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Supporting Information

Ultrastable dihydrophenazine-based polymer from industrial waste as sustainable lithium-ion battery cathode material

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Reagents

Phenazine was obtained from Sennics CO., LTD. Shandong. Dry tetrahydrofuran (THF, 99.5%), acetonitrile, sodium carbonate were purchased from Greagent; Sodium dithionite was purchased from Energy Chemical; Methacryloylchloride, methyltributylammonium chloride (MTBAC), 4-dimethylaminopyridine (DMAP), 2-bromoethanol, trimethylamine (99.5%), dry dichloromethane (DCM, 99.9%), N-methyl-2-pyrrolidinone (NMP, 99.5%), azobisisobutyronitrile (AIBN, 98%) were purchased from Adamas. And AIBN was crystallized from ethanol and dried under vacuum prior to use and kept in the refrigerator.

Materials characterizations

Fourier transform infrared (FTIR) spectra were obtained from PerkinElmer Spectrum Two FT-IR with a range from 400 to 4000 cm^{-1}. Thermogravimetric analysis (TGA) was measured on the NETZSCH STA 409 PC/PG apparatus in a wide temperature range of 25-800 °C with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Scanning electron microscopes (SEM) was detected on JEOL JSM-7810F. X-ray diffraction (XRD) patterns were gained on an X'pert PRO instrument. Proton nuclear magnetic resonance (^1H NMR) was acquired on a Bruker AVANCE III 400M.

Materials preparation

Synthesis of 5,10-bis-2-(hydroxyethyl)-phenazine (**BHEP**). [1] Phenazine (0.901 g, 5.0 mmol), sodium dithionite (1.306 g, 7.5 mmol), sodium carbonate (1.061 g, 10 mmol), MTBAC (0.316 g, 1.3 mmol) were added in a 100 mL tube-type schlenk flask, respectively. Then, adding H_2O (1 mL), acetonitrile (10 mL) and 2-bromoethanol (1.5 mL, 20 mmol) into the flask under N_2 atmosphere and stirred for 48 h at 100 °C. To the reaction mixture, 50 mL of water was added via addition funnel and then cooled to room temperature. The crude product was obtained by suction filtration as the filter cake and washed with water. The product was then recrystallized from methanol to give the green, needle-shaped solid **BHEP** (0.681 g, 2.5 mmol) in 50% yield. ^1H NMR (400 MHz, DMSO-d_6): δ 4.92 (s, 2H), 3.57 (q, 8H).

Synthesis of 5, 10-bis-(ethyl methacrylate)-phenazine (**BEMP**). **BHEP** (300 mg, 1.11 mmol), DMAP (6.8 mg, 0.056 mmol), degassed trimethylamine (247 mg, 2.44 mmol) and DCM (4 mL) were added in a 50 mL tube-type schlenk flask, respectively. Then MTBAC (232 mg, 2.22 mmol) was added at 0 °C under N_2 atmosphere and stirred for 12 h. The resulting mixture was extracted with DCM and the organic phase was then dried with anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The crude product was further purified by using column chromatography to obtain the yellow powder **BEMP** (180.7 mg, 0.44 mmol) in 40% yield. ^1H NMR (400 MHz, DMSO-

d_6): δ 5.99 (s, 2H), 5.67 (s, 2H), 4.28 (s, 4H), 3.33 (t, 4H), 1.84 (s, 6H).

Synthesis of poly(5, 10-bis-(ethyl methacrylate)-phenazine) (**PBEMP**). [2] The monomer **BEMP** (100 mg, 0.25 mmol), AIBN (4.04 mg, 0.025 mmol) were added in degassed THF (1 mL) in a 10 mL tube-type schlenk flask under N_2 atomosphere. The solution was stirred at 60 °C for 24 h. After cooling down to room temperature, the mixture was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$, and the precipitate was washed with methanol and acetone, successively, and separated by centrifugation to get yellow solid **PBEMP** (89.1 mg, 0.22 mmol) in 89% yield.

Electrochemical measurements

Electrochemical measurements were performed using Standard CR-2016 coin-type half cells which consist of working electrode, Celgard 2400 membrane, nickel foam and stainless steel positive and negative shells. Lithium foil was used as the anode, **PBEMP**-based composite electrodes as the cathode, and 1 M $LiPF_6$ dissolved in ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (1:1:1 by volume) as the electrolyte. The composite electrodes was obtained by mixing active materials (**PBEMP**), conductive additives (multi-walled carbon nanotubes, MWCNTs) and binder (polyvinylidene fluoride, PVDF) based on their mass ratio of 5:4:1 and ball milled into a slurry at room temperature for 2 h. Then the slurry was coated on the carbon-coated aluminium foil followed by drying at 80 °C for 24 h in vacuum. The dried materials were cut into discs with 14 mm in diameter. The cells were assembled in the glove box ($H_2O<0.01$ ppm, $O_2<0.01$ ppm), and they have an equilibration time of 24 h before testing. The galvanostatic charge/discharge tests were performed in a voltage range of 2.0-4.5 V vs. Li/Li^+ on a NEWARE CT-4008 cell test instrument (Shenzhen, China). Cyclic voltammetry (CV) tests were recorded on the electrochemical workstation system (PGSTAT302N AutoLab, Metrohm, Switzerland). All the electrochemical tests were performed at room temperature.

Supporting Figures

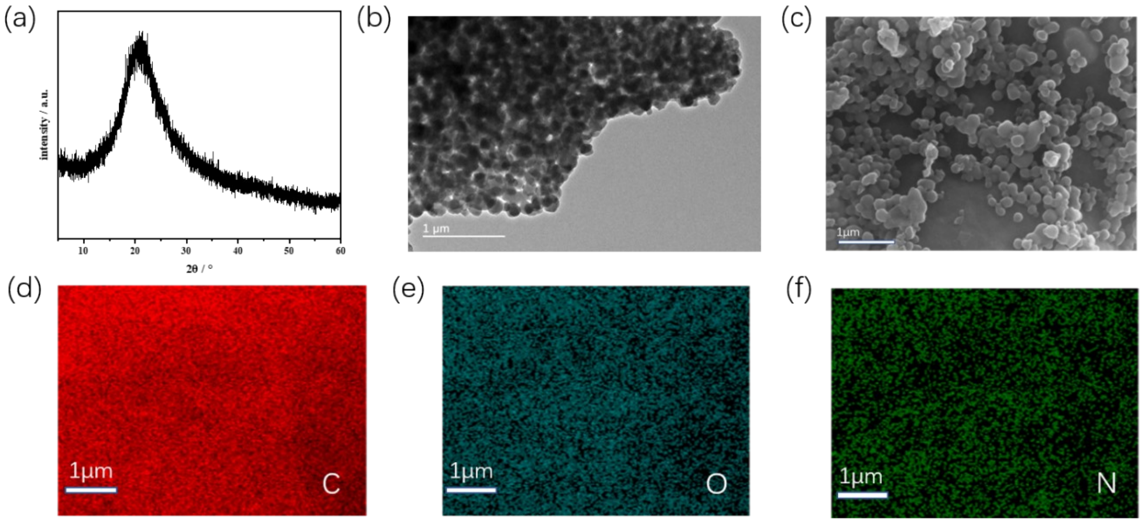

Fig. S1 (a) XRD pattern of **PBEMP**; (b) TEM images of **PBEMP**; (c-f) The C, O, N element mappings of **PBEMP**.

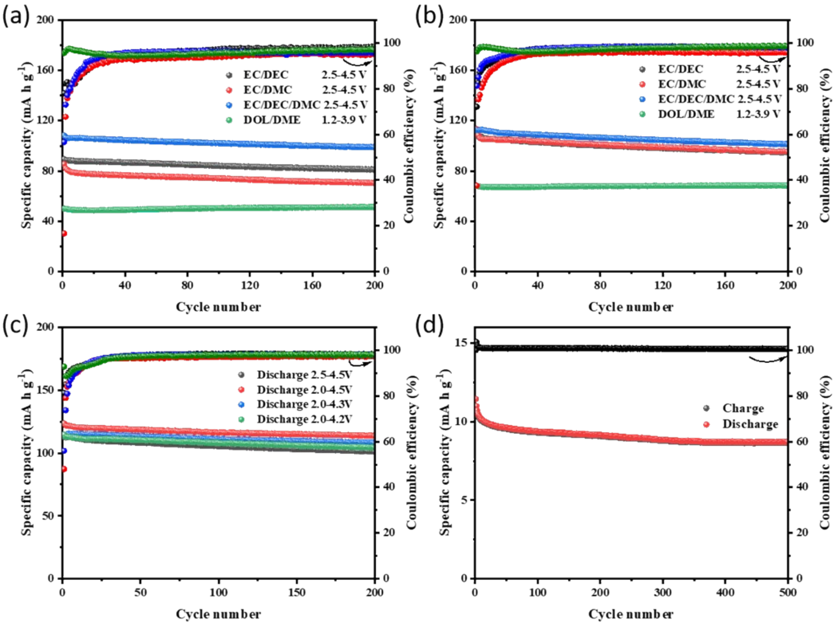

Fig. S2 The electrochemical performance of **PBEMP** at 0.2 A g^{-1} in four kinds of electrolytes using two different conductive additives (a) Acetylene black (AB); (b) Multi-walled carbon nanotubes (MWCNTs); (c) The specific capacity of **PBEMP** in EC/DEC/DMC at various voltage range at 0.2 A g^{-1}; (d) Capacity contribution of MWCNTs at 2.0-4.5 V.

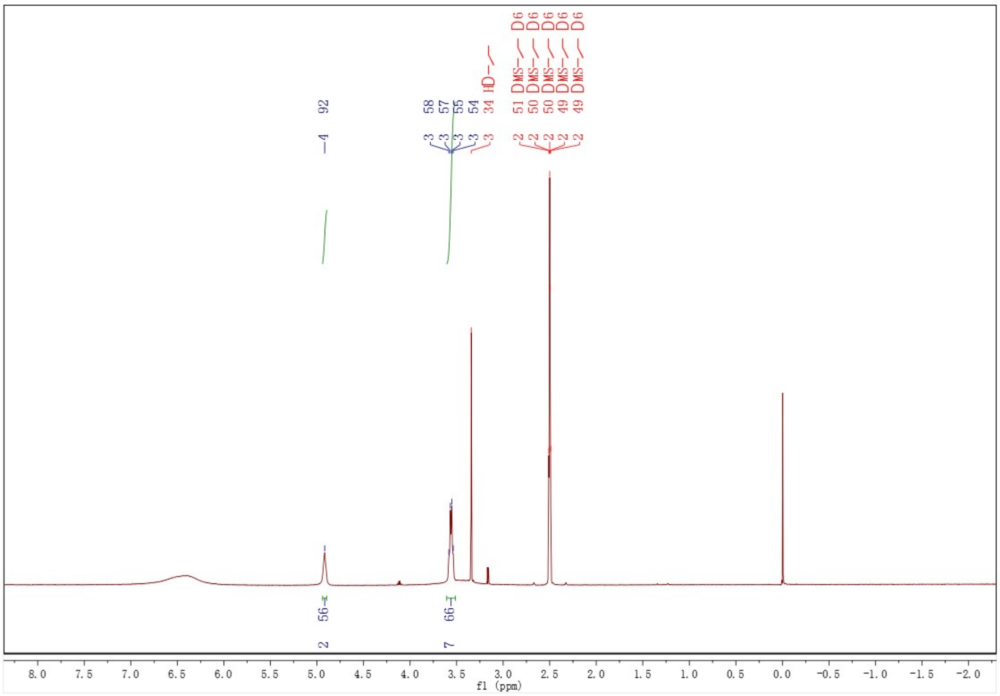

Fig. S3 400 MHz ^{1}H NMR spectrum of **BHEP** in DMSO-d$_6$.

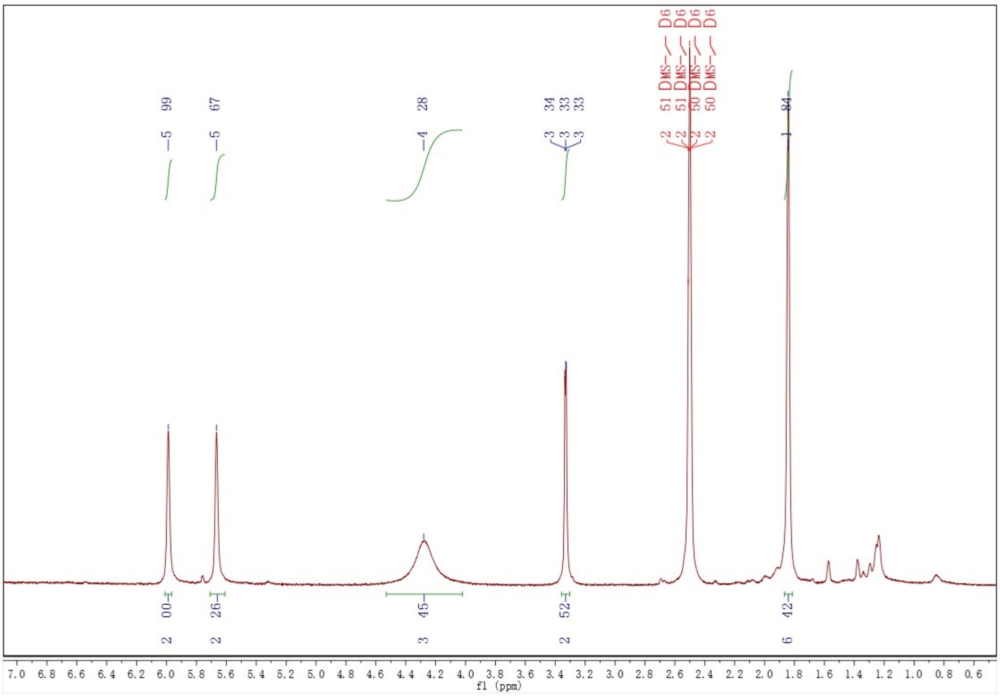

Fig. S4 400 MHz ^{1}H NMR spectrum of **BEMP** in DMSO-d$_6$.

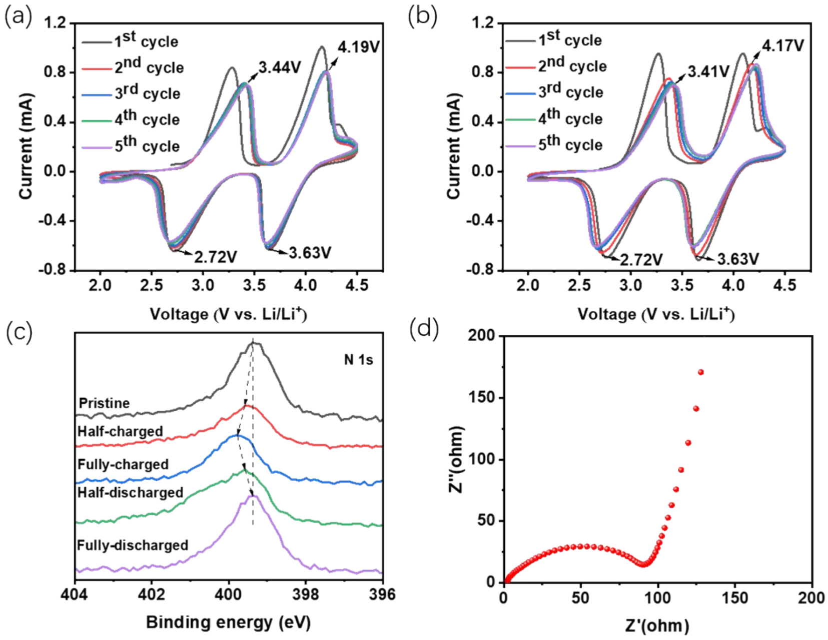

Fig. S5 Cyclic voltammograms of **PBEMP** in 1 M $LiPF_6$ in (a) EC/DEC and (b) EC/DMC electrolytes at a scan rate of 2 mV s^{-1}; (c) XPS characterization of N 1s region; (d) Electrochemical impedance spectra (EIS) for **PBEMP.**

1. *J. R. Lomprey, T. F. Guarr, K. L. Baumann and P. Giri*. US06445486 B1, 2002.
2. W. Guo, Y.-X. Yin, S. Xin, Y.-G. Guo and L.-J. Wan, *Energy Environ. Sci.*, 2012, **5**, 5221-5225.