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# Thioether Bond Containing Polymers as Novel Cathode Active Materials for Rechargeable Lithium Batteries

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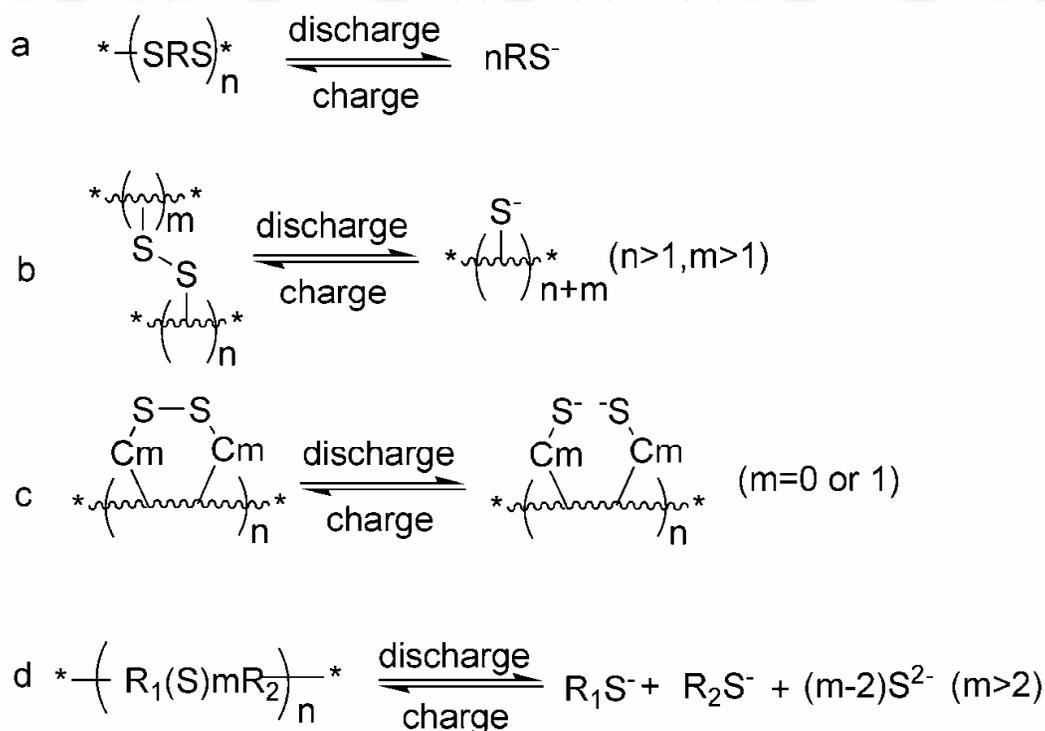
## 1. Introduction

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. To build high energy batteries, both the anode (negative electrode in batteries) and cathode (positive electrode in batteries) must have a high specific capacity. Lithium, with a theoretical specific capacity of  $3860 \text{ mA h g}^{-1}$  at the anode, may offer a high-energy density, if the cathode material also has a high capacity. Most of the cathode materials currently in use are inorganic materials, such as transition metal oxide, the specific capacity of which is very low (less than  $200 \text{ mAhg}^{-1}$ ) compared with lithium and limited the specific capacity of lithium secondary battery.

Sulfur is of high specific capacity, cheap, and environmentally benign as cathode material for rechargeable lithium batteries. It has attracted great interest and has being extensively studied. The shortcomings are its electric insulation, dissolution in solvents, and migration of  $\text{S}^{2-}$  from cathode.

Since Liu and Visco et al. (M. Liu et al., 1989; Visco et al., 1989) found that organic disulfide compounds could be used as cathode materials for rechargeable lithium battery in late 1980s, many researches have been focused on organic disulfide materials. These disulfide compounds could be divided into five categories (Scheme 1): (1) Small organic compounds (Scheme 1a), from which small molecular anions ( $-\text{SRS}-$ ) were formed in the reductive state (Z. J. Liu et al., 2005; Maddanimath et al., 2003; Tsutsumi et al., 1996, 1997, 2001). Therefore this kind of organic disulfide compounds has the similar disadvantage to elemental sulfur. (2) Disulfide ladder polymers (Scheme 1b) have polymeric backbone linking disulfide bonds and do not dissolve in solvents during discharge process. But it is difficult to recombine perfectly during charging process, so that the cycling property is poor (Huang et al., 2003; Naoi et al., 1998; Su et al., 2004). (3) Disulfide polymers have disulfide bonds as side-chains (Scheme 1c), in which the two S atoms of one disulfide bond ( $-\text{S}-\text{S}-$ ) are linked to the same polymeric main chain. Hence the recombination of disulfide bonds could be improved (Amaike & Iihama, 2006; Deng et al., 2006; J. X. Li et al., 2004; Uemachi et al., 2001; Xu et al., 2006; Xue et al., 2003). (4) Polysulfide compounds (Myachina et al., 2006; Trofimov et al.,

2002, 2006) (Scheme 1d) have high specific capacity in the first cycle and serious cycling fading due to its polysulfide structure. (5) Sulfurized polymers were synthesized through heating the mixture of organic polymer compounds and sulfur. Their structure is unclear; the electrochemical behaviors relied on the heating conditions. Some of them have high specific capacity and good cycling properties (Wang et al., 2002, 2003; Trofimov et al., 2002, 2003). The electrode reactions of all these compounds are based on the same mechanism: the cleavage-recombination of disulfide (S-S) bonds.



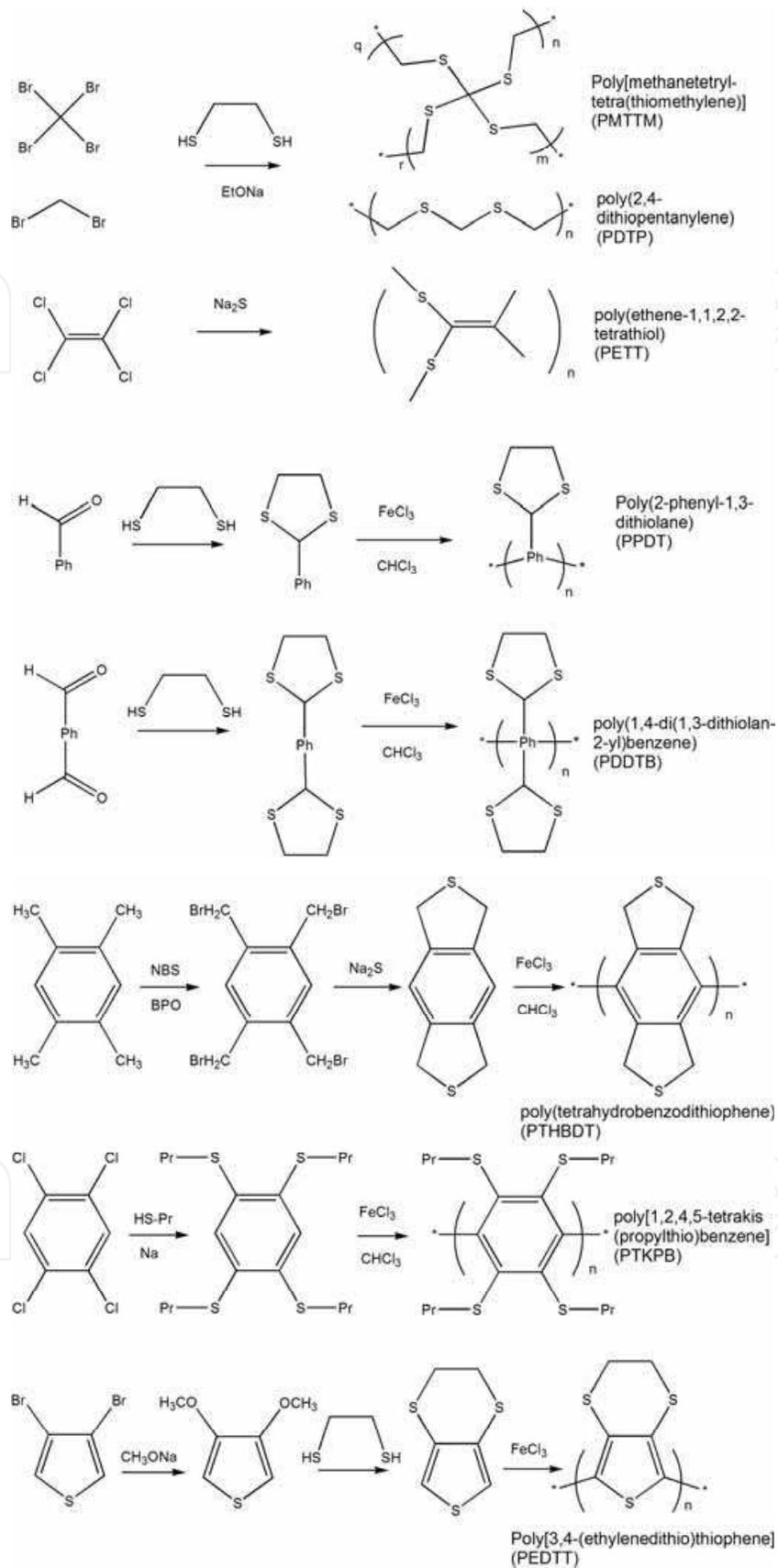
Scheme 1. Organic disulfide compounds for cathode active material in rechargeable lithium batteries

We found that thioether bond containing polymers (thioether polymers) other than conventional disulfides could also storage energy as cathode active materials and reported the research results in series papers since 2007 (Tang et al., 2008; Zhan et al., 2008, 2009; Zhang et al., 2007, 2008, 2009). The thioether polymers contain thioether (C-S-C) bonds instead of disulfide (-C-S-S-C-) bonds, in which the thioether bonds are the function groups to undergo electrode redox reaction. The redox reactions of thioether compounds (Scheme 3) do not involve bond cleavage, thus it may offer better stability as cathode active material. Furthermore, thioether bond may afford multi electron redox cathode reaction and higher specific capacity. As a novel structure, it showed some advantage and need further study and exploration. In this chapter, some thioether polymers as cathode active materials in lithium rechargeable battery are reviewed.

## 2. Structure, syntheses, and characterization of the thioether polymers

### 2.1 Structure and syntheses routes of the thioether polymers

The structure and synthesis routes of thioether polymers investigated as cathode active material in our project are summarized in Scheme 2.



Scheme 2. Structure and Synthesis Routes of thioether polymers

Here Poly[methanetetrayl-tetra(thiomethylene)] PMTTM, Poly(2,4-dithiopentanylene) PDTP, and Poly(ethene-1,1,2,2-tetrathiol) PETT are mainchain thioether polymers, in which sulfur atoms link carbon atoms to form polymeric backbones. The other polymers are side chain thioether polymers, those polymeric mainchains are consisted of conjugating aromatic moieties, with thioether side chains as pendants. Among them Poly(2-phenyl-1,3-dithiolane) PPDT, Poly(1,4-di(1,3-dithiolan-2-yl)benzene) PDDTB, poly(tetrahydrobenzodithiophene) PTHBDT, and poly[1,2,4,5-tetrakis(propylthio)benzene] PTKPTB have polyphenylene main chain, linking thiolane on benzene moieties as pendants. Similarly, Poly[3,4-(ethylenedithio)thiophene] PEDTT has polythiophene backbone, linking cyclo-thiolane on the 3,4- position on thiophene ring.

The syntheses of thioether polymers are facile and listed in Scheme 2. The mainchain thioether polymers were prepared by condensation polymerization. The conjugated polymers were prepared by facile oxidation coupling polymerization.

Most of thioether polymers were insoluble in organic solvents and were characterized by FT-IR, FT-Raman, XPS (X-ray photoelectron spectroscopy), and elemental analysis.

## 2.2 Materials characterization

In FT-IR spectra, the absorption peaks of C-S stretching vibration in C-S-C bonds usually appear around 700  $\text{cm}^{-1}$ . In FT-Raman spectra, the peaks of C-S stretching vibration are between 700-600  $\text{cm}^{-1}$ , and the peaks of C-S-C skeletal deformation are located at 270 to 380  $\text{cm}^{-1}$ . In XPS spectra, the binding energy peak of S2p in thioether is at 163.6 eV or 164.2 eV. Most of the thioether polymers show amorphous in XRD curves.

## 3. Electrochemical properties

### 3.1 Cyclic voltammetry measurement

The cyclic voltammetry (CV) tests were carried out at a scan rate of 50  $\mu\text{Vs}^{-1}$  between 1.5 and 4.4 V at room temperature. The cathode was prepared by mixing polymer powder with carbon black and Teflon in a weight ratio of 4:4:2, the Li foil was used as the reference electrode and counter electrode with 1M LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> (LiTFSI) in 1,2-dimethoxyethane (DME)/1,3-dioxolane(DOL) (1:2, by weight) as electrolyte. The cyclic voltammograms (CVs) results of the first cycle of various thioether polymers are summarized in Table 1.

Thioether Polymer	Oxidation Peaks/V <sup>b</sup>	Reduction Peaks/V <sup>b</sup>
poly[methanetetrayl-tetra(thiomethylene)] PMTTM	2.20, 3.9	1.89, 2.00
poly(2,4-dithiopentanylene) PDTP	2.16, 3.9	1.72, 1.85
poly(ethene-1,1,2,2-tetrathiol) PETT	2.23, 4.03	2.00, 2.38
poly(2-phenyl-1,3-dithiolane) <sup>a</sup> PPDT	2.71, 3.60	1.55, 1.85
poly(1,4-di(1,3-dithiolan-2-yl)benzene) <sup>a</sup> PDDTB	1.95, 3.60	1.65, 1.75
poly(tetrahydrobenzodithiophene) PTHBDT	3.4-4.2	1.7-2.2, 2.5-2.8

<sup>a</sup> Cyclic voltammograms were tests through powder microelectrodes packed with only the pure thioether polymers in 1M LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, 1,2-dimethoxyethane/1,3-dioxolane (1:2, by weight) solution at room temperature; scan rate, 5mVs<sup>-1</sup>.

<sup>b</sup> Li foil was used as the reference electrode

Table 1. CV redox peaks of the thioether polymers

There are two oxidation peaks and two reduction peaks for all of the thioether polymers. The two oxidation peaks usually appear around 2V and 4V, while the reduction peaks are between 1.5-2.5V. The high oxidative peak indicates that the polymer may be charged at higher voltage as cathode material. But the reductive peaks are in lower voltage, which imply a lower discharge voltage.

### 3.2 Charge-discharge tests

The charge-discharge tests were performed on Land Battery test system. Working cathodes was prepared by mixing specific polymer powder with carbon black and Teflon in a weight ratio of 4:4:2. Lithium foil was used as the anode and the tests was processed at a rate of 50 mA/g in 1M LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> (LiTFSI) in 1,2-dimethoxyethane (DME)/1,3-dioxolane(DOL) (1:2, by weight) solution. The cut-off voltages were 1.5V and 4.4V.

#### 3.2.1 The cycling specific capacity and proposed redox reaction

The cycling specific capacity of the thioether polymers is summarized. In Fig.1 Poly[methanetetrayl-tetra(thiomethylene)] (PMTTM) displays specific capacity of 504 mAhg<sup>-1</sup> at the third cycle, which decreases rapidly and maintains the value around 200 mAhg<sup>-1</sup> at the 16th cycle. Similarly, Poly(2,4-dithiopentanylene) (PDTP) exhibits a maximal specific capacity of 174 mAhg<sup>-1</sup> and a stable specific capacity about 100 mAhg<sup>-1</sup> between 16th and 50th cycles. The cycling capacity results of aliphatic thioether polymers suggest that polymers with thioether groups alone can offer energy storage without disulfide bond or conjugated polymeric main chain. There are only three kinds of bonds in PMTTM and PDTP: C-C, C-H, and C-S-C bonds. The saturated C-C and C-H bonds cannot afford redox reaction, hence it can be deduced that thioether bond is the only electrochemical active function group to offering energy storage. The oxidation of thioether had been studied and reported in literatures (Gilbert et al., 1973; Glass et al., 1977, 1990; Momose et al, 1987; Musker & Roush, 1978; Musker et al., 1978; Musker, 1980; Symons, 1974; Werst, 1991; Wilson, 1979), which illuminated the formation and existence of thioether cation.

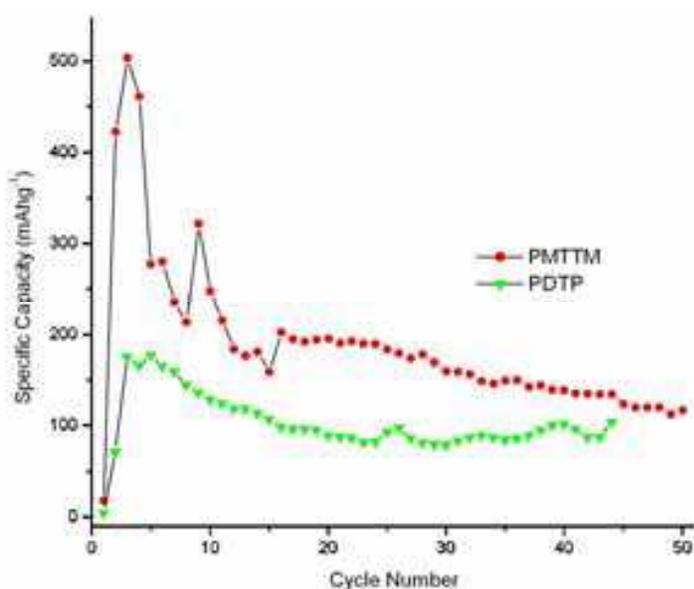


Fig. 1. Cycling capacity of poly[methanetetrayl-tetra(thiomethylene)] (PMTTM) and poly(2,4-dithiopentanylene) (PDTP)

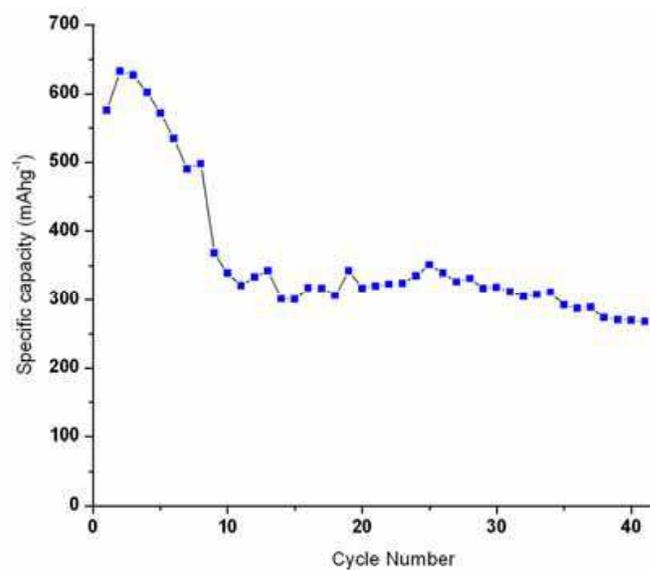


Fig. 2. Cycling capacity of Poly(ethene-1,1,2,2-tetrathiol) (PETT) In Fig.2 Poly(ethene-1,1,2,2-tetrathiol) (PETT) displays a stable discharge specific capacity value of ca. 300 mAhg<sup>-1</sup> from the 10th cycle to the 40th cycle and shows maximal specific capacity of 632 mAhg<sup>-1</sup> at the second cycle. The coulomb efficiency is at high level of 90% from the 10th cycle to the 40th cycle. It shows more stable discharge specific capacity compare to saturate aliphatic thioether polymers; indicating vinyl structure benefits the electrode reaction.

In Fig. 3 Poly(2-phenyl-1,3-dithiolane) (PPDT) displays a specific capacity of 129 mAhg<sup>-1</sup> at the first cycle and a specific capacity of 238 mAhg<sup>-1</sup> at the second cycle, and then it decreases and maintains the value around 100 mAhg<sup>-1</sup>. But Poly(1,4-di(1,3-dithiolan-2-yl)benzene) (PDDTB) exhibits a maximal specific capacity of 378 mAhg<sup>-1</sup>, and a stabilized specific capacity of about 300 mAhg<sup>-1</sup>. The two polymers have same mainchain and pendant but different thiolane contents; hence the specific capacity value is determined by its dithiolane contents.

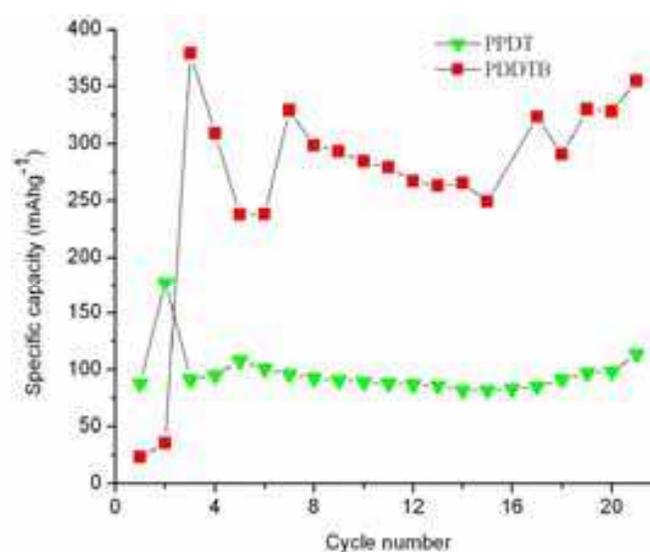


Fig. 3. Cycling capacity of Poly(2-phenyl-1,3-dithiolane) (PPDT) and Poly(1,4-di(1,3-dithiolan-2-yl)benzene) (PDDTB)

The initial discharge specific capacity of Poly[1,2,4,5-tetrakis(propylthio)benzene] PTKPB is around  $200 \text{ mAhg}^{-1}$ . From the second cycle on, the specific capacity decreases dramatically and becomes stable after the tenth cycle (Fig. 4).

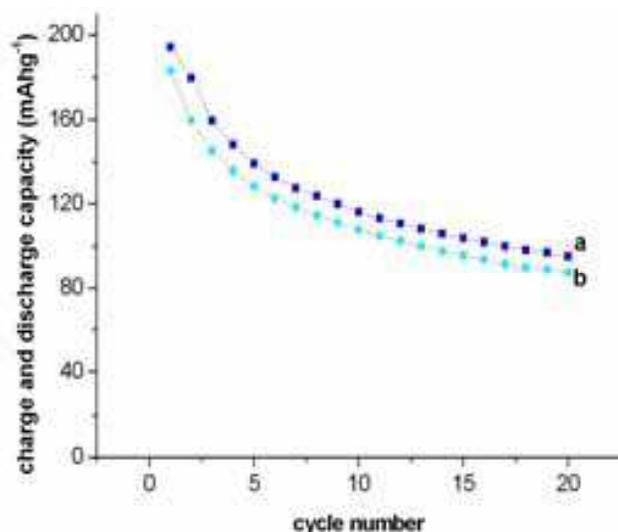


Fig. 4. Cycle life of Poly[1,2,4,5-tetrakis(propylthio)benzene] PTKPB (a) charge and (b) discharge

The discharge specific capacity of Poly(tetrahydrobenzodithiophene) PTHBDT was above  $550 \text{ mAhg}^{-1}$ . The maximal specific capacity of  $820 \text{ mAhg}^{-1}$  was obtained at the 9th cycle. After 16 cycles, the specific capacity was above  $550 \text{ mAhg}^{-1}$  (Fig.5). Similarly, the polythiophene mainchain thioether polymer, Poly[3,4-(ethylenedithio)thiophene] PEDTT showed discharge specific capacity of  $600 \text{ mAhg}^{-1}$  at 3rd cycle and ca.  $400 \text{ mAhg}^{-1}$  from 19th cycle to 34th cycle (Fig. 6) [29].

Generally, the specific capacity of polyphenylene and polythiophene mainchain thioether polymers, PPDT, PDDTB, and poly[1,2,4,5-tetrakis(propylthio)benzene], looked more stable than that of aliphatic thioether polymers, PDTP and PMTTM. It means that electric conductive mainchain is benefit to the charge-discharge behavior of the thioether polymers.

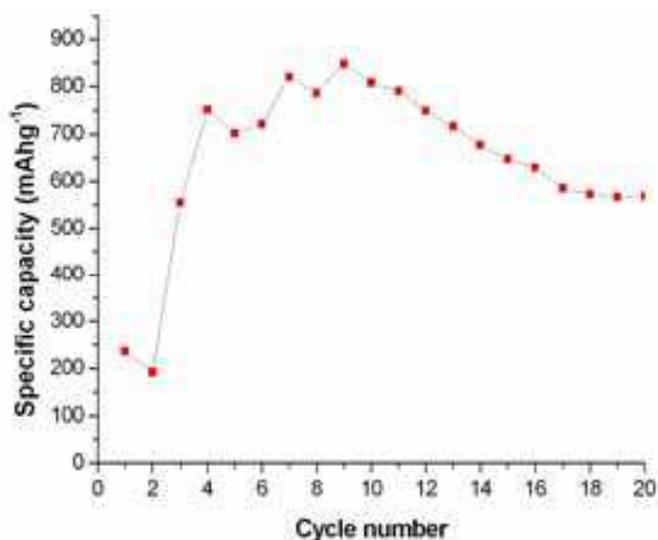


Fig. 5. Specific capacity ( $\text{mAhg}^{-1}$ ) of poly(tetrahydrobenzodithiophene) vs. cycle numbers.

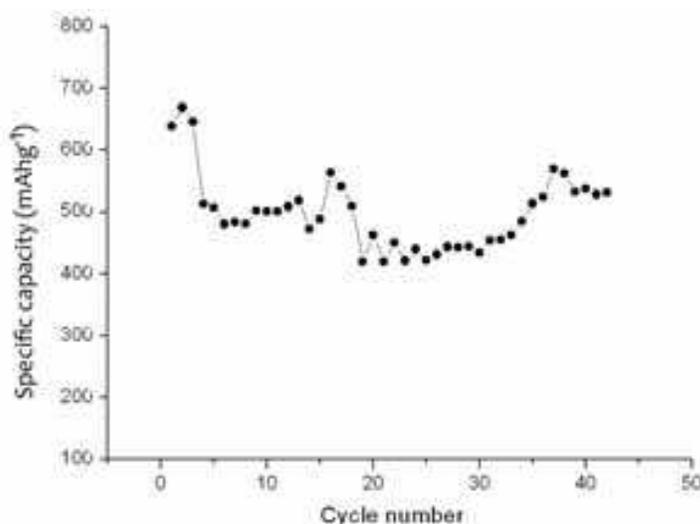
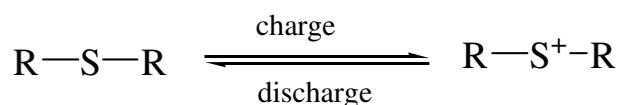


Fig. 6. Specific capacity of poly[3,4-(ethylenedithio)thiophene]

The measured maximal specific capacity of the thioether polymers are listed in Table 2. According to proposed redox reaction on S atom of thioether bond (Scheme 3), the theoretic specific capacity of the thioether polymers was calculated and listed in Table 2. It is very know that conjugated electro conductive polymers have discharge specific capacity come from “doping” mechanism as cathode active materials in lithium batteries, but the values are very lower hence are neglected in this paper. It can be seen that for most of thioether polymers their maximal specific capacity value is roughly agree with the theoretical specific capacity. One exception is Poly[3,4-(ethylenedithio)thiophene] PEDTT, its maximal specific capacity is 650 mAh g<sup>-1</sup>, higher than its theoretic value. But from the 19th cycle to the 34th cycle, the discharge specific capacity is ca. 400-450 mAh g<sup>-1</sup> (Fig.6), still agrees with the theoretic value. Generally, the results give support to our proposed mechanism.

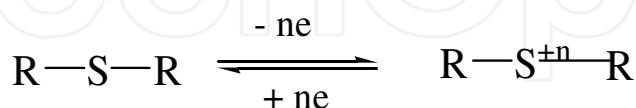


Scheme 3. Single electron cathode redox of the thioether polymers

Thioether Polymer	theoretic value	Practical maximal value
poly[methanetetryl-tetra(thiomethylene)] PMTTM	570	504
poly(2,4-dithiopentanylene) PDTP	505	200
poly(ethene-1,1,2,2-tetrathiol) PETT	595	632
poly(2-phenyl-1,3-dithiolane) PPDT	294	238
poly(1,4-di(1,3-dithiolan-2-yl)benzene) PDDTB	374	378
poly[1,2,4,5-tetrakis(propylthio)benzene] PTKPB	288	200
poly(tetrahydrobenzodithiophene) PTHBDT	279	820
Poly[3,4-(ethylenedithio)thiophene] PEDTT	467	650

Table 2. The theoretic and practical maximal specific capacity of thioether polymers (mAhg<sup>-1</sup>)

But Poly(tetrahydrobenzodithiophene) PTHBDT has much higher specific capacity than its theoretic specific values. The theoretic specific capacity of PTHBDT is only 279 mAhg<sup>-1</sup>, but its practical discharge maximal specific capacity is of 820 mAhg<sup>-1</sup> at the 9th cycle and at most cycle the discharge specific capacity is above 500 mAhg<sup>-1</sup> (Fig 5). New redox mechanism can be deduced from the rare high specific capacity: multi electrons are transferred on one sulfur atom in this thioether polymer [28]. To represent multi-electron redox reaction, a general reaction formula is proposed in Scheme 4. Here n is the electron number involved in the electrode redox. Corresponding to the specific capacity of 500 mAhg<sup>-1</sup> and 820 mAhg<sup>-1</sup>, the electron number is 2 and 3 respectively.



Scheme 4. Multi-electron Redox reaction of thioether polymer in lithium battery

Poly[3,4-(ethylenedithio)thiophene] PEDTT showed high discharge specific capacity above 650 mAhg<sup>-1</sup> (Fig. 6) at 3rd, the maximal value is also higher than that of theoretic value of single electron redox, which may due to the multi-electron redox reaction too.

In addition, solvents are important to the cathode redox reaction. The oxidation of thioether can be facilitated by electro-donating group (Glass, 1977), and thioether cation can be stabilized by electron donation (Wilson et al., 1979). The specific capacity results of thioether polymers were tested with 1, 2-dimethoxyethane and 1, 3-dioxolane mixture as electrolyte. Both two electrolytes are electron donors; the electrolyte may be helpful to the redox of thioether group.

### 3.2.2 The charge-discharge curves

The charge-discharge curves of various thioether polymers are summarized and shown in Fig. 7 to Fig.12.

The charge-discharge curves of poly[methanetetryl-tetra(thiomethylene)] PMTTM are shown in Fig.7. It can be seen that the capacity plateaus of the two polymers are at ca. 2.2V on discharge and 2.8 and 3.8V on charge, corresponding to the oxidative potential and reduction potential in CV (Table 2).

The charge-discharge curves of poly(ethene-1,1,2,2-tetrathiol) PETT are shown in Fig.8. The charge curve contains two plateaus: the low plateaus are at 2.6–2.8V and the high plateaus are between 3.3 and 3.8 V. But the discharge voltage is at 2.7–2.0 V. It showed higher discharge voltage than saturate aliphatic thioether polymer, poly[methanetetryl-tetra(thiomethylene)]. The results suggest that molecular structure played important role in the electrochemical behavior of thioether polymer. However, the discharge voltage fading was dramatic for the two mainchain thioether polymers. Fig. 9 to Fig. 11 show charge - discharge curves of the three polyphenylene mainchain thioether polymers—Poly(1,4-di(1,3-dithiolan-2-yl)benzene) PDDTB, Poly[1,2,4,5-tetrakis(propylthio)benzene] PTKPB, and poly(tetrahydrobenzodithiophene) PTHBDT. There are well-defined plateau for charge and discharge curves, the voltages are very close to each other : 2.4 V on charge and 2.3 V on discharge. These results indicated that high voltage may come from the polyphenylene backbone, those high oxidation potential afforded high discharge voltage. In addition, their charge-discharge voltages are very close to each other, which mean higher voltage efficiency than the mainchain thioether polymers.

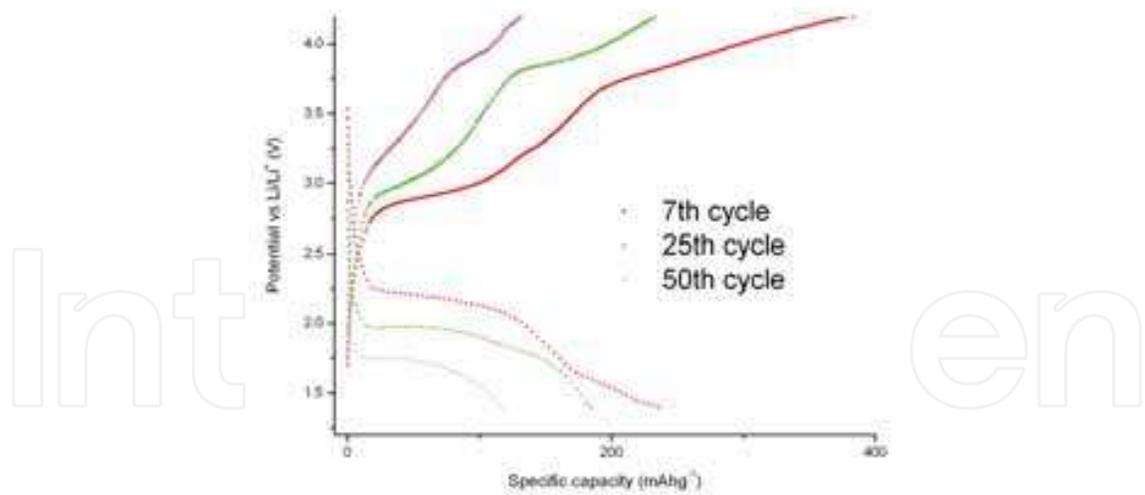


Fig. 7. The charge-discharge curves of poly[methanetetrayl-tetra(thiomethylene)]

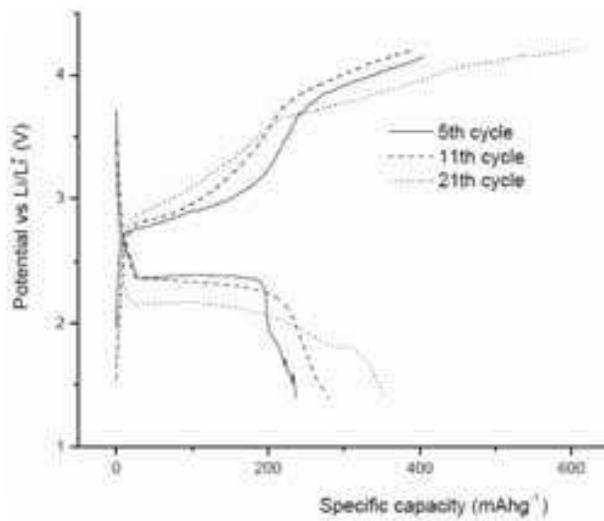


Fig. 8. The charge-discharge of poly(ethene-1,1,2,2-tetrathiol) PETT

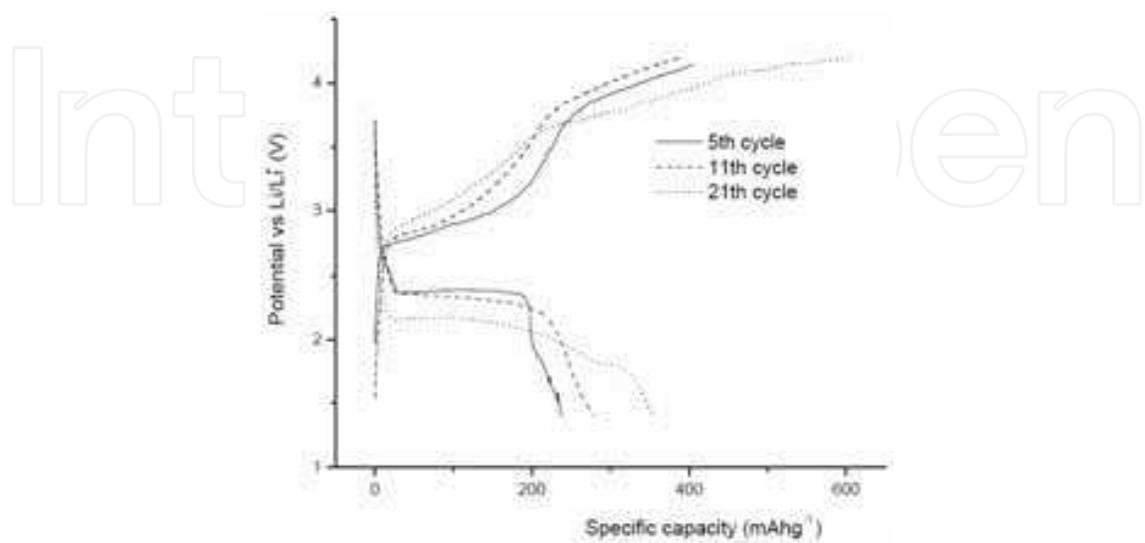


Fig. 9. Charge-discharge curves of poly(1,4-di(1,3-dithiolan-2-yl)benzene) PDDTB

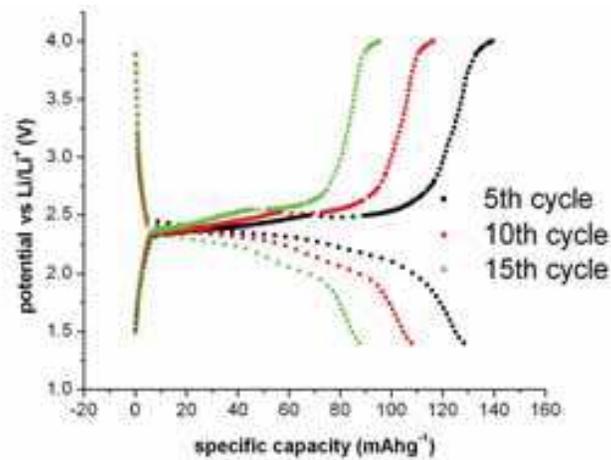


Fig. 10. Charge-discharge curves of poly[1,2,4,5-tetrakis(propylthio)benzene] PTKPB

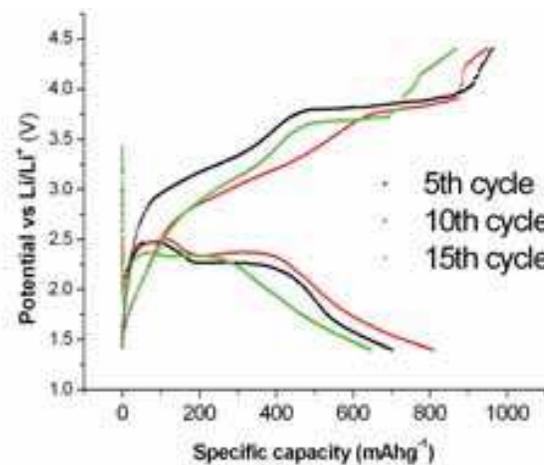


Fig. 11. The charge-discharge curves of Poly(tetrahydrobenzodithiophene) PTKP

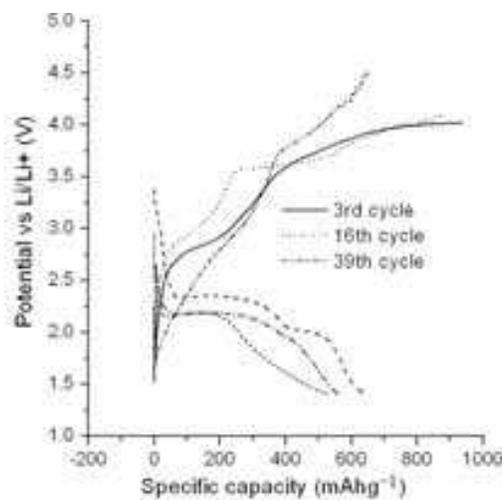


Fig. 12. Charge-discharge curves of Poly[3,4-(ethylenedithio)thiophene] PEDTT

Further, the voltage fading is slighter than those mainchain thioether polymers. The results mean that electric conductive mainchains improved the charge-discharge behavior of the thioether polymers.

The charge - discharge curves of Poly[3,4-(ethylenedithio)thiophene] PEDTT (Fig. 12) show two charge plateaus at ca. 2.8V and 4.0 V and discharge plateaus at ca. 2.2 V, respectively. The charge voltage and discharge voltage correspond to the oxidative potentials and reductive potentials in the CV test, as shown in Table 1. The gap between charge voltage and discharge voltage indicates the lower voltage efficiency.

#### 4. Conclusion

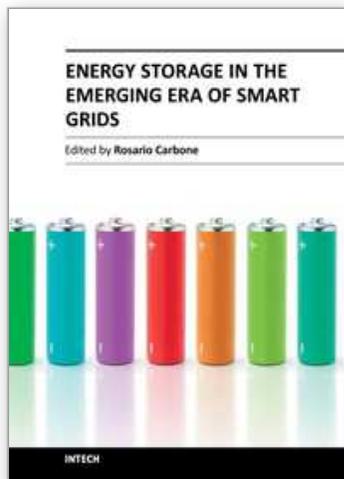
Thioether polymers were prepared by facile methods and tested as novel cathode active materials in lithium secondary batteries. The thioether polymers showed high discharge specific capacity up to 800 mAhg<sup>-1</sup>, discharge voltage above 2V, and good cycling stability. The results demonstrated that thioether polymers are cathode active material and thioether bond(C-S-C) is the function group to offer cathode redox reaction. It is proposed that S cation formed during charge-discharge process and somehow multi-electron redox reaction took place, which imparted high specific capacity. Electric conductive mainchain can improve the charge -discharge performance of the thioether polymers.

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## **Energy Storage in the Emerging Era of Smart Grids**

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Reliable, high-efficient and cost-effective energy storage systems can undoubtedly play a crucial role for a large-scale integration on power systems of the emerging “distributed generation” (DG) and for enabling the starting and the consolidation of the new era of so called smart-grids. A non exhaustive list of benefits of the energy storage properly located on modern power systems with DG could be as follows: it can increase voltage control, frequency control and stability of power systems, it can reduce outages, it can allow the reduction of spinning reserves to meet peak power demands, it can reduce congestion on the transmission and distributions grids, it can release the stored energy when energy is most needed and expensive, it can improve power quality or service reliability for customers with high value processes or critical operations and so on. The main goal of the book is to give a date overview on: (I) basic and well proven energy storage systems, (II) recent advances on technologies for improving the effectiveness of energy storage devices, (III) practical applications of energy storage, in the emerging era of smart grids.

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