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Carbon anode materials from polysiloxanes for lithium ion batteries

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Abstract Three kinds of silicon-containing disordered carbons have been prepared by pyrolysis of polysiloxanes with different amounts of phenyl side groups. X-ray powder diffraction, X-ray photoelectron spectroscopy and electrochemical capacity measurements were performed to study their behaviors. Graphite crystallites, micropores, and silicon species affect their electrochemical performances. All of them present high reversible capacities, >372 mAh/g. Since the graphite crystallites are very small, they contribute very little to reversible capacity. The number of micropores produced by gas emission during the heat-treatment process decides whether they exhibit reversible capacity. Si mainly exists in the form C–Si–O and influences the irreversible capacity. There is no evident capacity fading in the first ten cycles, indicating promising properties for these disordered carbons.

Keywords Lithium ion battery · Anode material · Disordered carbon · Polysiloxane

Introduction

Research into disordered carbons prepared at low temperatures (<1200°C) as anode materials for lithium secondary batteries peaked in the mid and late 1990s [1–4], and the introduction of heteroatoms has been widely used to modify the electrochemical performances of

many anode materials [5–14]. Their cycling behaviors are usually unsatisfactory, although their reversible capacities can exceed the theoretical capacity for graphite, 372 mAh/g. Here we prepared Si-doped disordered carbons by heat-treatment of polysiloxanes containing phenyl groups, and their electrochemical performances were measured. Preliminary results show that they have high reversible capacities and their cycling behaviors are very good.

Experimental

Polysiloxanes with different contents of phenyl, $(\text{Ph}_2\text{SiO})_{0.5} [(\text{CH}_3)_2\text{SiO}]_{0.5}$, $(\text{Ph}_2\text{SiO})_{0.28} [(\text{CH}_3)_2\text{SiO}]_{0.72}$, and $(\text{Ph}_2\text{SiO})_{0.16} [(\text{CH}_3)_2\text{SiO}]_{0.84}$, were kindly supplied by Prof. Z. Xie (Institute of Chemistry, Chinese Academy of Sciences, Beijing). They were placed in a tube furnace for heat-treatment. Prior to the heat-treatment, oxygen was flushed out with argon gas. After heating at 800 °C for 3 h, the products obtained were ground and passed through a sieve of 325 meshes for test and analysis. The products from this were designated as samples A1, A2 and A3, respectively.

X-ray powder diffraction patterns were recorded with an X-ray diffraction meter (Rigaku D/max–2500) in the range of $2\theta=10\text{--}100^\circ$. X-ray photoelectron spectroscopy was carried out with a VG ESCALAB220i-XL spectrometer using Al k_α as an X-ray source, and the pressure in the analysis chamber was around 10^{-9} mbar.

The electrodes were prepared as follows. 88% Active material, 5% acetylene black and 7% polyvinylidene fluoride (PVDF) binder in *N*-methylpyrrolidone (NMP) were homogeneously mixed, and the slurry was coated onto a copper foil to form a film. After the evaporation of the solvent, the coating was dried under vacuum at 120 °C and finally pressed at 4 MPa. The area of the prepared electrode was 0.64 cm², and the mass of the active carbon materials was precisely weighed (about 10 mg). Coin-type model cells were assembled in a box filled with argon gas in order to evaluate the electro-

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chemical properties of the active materials. Lithium metal was used as the reference and counter electrode, and 1 M LiPF₆/EC+DEC (1:1 in volume) as the electrolyte solution. The cells were cycled galvanostatically at a current density of 0.15 mA/cm² between 0 and 2.0 V versus Li⁺/Li.

Results and discussion

Table 1 shows the carbon yield from pyrolysis of three kinds of polysiloxanes. The lower the content of phenyl side groups in the precursors, the higher the carbon yield and the lower the weight loss. It was found that the release of benzene was primarily responsible for the major weight loss during the pyrolysis of polysiloxanes containing phenyl side groups [9]. Above 500 °C, the polymer began to decompose rapidly and benzene was given off as the predominant gaseous species. When the temperature was above 600 °C, the evolution of methane and hydrogen began. The main reason for this is that the phenyl side groups can easily form phenyl radicals and benzene gas is given off at lower temperatures. As a result, the carbon yield decreases with the content of phenyl side groups in the precursors. It is known that the release of small molecules will produce micropores at the nanometer level [15, 16]. If the carbon yield is lower, more gases are given off and more micropores will be created.

Figure 1 shows the X-ray powder diffraction patterns of the carbon samples obtained. These materials are typically disordered, since only the diffraction peak of the 002 plane can be clearly identified; this is similar to previously reported disordered carbons [1–15]. They mainly consist of amorphous areas that include micropores and graphite crystallites. The interlayer distance of the graphite crystallites, d_{002} , was estimated according to Eq. 1:

$$d_{002} = \frac{\lambda}{2 \sin \theta}, \quad (1)$$

where λ is the wavelength of the X-ray, β the full width at half-maximum of the peak in radians, and θ is the Bragg angle. The results are presented in Table 1. The interlayer distance d_{002} increases with the content of phenyl side groups in the precursors. Since it is difficult for silicon to form sp² hybrid bonds (necessary for its substitution of carbon atoms in the graphene planes), the difference in d_{002} does not result from the doping of

Table 1 Selected results from the analysis of the carbons obtained

Sample	Carbon yield(%)	XRD analysis		Capacity in the first cycle (mAh/g)	
		d_{002} (Å)	L_c (Å)	Reversible	Irreversible
A1	30	3.83	7.538	528	389
A2	40	3.72	7.717	442	423
A3	50	3.64	7.479	387	442

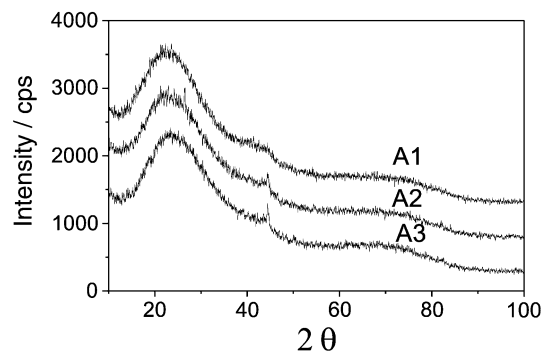


Fig. 1 XRD patterns of samples. The curves of A2 and A3 have been shifted upward successively by 500 counts for clarity

silicon. From the carbon yield it is known that a lot of gases were given off during the heat treatment. When the content of phenyl groups is larger, more gases are released and the probability of combining two graphene sheets is lower. As a result, the interlayer distance d_{002} increases with the content of phenyl groups. We tried to evaluate the size of the graphite crystallite along the c -axis L_c according to Eq. 2 below:

$$L_c = \frac{0.89\lambda}{\beta \cos \theta}. \quad (2)$$

However, since the calculated size of the graphite crystallite is too small the result cannot be correct, although it is also presented in Table 1. Compared with other kinds of disordered carbons [17, 18], the sizes of the graphite crystallites in our prepared carbons are much smaller. In this case, Raman spectroscopy is recommended to measure them.

The XPS spectra of these samples are shown in Fig. 2, and the selected results are also presented in Table 1. It shows that all prepared carbons consist of C, Si and O. The binding energies for C, O and Si in these samples are almost the same, and there is little difference between their peak areas. Oxygen atoms are mainly present in O–Si bonds, whose binding energy peak is at about 532.7 eV. Carbon atoms mainly exist in C–C bonds, whose binding energy peak is at about 284.4 eV, corresponding to carbon atoms in the graphene planes, and small amounts of carbon combine with oxygen and silicon in various forms. The binding energy of silicon atoms here is lower than that in SiO₂ (103.8 eV), but higher than that in SiC (101 eV). This suggests that silicon combines with both carbon and oxygen atoms and exists in the form of C–Si–O, which is in agreement with the Auger electron spectroscopic analysis of the pyrolyzed epoxy-silane composites [19]. From the XPS data, the ratio of O/Si for these carbons is calculated to be about 1.5, indicating that silicon can combine with one, two or three atoms, although their binding energies could not be clearly differentiated in Fig. 2c.

The discharge/charge profiles for the first cycle for the three carbon samples are shown in Fig. 3; selected data

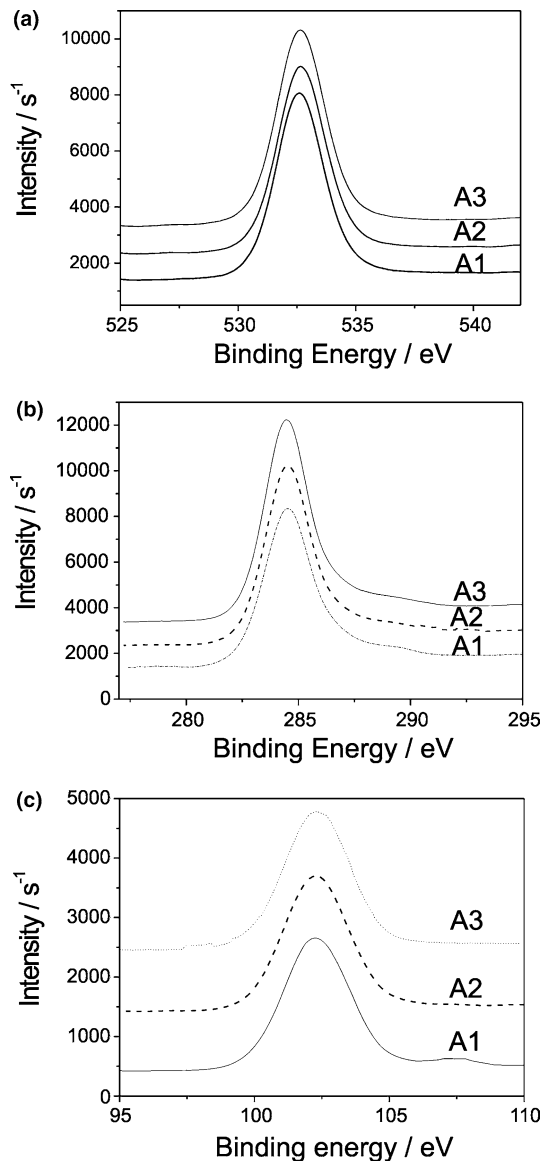


Fig. 2 X-ray photoelectronic spectra of (a) O_{1s} , (b) C_{1s} and (c) Si_{2p} of samples A1–A3. The curves have been shifted upward successively by 1000 counts for clarity

are presented in Table 1. There is no apparent voltage plateau in the charge profiles, which are similar to those of most disordered carbons. The charge capacities of all samples, which are reversible from the discharge profiles in the second cycle, are greater than the theoretical value of graphite, 372 mAh/g. The reversible capacity below 0.5 V, corresponding to lithium de-intercalation from graphite crystallites, is small. Perhaps it is consistent with the above measurement of X-ray diffraction. Many other kinds of disordered carbons show larger graphite crystallites and exhibit an evident capacity for lithium de-intercalation as a slow slope of voltage below 0.5 V [17, 18]. Since the heat treatment time is not long, only 3 h, the size of the graphite crystallites is small. As a result, their contribution to the reversible capacity is not much. If the heat treatment time was longer, then a

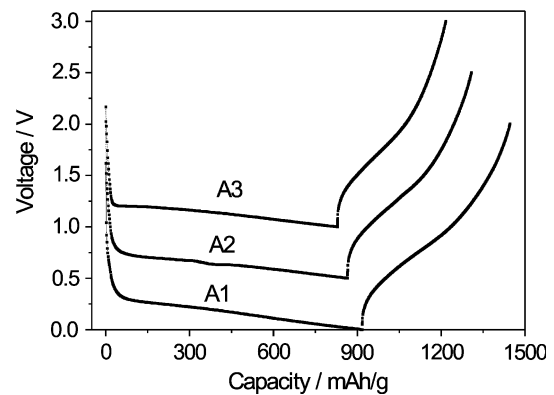


Fig. 3 Discharge/charge voltage profile of the samples A1–A3 in the first cycle under a constant current of 0.15 mA/cm^2 . The discharge rate is about C/20 and the charge rate is about C/10. The data have been offset sequentially for clarity. The shifts are 0.5 and 1.0 V for samples A2 and A3, respectively

larger contribution from the graphite crystallites to the reversible capacity would be obtained [17].

The reversible capacity increases with the content of the phenyl side groups in the precursors, and the highest one is 528 mAh/g. It has been reported that Si–O–C is an active species for lithium storage [14]. However, reversible capacity decreases with its content, which is contrary to our expectation that silicon would play a significant role in the reversible capacity. Consequently, the action of the silicon species cannot account for this increase in capacity, although the silicon species contribute to the reversible capacity, which is evidenced from a peak close to 0.7 V in the curves of differential capacity versus cell voltage (not shown here). As discussed above, more gas is released when the amount of phenyl side groups in the precursor is high, and this tendency can be ascribed to the action of micropores, which contribute to reversible capacity [15, 20, 21, 22].

Figure 3 also shows that the irreversible capacity increases with the content of silicon atoms. In our case, the amount of O is very large from the XPS measurement, about 1.5 O atoms per Si atom. Due to the existence of this O, irreversible capacity is produced [14]. As a result, the irreversible capacity increases with the content of silicon species.

The cycling behaviors of our three samples are shown in Fig. 4. All show good cycling behaviors, and in the first ten cycles there is no evident capacity fading, which is quite different behavior to most disordered carbons [1–14, 23]. Perhaps the main reason for this is their unique structural feature—graphite crystallites—which are mostly unstable during cycling [15] and contribute little to the reversible capacity. Consequently, the reversible capacity does not fade significantly. Of course, the detailed mechanism needs further investigation. These results indicate that these kinds of disordered carbons are promising materials, although some modification is needed to decrease the irreversible capacity in the first cycle and the voltage hysteresis.

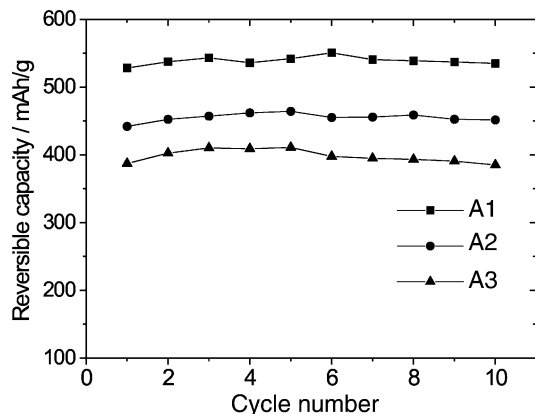


Fig. 4 Cycling behaviors of the prepared Si-doping samples at a current density of 0.15 mA/cm^2 and a voltage range of 0–2 V

Conclusions

In this work, three kinds of polysiloxanes with various amounts of phenyl content were pyrolyzed at low temperature (800°C) in order to prepare disordered carbons. In these carbons, the graphite crystallites are very small. Due to the existence of phenyl side groups, large number of micropores are produced during the heat treatment. Si mainly exists in the form of C–Si–O in these materials. These three factors evidently affect the electrochemical performances of the materials. Since the content of graphite crystallites is very small, their effect on reversible capacity is minor, and good cycling is exhibited. The micropores, acting as storage sites for lithium, are probably mainly responsible for the reversible capacity. Although the C–Si–O species contributes to reversible lithium storage, it mainly affects the irreversible capacity, since the atomic ratio of O/Si is large, about 1.5. These results show that these prepared carbons may be promising anode materials for lithium ion batteries.

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