Li / Li⁺) at a scan rate of 0.5 mV s^{-1} .

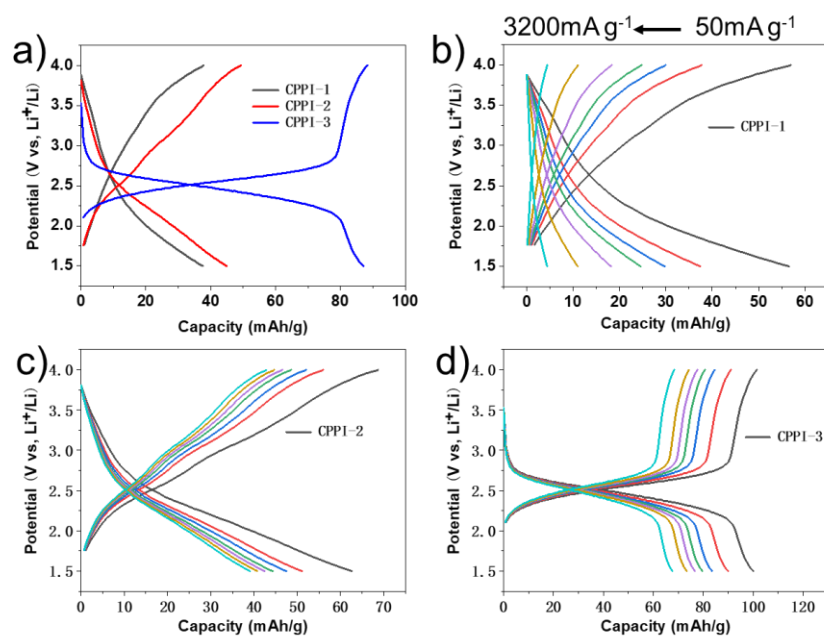


Fig.S1 (a) Galvanostatic discharge/charge curves of different samples at the rate of 100 mA g^{-1} ; Galvanostatic discharge/charge profiles of CPP1-1 (b), CPP1-2 (c) and CPP1-3 (d) at the rate of 50, 100, 200, 400, 800, 1600 and 3200 mA g^{-1} .