



Short communication

Poly(tetrahydrobenzodithiophene): High discharge specific capacity as cathode material for lithium batteries

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ABSTRACT

A novel thioether containing conjugative polymer, poly(tetrahydrobenzodithiophene) (PTBDT), with high discharge specific capacity as the cathode material for lithium batteries, has been synthesized chemically. The polymer has been characterized by elemental analysis, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The cyclic voltammogram of the polymer shows multiple redox peaks. The charge–discharge tests show stable discharge specific capacity about 560 mAh g⁻¹ and the maximal capacity of 820 mAh g⁻¹, and discharge voltage about 2.3 V. The results indicate that the thioether bonds of the polymer are involved in the electrode reaction. It is tentatively proposed that the thioether cations are formed during the redox reaction on the cathode. The reversible redox reaction on thioether bonds that is a multi-electron process offers a high specific capacity, and low discharge voltages.

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1. Introduction

The development of lightweight and high energy-density rechargeable batteries is of importance with the increasing demand for mobile power and the extensive use of portable devices. Conjugated conducting polymers, such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH) and poly-p-phenylene (PPP), have been used as cathode materials [1], even through their theoretical specific capacities are generally below 100 mAh g⁻¹. Based on the reversible cleavage–recombination process (RS–SR ⇌ 2RS⁻), disulfide compounds have been first proposed by Liu et al. as cathode materials for lithium batteries [2]. Among which, 2,5-dimercapto-1,3,4-thiadiazole (DMcT) is a well-known organodisulfide compound due to its high theoretical charge density [3]. Oyama and co-workers reported a composite cathode material that comprises DMcT and polyaniline (PANI), exhibiting an accelerated redox reaction by the electrocatalysis effect of PANI on the disulfide bonds [4,5]. Kiya et al. also reported same effect of poly(2,3-ethylenediothiophene) (PEDOT) as an electrocatalyst to accelerate the redox reaction rate of DMcT [6–8]. Although the redox reaction rate is accelerated by incorporation of PANI and PEDOT to the disulfide compounds, the overall energy capacity of the composites are decreased due to the low energy storage capability

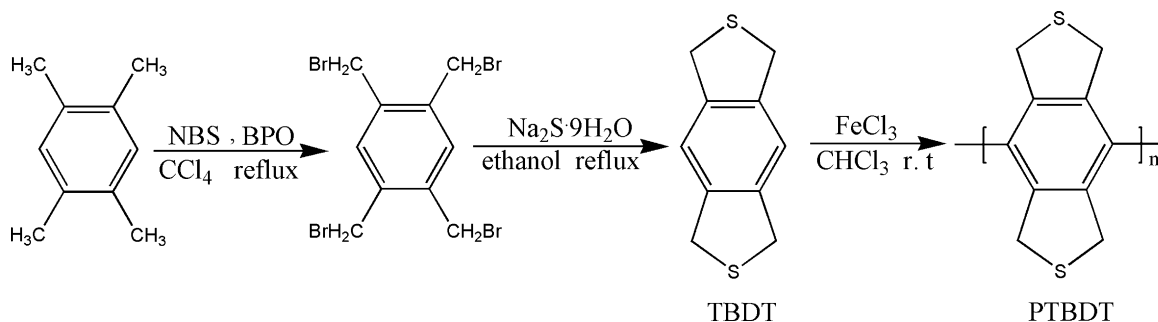
of PANi and PEDOT. The solubility of small molecules generated from the redox reaction results in the fading of discharge capacity, which jeopardizes the utilization of these materials in commercialized lithium batteries. With this in mind, two new polymers containing disulfide bonds have been synthesized. For the first type, the disulfide bonds are bonded between backbones to form “ladder polymer” [9–11] that are insoluble in electrolytes during the reduction process. However, the specific capacity fading remained, which may be caused by the difficult recombination of “intermolecular” disulfide bonds [11]. For the second type, the disulfide bonds are linked to the main-chain of a conducting polymer [12–16]. This “intramolecular” disulfide bonds could improve the recombination of disulfide bonds. However, the same problem observed to the ladder disulfide polymers occurs to these disulfide polymers, and the decay of the discharge capacity is still fast.

In our group, we reported that the thioether containing polymers, poly(2-phenyl-1,3-dithiolane) and poly(1,4-di(1,3-dithiolan-2-yl) benzene), show specific capacity of 117 mAh g⁻¹ and 378 mAh g⁻¹, respectively as cathode active materials in rechargeable lithium batteries [17]. The discharge specific capacity is much higher than their main-chain polyphenylene without thiolane groups, suggesting that thiolane groups are the function groups to offer energy storage. It is noted that the thiolane groups attached to the main-chains are non-coplanar to the phenyl rings of polyphenylene in both polymers, discouraging the electric charge transfer. Therefore, here we report a novel molecule, poly(tetrahydrobenzodithiophene) (PTBDT), that has coplanar thioether bonds to polyphenylene main-chains. The polymer has

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Scheme 1. The synthetic route of PTBTD.

a polyphenylene main-chain to offer electron conductivity. Moreover, each unit of tetrahydrobenzodithiophene has two coplanar thioether bonds to offer electrode reactions. Characterizations are carried out for the polymer and, its electrical properties as well as the discharge/charge performance are reported. The synthetic route is depicted in Scheme 1.

2. Experimental

2.1. Apparatus and procedures

FT-IR spectra were recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets. Powder XRD patterns were obtained from a D8ADVANCE X-ray diffractometer. NMR spectra were obtained from a Varian Mercury-VX 300 spectrometer. Elemental analysis was determined by a Thermo Quest Italia S.P.A. Flash EA1112 SERIES. XPS test was carried out on a KRATOS XSAM800 Instrument with the magnesium source Mg Ka 1253.6 eV operated at 12.5 kV and 16 mA. Thermal analysis of the samples was performed on a Diamond DSC TG-DTA 6300 instrument under nitrogen flow at a heating rate of $20^{\circ}\text{C min}^{-1}$. For electrochemical evaluation, the cyclic voltammetry (CV) tests were carried out on CH Instruments electrochemical workstation (CHI 660B) in 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2(\text{LiTFSI})/1,2\text{-dimethoxyethane}/1,3\text{-dioxolane}$ (1:2 by weight) solution at a scan rate of $50 \mu\text{V s}^{-1}$ between 1.5 V and 4.2 V. The cathodes were prepared by mixing specific polymer powders with carbon black and Teflon in a weight ratio of 4:4:2, the Li film was used as the reference electrode and counter electrode. The charge–discharge tests were performed on Land Battery test system. Working cathodes were prepared by mixing active material powders with carbon black and Teflon in a weight ratio of 4:4:2. Lithium foil was used as the anode and the tests were processed at a rate of 50 mA g^{-1} in 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2/1,2\text{-dimethoxyethane}/1,3\text{-dioxolane}$ (1:2 by weight) solution. The cut-off voltages were 1.4 V and 4.2 V.

2.2. Synthesis of TBDT and PTBTD

2.2.1. Synthesis of 1,2,4,5-tetrakis (bromomethyl)benzene

The synthesis is performed according to literature [18]. Carbon tetrachloride and chloroform were refluxed twice for 8 h over P_4O_{10} and then kept under dry argon. 1,2,4,5-Tetramethylbenzene (7.5 g, 56 mmol), N-bromosuccinimide (40 g, 24 mmol) and benzoyl peroxide (3 g) were added to 150 ml carbon tetrachloride; the mixture was carefully heated under reflux until the red-brown color vanished. The hot mixture was filtered, the residue was washed with hot carbon tetrachloride and the solution was concentrated to about 50 ml. After cooling at 0°C for several hours, white crystals were formed, which were separated and re-crystallized from chloroform to yield 2.93 g (12%) of 1,2,4,5-tetrakis (bromomethyl)benzene (m.p. 159.3°C). $^1\text{H NMR}$ (300 MHz, CDCl_3): 4.6 (s, 8H), 7.38 (s, 2H).

2.2.2. Synthesis of tetrahydrobenzodithiophene

Tetrahydrobenzodithiophene was synthesized accordingly [19]. Tetrabromodurene (1.99 g, 4.44 mmol) was added to a solution of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (2.14 g, 8.88 mmol) in ethanol (100 ml) and refluxed for 6 h. Removal of solvent resulted in an off-white residue that was partitioned between CH_2Cl_2 (100 ml) and H_2O (50 ml). The aqueous layer was separated and further extracted with CH_2Cl_2 (2×100 ml). The organic fractions were combined and dried (MgSO_4). After evaporation of solvent and dried in oven at 80°C to constant weight, 0.84 g white powder (TBDT) was obtained (4.34 mmol, yield 97%; m.p. $218\text{--}221^{\circ}\text{C}$, lit. $220\text{--}223^{\circ}\text{C}$). $^1\text{H NMR}$ (300 MHz, CDCl_3): d.7.08 (s, 2H, arom.), 4.19 (s, 8H, CH_2). Elemental analysis (%): C 61.76, H 5.08, S 33.92 (found); C 61.85, H 5.15, S 32.99 (calcd.).

2.2.3. Synthesis of poly(tetrahydrobenzodithiophene)

TBDT was polymerized by facile oxidative coupling reaction of PTBTD in the presence of FeCl_3 in chloroform at room temperature for 48 h. After reaction, chloroform was filtered off; FeCl_3 was removed by washing with dilute hydrochloric acid then water till colorless. The black powder was collected and extracted by ethanol in a Soxhlet extractor for 24 h. The black polymer was dried at 60°C in oven to constant weight. Elemental analysis (%): C 62.37, H 4.28, S 33.35 (found); C 62.50, H 4.17, S 33.33 (calcd.).

3. Results and discussion

3.1. Material characterizations

The monomer TBDT and polymer PTBTD have been characterized by FT-IR, as shown in Fig. 1(a) and (b). It is noted that the absorption bands of the polymer are broader than that of the monomer, while the vibration bands of PTBTD are similar to that of TBDT. The strong absorption at 1384 cm^{-1} is attributed to the C–H bending vibration of the methylene; the weak absorp-

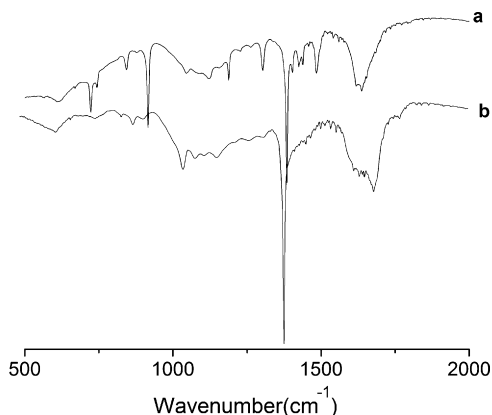


Fig. 1. FT-IR spectra of TBDT (a) and PTBTD (b).

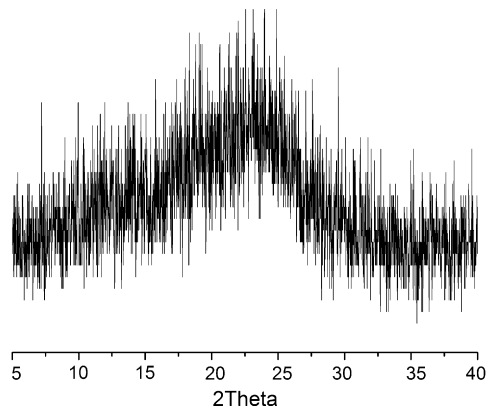


Fig. 2. X-ray diffraction spectrum of PTBDT.

tion at 717 cm^{-1} is assigned to the C–S stretching band [15]. The absorption at 843 cm^{-1} of the monomer is attributed to the single hydrogen on benzene ring, which is very weak in the FT-IR spectrum of the polymer. The spectra around 1630 cm^{-1} are attributed to the skeletal vibrations of benzenoid ring. Moreover, the FT-IR spectrum of PTBDT has no peak associated to sulfone or sulfonate groups at 1100 cm^{-1} [20]. These results suggest that side reaction does not occur to the thioether groups during the chemical polymerization.

The hydrogen content of PTBDT (4.28%) is lower than that of monomer TBDT (5.08%), indicating the occurrence of a dehydrogen polymerization. The XRD pattern in Fig. 2 shows that the polymer is amorphous. Fig. 3 presents the XPS spectrum of the polymer. The main peak of S2p shows a binding energy of 163.6 eV, similar to poly(1,4-phenylene sulfide) (163.6 eV) [21]. This binding energy indicates the presence of C–S–C bond in the polymer. Thermal gravity analysis (TGA, Fig. 4) reveals that the decomposition of PTBDT starts at 240°C (5% weight loss). It is well known that polyphenylene has very high decomposing temperature up to 400°C , so that the low thermo-stability is owing to the presence of thioether groups.

3.2. Electrochemical properties

Fig. 5 shows the cyclic voltammograms (CVs) of the first cycle of PTBDT. There are four oxidation peaks at 3.44 V, 3.64 V, 3.89 V and 4.13 V, and two broad reduction bands at 1.7–2.2 V and 2.5–2.8 V. The results indicate there are multi-oxidation reactions at high voltage in PTBDT. The broad reduction peaks, which may be the overlap of multi-reduction peaks, imply that the reduction reaction of PTBDT is complicated. On the other hand, the CV curve of polyphenylene shows one pair of redox peaks only, so that the

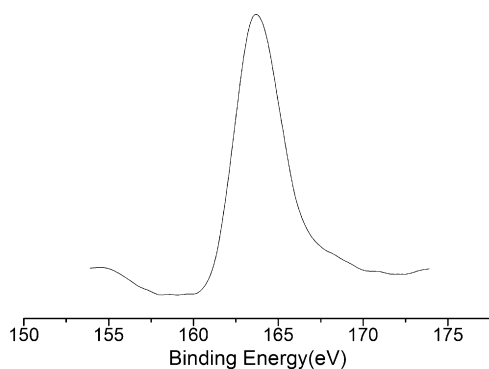


Fig. 3. XPS spectrum of PTBDT.

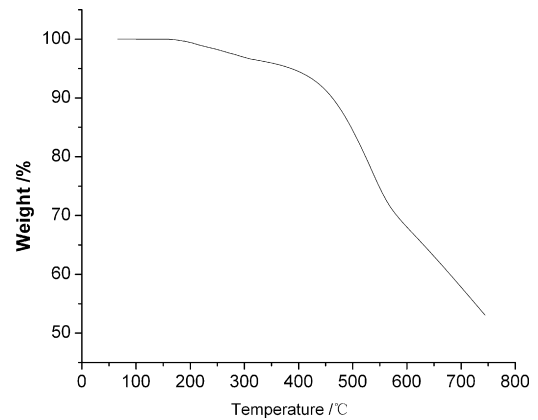


Fig. 4. TGA curve of PTBDT.

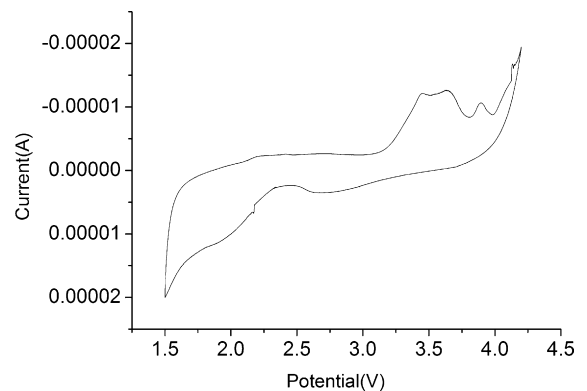


Fig. 5. Cyclic voltammogram of PTBDT.

extra oxidation peaks may be attributed to the oxidation reaction of thioether bonds. In addition, the low voltage is similar to that of other thioether containing polymers [17,22], which implies the reduction reaction occurring on S atoms rather than de-doping process on PPP main-chains.

Fig. 6 shows charge–discharge curves of PTBDT in 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ /1,2-dimethoxyethane/1,3-dioxolane solution. The charge voltage and discharge voltage correspond roughly to the oxidation and reduction potential in the CV (Fig. 5). Meanwhile the discharge curves are well defined with two discharge plateaus at ca. 2.4 V and 2.2 V, respectively; the former corresponds to specific capacity ca. 100 mAh g^{-1} and the later corresponds to capacity

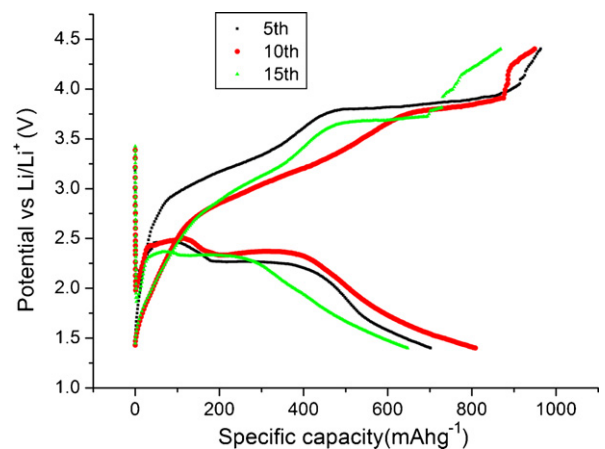


Fig. 6. The charge–discharge curves of PTBDT.

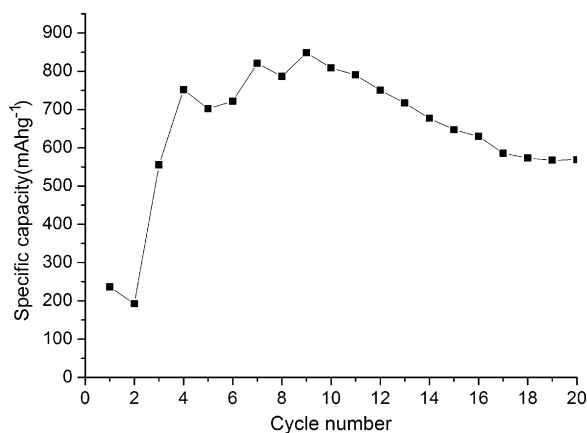


Fig. 7. Specific capacity of PTBTD vs. cycle number.

from 200 mAh g⁻¹ to 400 mAh g⁻¹. In addition, the high specific capacity of 400–800 mAh g⁻¹ is obtained with a low voltage of 2.1–1.5 V. The results indicate that the charge–discharge behavior, as a result from its complicated electrode reactions, is complicated.

The high charge voltage and low discharge voltage are the characteristics of PTBTD cathode in LiTFSI/DOXL-DME electrolyte. The charge voltage is similar to that of its main-chain polyphenylene; but the discharge voltage is much lower than that of polyphenylene (3–4 V) [1]. On the other hand, the charge–discharge voltages are similar to the previously reported thioether containing polymers poly(2-phenyl-1,3-dithiolane), poly(1,4-di(1,3-dithiolan-2-yl) benzene), and aliphatic thioether polymers [17,22]. Obviously, the multi-plateaus and low discharge voltage are the characteristic of thioether containing polymers and mainly attributed to the redox reaction of thioether bonds.

The cycle life of PTBTD is shown in Fig. 7. Except the activation process of first two cycles, the discharge specific capacity is above 550 mAh g⁻¹. The maximum specific capacity of 820 mAh g⁻¹ is obtained at the 9th cycle. The values are higher than those of disulfide polymers (<400 mAh g⁻¹) [10,11,13–16] and polyphenylene (<159 mAh g⁻¹) [1]. In addition, the decay of capacity of PTBTD is not as significant as that of disulfide polymers. The results show higher discharge specific capacity and stability of PTBTD than that of disulfide polymers as cathode materials.

3.3. Electrode reaction of PTBTD in LiTFSI/DOXL-DME

Obviously, PTBTD has fairly different electrode reactions from conventional conducting polymers and disulfide polymers. It is tentatively proposed that the thioether cations are formed and enable

a reversible electrode reaction to store energy. In the literature, thioether cations have been extensively investigated and reported long life in some systems [23–25]. In addition, it is known that conjugating aromatic π system may stabilize the thioether cations. Moreover, with electron donating C–O–C groups, the LiTFSI/DOXL-DME electrolyte promotes the stability of thioether cations. The proposed redox reaction on PTBTD is depicted in Scheme 2. During the oxidation process, the phenyl ring loses an electron to form a radical cation, which is subsequently electro-neutralized by gaining an electron from a neighboring S atom; meanwhile the S atom is oxidized to form a thioether cation. This oxidation–electron transfer process can be repeated further at higher voltage till S⁴⁺ cations are formed. Meantime, each tetrahydrobenzodithiophene unit carries 8 positive charges. The multistep reaction is proposed to explain the four oxidation peaks in CV curve of PTBTD (Fig. 5). It also means that high voltage remove more electrons from S to form high valent thioether cations, which result in high capacity (Fig. 6). This process affords a theoretical specific capacity of 1116 mAh g⁻¹, which is roughly in agreement with the stable discharge specific capacity. On the other hand, the discharge process is the reduction reaction of thioether cations, which offers a low voltage.

4. Conclusions

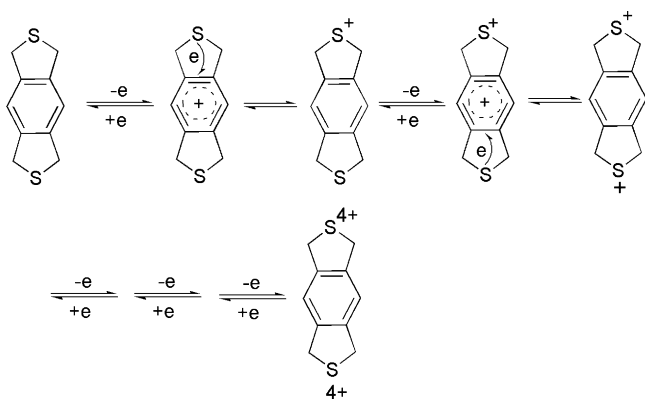
A novel thioether containing polymer, poly(tetrahydrobenzodithiophene), has been successfully synthesized by facile oxidative-coupling polymerization and characterized by XRD, EA, XPS and TGA. The electrochemical tests show that the thioether containing polymer is electro-active as the cathode material with a high discharge capacity. Thioether bonds are the function groups to impart the energy storage ability of poly(tetrahydrobenzodithiophene). ‘Thioether cation formation’ mechanism has been proposed to rationalize the electrode reaction. The reversible redox reaction on thioether bonds affords poly(tetrahydrobenzodithiophene) a high discharge specific capacity and a low discharge voltage as the cathode material for lithium batteries.

Acknowledgement

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Scheme 2. Tentatively proposed cathode reaction of PTBTD.

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