Supporting Information

Phenazine-based Spiroborate Complex with Enhanced Electrochemical Stability for Lithium Storage

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Reagents

O-Phenylene diamine (99%), 2,5-dihydroxy-p-benzoquinone (98%), lithium hydroxide (99%), orthoboric acid (99%), phosphorus (V) oxide (P_2O_5, 98%), ethanol (EtOH, 99.7%), methanol (MeOH, 99.5%), hexane (97%), diethyl ether (99.5%), ethyl acetate (99.5%), tetrahydrofuran (THF, 99%) was purified by distillation prior to use.

Materials characterizations

The prepared compounds were confirmed by nuclear magnetic resonance (NMR) using a 400 MHz Brucker. The Fourier Transform infrared spectroscopy (FT-IR) spectra of **DHP** and **LDPB** were recorded on PerkinElmer Spectrum Two, and the wavenumber from 400 cm^{-1} to 4000 cm^{-1}. The TGA profiles of the **DHP** and **LDPB** was measured carried out METTLER TGA2 model with a temperature ramp of 10 °C min^{-1} from 30 °C to 800 °C under a N_2 atmosphere. The Powder X-ray diffraction of **DHP** and **LDPB** were conducted on Smartlab (3KW). Scanning electron microscopes (SEM) is measured on Quanta FEG 250. The ex-situ XPS spectra of **LDPB** was tested on Thermo Scientific K-Alpha. The discharge and recharge of **LDPB** were measured by ex-situ FT-IR and XPS after the first discharge and a complete cycle, respectively. Before the ex-situ FT-IR and XPS test, the batteries were disassembled in an argon-filled glovebox, the collected samples were gently washed with DOL (about 5 mL) and dried at 60 °C for 12 h in a vacuum drying oven.

Materials preparation

Synthesis of 2,3-dihydroxyphenazine (**DHP**).[1] Add o-phenylene diamine (3.57 mmol; 1 eq) and 2,5-dihydroxy-p-benzoquinone (7.14 mmol; 2 eq) to 386 mL ethanol solution. After the mixture was heated to reflux at 85 °C for 1.5 h, the ethanol was distilled off under reduced pressure. The residue was absorbed with a small amount of THF, and filtered with a sand core funnel. The filter cake was dried overnight in a vacuum drying oven (50 °C) to obtain a crude product. The crude product was recrystallized with ethyl acetate to obtain a pure product. Yield: 70%. FT-IR vmax / cm^{-1} 2703(O-H), 1508~1603(C=C), 1442(C-N), 1143~1307(C-O), 746~906(C-H), 586(benzene ring). ^1H NMR (400 MHz, DMSO-d6) δ 7.19 (s, 2H); 7.71 (d, 2H); 8.02 (d, 2H).

Synthesis of lithium bis(2,3-dihydroxyphenazine) borate (**LDPB**).[2] **DHP** (1.41 mmol; 2 eq) and lithium hydroxide (0.71 mmol; 1 eq) were dissolved in 1.2 mL methanol solution to make the system uniform. Add boric acid (0.71 mmol; 1 eq), heat and stir at 60 °C. Methanol was distilled off under reduced pressure, the crude residue was absorbed with 1~2 mL THF, the desired product was precipitated with n-hexane (~3 mL), and the solvent was removed by suction filtration. The filter cake was washed successively with n-hexane and anhydrous ether. The filter cake was vacuum dried (30 °C) overnight on P_2O_5 to obtain a crude product. The crude product was recrystallized with anhydrous ether for a long time and then filtered again with suction. The filter cake was vacuum dried with phosphorus pentoxide to obtain a pure product. Yield: 65%. FT-IR vmax / cm^{-1} 1508~1603 (C=C), 1442 (C-N), 1213~1312 (C-O), 1044 (B-O), 746~906 (C-H), 586 (benzene ring).

Electrochemical measurements

DHP and **LDPB** as the cathode active material are assembled from 2016 coin cell in a glove box filled with argon. Contains active materials (30 wt %), CMK-3 (60 wt %), 10 wt % PVDF binder in N-methyl-2-pyrrolidone (NMP). After ball milling the mixture for 2 hours, use a 200 µm thickness applicator to coat it on a 16 µm thickness single-gloss aluminum foil, and dry it in a vacuum drying oven at 80 °C for 12 hours. The dried pole piece was cut into circular slices with a diameter of 14 mm with a manual punching machine, and the active material loading was 0.4 mg cm^{-2}. The battery is assembled with a 14 mm diameter lithium sheet as the anode, polypropylene film (Celgard 2400) as the separator, 1 M LiTFSI DOL/DME (1:1 v/v) as electrolyte. Electrochemical cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were both instructed on electrochemical workstation (CHI660E) using the coin cells. The charge/discharge cycles were carried out on a Neware Battery Test System. All the electrochemical tests were performed at room temperature.

Supporting Figures

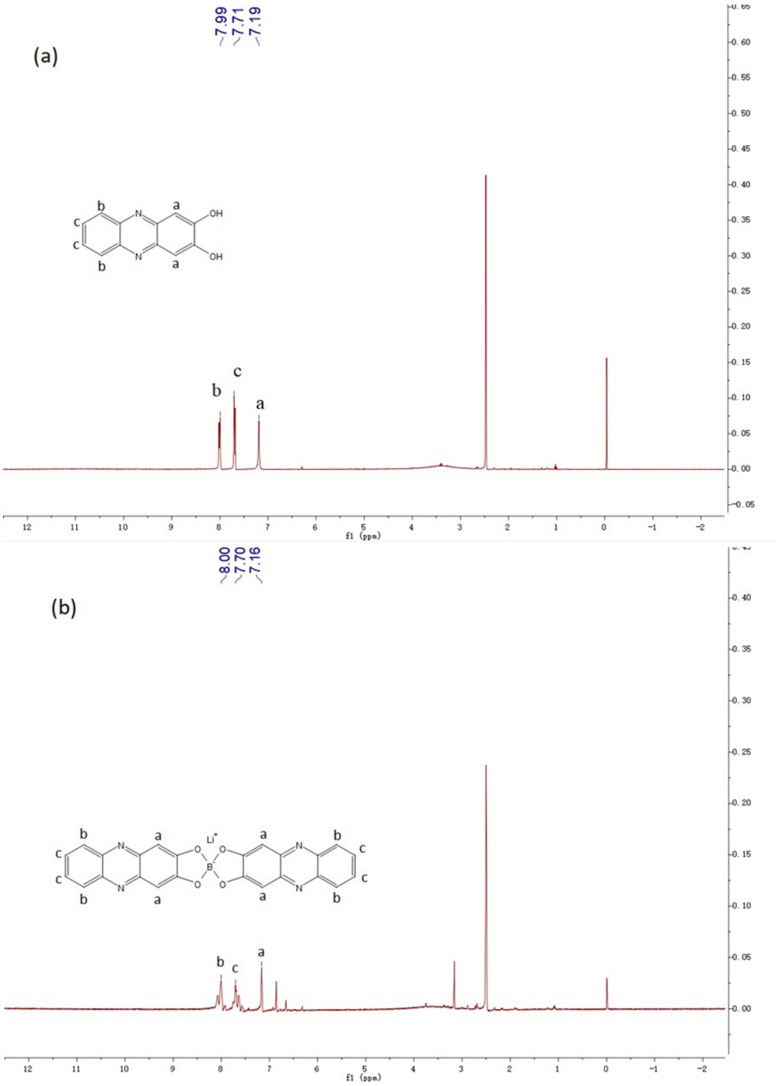

Fig. S1 (a) **DHP** ^{1}H NMR; (b) **LDPB** ^{1}H NMR.

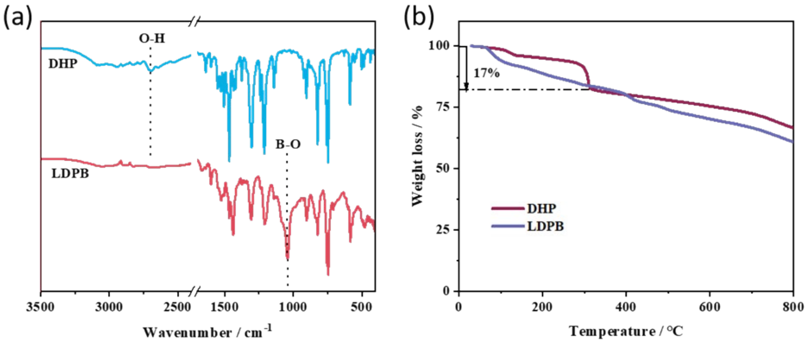

Fig. S2 (a) Ex-situ FT-IR diagram of **LDP** and **LDPB**; (b) Thermal gravimetric analysis (TGA) diagram of **DHP** and **LDPB**.

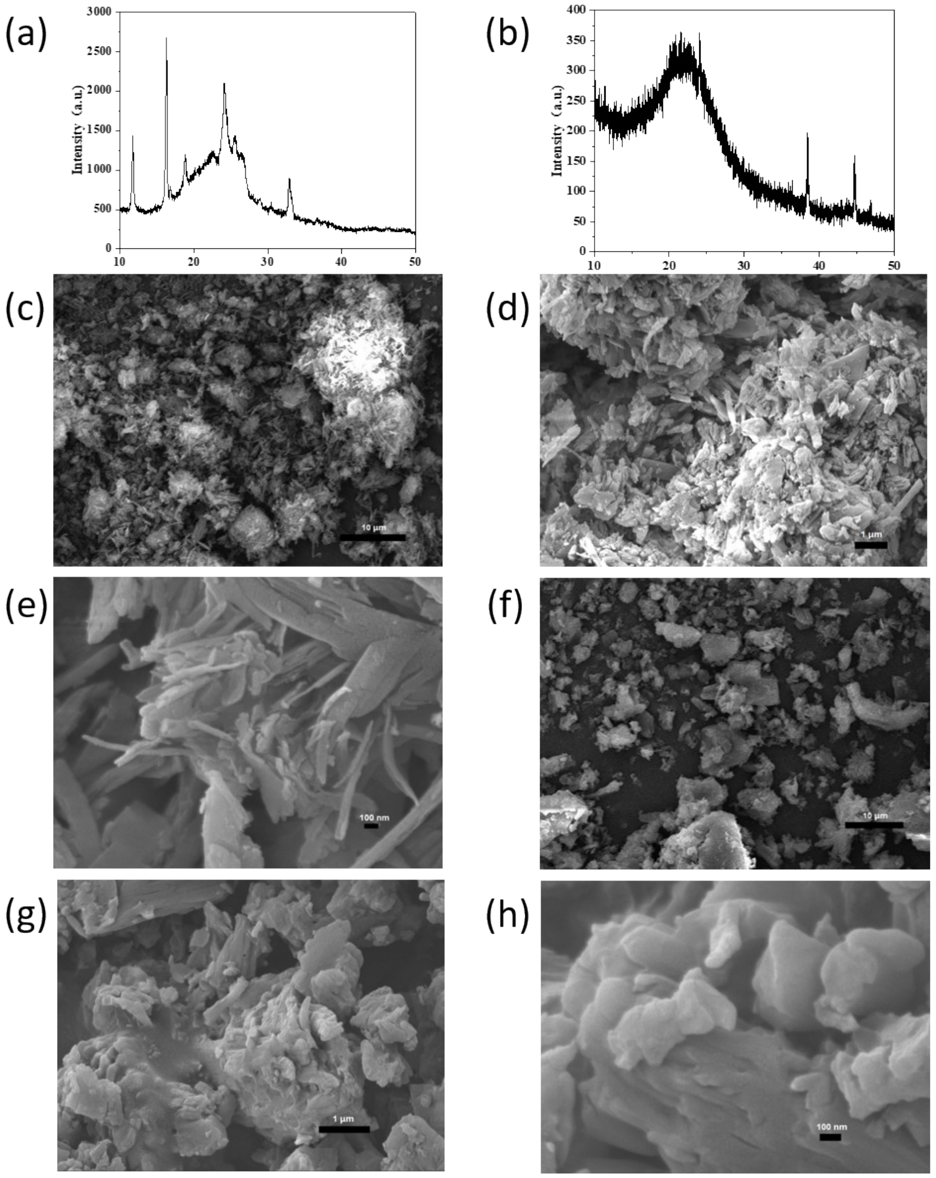

Fig. S3 (a) and (b) are the PXRD patterns of **DHP** and **LDPB**, respectively; (c), (d) and (e) are the SEM patterns of **DHP**; (f), (g) and (h) are the SEM patterns of **LDPB**.

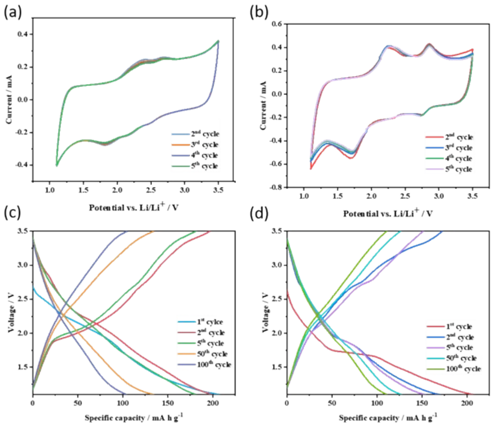

Fig. S4 (a) and (b) are CV graphs of **DHP** and **LDPB** at a sweeping speed of 2.0 mV s^{-1}; (c) and (d) are the galvanostatic charge/discharge profiles of **DHP** and **LDPB** electrodes under 1st, 2nd, 5th, 50th, 100th, respectively. Current: 200 mA g^{-1}. Electrolyte: 1 M $LiPF_6$ EC/DMC (1:1 v/v).

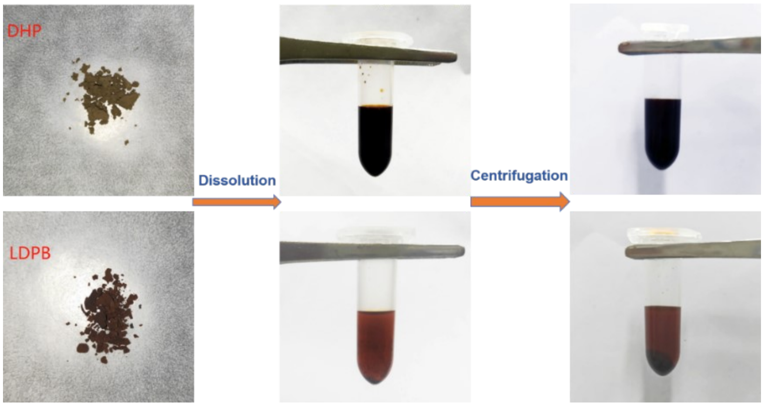

Fig. S5 The solubility of **DHP** and **LDPB** (5 g/L) in a solution of 1 M LiTFSI DOL/DME (1:1 v/v).

In this figure, we can see that when the same amount of **DHP** and **LDPB** (5 mg) are added to the same amount of electrolyte (1 mL) and centrifuged, **DHP** is dissolved in the electrolyte. In contrast, **LDPB** is only partially dissolved, and there is a precipitate at the bottom. This shows that the solubility of **LDPB** in the electrolyte is significantly lower than that of **DHP**, which explains the improvement of **LDPB**'s cycle performance.

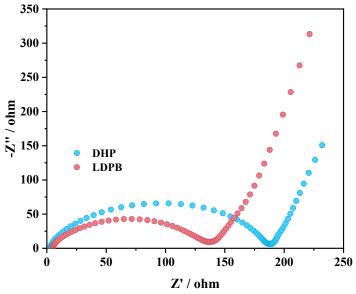

Fig. S6 Electrochemical impedance spectra (EIS) for **DHP** and **LDPB.**

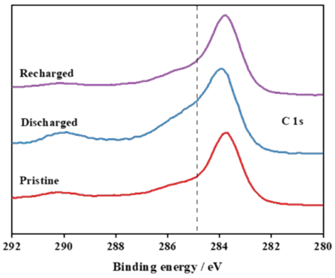

Fig. S7 XPS characterization of C 1s region.

1 Olivier S , Claire S . EP2078720 A1, 2009 .
2 M. J. Sevrin, L. Furst, J. D. Nguyen, J. L. Collins and C. R. J. Stephenson, *Tetrahedron*, 2018, **74**, 3246-3252.