Synthesis and Properties of Copolymer of 3-Thienylmethyl Disulfide and Benzyl Disulfide for Cathode Material in Lithium Batteries

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ABSTRACT: The copolymerization of 3-thienylmethyl disulfide and benzyl disulfide has been investigated. Two monomers were synthesized in a novel facile way. Copolymer of them, especially poly (3-thienylmethyl disulfide-*co*-benzyl disulfide), ratio 1 : 4, namely, $TcB_{1:4}$, was easily electrocopolymerized to form a stable and higher conductive structure at a lower potential on Pt, Au, or glass carbon electrode. $TcB_{1:4}$ and $TcB_{4:1}$, especially the former, exhibit better conductivities than those of pure poly 3-thienylmethyl disulfide and poly benzyl disulfide. The copolymer has larger areas than that of monopolymer by cyclic voltammogram measurement. The copolymer shows a capability of supplying more power and energy than monopolymer itself. Copolymers could be used as cathode materials for lithium secondary batteries because their functional groups could not be destroyed before 80°C. In scanning electron micrography, the copolymers show larger compacter structure. The results of the copolymer systems show that they are potentials as cathode materials for lithium batteries. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 727–735, 2010

Key words: copolymerization; conducting polymers; redox polymers; cathode material; lithium battery

INTRODUCTION

Various kinds of materials have been investigated as cathode materials for lithium batteries such as $LiCoO_2$, V_2O_5, transition metal oxides, Ni-rich cathode, multi-metal oxide, etc.[1–3] However, conducting polymers have caught a great deal of attention because of their potential applications in many ways such as electrochemical windows, biosensors, lithium batteries, redox capacitors, antistatic coatings, and semiconductor devices.[4–7] Among the organic conducting polymers, electroactive polyorganodisulfides are promising cathode materials for lithium batteries in view of their high specific capacity and power density.[8] Masato et al. reported that the experimental capacity of poly 2,5-dimercapto-1,3,4-thiadiazole (PDM_CT) and polyanthra [1,9,8-b,c,d,e][4,10,5-b,c,d,e] bis-[1,6,6a(6a-S)trithia] pentalene (PABTP) are about 362 Ah kg^{-1} and 300 mAh g^{-1}, respectively.[9–11] Polyorganodisulfides have several advantages to benefit the practical application such as environment-friendly, low-cost, and facile preparation. Moreover, the charge and discharge are feasible in high efficiency at ambient conditions.[12–16] However, these cathode materials also exhibit several drawbacks such as poor conductivity, low stabilization and poor electrical performance.[15,16]

Here, copolymerization has been taken to improve the physical properties and processability of polyorganodisulfides and their electrical conductivity is still exploited. In fact, most poly-organodisulfides are insoluble and nonfusible such as poly 3-thienylmethyl disulfide (PTD) and poly benzyl disulfide (PBD). We have synthesized their monomers 3-thienylmethyl disulfide (TD) and benzyl disulfide (BD) in a new facile way. Electro-polymerization, which has been used more widely than chemical oxidative polymerization for the product, can be obtained pure products and divided into two categories: one involving deposited of conjugated polymer within a polymer matrix deposited on an electrode surface and another involving the electropolymerization in the presence of a soluble polymeric electrolyte.[17]

Both methods are propitious to improve the mechanical and physical properties of conjugated polymers.[18–25] However, most of these blend polymers gradually lose their conductivity upon aging. Copolymerization is often used to prepare a new polymer with properties different from the constituent monomers.[17,18] Copolymerization could be a better choice owing to the chemical linkage between the matrix and the conjugated polymer can improve the aging properties.[26] Ordinarily the chemical and physical properties of a copolymer are in the range of those of a composite and a blend, but not all. Conductivity and thermal stability has been improved by copolymerization.[27–29]

To perform well in the electropolymerization or electro-copolymerization, the anode electrode is critical as the high potential will lead to overoxidation, which means the loss of π-electron of aromatic ring.[30] Deposition of conjugated polymers or copolymers from electropolymerization or electro-copolymerization had been carried out on work electrode such as platinum, gold, and carbon.[31–34] Copolymer was found to be one of the best promising cathode materials for lithium batteries. Most importantly, the resulting copolymer films performed well in conductivity, thermal stability, and electrical property. With the improvement of assembly technology, it is believed that organosulfur copolymers are the most promising cathode material for lithium batteries because of their high theoretical capacities.[11,15,16]

EXPERIMENTAL

Chemicals

Anhydrous acetonitrile was doubled distilled from calcium hydride to lower water content. Acetonitrile (ACN) was stored over molecular sieves. Tetrabutylammonium hexafluorophosphate ([Bu_4N][PF_6]) was obtained from Acros and dried under reduced pressure at 80°C for 24 h before use. All other chemicals were of reagent grade.

3-Thienylmethyl disulfide

Benzoyl peroxide (0.48 g, 2.00 mmol) and 3-methyl-thiophene (3.92 g, 40 mmol) were dissolved in CCl_4 (80 mL) and solely refluxed for 30 min at 80°C (Scheme 1). The mixture was then cooled to 0°C, and succinimide was removed by filtration. The filtrate was dropped directly into 80 mL 0.64 mol L^{-1} thiourea solution with ethanol as solvent at 76°C. The mixture was refluxed for 2.5 h at 70°C. After the reaction was completed, 70 mL 0.71 mol L^{-1} NaOH aqueous solution was added step by step. $FeCl_3$ (0.5 g) was added and stirred for 30 h. The obtained yellow solid was filtered and washed with ethanol. Col-
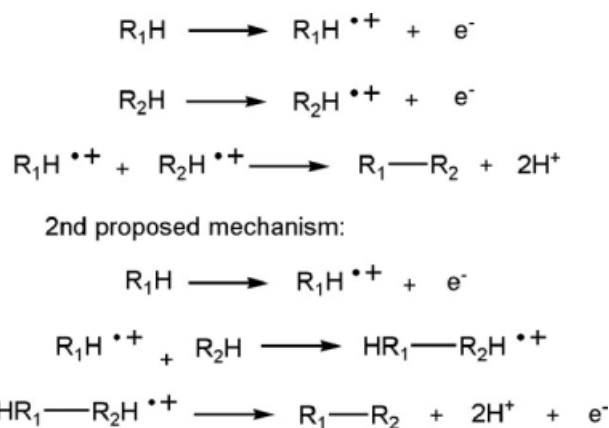
Scheme 1 Possible mechanism of the electrochemical copolymerization.

umn chromatography on silica gel with hexane gave a colorless crystalline solid (3.01 g, R_f = 0.43, 58%). EA ($C_{10}H_{10}S_4$): =C: 46.52 (46.47); H: 3.98 (3.90); S: 49.69 (49.63). H^{1}NMR (CDCl$_3$): δ = 3.633 (s,4H,CH$_2$), δ = 7.020 (d,2H,H-4&H-4'), δ = 7.095 (d,2H,H-2&H-2'), δ = 7.259 (d,2H,H-5&H-5'). Masse (EI): [M]$^+$ = 258. The products were purified by silica gel chromatography and dried at 30°C in vacuum oven to constant weight.

Benzyl disulfide

Benzyl chloride (2 g, 15.8 mmol) was added directly into a solution of thiourea (1.2 g, 15.8 mmol) in 70 mL ethanol and refluxed for 2 h at 78°C (Scheme 1). Then a solution of NaOH (2 g, 50 mmol) in 100 mL H_2O was added and stirred. $FeCl_3$·$6H_2O$ (0.1 g, 0.37 mmol) was then added into it and stirred for a day. After filtration, the white precipitation was recrystallized with ethanol to give a pure product. Yield: 2.6 g (66.7), white acicular. EA ($C_{14}H_{14}S_2$): = C: 68.16 (68.29); H: 5.59 (5.69); S: 26.25 (26.02). H^{1}NMR (CDCl$_3$): δ = 4.13 (s,4H,CH$_2$), δ = 7.28 (d,Ar-5H). Masse (EI): [M]$^+$ = 246.

General procedure for the synthesis of monopolymers and copolymers

To obtain a sufficient amount of polymer/copolymer for thermal analysis and charge/discharge test, chemical oxidation were used as a facile way. Anhydrous $FeCl_3$ (4.8 g, 30 mmol) was added to a solution of 1,4-dihydrothieno[3,4-*d*] [1,2] dithiine (0.2 g, 1.15 mmol) in 15 mL CHCl$_3$ under slow nitrogen flow. Then the solution was stirred at 50°C for 36 h. After the reaction was completed, the chloroform was removed under reduced pressure. The solid residue was washed with water and then dried at 60°C in oven. The crude was extracted by ethanol in soxhlet extractor to give pure.

General electrochemistry

Cyclic voltammograms (CVs) were performed on a EG&G PAR 283 electrochemical workstation (Princeton, USA) at 25°C. Electrocghemical polymerizations were carried out in a conventional three electrode cell using Pt, Au, or glass carbon (GC) disk work electrodes with a 0.5 mm diameter. A platinum foil (3.0 cm^2) and saturated calomel electrode (SCE, 0.241 V versus SHE) were used as counter and reference electrodes, respectively. Additionally the electrodes were treated with sulfuric and nitric acids for 5 h followed by rinsing with distilled water and ethanol. Electrodes were dried over silica gel in vacuum before starting the electrochemical investigation or the copolymerization experiments. Solutions used for the electrochemical studies were prepared from 5 mL ACN and contained 1 mmol L^{-1} monomer and 0.1 mol L^{-1} [Bu$_4$N][PF$_6$] electrolyte. For copolymerization studies, the concentration of each monomer was proportioned to give a total monomer concentration of 10 mmol L^{-1}. The peak potentials for oxidation are determined at a potential range of 0 V to 1.3 V. This cycle was repeated 10 times. The scanning rate was 50 mV s^{-1}. All solutions were deaerated with nitrogen before the measurements for 10 min, and during the measurements the solutions were passed over by a stream of nitrogen. Deposited polymers/copolymers were then washed with ACN before carrying out electrochemical characterization in monomer-free electrolyte solution.

Conductivity

Ionic conductivity of the polymer/copolymer film was determined by complex impedance spectra measured using PAR 283 with the help of frequency response analysis Zview system software under an oscillation potential of 10 mV over a frequency range of 1 MHz–0.1 Hz. The cell is consisted of a work electrode (Pt/Au/GC + polymer/copolymer film). The electrolyte is 0.1 mol L^{-1} [Bu$_4$N][PF$_6$] in ACN solution. The polymer/copolymer films were electrochemically prepared on Pt, Au, and GC electrodes at a constant cycle potential of 0–1.3 V for 10 times. Before the test, the films were washed with ACN.

Characterizations

The thermogravimetric analysis (TGA) was performed with a thermal analyzer of NETZSCH TG 209. Thermal analysis was performed under a nitrogen stream in the temperature range of 303–623 K with a heating rate of 10 K min^{-1}. Scanning electron microscopy (SEM) measurements were taken using a JEOL JSM-6330F scaning electron microscopy. Infrared spectra were recorded using vertex 70 FTIR
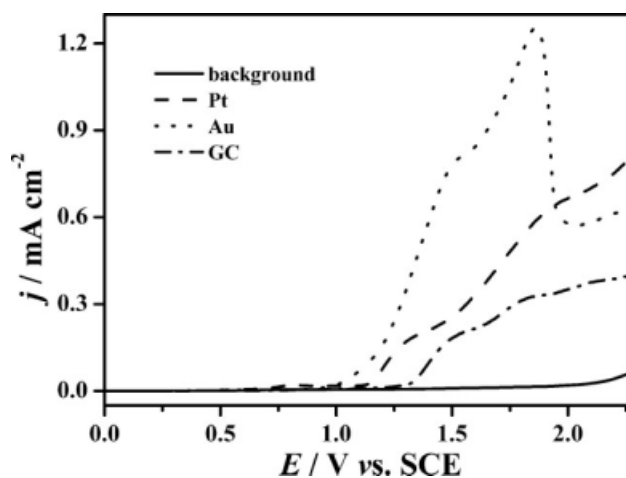

Figure 1 First anodic scan showing the onset oxidation potentials for TcB$_{1:1}$ on Pt, Au, and GC in 0.1 mol L^{-1} [Bu$_4$N][PF$_6$]/ ACN.

spectrophotometer with KBr pellets. Elementary analysis was performed on Vario EL.

Charge and discharge test

The test of cycling capacity was performed on Land Battery (Wuhan Land) test system. Working cathodes were prepared by mixing active material with carbon black and Teflon in a weight ratio of 4:3:3 (total weight: 0.9 g). Lithium foil with 250 μm thickness was used as the anode and the tests were processed at a rate of 50 mA g^{-1} in 1.0 mol L^{-1} LiPF$_6$, Ethylene Carbonate /Diethyl Carbonate (1:1, by weight) solution. The cut-off voltages are 1.0 and 4.0 V.

RESULTS

Cyclovoltammetric copolymerization

Figure 1 shows the first anodic polarization curves of TcB$_{1:1}$ on different electrode materials. When the anodic potential rises, TcB$_{1:1}$ begins to polymerize at 1.152 (Pt), 1.062 (Au), and 1.324 V (GC), respectively. In a representative electrochemical polymerization to prepare intrinsically conductive copolymer, one of the monomers is first oxidized by the application of an appropriate oxidation potential to prepare the corresponding monomer radical cation, which then becomes concentrated at the electrode surface.[35] Radical cations are the most likely species initiating the copolymerization. The monomer radical cations can react with a compound, which forms stable radical cation intermediates because they are conjugated with the aromatic rings.[17] There are two proposed mechanisms about it: (i) radical cations undergo electrophilic substitution with neutral monomers to prepare oligomers that further oxidize and then
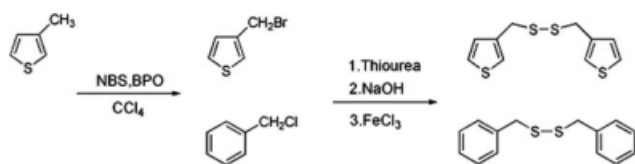
Scheme 2 Schematic illustration for the preparation of TD and BD and their copolymer.

electroprecipitate onto the electrode surface;[36](ii) radical cations couple to prepare oxidized oligomers which electroprecipitate onto the electrode surface.[37] The possible mechanism of this electrochemical copolymerization of TD and BD is illustrated in Scheme 2. As far as we know, high onset potential of oxidation of monomer may lead to overoxidation, which has some negative effects on the aromatic structure. The thiophene or benzene units could have been destroyed to become nonconductive. Therefore, it is a better choice to perform electrochemical polymerization or electrochemical copolymerziation at a lower oxidative potential.

Table I shows a comparison of the onset potential of oxidation of the monomer (E_{ox} onset) and the diffusion-limited oxidation peak potential (E_{ox} peak) of the polymer precipitated on the surface of the electrode. As seen in Table I, the polymerization behavior of the five cases uses three different electrodes. In accordance with Figure 1, TcB$_{1:1}$ and TcB$_{4:1}$ begin to polymerize at 1.062 and 0.958 V on Au electrode respectively, which is an intermediate value to that of PTD or PBD by itself. TcB$_{1:4}$ begins to polymerize at 0.899 V on Au electrode, which is a lower value than that of PTD or PBD by itself. This could indicate that there is an easier trend for copolymer to form a stable and higher conductive structure at a lower potential. Experiments prove this conclusion to be true. It's worthy noting that different proportion has different strong point. The oxidation potentials of the two monomers do not change significantly when different electrodes are used. However, when Au is used as the electrode, the peak oxidation potential for all monomers shifts approximately by 01–0.6 V lower with respect to those for the polymerization carried out on Pt and GC electrodes. Jin et al. performed electropolymerization of two monomers and found that the product polymer was a copolymer instead of composite or blend.[17] Many studies obtained the same things.[30,34] In accordance with other experimental results, it is believe that TcB is a copolymer instead of composite or blend of TD and BD.

Conductivity

Electrochemical impedance spectroscope (EIS) was used to characterize the electrochemical behavior of

the monopolymer and copolymer. Figure 2 illustrates typical EIS response for the TD-co-BD composite polymer film in a three-electrode cell system. As illustrated in the inset of Figure 2, all the profiles show semi-arcwise span from high-frequency to low-frequency. The cells are consisted of a working electrode (Pt/Au/GC + polymer film), a reference electrode (SCE), and a counter-electrode (platinum wire). The electrolyte is 0.1 mol L^{-1} [Bu$_4$N][PF$_6$] in ACN solution. A single (R$_1$R$_2$C) circuit may give adequate description of the rate control of diffusion.[38,39] To be specific, the constant phase element (CPE1) is necessarily introduced to account for the nonideality of the interface between the electrode and electrolyte in the practical impedance spectrum.[40,41]

As shown in the inset of Figure 2, the equivalent circuit consists of a bulk-electrolyte resistance (R_1) in series with a parallel circuit of CPE1 and the charge transfer resistance (R_2). The impedance of a CPE may be associated with the double-layer capacitances and can be expressed as following

$$Z_{CPE} = A(j\omega)^{-n} \tag{1}$$

$$\alpha = (1 - n)\frac{\pi}{2} \tag{2}$$

where $n = 1$, $A = C^{-1}$. α refers to the deviation from the vertical of the line in the $Z' — Z''$ plot.

Therefore, with the help of the Zview system software, the equivalent circuit is used to fit the experiment data. The R_1, R_2, and CPE1 can be estimated from this fitting procedure. The ionic conductivity S of the polymer film is calculated by

$$S = \frac{1}{RA} \tag{3}$$

where R is the radius of the semi-arcwise and A is the area of the working electrode (0.19625 cm^2). The smaller the radius of the semi-arcwise is, the higher the conductivity is.[39]

As shown in Table II, TcB exhibits a good conductivity on every occasion. It can be clearly seen from

TABLE I
Oxidation of Monomer (E_s) and the Diffusion Limited Oxidation Peak (E_p)

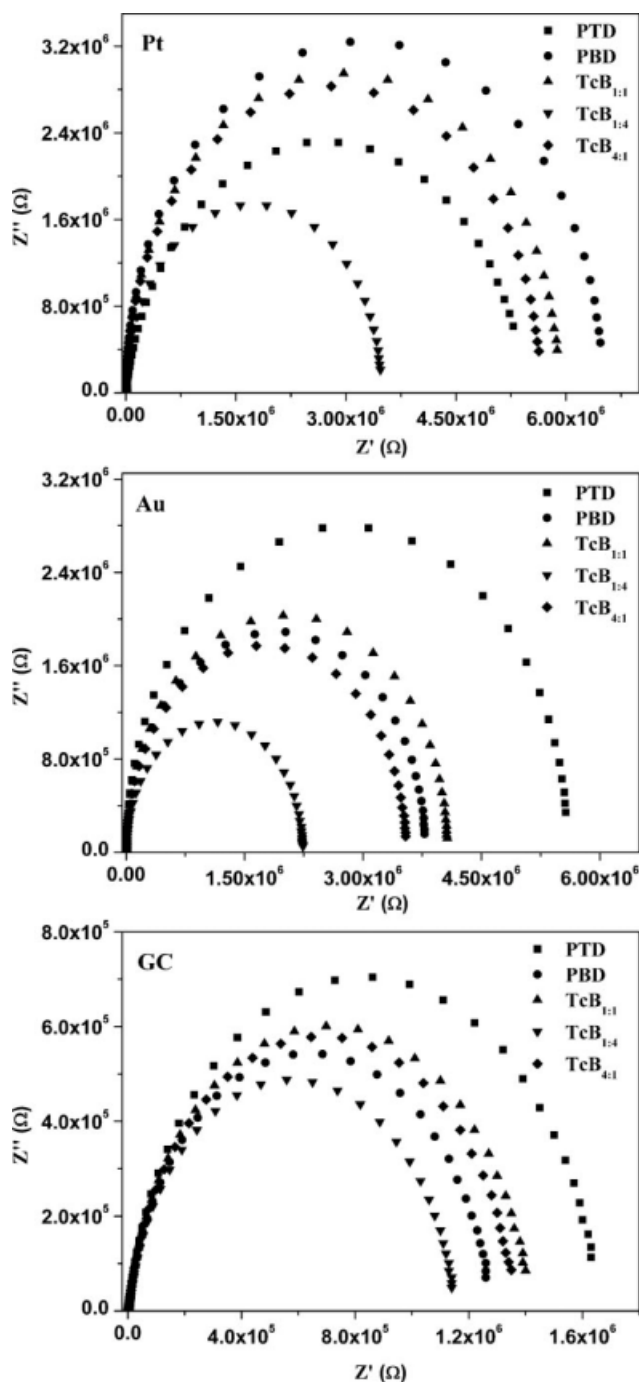| Electrode	Potential/V	PTD	PBD	TcB$_{1:1}$	TcB$_{1:4}$	TcB$_{4:1}$
Pt	Eox(onset)	1.297	1.218	1.152	1.080	1.148
	Eox(peak)	1.934	2.023	>2.3	2.142	1.663
Au	Eox(onset)	1.053	0.944	1.062	0.899	0.958
	Eox1(peak)	1.378	1.482	1.862	2.237	1.631
	Eox2(peak)	1.803	1.631			2.043
GC	Eox(onset)	1.243	1.265	1.324	1.098	1.256
	Eox1(peak)	1.487	1.726	>2.3	2.205	1.857
	Eox2(peak)	2.034				

Figure 2 Impedance simulated plots for the PTD, PBD, and TcB on Pt, Au, and GC electrode. Its corresponding equivalent circuit is shown in inset. Symbols Z' and Z'' refer to the real and imaginary components.

Table II that most of the conductivities of copolymers are between those of pure PTD and PBD, indicating that the combination of TD and BD is helpful to improve the conductivity of polymer which may be beneficial to extend the applications of these materials. However, there is always an exception to any rule. Hence, if only TD or BD is oxidized to produce blend polymer, the performance data for the copolymer system should be half that of either of the two pure systems. In accordance with performance test result, it is highly likely that they are copolymerized to produce a more excellent polymer consisting of both TD and BD repeat units. $TcB_{1:4}$ and $TcB_{4:1}$ exhibits better conductivities than those of pure PTD and PBD. Comparing with the copolymers prepared on different electrodes, $TcB_{1:4}$ shows the highest conductivity in every case, respectively. This is in accordance with the part 1 analysis results. The lower Eox onset potential, the best performance copolymer film can we have. Therefore, 1 : 4 is the best proportion suitable for the electrocopolymerization of TD and BD.

Electrochemistry of polymer/copolymer film

Figure 3 shows the CV of PTD, PBD, and TcB on GC electrode. The redox pattern of the polymer/copolymer shows one redox peak at $-1.0 \sim -0.6$ V of $TcB_{1:1}$ and $TcB_{1:4}$ which gives a larger area of the current-potential curves than PTD and PBD, indicating a larger current densities in the copolymer, especially $TcB_{1:4}$. It also suggests that the anodic/cathodic transfer coefficient of copolymer especially $TcB_{1:4}$ and $TcB_{1:1}$, is much greater than monopolymer. Apparent values for the peak separation (ΔE_p) obtained from the CV data are 0.212 V (PTD), 0.173 V (PBD), 0.160 V ($TcB_{1:1}$), 0.159 V ($TcB_{1:4}$) and 0.201 V ($TcB_{4:1}$). The smaller separation of anodic and cathodic peak potentials of $TcB_{1:4}$ and $TcB_{1:1}$ indicates that the overall reaction rate is faster than PTD and PBD. As we know, kinetic reversibility is an important parameter for energy storage applications. The higher and easier the kinetic reversibility of the electrode reaction, the higher the power output at a given energy efficiency of the system, or the higher the energy efficiency at a given power output.[42]

TABLE II
Conductivities of PTD, PBD, and Copolymers Obtained from Different Electrodes

Electrode	Conductivity (S/cm)				
	PTD	PBD	$TcB_{1:1}$	$TcB_{1:4}$	$TcB_{4:1}$
Pt	9.66×10^{-7}	7.90×10^{-7}	8.66×10^{-7}	7.51×10^{-6}	4.63×10^{-6}
Au	9.17×10^{-7}	1.35×10^{-6}	1.26×10^{-6}	2.30×10^{-6}	1.44×10^{-6}
GC	3.13×10^{-6}	4.05×10^{-6}	3.64×10^{-6}	4.48×10^{-6}	3.78×10^{-6}
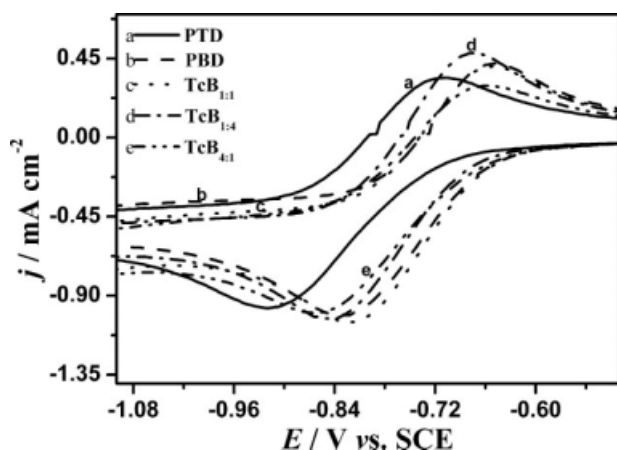
Figure 3 CV of PTD, PBD, and copolymers on GC electrode in 0.1 molL^{-1} [Bu$_4$N][PF$_6$]/ ACN.

Thermal analysis

Figure 4 shows the thermal analysis for the TD, PTD, PBD and those of the corresponding different copolymers. The thermal stability of these materials is very important for their potential applications. As can be seen from Figure 4, below 80°C, a light weight loss of each polymerized material is about 2–4%, mainly due to desorption of solvent trapped in the polymer. In accordance with Figure 5, an obvious weight loss of TD is observed in the range of 179–250°C. The total mass loss of TD is about 90% in the whole process. Two obvious endothermic peaks of all materials, indicating typical monomer TD, are observed at 60–120°C and 180–300°C. The first endothermic peak is believed to be associated with the decomposition of disulfide bond because it is a less stable functional group and the cleavage of disulfide bond is also an endothermic process. It can be seen clearly that polymers/copolymers show a change in the endothermic maxima and temperature of S—S bond cleavage, which means that polymer/
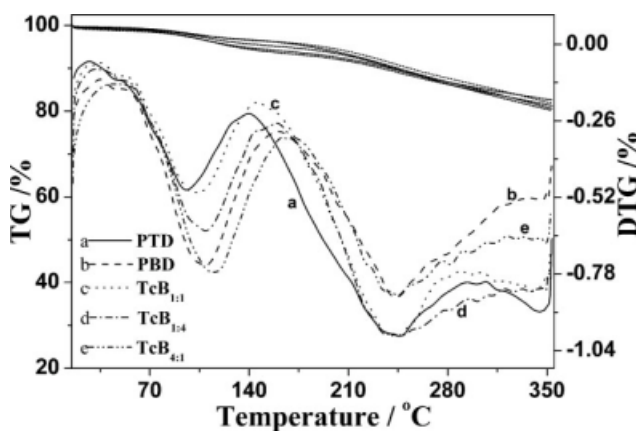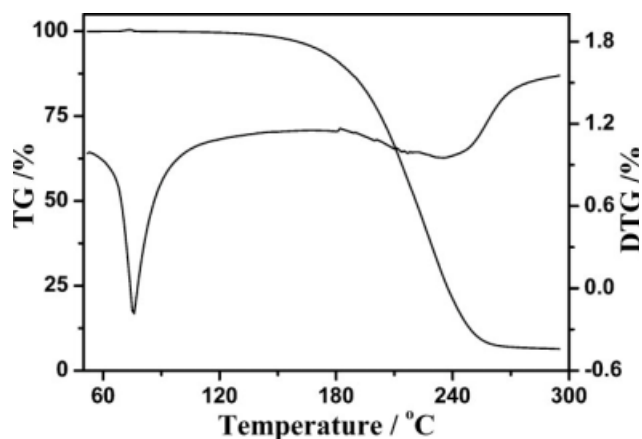

Figure 5 TG and DTG curves of TD.

copolymer has a better thermal stability than monomer. Moreover, the cleavage of disulfide bond of TcB$_{4:1}$ shows a highest value in the endothermic maxima. Next came PBD, and the rest rank is given to TcB$_{1:4}$, TcB$_{1:1}$, and PTD. The second process is 180–300°C and mainly due to the decomposition of small molecular weight organic compounds. Comparing with the thermogravimetric and derivative thermogravimetry analysis (TG/DTG) of monomer TD, polymer/copolymer shows a better thermal ability and total mass loss is about 20%. It is known that thermogravimetric analysis (TGA) is a significant dynamic way of dectecting the degradation behaviors. However, the weight loss of a polymerized material is useless, especially for these materials which are used as cathode materials for the lithium secondary batteries. After the decomposition of the functional group of the functional material, there is no use for it. Therefore, it doesn't matter about the weight loss at high temperature. The service temperature for lithium secondary battery is about −20°C
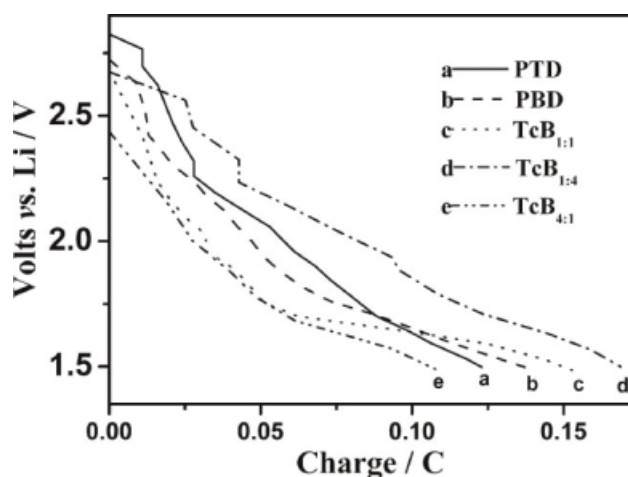

Figure 4 TG and DTG curves of PTD, PBD, and copolymers.

Figure 6 Charge and discharge curves of PTD, PBD, and copolymers in a 1 mol L^{-1} LiPF$_6$ EC/ DEC solution.
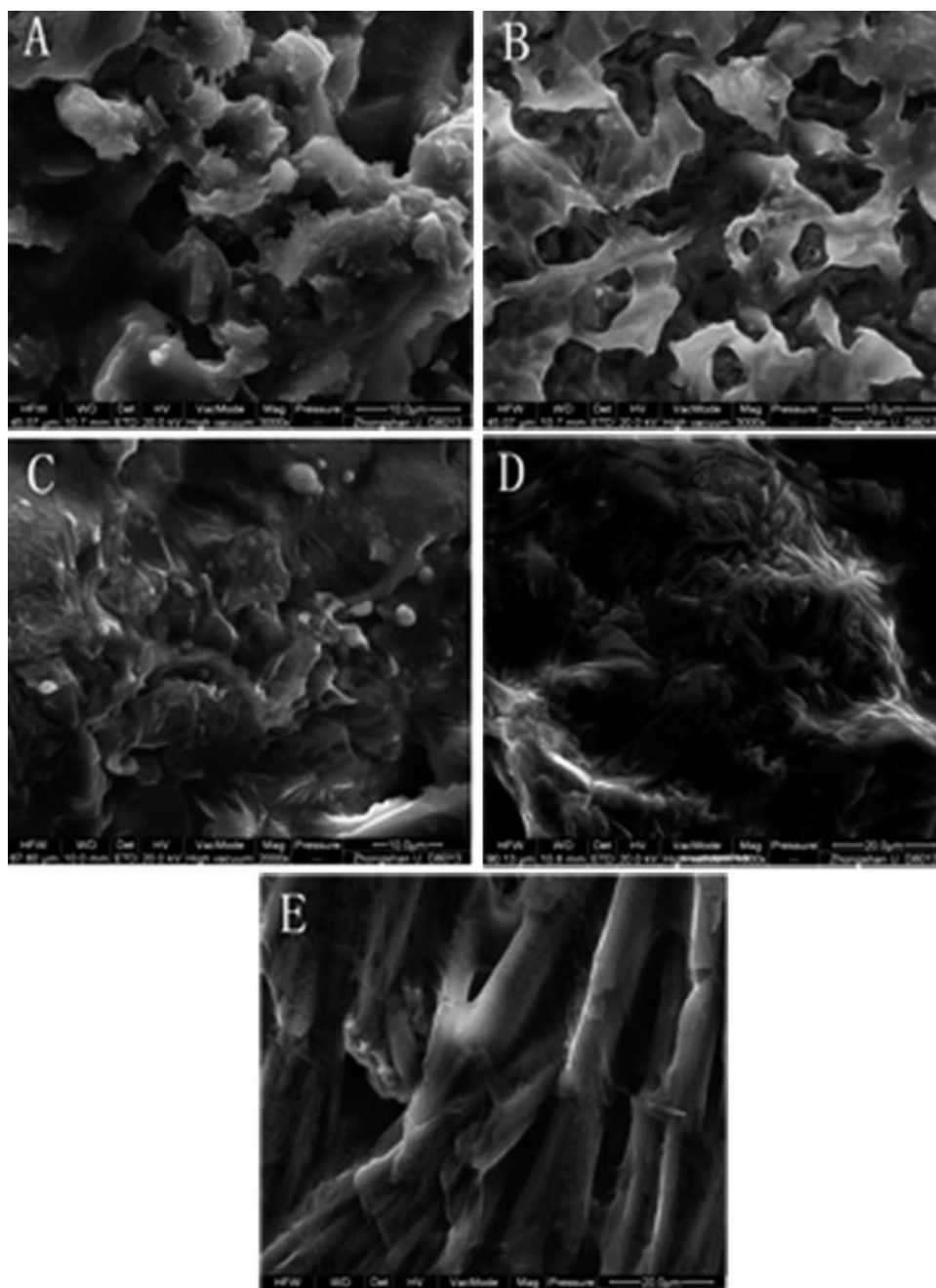
Figure 7 SEMs of the surface of (A) PTD, (B) PBD, (C) TcB$_{1:1}$, (D) TcB$_{1:4}$, and (E) TcB$_{4:1}$.

to 80°C. In other words, polymers/copolymers could be used as cathode materials for lithium secondary batteries because their functional group could not be destroyed below 80°C. All these results indicate that the combination of TD and BD contributes to the improvement of thermal property of copolymer. An investigation of low temperature performance of these materials is currently ongoing.

Charge and discharge curve

Figure 6 shows the result of the charge and discharge test of PTD, PBD and the copolymer of TD and BD. The samples were charged at 100 μ*A* to 4.0 V and then open-circuited for 60 s. The samples were then discharged at 200 μ*A*. In this figure the discharge has been converted to coulombs by multiplying the discharge current (200 μ*A*) by the time over which the discharge occurred. It can be clearly seen that TcB$_{1:1}$ and TcB$_{1:4}$ are capable of providing a greater power density. However, the stability and the choice of electrolyte remains an issue. As can be seen from Figure 6, TcB could not be charged above 2.67 V. Therefore, it is discharged to a lower potential about 1.50 V to maintain the voltage ranges

comparable. PTD was charged to 2.80 V and PBD to 2.71 V. In fact, these organodisulfide polymers could not be used for high power vehicle as a result of their low charge/discharge potential. Moreover, the polymerized materials are unstable in the repeated charge and discharge tests due partly to the choice of electrolyte. However, TcB$_{1:4}$ shows very interesting properties. From the curve, it is clear that TcB$_{1:4}$ is able to supply higher energy and power, as indicated by the others' steeper slope. This result suggests that good performance will be proportional to the amount of monomer BD and well fits to the conclusion above.

Morphology

The surface of PTD, PBD and copolymers was analyzed by scanning electron micrography (SEM) because the properties of functional polymers are strongly depended on their morphology and structure. The SEMs of PTD, PBD, and the TcB copolymers showed a wide variation of surface morphology. PTD gives a "bumpy" sidewall morphology as shown in Figure 7(A), while PBD shows a porous structure with smooth surface. The different between PTD and PBD is the surface thickness of the latter is thinner than that of the former. It is probably a principal factor that influenced cell performance. However, copolymers of TD and BD give different morphologies as shown in Figure 7(B,D,E). The copolymers, except TcB$_{4:1}$, show larger compacter structure. Despite the differences observed in the surface morphology depending on feed ratios, all the copolymers are covered with layer of yarn, and TcB$_{1:1}$ and TcB$_{1:4}$ are the most obvious. It is assumed that different physical and chemical material is produced during the process of copolymerization or this is a unique physical property of p-doping TcB. As we seen, the layer of yarn decreases with the increase of ratio of TD. In accordance with Figure 6, there must be an affinity in it. In other words, although the types of doping ion are not the same, the higher conductivity of TcB, especially TcB$_{1:4}$, can be also ascribed to this primary conclusion.

Structural characterizations

The TD, BD and their polymers/copolymers were characterized by FTIR spectroscopy. The main vibrations observed in the spectra together with their assignments are given in Table III.

For the qualitative analysis of the FTIR spectra of aromatic substituted disulfide two criteria have been proposed, namely the absorption of the aromatic C—H out-of-plane vibration (υring$_{C—H}$) and the C—S stretching vibration. According to the first criterion, the band at >3000 cm^{-1} of the υring$_{C—H}$ vibration is

TABLE III
Characteristic IR Bands and Their Structure Assignments

Polymer/monomer	υring$_{C—H}$	υring$_{C=C}$	$\delta_{C—H}$	$\upsilon_{C—S}$
TD	3085	1766–1407	785	676
BD	3047	1632–1385	763	695
PTD	3090	1718–1386	788	669
PBD	3065	1718–1376	762	703
TcB$_{1:1}$	3013	1716–1317	788	695
TcB$_{1:4}$	3072	1725–1325	763	694
TcB$_{4:1}$	3030	1720–1323	787	677

clearly observed. For each proportional TcB the same band appears at about 3013–3072 cm^{-1}, indicating an ordered polymer chain. The bands at 1766–1317 cm^{-1} corresponds to C=C stretching vibration. The bands at 762–788 cm^{-1} are due to the vibration frequency of the bending vibration of C—H. The bands at 669–695 cm^{-1} correspond to C—S stretching vibration, which points to a C—S—S—C structure. The results show that TcB was successfully obtained and can be used in mass production.

CONCLUSIONS

Two monomers, namely, 3-thienylmethyl disulfide and benzyl disulfide, were synthesized in a novel facile way and their copolymers were also investigated in this paper. TcB$_{1:4}$ is easily electropolymerized to form a stable and higher conductive structure on Pt, Au or glass carbon electrodes as a result of its lower onset oxidative potential. TcB$_{1:4}$ and TcB$_{4:1}$, especially the former, exhibit better conductivities than those of pure PTD and PBD. The cyclic voltammogram and charge/ discharge test show that copolymer is capable of supplying more power and energy than monopolymer itself. Copolymers could be used as cathode materials for lithium secondary batteries because functional group of copolymers could not be destroyed below 80°C. Hence, they could be cyclic utilization as cathode materials for lithium secondary batteries. In scanning electron micrography, the copolymers, except TcB$_{4:1}$, show larger compacter structure. The results of characterization show that TcB is a copolymer instead of composite or blend. Optimization of various conditions, such as the type of the electrolyte, the mixing ratio of conducting polymer and current density, should be performed in order to improve the performances of the cell. With the development of assembling technology, the copolymer of organodisulfide could be made a better use as cathode material for lithium batteries.

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