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# Aliphatic thioether polymers as novel cathode active materials for rechargeable lithium battery

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ABSTRACT

Two aliphatic thioether polymers, poly[methanetetryl-tetra(thiomethylene)] (PMTTM) and poly(2,4-dithiopentanylene) (PDTP) were designed, synthesized, characterized and tested as cathode active materials. The chemical structure of polymers was confirmed by FT-IR, FT-Raman, and XPS spectral analysis. Both polymers were found to have electrochemical activity as cathode materials for rechargeable lithium battery by the electrochemical tests. The specific capacity of PMTTM was 504 mA h $g^{-1}$ at the third cycle and faded to 200 mA h $g^{-1}$ after 10 cycles; PDTP showed low and stable specific capacity around 100 mA h $g^{-1}$ even after 50 cycles. The specific capacity of fully saturated aliphatic thioether polymers demonstrated that thioether bonds offered energy storage. It was proposed that thioether bond was oxidized to form thioether cations with the help of ether solvents.

## 1. Introduction

Since Liu and Visco et al. [1,2] found organic disulfide compounds could be used as cathode active materials for rechargeable lithium battery in the late of 1980s, many researches have been focused on the development of organic disulfide materials [3–14]. The electrode reactions of the disulfide compounds are based on the reversible cleavage-combination of S–S bond. However, we found recently that two organic thioether compounds, poly[1,4-di(1,3-dithiolan-2-yl)benzene] and poly(2-phenyl-1,3-dithiolane), could also store energy as cathode active materials [15], and thioether function group was proposed as a functional group to offer electrode reactions: $C–S–C \leftrightarrow C–S^{+}–C$. Both the two polymers are composed of conjugated polyphenylene chains with thiolane as pendents. Since polyphenylene is well known cathode active material with specific capacity of tens mA $hg^{-1}$ [16], it is essential to examine whether the thioether structure alone is enough to offer specific capacity in polymers. To investigate the redox function of thioether groups, two novel aliphatic thioether polymers, poly[methanetetryl-tetra(thiomethylene)] (PMTTM) and poly(2,4-dithiopentanylene) (PDTP), were designed, synthesized, and their electrochemical activity was also tested. There are three kinds of bonds in PMTTM and PDTP: C–C, C–H, and C–S–C bonds. Since the saturated C–C and C–H bonds cannot afford redox reaction, thioether bond is the only possible electrochemical active function group among them. Therefore, we can estimate the electrochemical activity of thioether function group by electrochemical behaviors of PMTTM and PDTP.

## 2. Experimental

### 2.1. Materials

Sodium, anhydrous ethanol, perbromomethane and bibromomethane were AR purity and ethane-1,2-dithiol was 98% purity. All reagents were used as received unless otherwise indicated.

The synthetic routes and structures of the polymers are described in Scheme 1a. A typical synthetic procedure of PMTTM was described as below. In a three-neck flask equipped with gas conductor, condenser, and magnetic stirrer, sodium granules (2.0 g, 87 mmol) were added to 30 ml anhydrous ethanol and stirred under nitrogen atmosphere at room temperature till sodium dissolved completely. Ethane-1,2-dithiol (3.0 ml, 35 mmol) was added to the solution and the reactants were stirred for one more hour at room temperature. Then 10 ml ethanol solution of perbromomethane (5.3 g, 16 mmol) was added dropwise to the flask and the reaction mixture was stirred overnight. The white solid was collected by filtration and washed with distilled water (50 ml × 3). The product was dried in oven at 50 °C for 12 h and 1.98 g (63% yield). IR: 2915, 1411, 1182, 1108, 1051, 733, and 676 $cm^{-1}$; Raman: 2928, 1398, 761, 690, 635, 510, 377, 348, and 283 $cm^{-1}$.

The synthetic procedure of PDTP was same to that of PMTTM; but bibromomethane was used instead of perbromomethane. The product was white solid and the yield was 57%. IR: 2924, 1426,

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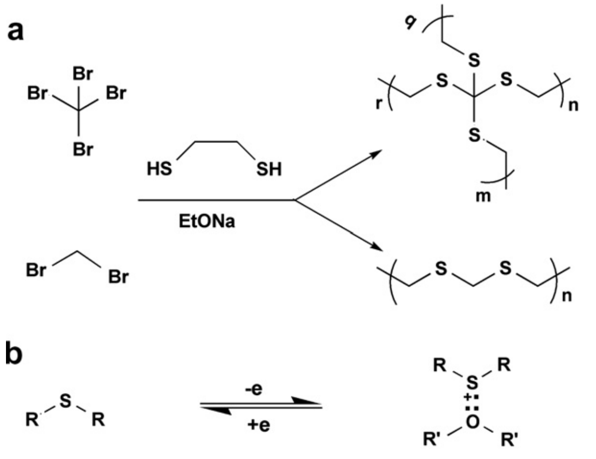

**Scheme 1.** (a) Synthetic routes of PMTTM and PDTP and (b) possible charge–discharge process of thioether in ether solvent.

1185, 1143, 719, and 673 $cm^{-1}$; Raman: 2934, 2901, 1401, 749, 688, 627, 504, 371, 336, and 279 $cm^{-1}$.

### 2.2. Apparatus and procedures

FT-IR spectra were recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets and FT-Raman was recorded on a Nexus 670-FT-Raman Module spectrometer. X-ray photoelectron spectroscopy (XPS) analysis data were obtained with the magnesium source radiation (1253.6 eV) operating at 10 kV and 10 mA. Thermal analysis of all samples were performed on a Diamond DSC TG-DTA 6300 instrument under nitrogen flow at a heating rate of 20 °C/min. XRD patterns of the powder specimens were obtained on a D8ADVANCE X-ray diffractometer.

The cyclic voltammetry (CV) tests were carried out on CH instruments electrochemical workstation (CHI 660B) at a scan rate of 50 $\mu V\ s^{-1}$ between 1.5 and 4.0 V at room temperature. 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 with 1 M $LiN(CF_3SO_2)_2$ (LiTFSI) in 1,2-dimethoxyethane (DME)/1,3-dioxolane (DOL) (1:2, by weight) as electrolyte.

For electrochemical evaluation, the charge–discharge tests were performed on Land Battery test system. Working cathodes were prepared by mixing specific polymer 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 in 1 M LiTFSI in DME/DOL (1:2, by weight) solution. The cut-off voltages were 1.4 and 4.2 V.

## 3. Results and discussion

### 3.1. Material characterization

The polymers were insoluble and were characterized by FT-IR, FT-Raman, XPS, XRD, and TGA. PMTTM and PDTP showed similar FT-IR and FT-Raman spectra, this is in good agreement to their molecular structures. The FT-IR spectrum of PDTP (Fig. 1a) show bonds at 2924 $cm^{-1}$ and shoulder at 2850 $cm^{-1}$, which are stretching vibration of $CH_2$. The presence of C–S bond in the polymer backbone is supported by the absorption peaks at 718 and 673 $cm^{-1}$ ($\nu_{C-S}$). There is no peak between 600–500 $cm^{-1}$ and at 2480 $cm^{-1}$, indicating that the polymers do not contain C–Br and S–H bonds. The FT-Raman spectrum of PDTP (Fig. 1b) showed the absorption peaks at 2934 and 2901 $cm^{-1}$, which is attributed to $CH_2$ stretching vibration. The peaks at 688 and 627 $cm^{-1}$ are assigned as C–S stretching vibration, while the peaks at 279, 335, 371 $cm^{-1}$ are assigned as C–S–C skeletal deformation [17,18]. The results suggest that the polymerizations between the bromomethanes and ethane-1,2-dithiol were successful. The X-ray photoelectron spectroscopy (XPS) spectra of PMTTM and PDTP are also examined. The S2p peaks of both two polymers are located at 163.6 eV, indicating the existing of thioether sulfur in the polymers [19,20]. The S2p spectra also show that sulfur in polymers has only one valence state, which suggest the completely reaction of $Na_2S$. The FT-IR, FT-Raman, XPS spectra results confirmed that both two polymers were assuredly obtained.

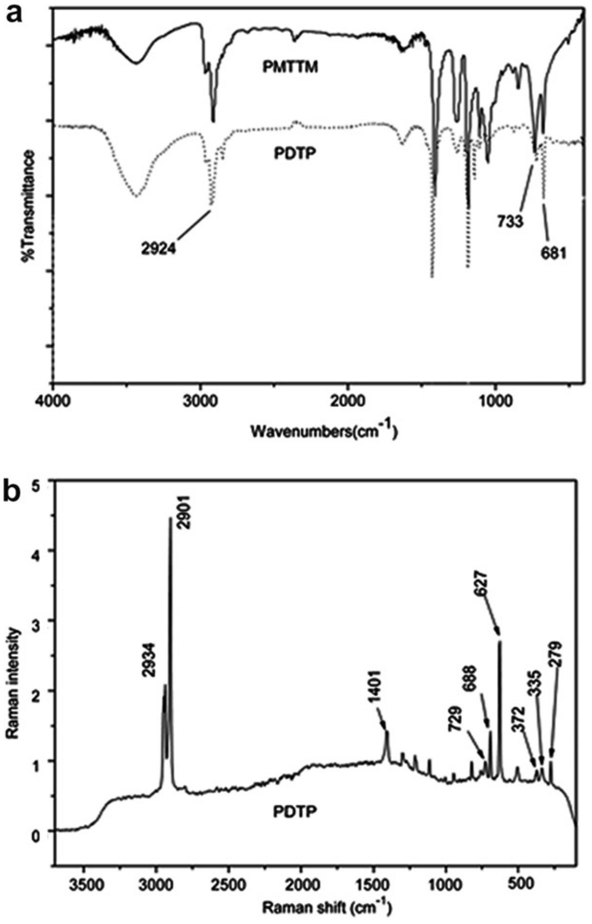

**Fig. 1.** (a) FT-IR spectra of PMTTM and PDTP and (b) Raman spectra of PDTP.

Thermal gravity analysis (TGA) of PMTTM and PDTP showed 5% weight loss at 211 and 71 °C, respectively. The decomposition temperature of PMTTM closes to that of our previous reported thioether polymer [15]. However, PDTP had much lower thermal stability than PMTTM, due to existence of low molecular weight oligomer. The X-ray diffraction (XRD) patterns showed amorphous structure for PMTTM and semicrystalline for PDTP, respectively. The morphology was consistent with their molecular structure (Scheme 1a): PMTTM was hyperbranched with S atoms in 4-dimension that was difficult to form order stacking; nevertheless, PDTP had linear molecular structure and easy to form regular stacking.

### 3.2. Electrochemical properties

Fig. 2 exhibits the cyclic voltammograms (CVs) of the first cycle of PMTTM and PDTP. PMTTM and PDTP have similar CV curves,