

Sulfonated polybenzothiazole cathode materials for Na-ion batteries

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Experimental Section

Materials synthesis

Synthesis of sPBT-SE55 polymer

The synthesis of sPBT-SE polymer was shown in Fig. 1a. Polyphosphoric acid (PPA) (15 g, 80%) was firstly added into a three-month flask with the N₂ inlet/outlet and a mechanical stirrer. Subsequently, 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) (0.45 g) was added to the flask and stirred for 12 h at room temperature, then the reaction continued for the other 24 h at 70 °C to remove hydrogen chloride completely. Bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCS) (0.5152 g) and 4,4'-Dicarboxydiphenyl Ether (PE) (0.2133 g) were then added to the mixture and reacted at 100 °C for 8 h. After cooling completely, P₂O₅ (3.8 g) was added into the flask and reacted at 120 °C for 2 h followed by another portion of P₂O₅ (2.23 g) was added into the system, and stirring at 120 °C for another 10 h. Subsequently, temperature increasing step went on for 12 h at 120 °C, for 12 h at 150 °C, for 12 h at 170 °C, for 17 h at 190 °C, for 17 h at 210 °C. The mixture was put into water to get noodle-like product, which was washed, filtrated, immersed in 5 wt.% Na₂CO₃ for 24 h, washed with several times to pH=7, and dried in vacuo for 24 h at 100 °C to get sPBT-SE55

product.

Yield: 94%. ¹H NMR (in DMSO-*d*₆, ppm, TMS): 9.00–8.75, 8.55, 8.25, 8.20–8.00, 7.30. FT-IR (film, cm⁻¹): 1478, 1402, 1313, 682 (stretching of benzothiazole ring), 960 (breathing of benzothiazole ring), 737 (deformation of benzothiazole ring), 1081, 1030, 612 (sulfonate).

Synthesis of sPBT-S polymer

The synthesis of sPBT-S was similar to that of sPBT-SE55 polymer, except that only Bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCS) (0.9368 g) was added after hydrogen chloride removed completely.

Yield: 90%. ¹H NMR (in DMSO-*d*₆, ppm, TMS): 8.76–8.74, 8.50–8.48, 8.26, 8.22–8.20. FT-IR (film, cm⁻¹): 1080, 1024, 612 (sulfonate), 960 (breathing of benzothiazole ring), 738 (deformation of benzothiazole ring), 680 (stretching of benzothiazole ring).

Synthesis of sPBT-SP polymer

The synthesis of sPBT-SP was similar to that of sPBT-SE55 polymer, except that Bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCS) (0.5152 g) and Biphenyl-4,4'-dicarboxylic acid (BP) (0.2 g) were added after hydrogen chloride removed completely.

Yield: 92%. ¹H NMR (in DMSO-*d*₆, ppm, TMS): 8.94, 8.88–8.81, 8.34–8.23, 8.07, 7.73–7.63, 7.22, 6.66. FT-IR (film, cm⁻¹): 1480, 1398, 1311, 680 (stretching of benzothiazole ring), 960 (breathing of benzothiazole ring), 738 (deformation of benzothiazole ring), 1080, 1024, 612 (sulfonate).

Synthesis of PBT-E polymer

The synthesis of PBT-E was similar to that of sPBT-SE55 polymer, except that only 4, 4'-dicarboxydiphenyl ether (PE) (0.4739 g) was added after hydrogen chloride removed completely.

Yield: 94%. ¹H NMR (in DMSO-*d*₆, ppm, TMS): 7.38–7.33, 7.27–7.18, 6.89–6.78. FT-IR (film, cm⁻¹): 1480, 1398, 1311 (stretching of benzothiazole ring), 960 (breathing of benzothiazole ring).

Measurements

Structure Characterizations

¹H NMR spectra was recorded on a Bruker BioSpin GmbH plus 400MHz spectrometer, using deuterated dimethyl sulfoxide (DMSO-*d*₆) as solvent and tetramethylsilane (TMS) as internal standard. FT-IR spectra of power sample was measured by PerkinElmer Spectrum Two in the range of 400-4000 cm⁻¹. XRD pattern was obtained from 2θ = 10~90° by using Rigaku MiniFlex 600 which equipped with a Cu Kα Radiation (λ = 0.15418 nm) at a current of 40 mA and a voltage of 40 kV, respectively. The differential thermal analysis was conducted on a PerkinElmer differential scanning calorimeter (DSC) 8000. The acid powder samples were preheated at 150 °C for 30 min in a N₂ atmosphere to remove moisture. After cooling to 90 °C, the temperature was heated to 300 °C at a heating rate of 10 °C/min, and the DSC curve within this temperature range was recorded. Thermogravimetric analysis (TGA) was run on a TG 209 F1 Libra instrument in the N₂. The acid powder sample was preheated at 180 °C for 30 min to remove the moisture. Recording TGA curves in the range of 200-700 °C at 20 °C/min. The morphology of power sample was examined by scanning electron microscope (SEM, Zeiss Gemini 300) and transmission electron microscope (TEM, JEM 2100F). The chemical components were obtained by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi).

Electrochemical measurements

sPBT-SE55 polymers were ground in agate mortar for about 10 mins to get polymer powder. Both conductive agent and adhesive were added into sPBT-SE55 polymer powder to make sPBT-SE55 cathode. sPBT-SE55, KB (Ketjen Black), 5% PVDF (polyvinylidene fluoride, the mass ratio of PVDF to N-methyl pyrrolidone (NMP) is 1:19) binder was blended by the mass ratio of 6:3:1, and a suitable amount of NMP was then added and mashed into a uniformly mixed slurry. The combined slurry was evenly coated on the aluminum foil and then vacuum dried for 12 h at 60 °C. Finally, the dried film was cut into 12 mm diameter sheets as the cathode. The 1 M NaClO₄ in diethyl

carbonate (DEC) and ethylene carbonate (EC) (DEC: EC = 1:1, by volume ratio) solution was served as the electrolyte, and metal Na as the counter electrode, and encapsulated into the CR2016 button cell in an argon - filled glove box. The galvanostatic charging/discharging tests were carried on a LAND multichannel battery tester (CT2001A) at the current density of 30 mA g^{-1} in a voltage range of 1.5–4.0 V.

Figure captions

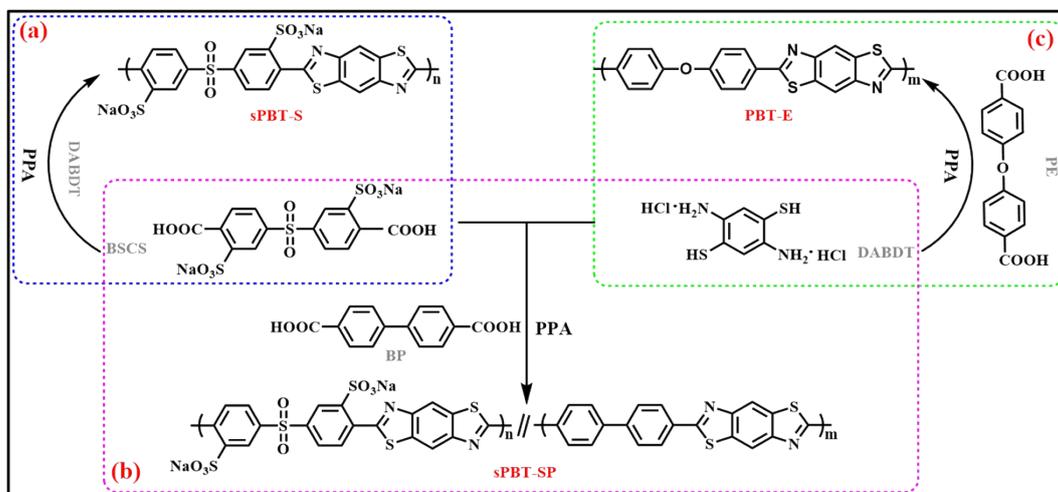


Fig. S1 Synthesis routes of (a) sPBT-S, (b) sPBT-SP, and (c) PBT-E.

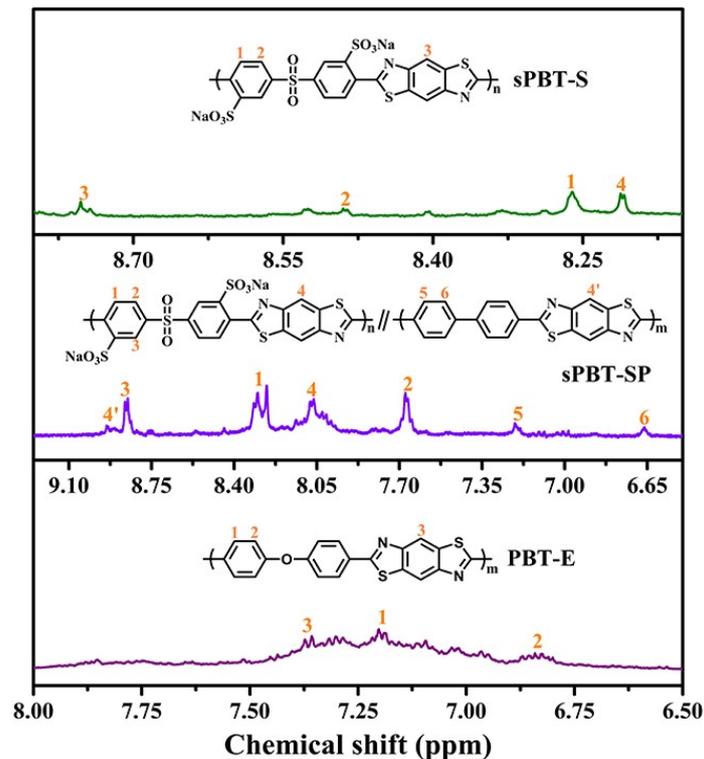


Fig. S2 ^1H NMR spectra of sPBT-S, sPBT-SP, and PBT-E polymer.

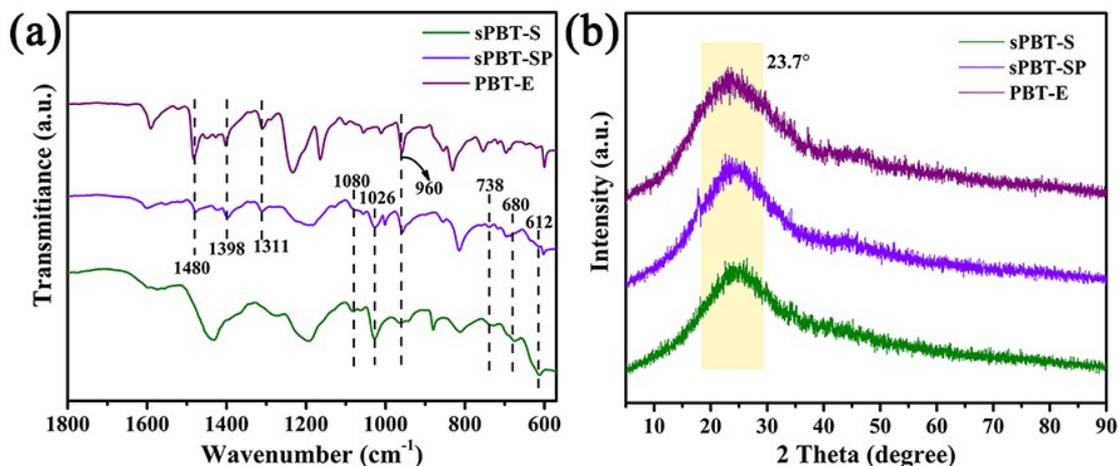


Fig. S3 (a) FT-IR spectra, (b) XRD pattern of sPBT-S, sPBT-SP, and PBT-E polymer.

Description : As shown in Fig. S2, the hydrogen signal peaks of sPBT-S, sPBT-SP, and PBT-E polymer were assigned in their respective ^1H NMR spectra. Therein, H4 and H4' of sPBT-SP exhibited different peak shapes as they were in different chemical environment. H4 had a double peak shape, which was similar to the H3 peak in sPBT-S, while PBT-E without sulfonated groups did not show similar signal peak. As displayed in the FT-IR spectra of sPBT-S, sPBT-SP, and PBT-E polymer (Fig. S3a),

the characteristic stretch peaks of benzothiazole rings (1480, 1398, and 1311 cm^{-1}) were appeared in PBT-E. Another characteristic stretch peaks of benzothiazole rings (680 cm^{-1}), the deformation peak (738 cm^{-1}) of the benzothiazole ring, and the peaks of sulfonate groups (1080, 1026, and 612 cm^{-1}) were appeared in sPBT-S and sPBT-SP. Meanwhile, the breath peak (960 cm^{-1}) of benzothiazole rings was exhibited in the spectra of all the three polymers.^{1, 2} ^1H NMR and FT-IR results demonstrated the successful synthesis of the three polymers. Similar to the XRD pattern of sPBT-SE55, all three polymers showed a wide peak with a center peak of $2\theta = 23.7^\circ$, which indicated that they were amorphous polymers (Fig. S3b).



Fig. S4 solubility analysis results of sPBT-SE55 polymer.

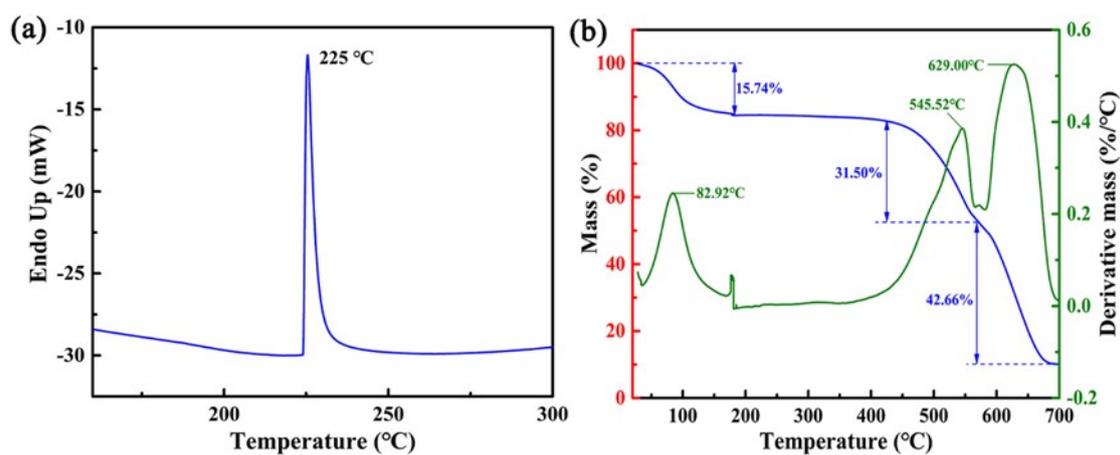


Fig. S5 (a) DSC, (b) TGA curve of sPBT-SE55 polymer.

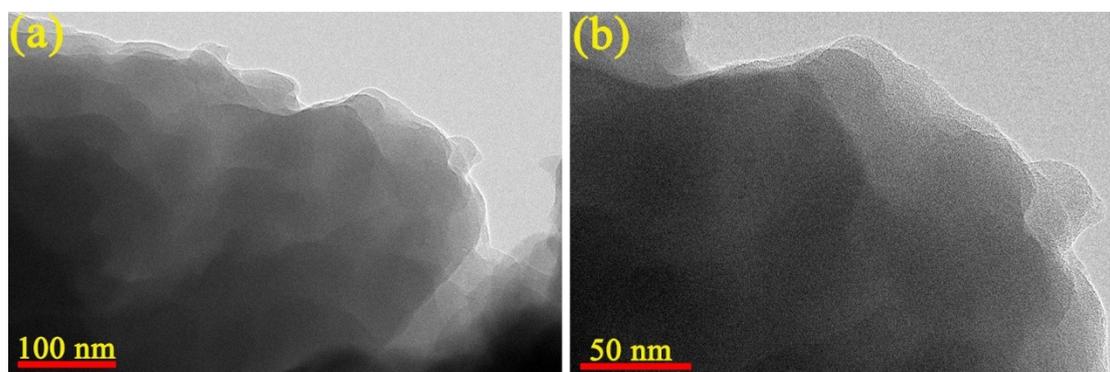


Fig. S6 TEM images of sPBT-SE55 polymer.

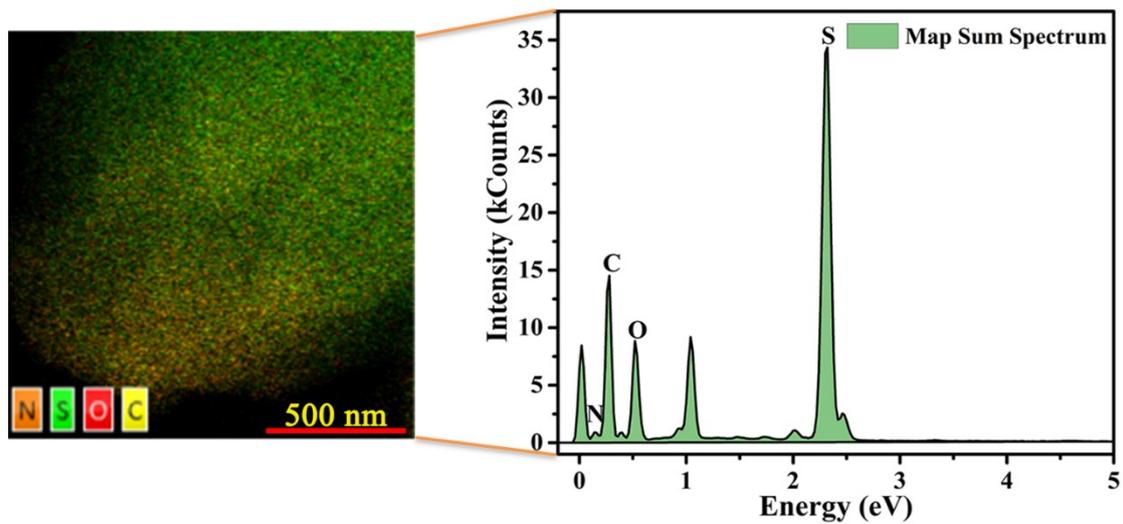


Fig. S7 EDS analysis of sPBT-SE polymer.

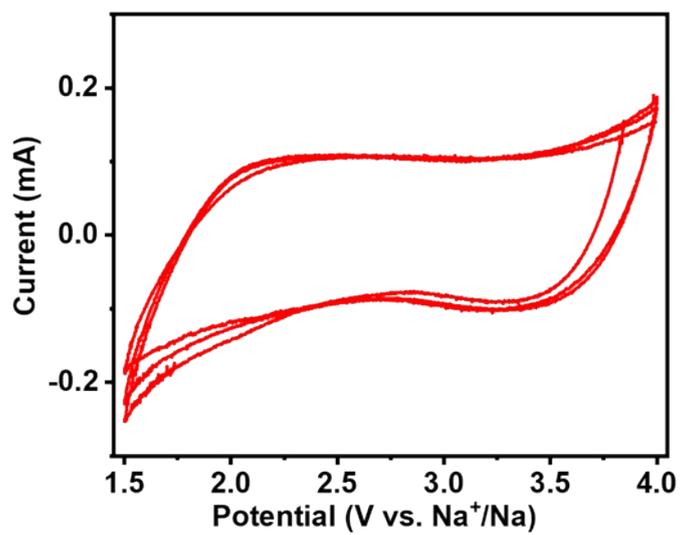


Fig. S8 The CV of first three cycles of sPBT-SE55.

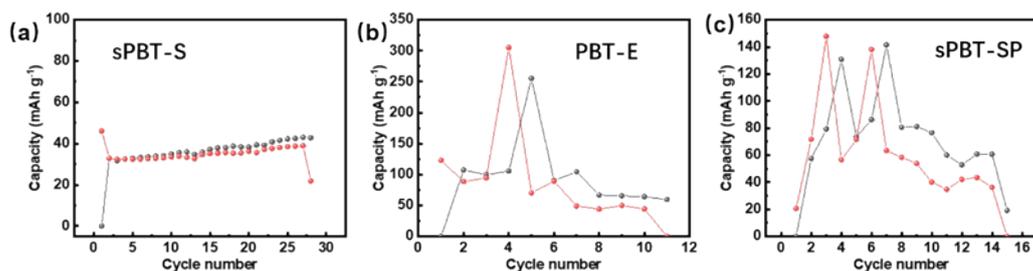


Fig. S9 Charge and discharge cycle performance of sPBT-S (a), PBT-E (b) and sPBT-SP (c).

Description : It can be seen from the charge discharge cycle performances diagram of the sPBT-S and sPBT-SP materials that the capacities of the materials were very low, basically unable to charge and discharge normally, which were far lower than that of sPBT-SE55. In addition, Fig. S9a shows that although the specific capacity of material sPBT-S was low, the coulomb efficiency was always high, while the capacity of materials PBT-E and sPBT-SE corresponding to Fig. S9b and c was high in a certain cycle, but the capacity was very unstable and the coulomb efficiency was very low. From the above analysis, we could also guess that the group that makes a great contribution to the capacity here may be $-SO_2$, and the ether bond might increase the flexibility, so as to stabilize the electrochemical cycle of the material.^{3, 4} In a word, the functional groups in sPBT-SE55 material played a synergistic role in the electrochemical performance of the whole material.

Notes and references

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