

Improved disordered carbon as high performance anode material for lithium ion battery

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Abstract A sulfur-substituted disordered carbon is explored as anode material for lithium-ion battery. Its physical and electrochemical properties are characterized by a variety of techniques such as powder X-ray diffraction, element analysis, Fourier transform infrared spectrum, scanning electron microscopy, and typical electrochemical tests. Electrochemical tests show the activated carbon displays a first cycle discharge capacity of $1,216 \text{ mAh}\cdot\text{g}^{-1}$. It also has a remarkable cycling stability with an average capacity fade of 0.92% per cycle from 11th to 100th cycle in the range of 0.01–3.00 V versus metallic lithium at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$. After 100 cycles, the electrode still maintained a capacity of $420 \text{ mAh}\cdot\text{g}^{-1}$.

Keywords Disordered carbon · Lithium-ion battery · Anode

Introduction

As one of the most advanced power source, lithium-ion battery has been investigated intensively in the past decade. Carbonaceous materials have been currently used in most commercial Li-ion battery due to its low cost and relative safety upon cycling when compared to lithium metal. Hence, extensive researches are directed towards various types of carbonaceous materials, such as graphitic carbon

[1, 2], carbon nanotubes [3, 4] and disordered carbon [5–7] and so on.

Among these carbonaceous materials, graphite and graphitized carbon are widely used due to their very flat potential and structural stability upon cycling. However, low lithium storage capacity (normally below $372 \text{ mAh}\cdot\text{g}^{-1}$) corresponding to the LiC_6 stage is the main drawback of graphite. Recently, carbon nanotubes with a large surface area become appealing anode materials because they exhibit an increased capacity as an active material, and induce highly improved cyclic characteristics as an additive to the anode material [8, 9]. However, they maybe not useful in Li-ion cells because of their relatively low reversible capacity ($100\text{--}500 \text{ mAh}\cdot\text{g}^{-1}$) [9, 10]. Disordered carbons, despite their large irreversible capacity and hysteresis [11, 12], have been an alternative anode material due to their appealing features like high uptake of lithium and excellent cycling ability [13–17].

Therefore, in the immediate search for high-performance anode materials, more attentions are being paid on the optimization of disordered carbons. Up to now, many kinds of low-crystallized carbon has been obtained by pyrolysis of condensed aromatic ring compounds and carbon abundant polymer, such as hexa(phenyl)benzene [5, 6], acrylonitrile-butadiene-styrene terpolymer [7], polyacrylonitrile [16, 17] and so on.

3, 4, 9, 10-perylene-tetracarboxylicacid-dianhydride (PTCDA), with their unique π -conjugated structure, is a well-known organic molecule semiconductor and precursor for functional dyes [18, 19]. PTCDA is expected to be a wonderful precursor for carbonaceous material for its unique stacking-layer structure [20] and high carbon content. The use of disordered carbon made from PTCDA as anode material for lithium ion battery had been reported by Takami et al. [21].

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In this work, sulfur is introduced into PTCDA and a new kind of disordered carbon is obtained by pyrolysis of sulfide PTCDA at relative low temperature (600 °C). Electrochemical tests show that the introduction of sulfur greatly improves the capacity and cycling properties of the disordered carbon.

Experimental

Materials and preparation

PTCDA (bright red) and sublimed sulfur were mixed with a mass ratio of 1:1. The resulted mixture were fully grinded and reacted at 450 °C (the product is marked as PS450), 550 °C (PS550), 600 °C (PS600) and 700 °C (PS700) in argon atmosphere for 3 h to give the powders.

Characterization and electrochemical measurements

Element analysis (EA) of the sample was conducted on a VarioEL III element analysis instrument. The powder X-ray diffraction (XRD) was carried out on a Shimadzu 6000 X-ray diffractometer, using Cu $K\alpha_1$ radiation ($\lambda=1.54056 \text{ \AA}$). The morphological features were observed by a scanning electron microscope (Hitachi SEM X-650). Fourier transform infrared spectrum (FT-IR) was recorded using KBr pellets on a Nicolet AVATAR-360 spectrometer in range of 400–4,000 cm^{-1} .

The coin-type cells (size: 2016) were utilized in electrochemical testing. The cells were made by a working electrode and a lithium foil counter electrode separated by a Celgard 2300 microporous membrane. The working electrode was prepared by mixing sulfur-substituted carbon powders with polytetrafluoroethylene binders in a weight ratio of 95:5,

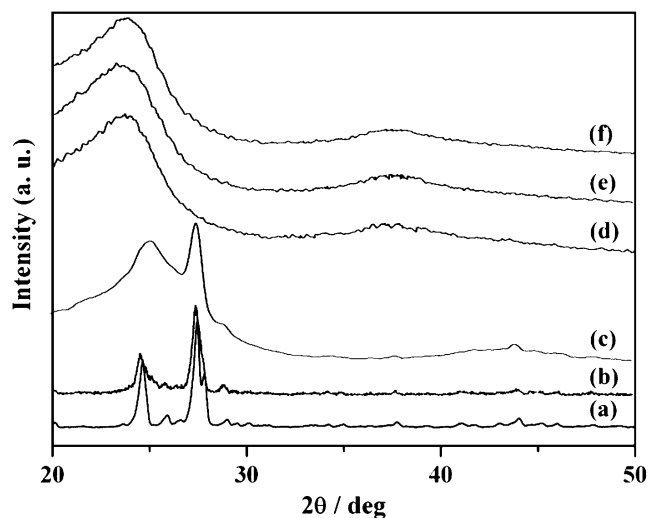


Fig. 1 The XRD patterns of (a) PTCDA, (b) PS450, (c) PS550, (d) PS600, (e) PS700, (f) C600

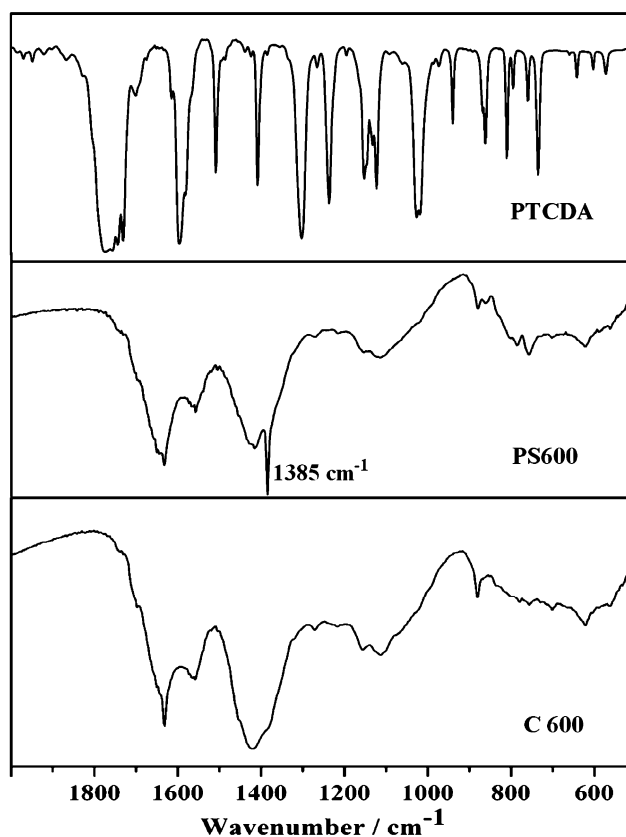


Fig. 2 FT-IR spectra of PTCDA, PS600 and C600

compressing the mixture onto a stainless steel mesh current collector. A 1 $\text{mol}\cdot\text{L}^{-1}$ solution of LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate (EC/DEC, 1:1 vol.%) was used as the electrolyte. The cells were assembled under highly pure argon atmosphere in a glove box (Mikrouna Super 1220/750, China). The discharge–charge tests were examined on a Neware battery test system in the range 0.01–3.00 V vs. Li/Li^+ , using current rate of $100 \text{ mA}\cdot\text{g}^{-1}$.

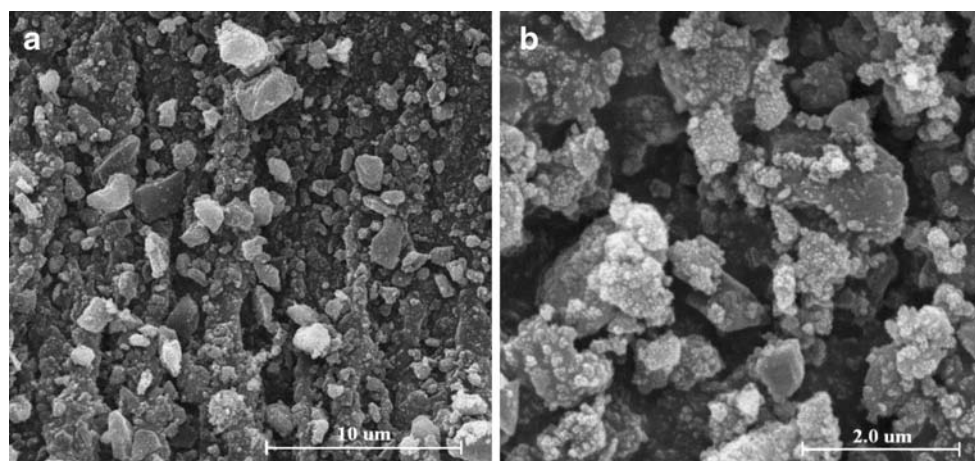
Results and discussion

XRD patterns, FT-IR, and EA

Recently, our group has reported as high-performance cathode materials for Li-ion battery. PS450 has been proved

Table 1 Results from EA and XRD of prepared materials

	PTCDA	PS 450	PS 550	PS 600	PS 700	C 600
Found (%) C	–	70.490	82.870	82.390	89.450	90.400
S	–	7.710	11.470	14.690	6.713	–
H	–	1.529	1.697	1.210	0.820	1.216
d_{002} (Å)	–	–	–	3.578	3.525	3.477

Fig. 3 Scanning electron micrographs of PS600

to be a sulfide polymer with PTCDAs as the main components that cross-linked by thioether (C-S-C) bonds [22]. Figure 1 shows the XRD patterns of PTCDA, the product of pyrolysis of PTCDA at 600 °C (marked as C600) and products obtained by calcining the mixture of PTCDA and sulfur (PS450, PS550, PS600, and PS700).

As shown in Fig. 1, the XRD pattern of PS450 fits well with that of PTCDA. When calcined at temperatures higher than 550 °C, PTCDA begin to decompose and change to disordered substance. From the XRD patterns of PS600 and PS700, the two weak and broad (002) and (100) diffraction peaks, located at about 25.6° and 43.8°, indicate that the amorphous carbons consist of graphite crystallites, while no peaks of elementary sulfur is observed. However, sulfur can be detected by EA in both of PS600 and PS700. Based upon our previous work [22], we believe that in PS600 and PS700, the disordered carbon atoms are interconnected by sulfur atoms. This is also verified by FT-IR spectra shown in Fig. 2. Figure 2 presents the FT-IR spectra of PTCDA, PS600, and C600. It can be seen that in the spectra of PS600 and C600, PTCDA has decomposed completely and they have similar bands. However, a new band of 1385 cm⁻¹ appears in the spectrum of PS600, which can be assigned to the stretching vibration of thioether bonds [23].

Compared to natural graphite (about 3.35 Å), the interlayer distances (d_{002} values) of C600, PS600, and PS700 are larger. On the other hand, d_{002} values of PS600 and PS700 are a little larger than that of C600. Since the covalent diameter of sulfur is larger than that of carbon, 0.77 versus 1.02 Å, the substitution of carbon by sulfur will cause increase in the spacing between adjacent sheets. Larger interlayer spacing may be favorable for lithium insertion and extraction, for maintaining the structure stability of electrode during cycling.

More details of EA are shown in Table 1. From their comparison, it can be seen that the contents of H decrease when the heat-treatment temperature increases. However, the sulfur content increases in the temperature range of

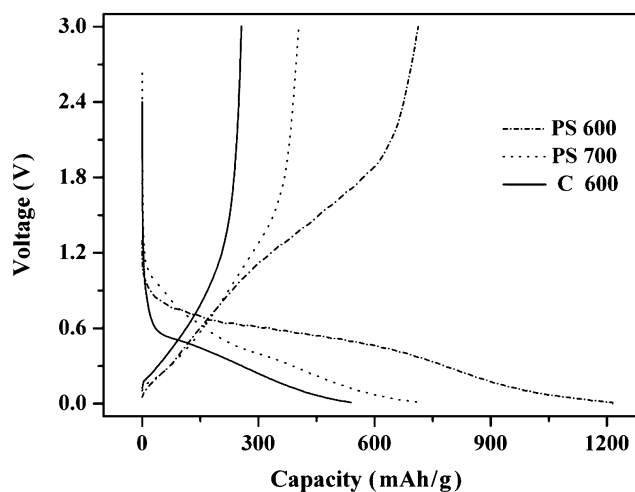
450–600 °C. It can be presumed that most of hydrogen atoms are substituted by sulfur in PS600. This is confirmed by the largest d_{002} value of PS600. Thus, it may affect the physicochemical properties of the prepared carbons. However, in PS700, the sulfur content is lower than that of PS600. This may be due to the sublimation of sulfur at higher temperature.

Size and morphology of PS600

The morphology and particle sizes of the disordered carbon were observed by SEM. Electronic micrographs are shown in Fig. 3. Basically, the graphs show block in morphology with irregular dispersion. The particle size varies from 0.5 to 5 μm. It also can be seen in Fig. 3b that big bulks are coated by small particles on the surface.

Electrochemical properties

The initial discharge–charge curves of different disordered carbons are shown in Fig. 4. There is an inconspicuous

**Fig. 4** Initial discharge–charge curves of PS600, PS700 and C600

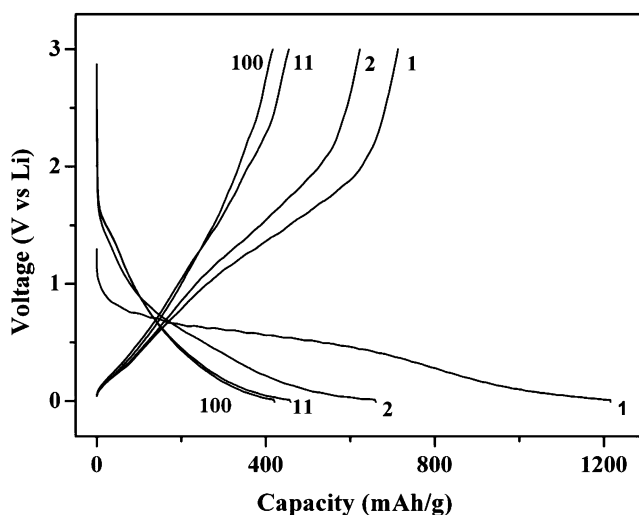


Fig. 5 Voltage profiles of PS600 in different cycles

plateau between 0.9 and 0.3 V in the first discharge curve of PS600 while this plateau is compressed in the first discharge curve of PS700. This plateau may correspond to the formation of Li_2S and Li_2O [24]. There is a plateau at 0.8–0.6 V in the first discharge curve of C600.

Figure 5 shows the voltage profiles of PS600 in different cycles. It can be clearly seen that the discharge plateau of first cycle disappears from the second cycle. The discharge curves of subsequent cycling are similar to that of the second cycle, which has a circular arc shape. But the charge curves are approximately presented as beelines.

The capacity and stability of the disordered carbons are investigated by model test cells using Li-metal as counter

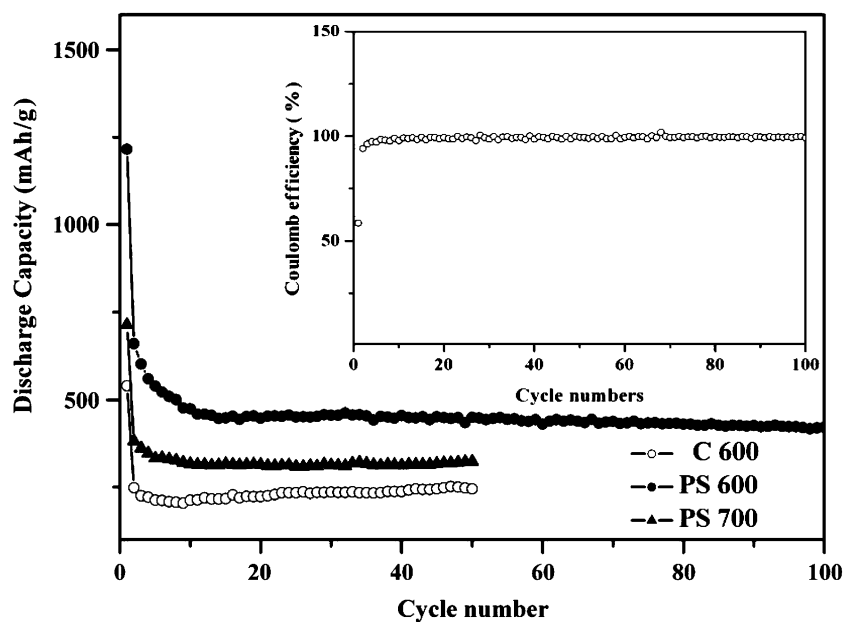
electrode. The cells were firstly discharged (Li-ion insertion) to 0.01 V, and then charged (Li-ion extraction) to 3.00 V at a constant current density of $100 \text{ mAh}\cdot\text{g}^{-1}$. Figure 6 shows the cycling behavior of the electrodes. For PS600, an initial discharge capacity of $1,216 \text{ mAh}\cdot\text{g}^{-1}$ is obtained whereas the capacity for the following discharge is $660 \text{ mAh}\cdot\text{g}^{-1}$. The irreversible capacity loss upon the first cycle is about 45.7%. However, the capacity retention upon subsequent cycling is very good with a fading of 0.65% per cycle. Furthermore, the rate of the capacity decay from the second to the tenth cycle is much higher than that from the seventh to the 200th cycle. PS600 presents excellent cyclic stability with a capacity loss 0.08% per cycle between 11 and 100 cycles. After 100 cycles, this material still maintains a capacity of $421 \text{ mAh}\cdot\text{g}^{-1}$. Except the first cycle, coulombic efficiency of the electrode was 98% or above.

Sulfur can play an important role in the improvement of electrochemical properties of disordered carbon. In this work, the reversible capacity decreases when less sulfur is introduced. As shown in Fig. 6, PS700 and C600 have much lower capacity with initial discharge capacities of 713 and $539 \text{ mAh}\cdot\text{g}^{-1}$, followed by discharge capacities of 381 and $248 \text{ mAh}\cdot\text{g}^{-1}$ in the second cycle, respectively. They only display capacities of 323 and $245 \text{ mAh}\cdot\text{g}^{-1}$ after 50 cycles.

Conclusions

Novel sulfur-substituted disordered carbons have been synthesized by pyrolysis of sulfide PTCDA. The introduction of sulfur enhances the reversible capacity of the

Fig. 6 Cycling stability of PS700, PS600 and C600. Inset means the coulombic efficiency of PS600



disordered carbon. The very good electrochemical performance made it a promising substitute for the conventional graphite materials. However, the mechanism of lithium insertion still needs to be investigated.

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