Short communication

Poly[3,4-(ethylenedithio)thiophene]: High specific capacity cathode active material for lithium rechargeable batteries

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ABSTRACT

Poly[3,4-(ethylenedithio)thiophene] (PEDTT) has been synthesized by oxidative-coupling polymerization of 3,4-(ethylenedithio)thiophene (EDTT) in the absence of solvent at ambient conditions. The resulting polymer has been characterized by FT-IR, XRD, TGA, UV–vis and solution NMR analyses. In addition, PEDTT has been evaluated as the cathode active material for rechargeable lithium batteries. The charge–discharge tests are carried out at room temperature. PEDTT shows discharge specific capacity above 425 mAh g^{-1}. It is tentatively proposed that electrode reaction involves the formation of thioether cation, which imparts multi-electron redox reaction, high discharge specific capacity, high charge voltage and low discharge voltage.

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1. Introduction

Cathode materials with high energy density are required to develop high-performance rechargeable batteries. Electro-active polymers, including polythiophene (PTH), have been utilized as cathode materials for lithium batteries since 1980s [1–3]. With excellent environmental stability in both doped and de-doped states and desired electrochemical properties, PTH is suitable to be used as the cathode active material for lithium secondary batteries. A Li/PTH cell using chemically synthesized PTH in LiBF$_4$/PC showed stable and high discharge voltage (i.e. 3.8 V at the plateau region), with 96% and 87% charge–discharge coulombic efficiencies at charge capacity of 17 mAh g^{-1} and 33 mAh g^{-1}, respectively [4]. PTH powders that was chemically polymerized in chloroform solution was used as the cathode active material to build Li/PTH cell with 1 M LiPF$_6$/ethylene carbonate (EC)/dimethylcarbonate (DMC) solution. This cell exhibits a significant capacity of 20 mAh g^{-1} with an average voltage above 3.6 V, and desired cyclability [5]. In addition, the derivatives of PTH are also cathode active. For example, poly(3-octylthiophene) performs well as the electrode in 0.1 M tetrabutylammonium tetrafluoroborate/nitrobenzene solu-

tion. The coulombic efficiencies were 94% with 33% of doping level (monomer unit basis) [6,7]. In particular, when poly(ethylene-3,4-dioxythiophene) (PEDOT) was utilized as the cathode active material in 0.1 M Bu$_4$NPF$_6$/PC and 0.1 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$, a significantly capacity of 140 mAh g^{-1} that is higher than other conducting polymers (e.g. polyaniline, polypyrrole and polyphenylene) can be obtained [8,9]. However, the discharge specific capacity of PTH and its derivatives are generally too low to be utilized in commercial batteries [1]. Meanwhile, thiolane-containing polyphenylene that exhibits high specific capacity has also been reported [9]. It shows that the thioether bonds on thiolane can offer high electron storage, and therefore, polythiophene derivatives with thioether bonds may be used as high-performance cathode active materials.

Poly[3,4-(ethylenedithio)thiophene] (PEDTT), the sulfur analogue of poly(3,4-ethylenedioxythiophene) (PEDOT), is the polymer with thioether and polythiophene structure and has never been reported as a cathode material, to the best of our knowledge [10]. Comparison of molecular structure and properties between PEDOT and PEDTT has been reported in the literature [11–17]. It shows that PEDTT presents a higher oxidation potential, larger band gap and poor electro-conductivity, while its cathode activity remains unknown to date.

In this study, therefore, we are interested in synthesizing PEDTT and investigating its electro-active properties. PEDTT is synthesized by chemical polymerization with the absence of solvent at ambient conditions, and then used as cathode materials in rechargeable batteries with LiN(CF$_3$SO$_2$)$_2$ (LiTFSI)/1,2-dimethoxyethane
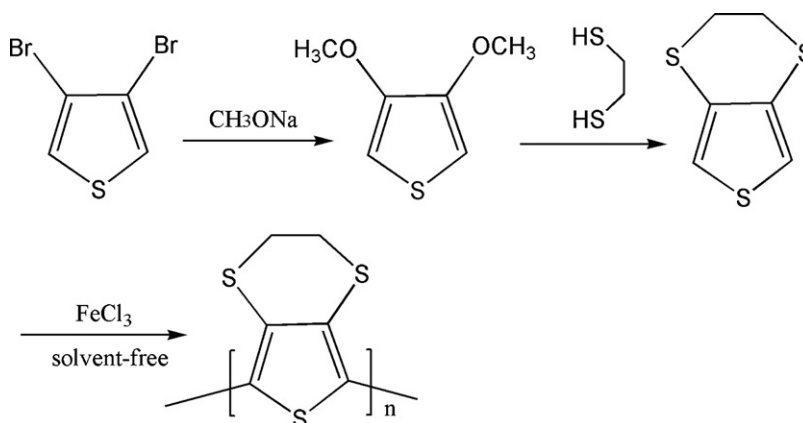
Scheme 1. Synthesis route of PEDTT.

(DME)/1,3-dioxolane (DOL) electrolytes. In addition, the discharge specific capacity of PEDTT is observed and its electrochemical behavior and mechanism are rationalized.

2. Experimental

2.1. Reagents and chemicals

3,4-Dibromothiophene, $FeCl_3$ and CuBr were purchased from Aldrich Co. and used without further purification. Methanol, sodium, ethanol and dimethyl formamide (DMF) were purchased from Shanghai Reagent Company and purified by distillation under reduced pressure. LiTFSI, DOL and ethylene glycol dimethyl ether (DME) were purchased from Ferro Inc. and used without further purification.

2.2. Monomer and polymerization

3,4-(Ethylenedithio)thiophene (EDTT) was prepared by the acid catalyzed nucleophilic substitution of 3,4-di(methoxy)thiophene with ethylenedithiol according to the literature procedure [18]. The molecular structure of EDTT is confirmed by ^{1}H NMR and FT-IR. ^{1}H NMR (CDCl$_3$, 300 M): δ 6.98(s, 2H), δ 3.23 (s, 4H). IR (KBr): 3091m, 2954w, 2910m, 1469m, 1409m, 1382w, 1322m, 1284m, 1164w, 1126w, 968w, 924w, 870m, 853s, 771s, 690w, 673w, 630w, 521w.

The synthetic route of the PEDTT is shown in Scheme 1 and the synthetic procedure is described as follows. Anhydrous $FeCl_3$ (0.98 g, 6 mmol) was quickly weighed and put into a mortar. EDTT (0.35 g, 2 mmol) was dropped into the mortar and then the mixture was ground at ambient condition for 30 min. $FeCl_3$ was removed by washing the ground sample with 20 ml methanol for three times. The polymer obtained was de-doped by stirring in 50% aqueous hydrazine monohydrate (10 ml) for 24 h and then collected by filtration. Afterwards the polymer was extracted with methanol in a Soxhlet extractor for 2 days. The brown-red powder was dried at 50 °C in oven to constant weight (0.30 g, yield 86%). ^{1}H NMR (CDCl$_3$): δ 3.20 ppm (s, 4H). Elem. Anal. Calcd. for $C_6H_4S_3$ (%): C, 41.38; H, 2.30; S, 55.17. Found (%): C, 41.77; H, 2.18; S, 54.32. IR (KBr): 2915w, 1712w, 1643m, 1411m, 1391m, 1277w, 1127w, 1062w, 716w, 603m.

2.3. Instruments and measurements

FT-IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer with KBr pellets. The ^{1}H NMR spectra (300 MHz) were obtained using a Mercury-VX300 spectrometer with CDCl$_3$ as solvent and chemical shifts (δ values) were given in parts per million with tetramethylsilane as the internal standard. Powder X-ray diffraction (PXRD) measurements were performed on a Philips diffractometer composed of a Cu Kα (λ = 1.54 Å) source, a quartz monochromator and a goniometric plate. The thermogravimetric analysis (TGA) was determined on a PerkineElmer TGA-2 with a heating rate of 2 °C min^{-1} in N_2 stream.

Cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (CHI660B) at a scan rate of 10 mV s^{-1} between 1.5 V and 4.0 V. The curves were measured with two electrodes using Li film as the reference electrode and the cavity microelectrode packed with polymer powders as working electrode. Charge–discharge tests were performed on a Land Battery Test System. Working cathodes were prepared by mixing polymers with carbon black and Teflon in a mass ratio of 4:4:2. Lithium foil was used as the anode and the tests were performed at a rate of 50 mA g^{-1} in 1 M LiN(CF_3SO_2)$_2$/ethylene glycol dimethyl ether/1,3-dioxolane (1:2, w/w) solution. The temperature was 30–40 °C and the cut-off voltages were 1.4 V and 4.5 V.

3. Results and discussion

3.1. Material characterization

The polymer PEDTT is slightly soluble in $CHCl_3$, CH_2Cl_2 and THF, and insoluble for the rest of ordinary solvents. Therefore, the molecular weight measurement cannot be easily performed. The polymer has been characterized by FT-IR, ^{1}H NMR, PXRD, TGA and UV–vis analyses. Fig. 1 shows the FT-IR spectra of EDTT monomer and de-doped PEDTT. Both spectra show C–Hα stretching at 2954 cm^{-1}, C (ring)–S–C stretching band at 1060 cm^{-1} and the C–S stretching vibration at 603 cm^{-1}. In contract, the C–Hα vibration on the aromatic ring (818–831 cm^{-1}) is observed in the spectrum of monomer EDTT only. The ^{1}H NMR spectrum of PEDTT shows the chemical shift at δ 2.56 ppm (4H) but no clear peak at around 7 ppm, indicating its high molecular weight. The UV–vis spectra of EDTT and de-doped PEDTT in THF are compared in Fig. 2. The spectrum of EDTT (Fig. 2a) shows two absorption bands with peak values of 215 nm and 298 nm, respectively. The spectrum of PEDTT (Fig. 2b) shows three absorption bands with peak values of 215 nm, 341 nm and 419 nm, respectively. The red shift and new band at longer wavelength are assigned to the extension of conjugation on the PEDTT chain. The characterization results clearly demonstrate the polymerization of monomer EDTT. In addition, the PXRD profile of PEDTT powders indicates the amorphous nature of PEDTT. The
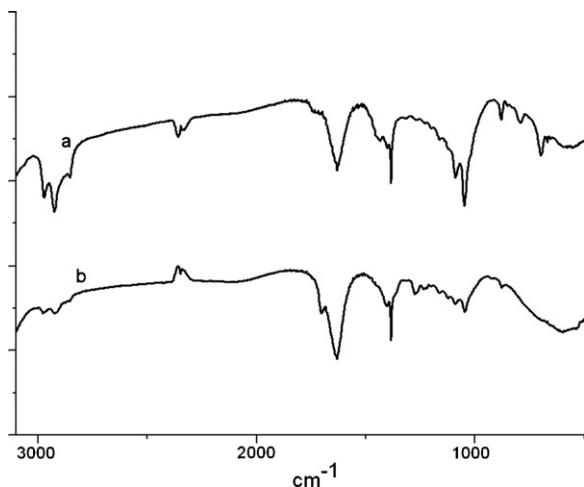
Fig. 1. FT-IR spectra of (a) EDTT monomer and (b) de-doped PEDTT.

TGA analyses of PEDTT under nitrogen atmosphere shows decomposition temperature started at 300 °C, which is in well agreement with the solution-prepared PEDTT [10]. The electric conductivity of PEDTT powders that were doped with I_2 was 10^{-3} S cm^{-1} at room temperature.

3.2. Electrochemical behavior

The CV curve of PEDTT is presented in Fig. 3, exhibiting two oxidative peaks. One peak locates at 2.7–3.7 V with a maximum value of 3.0 V, while the other peak locates at 3.5–4.0 V with a maximum value of 4.0 V. The reductive peak locates at 1.5–2.0 V with a maximum value of 1.7 V. The high oxidative potential and low reductive potential indicate that the polymer may offer high charge voltage and low discharge voltage as a cathode material. However, the strong and sharp reductive peak may be associated to a high discharge capacity.

The charge–discharge curves of PEDTT with two charge plateaus (i.e. 2.8 V and 4.0 V) are shown in Fig. 4. The discharge plateau is approximately at 2.2 V. The charge voltage and discharge voltage correspond to the oxidative potentials and reductive potentials in the CV test, as shown in Fig. 3. The gap between charge voltage and discharge voltage indicates the low voltage efficiency. However, the discharge profiles of PEDTT show high discharge specific capacity of 500–600 mAh g^{-1}, which is significantly higher than those of polythiophenes in Li/PTH batteries (i.e. high discharge of
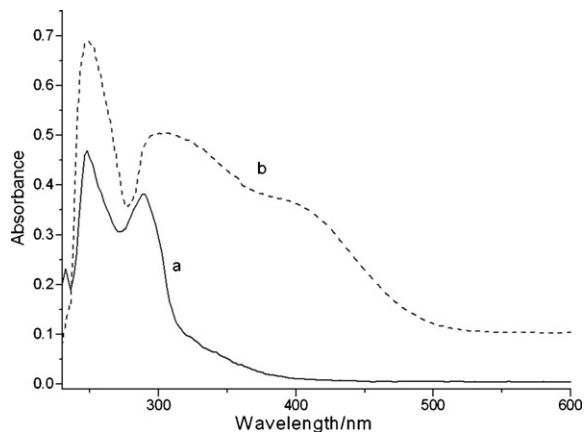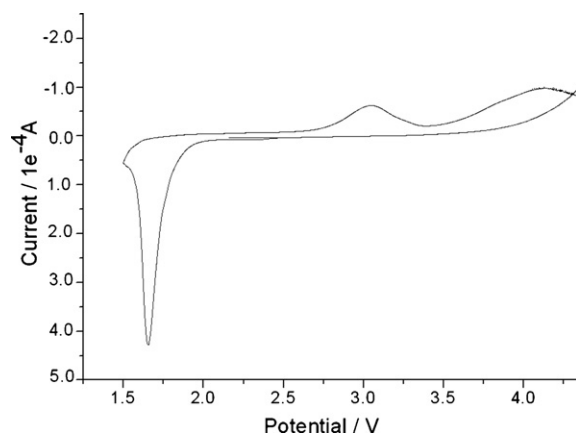

Fig. 3. CV curves of PEDTT powder microelectrodes packed with only the pure polymer, in 1 M LiTFSI/DOL/DME (1:2 by weight); scan rate 1 mV s^{-1} at room temperature.
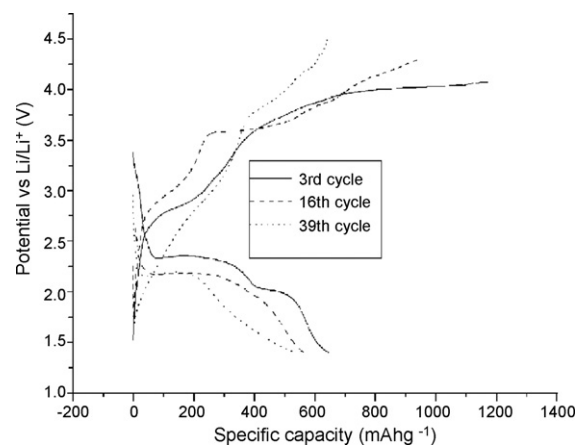

Fig. 4. Charge–discharge curves of PEDTT in LiTFSI/DOL/DME.

3 V and discharge specific capacity of 20–100 mAh g^{-1}) [1]. In the same time, the charge–discharge behavior of PEDTT is very similar to the thiolane-containing polymers [9].

A typical cycle life curve of PEDTT shows high discharge specific capacity (Fig. 5). The 1st to 3rd cycle shows a discharge specific capacity of ca. 600 mAh g^{-1}. From the 19th cycle to the 34th cycle, the discharge specific capacity is ca. 400 mAh g^{-1}. From 4th to 18th cycle and 35th to 44th cycle, the discharge specific capacity is ca.
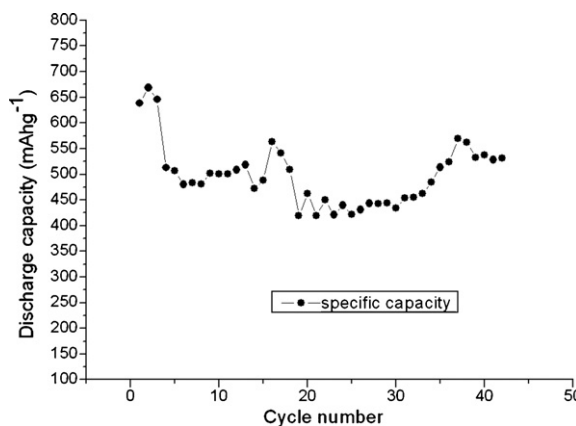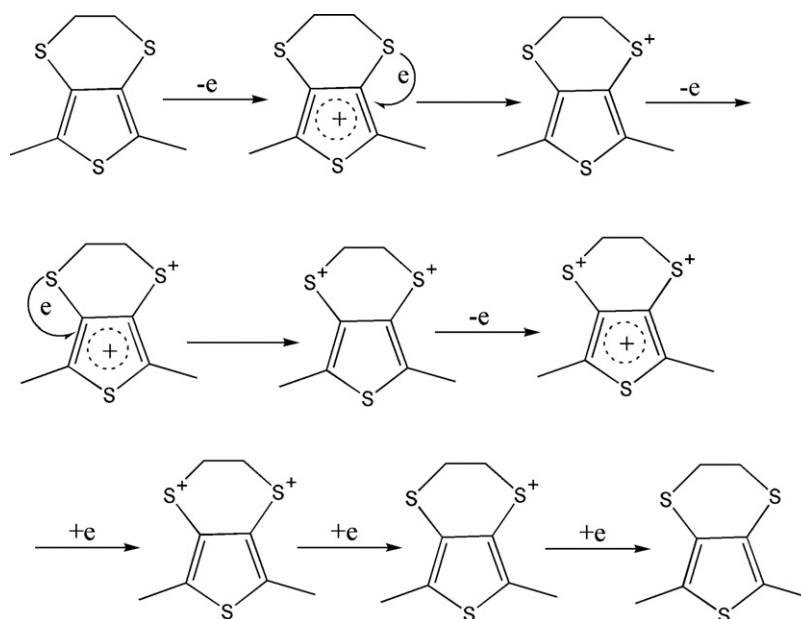

Fig. 2. UV–vis spectra of (a) EDTT and (b) de-doped PEDTT in THF.

Fig. 5. Cycle life of PEDTT in LiTFSI/DOL/DME.

Scheme 2. Tentatively proposed electrode reaction of PEDTT in LiTFSI/DOL/DME.

$500 \, mAh \, g^{-1}$. On the other hand, the value of discharge plateau starts from 2.3 V and decreases to 2.2 V at the 16th to 40th cycle. Although the discharge voltage of PEDTT is lower than those of conventional Li/PTH system, the energy density of PEDTT is higher than those of polythiophenes reported in the literature due to its high specific capacity [1]. The average discharge specific capacity is about $450 \, mAh \, g^{-1}$ and specific energy is close to $1000 \, Wh \, kg^{-1}$ based on the active material. In a typical Li/PTH cell, however, the discharge capacity is ca. $20 \, mAh \, g^{-1}$ with an average voltage of 3.6 V, corresponding to a specific energy of $72 \, Wh \, kg^{-1}$ [5].

3.3. Possible mechanism of PEDTT in cathode

The mechanism of PEDTT performing as a cathode of a Li/PEDTT cell remains unclear to date and here the rationalization of its performance is attempted. Clearly, the electrode reaction of PEDTT is different to the convenient "doping–de-doping" process. First of all, its discharge voltage at 2.2 V is remarkably lower comparing to those in de-doping processes that afford a discharge voltage of 3.3–3.8 V [1]. Secondly, the discharge specific capacity is one order of magnitude higher than those of "doping–de-doping" processes. For PEDTT, its theoretic discharge specific capacity is as low as $60 \, mAh \, g^{-1}$, even in a 100% doping–de-doping process.

On the other hand, the charge–discharge behavior is similar to that of thiolane-containing polymer (e.g. poly(2-phenyl-1,3-dithiolane) and poly[1,4-di(1,3-dithiolan-2-yl)benzene]). The specific capacity of thiolane-containing polymers is much higher than that of their mainchain polyphenylene and is sensitive to the contents of thiolane groups. Therefore, it is likely that the electrode reaction occurs on the S atoms of the thiolane groups [9]. PEDTT has the same thioether bond (C–S–C), works in the same electrolyte/solvents system and exhibits the same charge–discharge behavior to the thiolane polymers. Therefore, we believe that PEDTT has a similar electrode reaction to those of thiolane-containing polymers.

In fact, the formation of long-lived aliphatic thioether cation radical and dications (S^+–S^+) have been extensively studied and summarized by Musker [19]. Musker has predicted their utilization for electron transfer, power storage and recovery in biochemistry [19]. Moreover, thianthrene cations, an aromatic thioether compound with cations are more stable than the aliphatic thioether cations because its charge may be delocalized by the ring system [20]. Similarly, PEDTT has long aromatic conjugated chains that may offer more stable thioether cations than aliphatic thioether cations. Therefore, it is possible that thioether cations are formed during the charge process via electron transfer from S atom to the oxidized thiophene ring radical cation. Reversibly, during discharge process the electrons are injected into S cations from polymeric mainchains, as depicted in Scheme 2. According to this hypothesis, three electrons are involved on one EDTT moiety during a redox reaction. The corresponding theoretic specific capacity of PEDTT is $462 \, mAh \, g^{-1}$, which is in a relatively well agreement with the experimental measurements. In addition, the charge (oxidation reaction) process involves the formation of aromatic cation radicals, which may form doping complex with anions of TFSI. This process affords high voltage. On the other hand, the reductive reaction does not involve the de-doping process. The electron transfer directly onto the thioether cations from polythiophene mainchains, such that the electrical voltage is lower than that of charge process. Therefore, the discharge voltage is similar to that of thiolane polymers, rather than that of polythiophenes. As shown in Figs. 3 and 4, the oxidation potential and charge voltage are above 3.0 V, while the reductive potential and discharge voltage are ca. 2.0 V. The experimental values are compatible with the proposed process.

4. Conclusions

PEDTT has been chemically prepared by facile oxidative-coupling polymerization of EDTT at solvent-free conditions. The polymer has been utilized for cathode active materials for rechargeable lithium batteries and shows discharge specific capacity between $425 \, mAh \, g^{-1}$ and $550 \, mAh \, g^{-1}$ and a low discharge voltage between 2.0 V and 2.3 V. The electrode reaction involved is different to the conventional "charge–discharge" process. In order to rationalize the high discharge specific capacity and low discharge voltage of conjugate polymer PEDTT, we tentatively propose that the relevant electrode reaction involves the formation of thioether cation, which imparts the multi-electron redox reaction, the high discharge specific capacity, the high charge voltage and the low discharge voltage.

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