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ORIGINAL PAPER

Synthesis and properties of novel organic thiolane polymer as cathode material for rechargeable lithium batteries

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Abstract A novel thiolane polymer, poly[1,2,4,5-tetrakis(propylthio)benzene] (PTPB), was synthesized by facile oxidative-coupling polymerization, characterized by FT-IR, XPS, XRD, TGA and EA, and tested as cathode active material in rechargeable lithium batteries. The FT-IR, XPS and elemental analysis confirm the occurrence of polymerization and show the existence of C–S–C bonds. The results show that the thiolane polymer has electrochemical activity as cathode material in lithium batteries and thioether bonds may be the centers of the electrode reaction. A maximum specific capacity of 200 mAh g^{-1} was obtained and this agrees roughly with the theoretical prediction. In addition, high voltage efficiency was obtained first time from sulfide polymer.

Keywords Organic thioether polymer · Rechargeable lithium batteries · Cathode materials · Specific capacity

1 Introduction

There is an increasing need for rechargeable batteries with high specific energy for portable electronic equipment such as cell phones, digital cameras and portable PCs. Organic compounds with thiol or disulfide structure are candidates for cathode materials for high-energy density lithium secondary batteries [1–8]; for example, 2,5-dimercapto-1,3,4-thiadiazole (DMcT) [9] is one of the most well-known organic disulfide compounds with theoretical specific capacity of 362 mAh g^{-1}. It is accepted widely that the energy storage is based on the reversible cleavage-recombination process of disulfide bonds. Because of the instability of the S–S bond and the solubility of small molecules produced in the redox process, these materials have the disadvantage of rapid specific capacity fading. Recently, it has been found in our group that thiolane containing polymers also have the ability to store energy as cathode materials in rechargeable lithium batteries [10]. But it is still uncertain whether other thiolane containing polymers (thioether polymers) are electrochemically active as cathode materials. To examine the activity of organic thioether polymers, several new polymeric thioether compounds have been synthesized and investigated. In this paper we report a novel thioether polymer, poly(1,2,4,5-tetrakis(propylthio)benzene) (PTPB), its synthesis, characterization and properties. The polymer has conjugated polyphenylene mainchains with directly linked S atoms on benzene rings, which may be expected to offer better electron transport ability. The structure of the compound and the synthetic route is depicted in Scheme 1.

2 Experimental

2.1 Apparatus and procedure

FT-IR spectra were recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets. The XRD pattern of a powder specimen was obtained on a D8ADVANCE X-ray diffractometer. XPS tests were carried out on a KRATOS XSAM800 Instrument with the magnesium source Mg *Kα* 1253.6 eV operated at 12.5 kV and 16 mA. Thermal analysis was performed on a Diamond DSC TG-DTA6300

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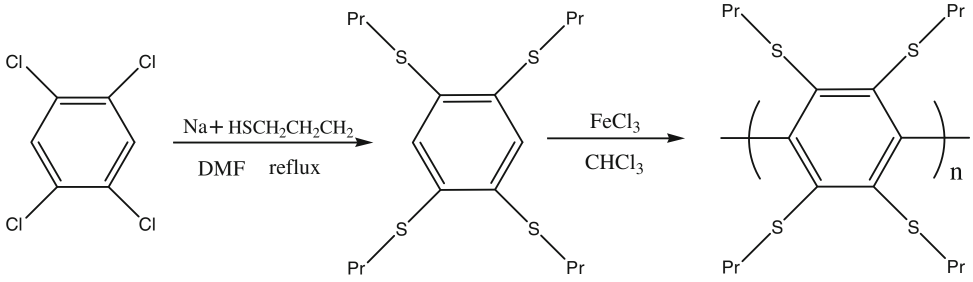
Scheme 1 Synthetic route of poly[1,2,4,5-tetrakis (propylthio) benzene]



instrument under nitrogen flow at a heating rate of 20 °C min^{-1}. Elemental analysis was determined on a Thermo Quest Italia S.P.A FlashEA1112 SERIES. For electrochemical evaluation, the charge–discharge tests were performed on a 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 $LiN(CF_3SO_2)_2$/1,2-dimethoxyethane/1,3-dioxolane (1:2 by weight) solution. The cut-off voltages were 1.4 and 4.2 V.

2.2 Materials preparation

All reagents were used as received unless otherwise mentioned. The monomer, 1,2,4,5-tetrakis(propylthio)benzene, was prepared by reaction of 1-propylthiol with 1,2,4,5-tetrachlorobenzene, according to a literature procedure [11] with a little modification and is depicted as follows. In an ice-cooled three-neck flask 3.04 g (40 mmol) 1-propylthiol was mixed with 0.92 g (40 mmol) sodium in 50 mL dried DMF and stirred under nitrogen. After the disappearance of sodium, 1.73 g 1,2,4,5-tetrachlorobenzene (8 mmol) was added and the temperature was increased to gentle reflux. The progress of the reaction was monitored by TLC (25:75 chloroform–hexanes). When more spots were observed on silica gel plate, heating was prolonged until there was only one spot. An excess of saturated aqueous sodium chloride solution was added to the reaction mixture until the product was precipitated as a white solid. For further purification, the crude product was chromatographed on silica gel using a mixture of chloroform and hexane (1:3) as eluant. After distillation of solvent, 1.70 g white crystal was obtained (57% yield). The structure of the monomer 1,2,4,5-tetrakis(propylthio)benzene (TPB) was confirmed by ^{1}H NMR and FT-IR. ^{1}H NMR: ($CDCl_3$, 300 M) δ7.17 (1H, s), 2.87 (4H, t), 1.70 (4H, m), 1.05 (6H, t). Elemental analysis (%): C: 57.87, H: 7.98, S: 34.12 (found); calculated: C: 57.75, H: 8.02, S: 34.22.

The polymerization procedure is described below. 2.65 g anhydrous $FeCl_3$ was added to a solution of 0.849 g 1,2,4,5-tetrakis(propylthio)benzene in 20 mL $CHCl_3$ and stirred at room temperature for 72 h. After the reaction was completed, chloroform was removed under reduced pressure. The solid powder was washed with dilute hydrochloric acid and distilled water and was then extracted by ethanol in a Soxhlet extractor for 24 h. The polymer was oven dried at 60 °C and 0.42 g brownish powder was obtained (49% yield). Elemental analysis (%): C: 58.31, H: 7.32, S: 34.32 (found); calculated: C: 58.06, H: 7.53, S: 34.41.

3 Results and discussion

3.1 Material characterization

The structure of the monomer was characterized by FT-IR, ^{1}H NMR. The polymer was insoluble and was characterized by FT-IR, XPS, TGA and XRD. The XRD pattern shows that the polymer is amorphous. FT-IR (Fig. 1) spectra show peaks at 2,966, 2,867 and 1,456 cm^{-1}, indicating the existence of CH_3– and –CH_2–. The vibration band around 1,600 cm^{-1} is attributed to the aromatic ring and the peak around 1,050 cm^{-1} is the C–S stretching vibration [7]. In addition, the peak at 750 cm^{-1} of monomer TPB is attributed to the C–H out of space vibration for the isolated hydrogen on 1,2,4,5-substituted benzene, which is absent in the IR of the polymer, indicating the occurrence of polymerization. The elemental analysis shows that the polymer

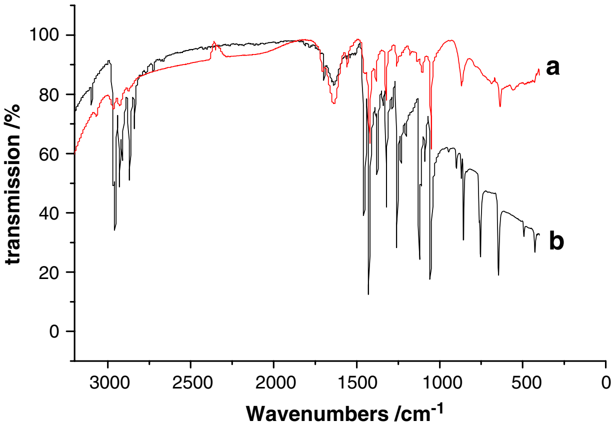


Fig. 1 FT-IR spectra of PTPB (a) and TPB (b)

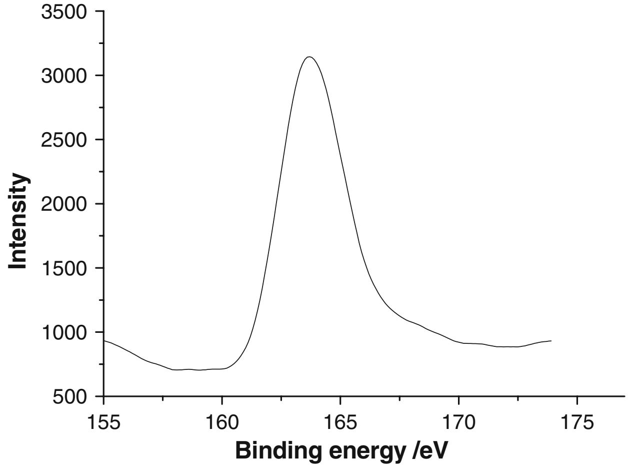


Fig. 2 XPS spectrum of PTPB

contains elemental C of 58.31% and S of 34.32%, very close to the theoretical value (C: 58.06%, S: 34.41%), indicating that the polymer is of high purity. In addition, the decrease of hydrogen content from 7.98% of the monomer to 7.32% of the polymer, indicates that a de-hydrogen polymerization has taken place.

Figure 2 shows the XPS spectrum of the polymer. The main peak of S2p shows binding energy at 163.6 eV, similar to poly(1,4-phenylene sulfide) (163.6 eV) [12]. This binding energy indicates the existence of C–S–C bonds in the polymer and agrees with the structure in Scheme 1.

Thermal gravimetric analysis (TGA) (Fig. 3) reveals that the polymer is stable before 170 °C; decomposition of the polymer started at 240 °C (5% weight loss). It is well known that its main-chain polyphenylene has very high decomposing temperature up to 400 °C, so that the low thermo-stability is due to the presence of thioether groups.

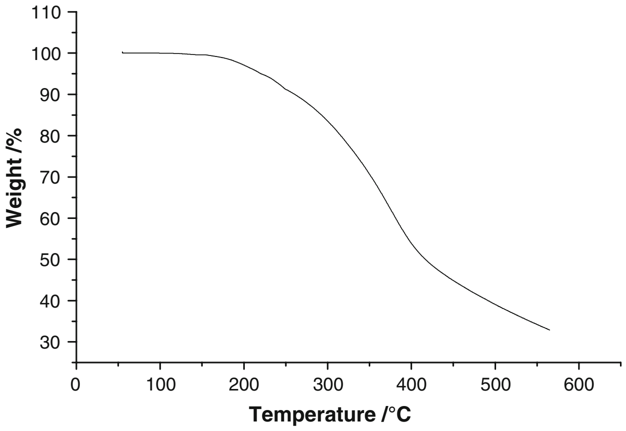


Fig. 3 Thermal gravity analysis curve of PTPB

3.2 Electrochemical tests

Figure 4 shows the charge and discharge curves of PTPB used as cathode materials. There is a well-defined plateau for charge and discharge curves, which are very close to each other: 2.4 V on charge and 2.3 V on discharge. The very close voltages mean high voltage efficiency, which is higher than those of disulfide polymers [6–8], also different from our previously reported sulfide polymers [10]. From the literature organic sulfur containing polymers have generally the drawback of low voltage efficiency. However, these results indicated that high voltage efficiency can be obtained from organic sulfide polymers. The reason is unclear at the moment and is still under investigation.

Figure 5 shows the cycle life of PTPB as cathode material. The initial discharge specific capacity is around 200 mAh g^{-1}. From the second cycle on, the specific capacity decreases dramatically and becomes stable after the tenth cycle. The capacity fading may be attributed to the migration of the molecules from the cathode. However, the results show that the thiolane polymer has the ability to store energy for lithium secondary batteries. Because there is no S–S bond in the polymer, the specific capacity cannot come from disulfide bonds. In addition, the specific capacity of polyphenylene main-chain is below 50 mAh g^{-1}; hence the specific capacity comes mainly from thiolane groups. Specifically, the redox reaction took place on the S atoms of thiolane groups. That is, during charge, one electron is removed from an S atom to form a S cation; in reverse, an S cation obtains one electron to be reduced to neutral thiolane. According to this hypothesis the theoretic specific capacity of poly[1,2,4,5-tetrakis(propylthio)benzene] should be 288 mAh g^{-1}. Generally, the practical discharge specific

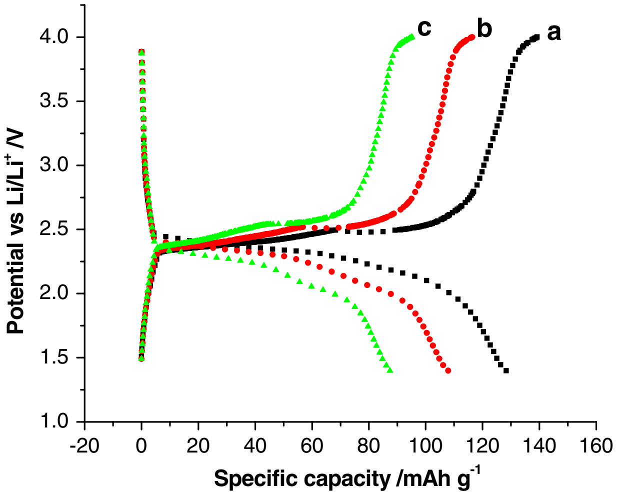


Fig. 4 Charge-discharge curves of PTPB: (a) 5th cycle, (b) 10th cycle, and (c) 15th cycle in 1 M $LiN(CF_3SO_2)_2$/1,2-dimethoxyethane/1,3-dioxolane (1:2 by weight), current density: 50 mA g^{-1}, cut-off voltage: 1.4–4.2 V

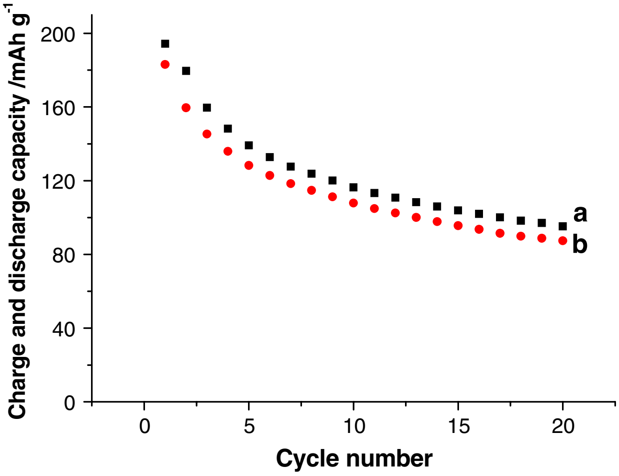


Fig. 5 Cycle life of PTPB (a) charge and (b) discharge curves in 1 M LiN(CF_3SO_2)$_2$/1,2-dimethoxyethane/1,3-dioxolane (1:2 by weight), cut-off voltage: 1.4–4.2 V, scan rate: 50 µV s^{-1}

capacity is lower than theoretical, so that our hypothesis accords roughly with experimental results.

4 Conclusions

In summary, a novel thiolane containing polymer, poly[1,2,4,5-tetrakis(propylthio)benzene] (PTPB), has been prepared by facile oxidative-coupling polymerization. The electrochemical tests show that PTPB is a potential cathode active material in lithium batteries. The results indicate that the thioether bonds may be the activity centers as cathode active material. A specific capacity up to 200 mAh g^{-1} has been obtained, which agrees with the single electron electrode reaction on one S atom. Moreover, high voltage efficiency has been obtained first time from organic sulfide polymer.

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