Short communication

Preparation and electrochemical properties of polysulfide polypyrrole

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ABSTRACT

A novel cathode material, polysulfide polypyrrole was successfully designed and synthesized for high-energy lithium–sulfur secondary batteries. The product was characterized by FT-IR, element analysis and DSC. Character results show that the polymer was obtained with polypyrrole as backbone and S–S side groups attached to it. Polypyrrole backbone in this polymer was used not only as container but also as conductivity passage. Cycle performances of the polymer was examined as active cathode material in lithium batteries, charge–discharge experimental results indicate that the polymer has a specific capacity of 515 mAh g^{-1} at the first cycle and 452 mAh g^{-1} at the 20th cycle. The improved cycle properties compared to other polymer disulfides and polysulfide polymers supply a good foundation for practical application of this material in rechargeable lithium batteries.

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1. Introduction

As a cogent candidate for the next generation high-energy lithium secondary battery, lithium sulfur batteries draw lots of researchers' interests [1–15] for its high specific energy, environmental friendly and low cost. However, lithium–sulfur batteries suffer from low active material utilization and poor cycle ability for the intrinsic low ionic conductivity of sulfur, as low as 5×10^{-19} S cm^{-1} [16] under ambient temperature. People do lots of work to modify the element sulfur, including to composite it with polymers [2–6,14,15], graphite [7,8], mesoporous carbon [9], carbon nano tubes [10], etc. On one hand, specific capacity has been improved to a high level, while, on the other hand, capacity retention rate after 50 cycles always less than 70% [1,2,8,10].

Organodisulfide polymers [16–20] and polysulfide polymers [14,15], with higher theoretical capacities than those of conventional cathode materials such as LiCoO$_2$, LiNiO$_2$ and LiMn$_2$O$_4$, have been introduced as a kind of novel energy storage materials for secondary lithium batteries based on the reversible two-electron reactions of the disulfide (S–S) bonds [16–20]. However, it has been proved that although these reactions are reversible, but very slow in dynamic [21–23], and that high temperature is required. What's more, as the active part in these molecules, sulfur occupying a small proportion, thus the specific capacity of cathode material is not high, and not suitable for commercial purposes.

In this work, a novel cathode material, polysulfide polypyrrole (SPPy) was synthesized. The conducting macromolecule polypyrrole (PPy) was used as stable backbones to provide electric conducting channels and long polysulfide lines were combined to polypyrrole as side chain in order to offer high specific capacity. This type of structure could efficiently prevent the dissolve and collapse of cathode material. Moreover, PPy could host Li$^+$-ion in the voltage range of 2.0–4.5 V versus Li/Li$^+$, with a theoretical capacity of 72 mAh g^{-1} [26–28], and when the H atoms were highly substituted by element sulfur, the capacity of pyrrole ring and that of element sulfur could be combined, on which a much higher capacity can be expected.

2. Experiment

2.1. Polysulfide polypyrrole synthesis

The SPPy was prepared by a 3 steps way. Firstly, the polypyrrole was synthesized via a traditional chemical oxidation way as literature reported [24]. A 0.671 g (1.0×10^{-2} mol) of freshly distilled pyrrole was placed in a 50 mL round-bottom flask at about -5 °C, and stirred vigorously. An aqueous solution (20 mL) containing FeCl$_3$·6H$_2$O (0.162 g, 6.0×10^{-4} mol) and HBF$_4$ (2.20 g, 48 wt% in H$_2$O, 1.2×10^{-2} mol) was added slowly through a dropping funnel. The resulting mixture immediately turned blue with the formation of a black precipitate. A 30 mL aqueous solution of H$_2$O$_2$ (2.43 g, 35 wt% in H$_2$O, 2.5×10^{-2} mol) was placed in a dropping funnel and a 12 mL portion of was added drop wise to the flask; the rest of the H$_2$O$_2$ solution was added in 6 mL portions at regular intervals of 1 h each. The reaction was allowed to proceed for further 90 min (i.e., for 4 h and 30 min in total) at -5 °C. The black precipitate obtained was recovered by vacuum filtration. The precipitate was washed with a copious amount of distilled water until the effluent was

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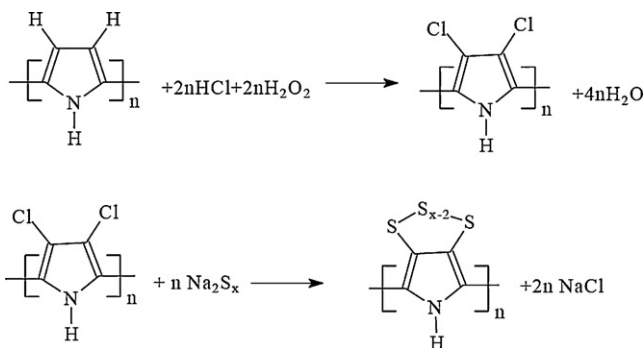
Scheme 1. The possible reaction process from PPy to SPPy.

Fig. 1. FT-IR spectrum of polysulfide polypyrrole (a) and polypyrrole (b).

colorless (about 300 mL). The precipitate was dried in the oven (about 70 °C) up to a constant weight.

Second, put the PPy powder into excessive hydrochloric acid (12 M), cooled to 5 °C in ice water, then equimolar amount of hydrogen peroxide (to HCl) was slowly dropped into the mixture (about 20 min) and stirred at 20–28 °C for about 1.5 h by mechanical stirrer, then the precipitation was filtered and immersed in ammonia solution (pH 8–9) overnight. Basically, the substitute reaction was as Scheme 1.

Subsequently, the product was washed with 0.1 M ammonia solution for several times and dried in vacuum to get the purple powder, chloropolypyrrole.

Thirdly, the mixture of $Na_2S \cdot 9H_2O$, sublimed sulfur (1:8 by mol. ratio) and dimethyl sulfoxide (DMSO) was put into a three-neck flask at certain proportion, refluxed at 100 °C under nitrogen protection for 4 h. Then chloropolypyrrole was added to the mixture and stirred rapidly at 120–130 °C for 24 h, then cool it to ambient temperature. After wash the product with water, immersed it into 0.1 M ammonia solution overnight, and then washed with 0.1 M ammonia solution several times, extracted with acetone until the filtrate were colorless. The final product was dried in vacuum for 12 h at 50 °C and the black powder SPPy was obtained.

2.2. Material characterization

Element analysis was performed on a Carlo Erba1106 analyzer. FT-IR spectra were recorded on a Bruker EQUINOX55 FT-IR spectrometer with KBr pellets. DSC analysis was carried out at a STA449C thermal analysis instrument with a temperature increasing rate 10 °C min^{-1}. The conductivity was measured with a standard four-probe way on a SB100A conductivity meter (Qianfeng Electronic Instrument Co., Ltd. Shanghai, China) with the materials pressed into pellets.

2.3. Electrochemical measurements

The SPPy cathode material was made by mixing 60% (wt) composite material with 30% carbon black and 10% LA-132 binder into a water–propanol (4:1, by vol.) mixing liquid to form homogeneous slurry, and then spread it onto aluminum foil substrates. The coated electrode was dried in a vacuum oven at 50 °C for 20 h. Subsequently, the electrode was cut into 1 cm × 1 cm rectangular. CR 2032 coin-type cells were assembled in an Ar-filled glovebox, with Celgard 2300 membrane as separator, Li foils as anode material, and 1 M LiClO$_4$/DOL-DME (volume ratio 50:50) as electrolyte. The cells were galvanostatically discharged and charged in the range of 1.5–3 V at different current densits of 0.1–0.4 mA cm^{-2} on a Neware battery test system. Cyclic voltammetry (CV) measurements were performed on a PARSTAT 2273 electrochemical workstation with a scanning rate of 0.1 mV s^{-1} for 3 cycles.
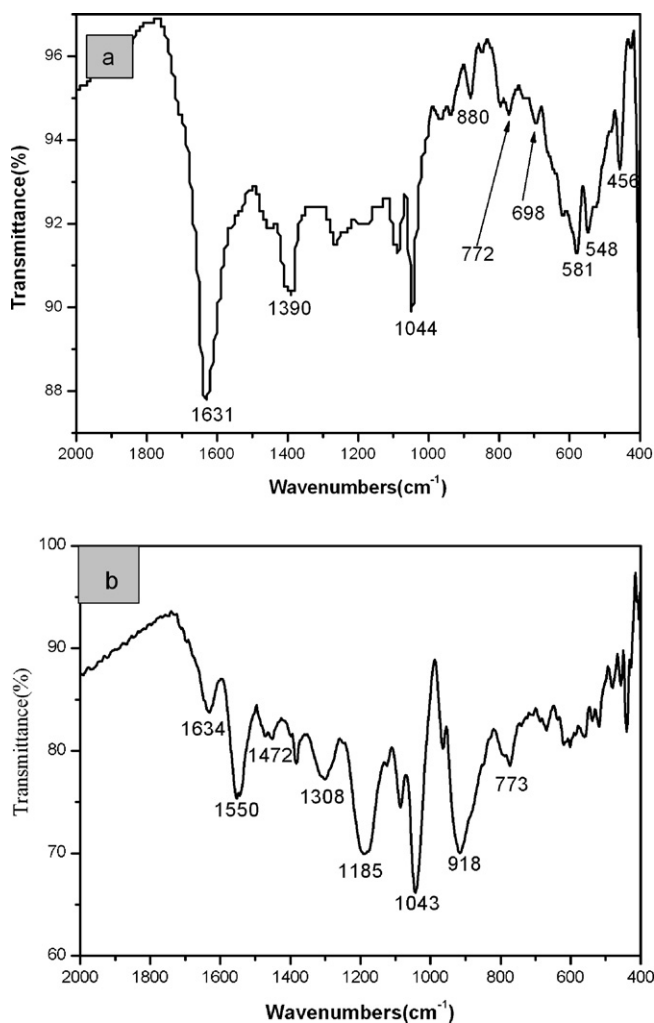
3. Results and discussion

3.1. Characterization of the polymers

Fig. 1 depicts the FT-IR spectrum of polymer obtained, in which line (a) and line (b) correspond to SPPy and PPy respectively. The presence of conjugated p-electron system gives broad bands in the FT-IR spectrum of electronically conductive polymers. The bands centered at 1634 cm^{-1}, 1550 cm^{-1} and 1472 cm^{-1} can be assigned to vibrations of pyrrole ring. The peaks at 1385 cm^{-1} and 1308 cm^{-1} is due to N–C vibration and deformation vibration, respectively. There is an obvious C β-H absorption band at 1043 cm^{-1} and 2 peaks in the range 750–930 cm^{-1}, while the C α-H absorption band does not exist in the spectrum, which indicates that pyrrole rings are mainly connected by α–α in PPy. Fig. 1(a) shows a new peak at 456 cm^{-1} which is attributed to vibrations of the S–S bonds (including elemental sulfur in residual amounts), and the absorption at 548, 581 cm^{-1} and 698 cm^{-1} is caused by the C–S bonds in structures [14,25]. There are still some peaks can be assigned to the absorption of C–H, which may because of that the H atoms in the polymer was not totally substituted by, moreover, they were influenced by the C–S and S–S bands, which cause them somewhat redshift.

Fig. 2 shows the DSC curve of element sulfur (a) and the polymer sulfuration product (b). Fig. 2(a) shows that sulfur would lose almost all its weight below 400 °C. While, there are 2 endothermic
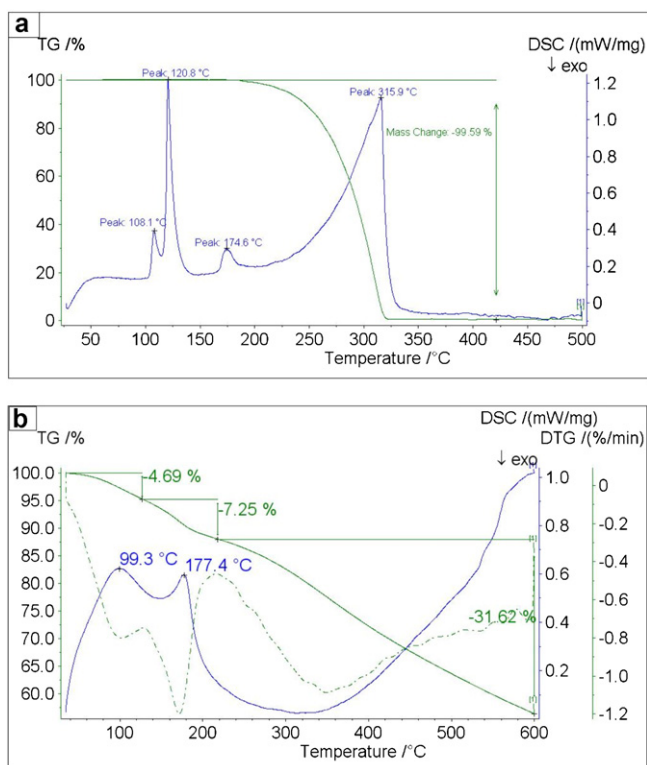
Fig. 2. DSC and TG curve of element sulfur and polysulfide polypyrrole.

Fig. 3. The cycle curve of SPPy/Celgard/Li battery of capacity (line a) and efficiency (line b).

peaks located at 99.3 °C and 177.4 °C in Fig. 2(b). The peak at 99.3 °C is the boiling point of H_2O, which means that the polymer contains some water, about 4.96% (wt). As cross linked structure polysulfide polypyrrole (alike to pure PPy) will never melt or dissolved, so the endothermic peak at 177.4 °C is possible up to the decomposition of SPPy. There is no peak at 120.8 °C, which correspond to the melting point of element sulfur, proves that sulfur in the polymer is in compound state other than elementary substance. TG curve indicates that the polymer lose weight continuously as the temperature increase, the possible reason is some decomposition or other redox reaction happened to the SPPy, thus some S, C, and N elements was lost. The weight loss of the SPPy is less than 10% under 200 °C, and its only 4.69% under 130 °C, therefore, this SPPy has good thermal stability and is suitable to be active material of secondary lithium battery.

Elemental analysis results indicate the polymer contains 26.41% (wt) C element, 7.89% and 64.59% for N and S element respectively, while the H is about 0.87%. According to this, the possible molecular formula of the polymer is $(C_4N_{0.97}H_{1.02}S_{3.71})_n$, which is in coincidence with the FTIR results, some H atoms were remained. No Cl was found in the polymer, which indicate that all Cl atoms are substituted be S. Moreover, the weight loss of SPPy is 23% (in which 4.96% is water) at 350 °C, while element sulfur would lost its weight of more than 90% in this temperature, therefore, the product is not simply mixture of S and PPy, at least a certain proportion of S atoms are chemical combined onto the polymer chain. Conductivity of the as prepared PPy is 95 S cm^{-1}, while it reduced to 17.2 S cm^{-1} for SPPy, therefore, carbon black was added to improve the conductivity of the electrode material.

3.2. The electrochemical properties

The cycle capability curve in Fig. 3(a) shows that the first discharge capacity reached 515 mAh g^{-1} when the current density was 0.1 mA cm^{-2}, and it remained as high as 452 mAh g^{-1} after
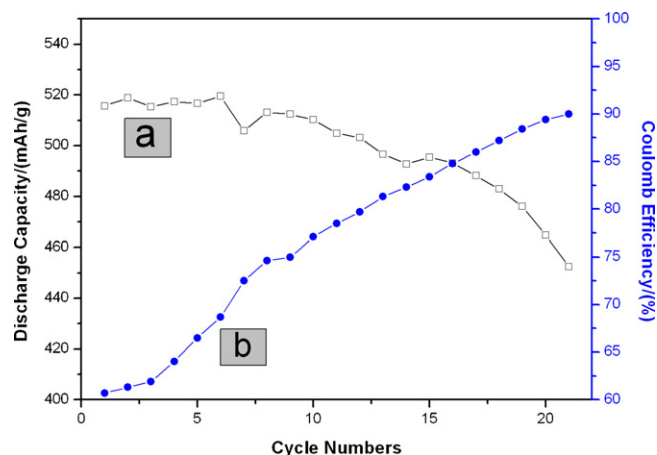
20 cycles. Along with the electrode reaction, the loss of S atoms on SPPy molecular chain would be unavoidable, part of the reaction products, Li_2S_x (in which $2 < x < 8$), would be solved into the liquid electrolytes and cause the loss of active material. Gradually, the polymer would turn into $(C_4N_{0.97}H_{1.02}S_2)_n$ (one S atom on each β–C in pyrrole ring). Moreover, PPy can act as a host material for Li$^+$-ion insertion/extraction in the voltage range of 2.0–4.5 V versus Li/Li$^+$, with a theoretical capacity of 72 mAh g^{-1} [26–28]. According to the formula of $C = 26.8n(m F^{-1}{}_w)$, in which n means the total electron number transferred in the reaction, and F_w corresponding to the molecular weight (or the minimum structure unit to obtain or lose ions) of the active material, theoretical capacity of $(C_4N_{0.97}H_{1.02}S_{3.71})_n$ is about 872 mAh g^{-1} (in which sulfur counts for 800 mAh g^{-1}, and the pyrrole ring for the other 72 mAh g^{-1}), and it is 496 mAh g^{-1} for $(C_4N_{0.96}H_{1.02}S_2)_n$. This could be simulated by the diagram as shown in Fig. 4, sulfur atoms were connected to long polymer chains. During discharge reaction, sulfur atoms may be reduced into S_x^{2-} or S^- ions, in which a portion of S_x^{2-} might be dissolved into the electrolyte as the form of Li_2S_x, while the sulfur atoms which are directly connecting to polymer chains could be saved.

High sulfur content influenced the ion transfer in the cathode, therefore the first discharge capacity is just 515 mAh g^{-1}, far behind the theoretical value, and the coulomb efficiency is as low as 61% (shown in Fig. 3insert b). While as the reaction goes on, part of the sulfur dissolved into the electrolyte in form of lithium polysulfides, which facilitate iron transfer in cathode material, thus the coulomb efficiency increased to more than 90% at the 20th cycle (see Fig. 3insert b). The battery capacity decreased 12.2% in the first 20 cycles, which was much improved compared with that of
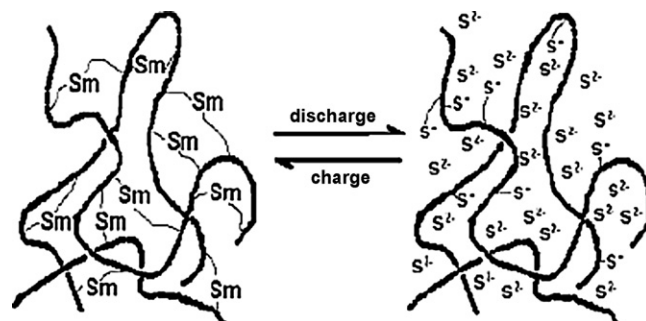

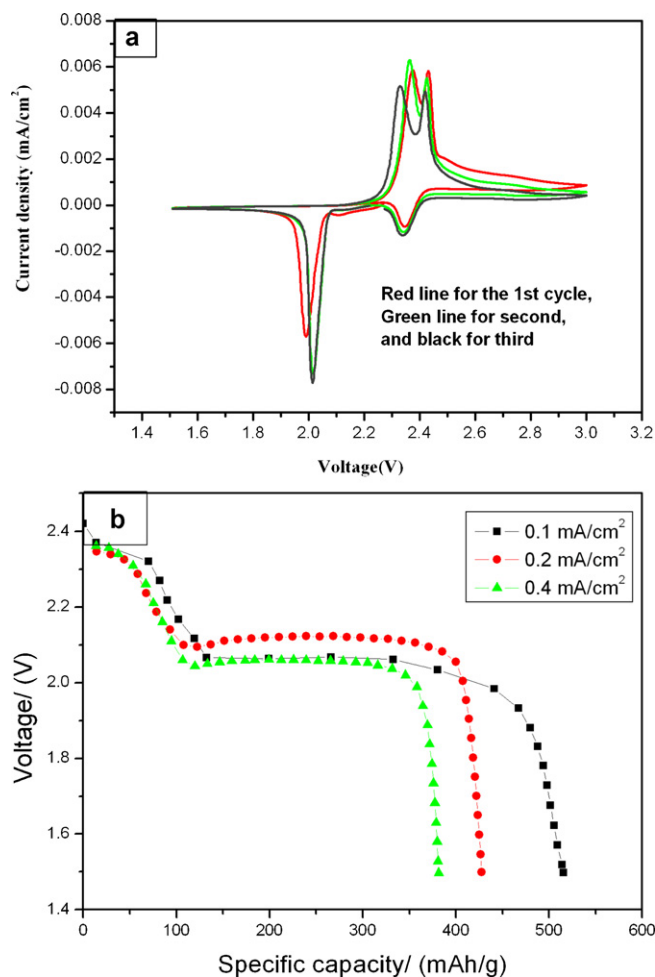**Fig. 4.** A simulative diagram of redox reaction in SPPy battery.

Fig. 5. Cyclic voltammograms (a) and discharge (b) curves of the electrode of SPPy.

when element sulfur or its composite materials were used as active material [17,20,29].

According to the CV performance in Fig. 5(a), it appears that the redox process took place in the range between 1.5 and 3.0 V (versus Li/Li$^+$), quite alike to other polymer-sulfur mixing composites [5,6], but the reduction peaks are split into two parts, which has not been appeared in other composites. As the Li$^+$-ion insertion/extraction reaction into PPy occurs in the range of 2–4.5 V, on which we inferred that one of the reduction peak, perhaps the narrow one at 2.43 V, was reinforced by it.

On basis of CV results, the potential range of 1.5–3.0 V (versus Li/Li) was selected for the continuous charge–discharge cycling. In Fig. 5(b) we can see the discharge curve of SPPy electrode shows two typical plateaus (2.34 and 2.1 V), which in accordance with the two-step reaction of SPPy with lithium during the discharge process as demonstrated in Fig. 5(a). The plateau at 2.34 V could be assigned to the lithium ion insertion to pyrrole ring and the formation of lithium polysulfides, which contribute specific capacity of about 110 mAh g^{-1} and changes little as the current density varies. The other plateau, which can be assigned to the formation of S^{2-} and polymer-S^{1-} (as shown in Fig. 4), takes a large share in the total specific capacity, but changes a lot as the discharge current varies.

4. Conclusions

A novel cathode material, polysulfide polypyrrole was prepared via a 3-step way. The characterization results show that the conducting polypyrrole chains act as backbones thus offer good electric conductivity, polysulfide chains are combined to polypyrrole backbones as side lines to offer high specific capacity in the as-prepared material. Electrochemical behavior of this material exhibited a high discharge capacity of 515 mAh g^{-1} at the first cycle, and a stable reversible capacity of 452 mAh g^{-1} after 20 cycles. Therefore, this cathode material is a good candidate for secondary lithium battery.

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