Short communication

Sulfides organic polymer: Novel cathode active material for rechargeable lithium batteries

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Abstract

Two novel sulfide polymers, poly(2-phenyl-1,3-dithiolane) and poly[1,4-di(1,3-dithiolan-2-yl)benzene], were prepared via facile oxidative-coupling polymerization under ambient conditions, characterized by FT-IR, XRD, TGA and elemental analysis, and were tested as cathode materials in rechargeable lithium battery. The charge–discharge tests showed that the specific capacity of poly[1,4-di(1,3-dithiolan-2-yl)benzene)] was 378 mAh g^{-1} at the third cycle, and retained at 300 mAh g^{-1} after 20 cycles. The specific capacity of poly(2-phenyl-1,3-dithiolane) was 117 mAh g^{-1} at the second cycle, and retained at 100 mAh g^{-1} after 20 cycles. The results indicated that thiolane group could be used as cathode active function group for lithium secondary batteries and the novel electrode reaction is proposed tentatively.
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Keywords: Organic sulfide polymers; Rechargeable lithium battery; Cathode active materials; Specific capacity

1. Introduction

Organic disulfides have attracted much attention as cathode materials since it was discovered that disulfide bridge could go through reversible redox reaction for energy storage and release in the 1980s [1,2]. Later, varies organic disulfide compounds have been synthesized and studied, such as poly(1,4-phenylene-1,2,4-dithiazol-3′,5′-yl) [3], cyclic disulfide polyamides [4], copolymer of 2,2-dithiodianiline and aniline [5], dimercaptan 2,5-dimercapto-1,3,4-thiadiazole (DMcT) [6], poly(bis(phenylamino)disulfide) [7], poly(4,6-dihydro-1H-[1,2]dithiino[4,5-c]pyrrole) [8], benzene-based polyorganodisulfide [9] and so on. We have reported the synthesis of anthracene based organic disulfide cathode active materials, anthra[1′,9′,8′-b,c,d,e] [4′,10′,5′-b′,c′,d′,e′] bis-[1,6,6a(6a-SIV)-trithia]pentalene (ABTH) and its homopolymer (PABTH) [10]. In the subsequent study, we have found that the S atom of the C–S–C bond could accept electrons or carry positive charges without the disulfide bridges. Moreover, C–S–C bonds are more stable than C–S–S–C bonds. Hence sulfide compounds may be potential candidates as cathode active materials. To this end, we designed novel polymers with sulfide side-chains to accept or donate electrons and polyphenylene as main chain to offer good electric conductivity. Two polymers, poly(2-phenyl-1,3-dithiolane) (PPDT) and poly(1,4-di(1,3-dithiolan-2-yl)benzene) (PDDTB) were synthesized, characterized and tested as cathode materials; the structure of the compounds and synthetic routes are depicted in Scheme 1; the electrochemical properties and energy storage abilities are described vide infra. The charge–discharge tests exhibited that both polymers were electrochemically active as cathode materials in rechargeable batteries, which provides potential for a new filed of rechargeable organic cathode materials.

2. Experimental

2.1. Materials

All reagents were used as received unless otherwise indicated. The monomers, 2-phenyl-1,3-dithiolane and 1,4-di(1,3-dithiolan-2-yl)benzene, were prepared by condensation of benzaldehyde and terephthalaldehyde with ethane-1,2-dithiol, respectively, according to literature procedure [11]. The structures of 2-phenyl-1,3-dithiolane (PDT) and 1,4-di(1,3-
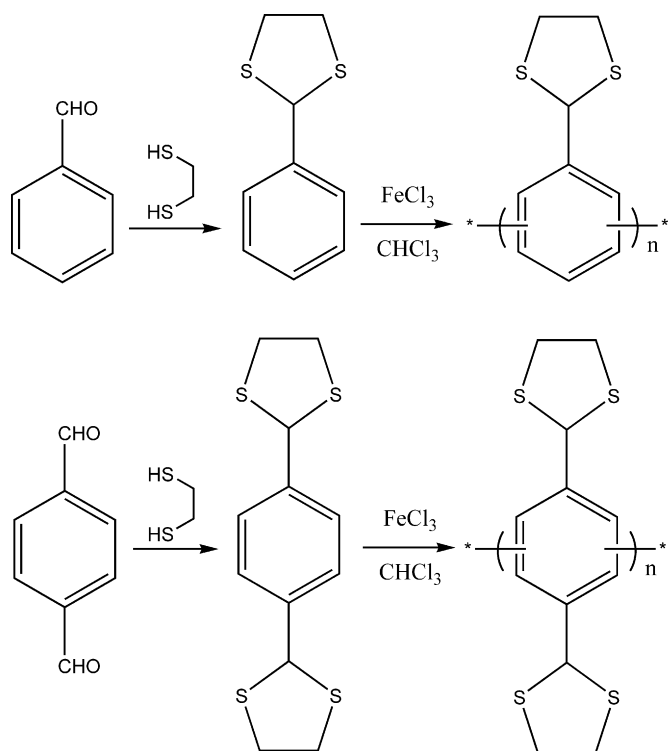
Scheme 1. The synthetic routes of poly(2-phenyl-1,3-dithiolane) and poly(1,4-di(1,3-dithiolan-2-yl)benzene).

dithiolan-2-yl)benzene (DDTB) were confirmed by FT-IR, ^{1}H NMR, and mass spectrometry. 2-Phenyl-1,3-dithiolane: IR: 3020, 2964, 2921, 1598, 1580, 1493, 1422, 1072, 852, 832, 776, 723, 697, 583 cm^{−1}; ^{1}H NMR (CDCl$_3$, 300 M) δ: 7.55–7.27 (5H, m), 5.66 (1H, s), 3.51–3.34 ppm (4H, m); MS (M[+], 182). 1,4-Di(1,3-dithiolan-2-yl)benzene: IR: 3020, 2924, 1509, 1420, 1280, 860, 810, 688, 671, 532 cm^{−1}; ^{1}H NMR (CDCl$_3$, 300 M) δ: 7.7.46 (4H, s), 5.61 (2H, s), 3.52–3.31 ppm (4H, m); MS (M[+], 286).

A typical polymerization procedure is depicted as below: 3.70 g anhydrous FeCl$_3$ was added to a solution of 1.17 g 1,4-di(1,3-dithiolan-2-yl)benzene in 30 ml CHCl$_3$ under slow nitrogen flow. Then the solution was stirred at room temperature for 72 h. After the reaction was completed, the chloroform was removed under reduced pressure. The solid residue was washed with dilute hydrochloric acid, distilled water, and then was extracted by ethanol in Soxhlet extractor. The polymer was dried at 60 °C in oven and 0.58 g brownish red powder was obtained. Poly(1,4-di(1,3-dithiolan-2-yl)benzene): IR: 3014, 2909, 1603, 1505, 1410, 1209, 1181, 1108, 1017, 911, 824, 730, 678, 650 cm^{−1}; element analysis (%) C 48.54, H 5.48, S 47.45 (found). Poly(2-phenyl-1,3-dithiolane): IR: 3015, 2915, 1594, 1578, 1445, 1405, 1205, 1173, 907, 771, 687, 646 cm^{−1}; element analysis (%) C 61.75, H 4.61, S 33.38 (found).

2.2. Apparatus and procedures

FT-IR spectra were recorded on a NICOLET AVATAR 360 FT-IR spectrometer with KBr pellets. 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^{−1}. XRD patterns of powder specimens were obtained on a D8ADVANCE X-ray diffractometer. Elemental analysis was determined on a Thermo Quest Italia S.P.A FlashEA1112 SERIES.

The cyclic voltammetry (CV) tests were carried out on CH Instruments electrochemical workstation (CHI 660B) in 1 M LiN(CF$_3$SO$_2$)$_2$/1,2-dimethoxyethane/1,3-dioxolane (1:2, by weight) solution at a scan rate of 5 mV s^{−1} between 1.5 and 4.0 V. The sulfide polymer powder microelectrode was used as working electrode, The Li film was used as the reference electrode and counter electrode. The preparation detail of powder microelectrode was described in article [12], and the powder is only the pure sulfide polymer without graphite. The cyclic voltammetry (CV) tests of monomer DDTB was carried out using Pt microelectrode as working electrode and Li film as the reference electrode and counter electrode.

For electrochemical evaluation, 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 LiN(CF$_3$SO$_2$)$_2$, 1,2-dimethoxyethane/1,3-dioxolane (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 structures of 2-phenyl-1,3-dithiolane (PDT) and 1,4-di(1,3-dithiolan-2-yl)benzene (DDTB) were characterized by FT-IR, ^{1}H NMR and MS. After polymerization, the products were insoluble and were characterized by FT-IR, XRD, TGA, and elemental analysis. FT-IR spectra of poly(2-phenyl-1,3-dithiolane) (PPDT) and poly(1,4-di(1,3-dithiolan-2-yl)benzene) (PDDTB) showed peaks around 1600 cm^{−1}, which were attributed to the C–C vibration of the benzene; the peaks at 684 cm^{−1} were attributed to the C–S stretching vibration, which also appeared in the FT-IR spectra of their monomers. The strong peak at 910 cm^{−1}, attributed to the isolated H of the benzene, was observed in the polymers but could not be found in the monomers, which indicated the polymerization of the monomers. The X-ray diffraction (XRD) patterns manifested that the two polymers were completely amorphous. It is envisioned that the large pendants of dithiolane resulted in irregular stacking of the polymer molecules. Thermal gravity analysis (TGA) of the polymers revealed that the decomposition of PPDT was started at 220 °C (5% weight loss) and PDDTB at 200 °C. It is well known that polyphenylene has very high decomposing temperature up to 400 °C, so obviously the low thermo-stability is owing to the introduction of thiolane groups.

3.2. Electrochemical properties

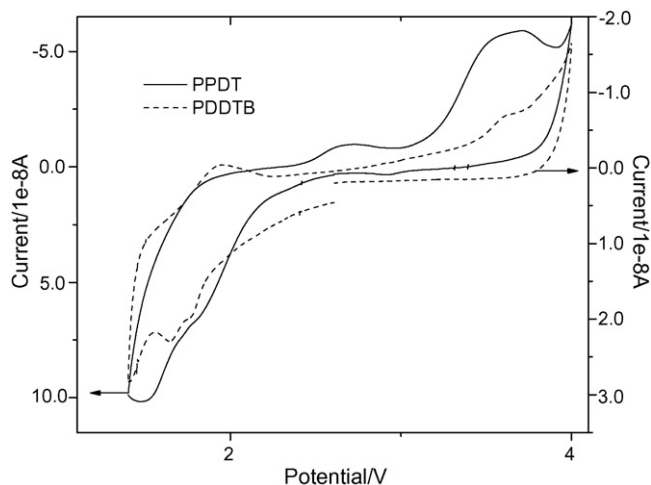Fig. 1 showed the cyclic voltammogramms (CVs) of the first cycle of pure PPDT and PDDTB powders without graphite in

Fig. 1. Cyclic voltammograms of powder microelectrodes packed with only the pure sulfide polymers in 1 M LiN(CF$_3$SO$_2$)$_2$, 1,2-dimethoxyethane/1,3-dioxolane (1:2, by weight) solution at room temperature; scan rate, 5 mV s^{-1}.

cavity microelectrode at a scan rate of 5 mV s^{-1} and potential between 1.4 and 4.0 V. It could be seen that PPDT had two oxidation peaks at 2.71 and 3.60 V versus Li/Li$^+$ and two reduction peaks at 1.55 and 1.85 V versus Li/Li$^+$. The oxidation peaks of PDDTB appeared at 1.95 and 3.60 V, and the reduction peaks at 1.65 and 1.75 V. There were two pairs of redox peaks for both of the polymers. The cyclic voltammogramms of DDTB showed two oxidation peaks at 1.95, 3.80 V and broad reduction peak between 1.5 and 2.4 V, which was similar to its polymer PDDTB.

The cycling capacity of the polymers is shown in Fig. 2. PPDT displayed a specific capacity of 129 mAh g^{-1} at the first cycle and a specific capacity of 238 mAh g^{-1} at the second cycle, and then it decreased and maintained the value at around 100 mAh g^{-1}. Similarly, PDDTB exhibited a maximal specific capacity of 378 mAh g^{-1}, and a stabilized specific capacity of about 300 mAh g^{-1}. This trend can also be found in the case of the organic disulfide polymer cathode materials that the specific
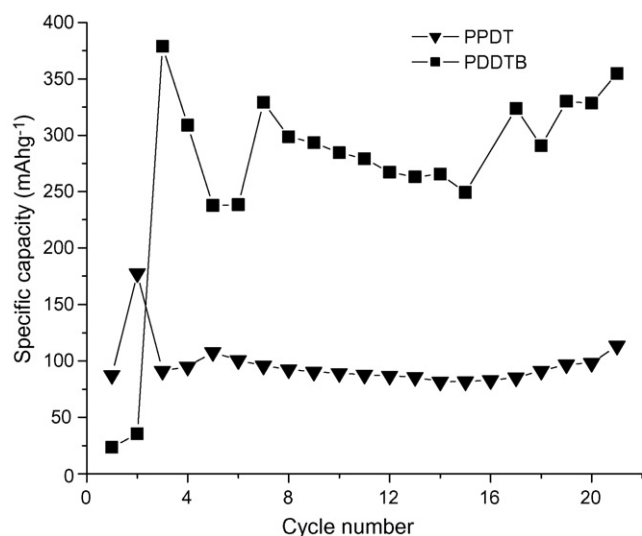

Fig. 2. Specific capacity (mAh g^{-1}) of polymers vs. cycle numbers (current density 50 mA g^{-1}).
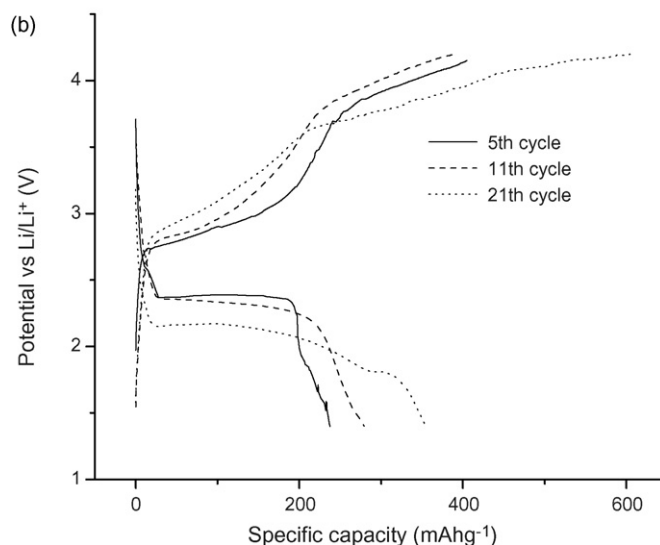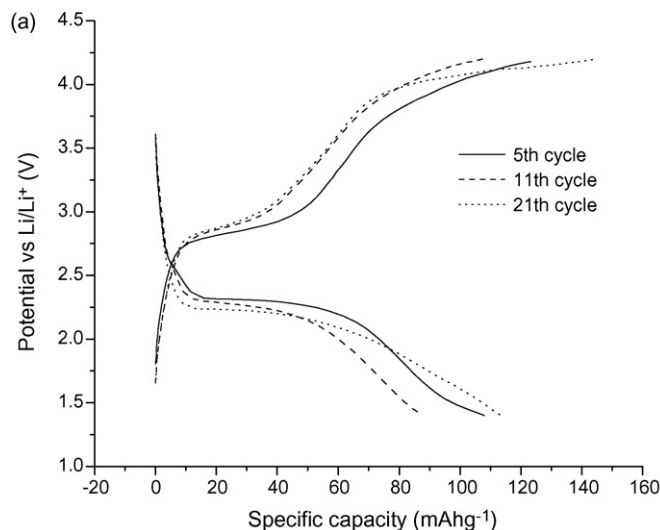

Fig. 3. (a) The capacity–voltage curves of charge–discharge of poly(2-phenyl-1,3-dithiolane). (b) The capacity–voltage curves of charge–discharge of poly(1,4-di(1,3-dithiolan-2-yl)benzene).

capacity decreased rapidly from the maximum to a stabilized value [8,9]. But the specific capacity of disulfides declined more dramatically than that of sulfides: the decrease of the disulfide was around 200 mAh g^{-1}; while that of the sulfide was only around 70 mAh g^{-1}. Therefore, sulfide polymers cathode electrodes should be more stable than the disulfide ones. The specific capacity of monomer DDTB reached 230 mAh g^{-1} at third circle but decreased dramatically to 75 mAh g^{-1} at the 10th cycle, indicating a rapid migration from the cathode during the charge–discharge process. The results illustrate that the polymers had better cycle stability than their monomers as cathode active materials. PDDTB, possessing four thiolane groups on one phenyl moiety, displayed much higher values of specific capacity than those of PPDT; which indicated that the specific capacity was related to the content of thiolanes and the electrode redox should take place on the S atom of the C–S–C bond.

The charge–discharge curves are shown in Fig. 3a and b. It can be seen that the capacity plateaus of the two polymers
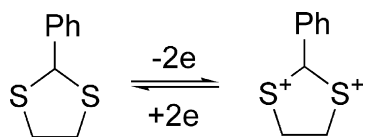
Scheme 2. Tentatively proposed mechanism for charge–discharge process of organic sulfide.

were at ca. 2.2 V on discharge and 2.8 and 3.8 V on charge. The charge behavior is quite different from those of disulfide polymers [4,8,13]: there is only one plateau above 3.0 V for disulfides but two plateaus for the sulfides. It clearly indicates that the electrode reaction of sulfide is different from that of disulfide. Though for the two sulfide polymers, limitations such as low coulombic efficiency and low voltage efficiency exist, we believe that this preliminary research provides potential of a new field for organic cathode material of lithium battery, and the electrochemical properties of sulfide compounds would be better in further study, just as when the organicdisulfide compounds were discovered and used as cathode materials in 1980s.

The electrode reaction mechanism is not clear yet and still under investigation at present, we envision that sulfide is the functional group to offer energy storage and the possible electrode reaction is proposed and depicted in Scheme 2. The anodic oxidation of dithioacetals including monomer 2-phenyl-1,3-dithiolane had been investigated and the mechanism was discussed by Simonet and co-workers [14], which was consistent with the existence of dicationic intemidiate of S. If the cations can be reduced to dithiolane, that is, the electrode reaction is reversible, then the reaction is an energy storage process and the compound can be used as electrode active material. To avoid bond-cleavage, sensitive nucleophiles were absent and the compounds worked as cathode of lithium batteries in this work. The electrode reaction is proposed as single electron redox reaction for one S atom, according to this reaction, the theoretic specific capacity of poly(2-phenyl-1,3-dithiolane) and poly(1,4-di(1,3-dithiolan-2-yl)benzene) is 294 and 374 mAh g^{-1}, respectively, which is roughly agrees with the maximum discharge capacity.

4. Conclusions

The two sulfide polymers, poly(2-phenyl-1,3-dithiolane) and poly(1,4-di(1,3-dithiolan-2-yl)benzene), showed obvious electrochemical activity as cathode active materials for rechargeable lithium battery. Sulfide was proposed as the functional group of energy storage. To our knowledge, this is the first example of thiolane as cathode active materials for rechargeable lithium battery. It is indicated that electrode redox reaction could take place on the S atoms of organic compounds apart from the cleavaging-combinating of S−S bond. The preliminary research provides potential of a new field for organic cathode material of lithium battery and further exploration is ongoing in our laboratory at present.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2007.02.043.

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