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Influence of pyrolyzing temperature and time on lithium storage properties of the synthesized SiO_x@C

nanocomposites

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Abstract

Polysiloxane@phenolic resin (Polysiloxane@RF) precursor is firstly synthesized by sol-gel method using resorcinol, formaldehyde and triethoxyethylsilanes as starting materials, and then pyrolyzed at a desired temperature for desired time. The as-prepared SiO_x@C samples are characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Raman spectroscopy, elemental analysis (EA), scanning electron microscope (SEM) and high resolution transmission electron microscopy (HRTEM), respectively. The synthesized SiO_x@C composites consist of nanorods and nanospheres. The electrochemical measurement shows that the composition, microstructure and lithium storage properties of the synthesized SiO_x@C nanocomposites are closely related with pyrolyzing temperature. Among them, the SiO_x@C nanocomposite synthesized at 1000 °C for 3 h delivers the best comprehensive electrochemical performance.

Keywords: SiO_x@C nanocomposite; lithium-ion batteries; anode; pyrolyzing temperature; electrochemical performance

1. Introduction

As advanced anode materials for lithium-ion batteries, silicon oxides are attractive due to high capacity, rich resource and relatively better cycle stability than element silicon [1-11]. Silicon oxides include stoichiometric compounds like SiO and SiO₂ [12-14], and nonstoichiometric compounds like SiO_x (0<x<2, $x \neq 1$)[15]. During initial lithiation, silicon oxides are firstly reduced in situ to form element silicon, Li₂O and a series of lithium silicates, which not only guarantees a high dispersion degree of the reduced silicon and the formed Li₂O and lithium silicates have a good buffer to the volume change of silicon in subsequent cycles, thus silicon oxide electrodes often show relatively better cycle stability [9, 16-20]. However, reducing silicon oxides particle sizes as much as possible and composing them with conductive matrix are still needed to overcome the volume change of silicon and improve the conductivity of the electrodes. Among them, the SiO_x/C composites synthesized by sol-gel route using siloxanes as starting materials are especially interesting because of facile preparation and low cost [8, 21-23]. Lately, some inspiring results have been reported. For instance, Zhao et al. reported that SiO_x/C composite with a core-shell structure delivered a reversible capacity of 817 mAh g^{-1} after 100 cycles [8]. Guo prepared hollow SiO_x nanotubular material by depositing SiO_x layer on a template of filter paper and subsequent calcination process, which showed a reversible capacity of 940 mAh g⁻¹ for 50 cycles [24]. However, to our best of knowledge, there is little work to investigate the influence of the pyrolyzing temperature and time of SiO_x precursor on the electrochemical performance of the synthesized SiO_x@C nanocomposite as an anode for lithium ion batteries. In the paper, we firstly prepare the polysiloxane@phenolic resin precursor by sol-gel method using resorcinol, formaldehyde and triethoxyethylsilanes as starting materials, and then investigate the effect of the pyrolysis temperature from 500 to 1000 °C with different time on the morphology, composition, microstructure and lithium storage properties of the synthesized SiO_x@C nanocomposite. The results show that both pyrolyzing temperature and time have significant influence on the aforementioned properties of the synthesized SiO_x@C nanocomposites except of morphology.

2. Experimental

Material preparation: The preparation procedure of the polysiloxane@phenolic resin precursor is similar to as described in our previous work with some modification.[18] Typically, after 0.2 g of resorcinol was dissolved in a solvent composed of 6 mL of absolute ethanol and 22 mL of distilled water, 0.2 mL of aqueous ammonia was added and continually stirred for 0.5 h at room temperature. Subsequently, 0.2 g of CTAB was added into the above solution and continually stirred for another 0.5 h. After 0.28 mL of formaldehyde was added with further stirring for 5 min, 1 mL of triethoxyethylsilanes were added dropwise and continually stirred for 24 h. Then, the mixture was kept at 80 °C under a static condition in a Teflon-lined autoclave for 24 h. The solid product was recovered by centrifugation and dried at 70 °C in a vacuum for 8 h. The synthesized precursors were transferred into a tube furnace and heated to a desired temperature at a ramp rate of 5 °C min⁻¹ and then kept at the temperature for desired time with an argon flux of 80 mL min⁻¹. The obtained SiO_x@C sample was labeled as S-T, in which T represented pyrolysis temperature.

Physical characterization: X-ray diffraction (XRD) patterns of the synthesized materials were detected using X'Pert PRO (PANalytical)) equipped with Cu K α ($\lambda = 0.15406$ nm) radiation at a scan rate of 5.0 ° min⁻¹ from 10 to 90 °. Thermogravimetric analysis (TGA, TA 2960, TA Instrument) was performed in argon at a heating rate of 5 K min⁻¹. The mass fraction of carbon, hydrogen and oxygen in the synthesized composites was determined by elemental analysis (Elementar analyzer, Elementar Americas INC). Silicon amount was calculated based on the determined carbon, hydrogen and oxygen content. Fourier-transform infrared reflection (FTIR) spectra were recorded from 400 to 4000 cm⁻¹ on a vertex 70 FTIR spectrometer (Bruker). Raman spectra were recorded from 200 to 2000 cm⁻¹ on a Raman spectrometer. Scanning electron microscopy (SEM, Leo-1530, Zeiss) and transmission electron microscopy (TEM, Philips CM12) were conducted to investigate the morphology and microstructure of the as-prepared composites.

Electrochemical measurements: 2032-type coin cells were assembled to evaluate the electrochemical characteristics of the as-prepared SiO_x@C nanocomposites. For preparing working electrode, the slurry mixed with as-prepared active material, carbon black (super P) and sodium alginate (SA) binder in a weight ratio of 75:10:15 in water solvent was pasted onto a Cu foil and then dried in a vacuum oven at 105 °C for 12 h. Mass loading of the active material on the current collector is 1.1-1.4 mg cm⁻². Lithium foil was used as the counter

electrode and reference electrode. The electrolyte was 1 mol L^{-1} LiPF₆ dissolved in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 by volume) with 2% vinylene carbonate (VC) and 10% fluoroethylene carbonate (FEC) as additives. The assembly of cells was performed in a glove box filled with high purified argon. Galvanostatic tests were conducted on the NEWARE multi-channel testing system over a potential window of 0.0-3.0 V versus Li⁺/Li. Unless stated otherwise, the mentioned capacity in this work was calculated on the total mass of the prepared materials. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a Bio-logic electrochemical workstation. After cell cycling ended and the cell was kept at open circuit state for 1 h, EIS measurements were performed at open circuit potential by applying a sine wave with an amplitude of 10 mV over a frequency range from 100 k to 0.01 Hz.

3. Results and discussion

Figure 1 (a) shows the thermogravimetric analysis curve of the polysiloxane@phenolic resin precursor. The weight loss mainly happened at less than 550 °C. After 600 °C, the weight has changed little with the increase of temperature. In this work, 500 °C was chosen as the lowest pyrolysis temperature for the polysiloxane@phenolic resin precursor. The XRD patterns, Raman spectra and FTIR spectra of the polysiloxane@phenolic resin precursor and SiO_x@C composites pyrolyzed at 500, 600, 800 and 1000 °C for 3 h are shown in Fig.1, respectively. From Fig.1 (b), for all tested samples, no sharp diffraction peaks are observed, indicative of their amorphous feature. A broad and weak diffraction peak appears at about 22.5°, which is associated with amorphous SiO₂ [25, 26]. In the XRD patterns of S-800 and S-1000, besides the peak at 22.5 °broadens and the peak position shifts higher angle, a new weak peak appears at about 43°, which are assignable to amorphous carbon.[3] No diffraction peaks for Si and SiC are observed for all samples. From Fig. 1 (c), before pyrolyzing, the FTIR spectrum of the polysiloxane/RF precursor presents the characteristic vibration peaks of methylene linkages at 2933 and 1463 cm⁻¹ and benzene ring at 1613 and 752 cm⁻¹. The broad peak at 3430 cm^{-1} and the sharp peak at 1253 cm^{-1} are attributed to the intermolecular hydrogen bond and the O-H in-plane deformation vibrations, respectively [27, 28]. The strong peak at about 1114 cm⁻¹ corresponds to asymmetric Si-O-Si stretching vibration [8]. These typical peaks indicate that the polysiloxane/RF precursor has successfully been synthesized. Comparing the FTIR spectra of the samples synthesized at different pyrolysis temperatures, it can be seen that the carbonization of phenolic resin at 500 °C is not complete, in which the weak peaks for C-H bonds still appear at 2920, 1276 and 887 cm⁻¹ [29]. With the increase of pyrolysis temperature, the carbonization degree of phenolic resin is enhanced, while three characteristic peaks at about 1090, 801 and 460 cm⁻¹ assigned to asymmetric stretching vibration, symmetric stretching vibration and bending vibration of Si-O-Si bond become stronger. In addition, the peak assigned to Si-O-Si asymmetric stretching vibration gradually shifts to high wavenumber with increasing pyrolysis temperature, indicating the particle size of the formed SiO_x increases [30]. The Raman spectra in Fig. 1 (d) reveal that pyrolysis temperature affects the carbonization degree of phenolic resin and the graphitization degree of the pyrolyzed carbon. No obvious characteristic peak for the pyrolyzed carbon is observed in the precursor, S-500 and S-600, while S-800 and S-1000 present two distinguishable vibration peaks around 1350 and 1599 cm⁻¹, respectively. The peak at 1350 cm⁻¹ is related to disorder carbon (D-band), while the peak at 1599 cm^{-1} is characteristic for graphitic sheets [31]. The fitting shows that the area ratios of the G to D band are 0.52 for S-800 and 0.62 for S-1000, respectively, implying the graphitization degree of carbon increases with the increase of pyrolysis temperature. The element analysis is used to determine the composition of the composites pyrolyzed at different temperatures for 3 h and the corresponding results are listed in Tab.1. Generally, with increasing heat-treatment temperature, the contents of hydrogen, oxygen and carbon decrease, while the content of silicon increases, indicating a high pyrolysis temperature is conducive to removing remnant hydrogen and oxygen. However, when the pyrolysis temperature exceeds 800 °C, the trend becomes slow, indicating that the remnant hydrogen and oxygen has gotten less and less. Herein, it should be pointed out that the rise of silicon content is due to the decrease of other components instead of the carbonthermal reduction of SiO_x. Zhao et al demonstrated that the carbothermal reduction temperature of SiO_x phase happened at about 1200 °C [25]. Our previous work also indicated that no element silicon could be detected in the SiO_x@C composite pyrolyzed at 1000 °C [32].

Figure 2 present the SEM images of the polysiloxane@RF precursor and SiO_x@C composites pyrolyzed at 600, 800 and 1000 °C for 3 h. All samples are composed of submicron-sized spheres and nano-scaled rods. Compared with the polysiloxane@RF precursor, the synthesized SiO_x@C particle size decreases due to phase contraction but they still preserve original morphology. The magnified SEM images show that these particles display crumpled surface like litchi rind. Such morphology and structure arise from the co-assembly of silicate oligomers and the RF precursors on CTAB soft template through electrostatic interactions. In combination with our previous studies [18, 21], it can be speculated that the morphology of

the products is closely related with the ratio of the used ethanol and water. When the ratio of the used ethanol and water is below 1:6, the synthesized SiO_x@C shows single rod-shaped morphology [21]. When the ratio of the used ethanol and water exceeds 2:5, the synthesized SiO_x@C is completely spherical [32]. When the ratio of the used ethanol and water is between 1:6 and 2:5, the synthesized SiO_x@C is the mixture of rods and spheres. Figure 3 shows the HRTEM images of the SiO_x@C nanocomposites pyrolyzed at 500, 600, 800 and 1000 °C for 3 h. For all samples, no crystalline lattice but a turbostratic structure is observed, indicating the amorphous feature of the synthesized SiO_x@C nanocomposites.

Figure 4 shows the charge-discharge profiles of the SiO_x@C nanocomposites pyrolyzed at 500, 600, 800 and 1000 °C for 3 h in the first two cycles at 100 mA g⁻¹. In the first discharge profiles, the slopes between 1.3-0.75 V are attributed to the decomposition of the electrolytes and the formation process of solid electrolyte interface (SEI) film, while the slope between 0.6-0.2 V corresponds to the reduction of silicon oxides, in which element silicon, Li₂O and a series of lithium silicates are formed [10, 18]. The voltage plateau between 0.2-0 V is assigned to the alloying process of the pyrolyzed carbon and reduced silicon. Due to low electronic conductivity of the Li₂O and lithium silicates formed during the first lithiation, there is not obvious alloying/dealloying voltage plateaus in subsequent cycles. From Fig. 4(a), the initial charge/discharge capacities increase with the rise of pyrolysis temperature. For instance, S-500 shows only an initial discharge capacity of 251 mAh g⁻¹ and an initial charge capacity of 95.4 mAh g⁻¹, while the initial discharge capacity and charge capacity of S-1000 increases to 1205 and 880 mAh g⁻¹, respectively. In addition, the lower the pyrolysis temperature is, the bigger the polarization degree of the charge-discharge profiles is. Incomplete pyrolysis of polymers and remnant hydrocarbyl should be responsible for the poor electrochemical performance of the SiO_x@C nanocomposites pyrolyzed at low temperatures. The incomplete pyrolysis of RF polymer leads to low conductivity of the synthesized composites, while the remained hydrocarbyl consumes extra lithium. In the second cycle, although the charge-discharge efficiency significantly increases, the serious polarization of the electrodes still exists at the materials synthesized at low pyrolysis temperatures.

Figure 5 displays the cycle performance profiles of the $SiO_x@C$ nanocomposites synthesized at different pyrolyzing temperature for 3 h at a current density of 100 mA g⁻¹. Since these samples are composed of one-dimensional and zero-dimensional nano-scaled/submicron-sized composites, and the Li₂O and lithium silicates formed during the first lithiation of SiO_x as well as the pyrolyzed carbon have good buffer to the volume change of silicon, they exhibit excellent cyclic stability. Although there is an obvious capacity fading in the first 30 cycles because the kind of materials experience complicate structural change in the initial phase of cycling, in which a part of active components cannot be recycled, no obvious capacity fading is observed in subsequent 200 cycles. However, the influence of pyrolysis temperature on the lithium storage properties of the synthesized samples is obvious. From Fig.5 (a), the initial discharge capacities of S-500, S-600, S-700, S-800, S-900 and S-1000 are 251, 446, 1088, 1144, 1139 and 1205 mAh g⁻¹, respectively. After 240 cycles, the discharge capacity is about 153 mAh g⁻¹ for S-500, 223 mAh g⁻¹ for S-600, 592 mAh g⁻¹ for S-700, 656 mAh g⁻¹ for S-800, 694 mAh g⁻¹ for S-900 and 757 mAh g⁻¹ for S-1000. From Fig. 5 (b), the lower pyrolysis temperature is, not only the lower the first coulombic efficiency is but also the bigger the fluctuation of the coulombic efficiency in subsequent cycles is. Figure 5 (c) shows the rate capability of S-600, S-700 and S-1000. These samples exhibit a stable discharge capacity at subsequent each current density except of the initial 30 cycles and excellent capacity recovery ability. However, the influence of pyrolyzing temperature on the rate capability of the synthesized samples is also obvious. At each tested current density, the sample synthesized at a higher temperature presents a higher discharge capacity than the sample synthesized at a lower temperature. At big current densities, the difference becomes more prominent. For instance, at 800 mA g⁻¹, S-1000 shows a stable discharge capacity of about 399 mAh g⁻¹, while S-700 shows only a stable discharge capacity of about 236 mAh g⁻¹. According to the aforementioned physical characterization results, the observed performance difference with different synthesis temperature should be attributed to the difference of the synthesized materials in composition and microstructure. With enhancing pyrolysis temperature, the remnant hydrogen or oxygen assigned to -OH, C-H, C=O and Si_x(OH)_y groups decrease while the graphitization degree rises, which contribute to the conductive improvement of the synthesized composites and the reduction of O:Si atomic ratio. A lower O/Si atomic ratio means a higher lithium storage capacity available [33]. Meanwhile, the improved conductivity can enhance the utilization of silicon oxide. Herein, it should be mentioned that a too long pyrolyzing time at 1000 °C is not good for the improvement of comprehensive electrochemical properties of the synthesized SiO_x@C nanocomposites because nano-sized SiO_x is readily sintered at a high temperature, which will lead to low a capacity or poor cyclic performance. Figure 6 (a) shows the cycle performance profiles of the SiO_x@C nanocomposites pyrolyzed at 1000 °C for different time. It can be seen that 3 h is optimized pyrolysis time. After pyrolysis time increases from 3 to 5 h, the lithium storage capacity of the synthesized SiO_x@C nanocomposites decreases. From Fig. 6 (b), with

prolonging the pyrolysis time from 2 to 5 h, the diffraction peak at 23.9° for SiO_x shifts to 21.2° and the full width at half maximum (FWHM) becomes more narrow, which is attributed to the sintering of SiO_x nanoparticles [10]. Evidently, the sintering deteriorates electrochemical performance of the synthesized SiO_x@C nanocomposites.

In order to further understand the cell performance shown in Fig. 5, the electrochemical impedance spectra of S-600, S-800 an-1000 electrodes after 15 cycles are recorded and the corresponding results are shown in Fig.7 (a). All profiles consist of two depressed semicircles and an oblique line. The intercept of the high-frequency semicircle with real axis mainly reflects the total resistance of solution and electronic contact (R₁ is used to describe the resistance), while the slope is the Warburg impedance related to the semi-infinite diffusion of lithium ions (Q_3) . The diameter of the high-frequency semicircle represents SEI film resistance (R_2) , while the diameter of the medium-frequency semicircle is associated with the charge transfer resistances (R₃) [34]. Based on equivalent circuit in Fig. 7 (b), in which constant phase angle element (Q) is used to substitute the corresponding capacitor or Warburg resistance, part fitting results are listed in Tab. 2. R₁ decreases successively with the increase of pyrolyzing temperature, indicating the SiO_x@C nanocomposite pyrolyzed at a high temperature is conducive to enhancing the electronic contact resistance of the electrodes. Although the SEI film resistance (R₂) for different electrodes is close, the charge transfer resistance shows significant difference, in which the charge transfer resistance of S-1000 is about one half of that of S-600, indicating the SiO_x@C nanocomposite pyrolyzed at a high pyrolysis temperature facilitates charge transfer.

4. Conclusions

In sum, we investigate the influence of pyrolyzing temperature on the morphology, composition, structure and lithium storage properties of the SiO_x@C nanocomposites from polysiloxane@phenolic resin precursor. The results show that with the increase of heat-treatment temperature from 500 to 1000 °C, it is avail of removing remnant hydrogen and oxygen and enhancing the graphitization degree of carbon. The observed electrochemical performance difference with different synthesis temperature should be attributed to the difference of the synthesized materials in composition and microstructure. In terms of lithium storage capacity, 1000 °C for 3 h is the optimized pyroyzing conditions of the polysiloxane@phenolic resin precursor.

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Table captions

Tab.1 Element composition and atomic ratio of O/Si of the $SiO_x@C$ nanocomposites pyrolyzed at different temperatures for 3 h

Tab. 2 Resistance comparison of S-600, S-800 and S-1000 electrodes after 15 cycles

Sample name	Element content (wt%)				Atomic ratio
	С	Н	0	Si	O/Si
S-500	37.81	1.82	31.81	28.56	1.95
S-600	37.02	1.40	29.32	32.26	1.59
S-700	36.72	0.98	28.82	33.48	1.51
S-800	36.41	0.73	28.36	34.50	1.44
S-900	36.33	0.57	27.92	35.18	1.39
S-1000	35.92	0.54	27.60	35.94	1.34

Tab.2

	R_1/Ω	R_2/Ω	R_3/Ω
S-600	20.3	1.5	97.7
S-800	8.8	1.6	51.6
S-1000	4.3	1.4	47.0

Figure Captions

Fig.1 TG curve of the polysiloxane/RF precursor (a); XRD patterns (b), FTIR spectra (c) and Raman spectra (d) of polysiloxane /RF precursor and the $SiO_x@C$ nanocomposites pyrolyzed at 500, 600, 800 and 1000 °C for 3 h;

Fig.2 SEM images of polysiloxane/RF precursor (a, b) and the $SiO_x@C$ nanocomposites pyrolyzed at different temperatures for 3 h: S-600 (c, d), S-800 (e, f) and S-1000 (g, h).

Fig.3 HRTEM images of the $SiO_x@C$ nanocomposites pyrolyzed at different temperatures for 3 h: S-500 (a), S-600 (b), S-800 (c) and S-1000 (d)

Fig.4 Discharge-charge profiles of the $SiO_x@C$ nanocomposites pyrolyzed at 500, 600, 800 and 1000 °C for 3 h in the first cycle (a) and second cycle (b) at a current density of 100 mA g^{-1}

Fig.5 Cycle performance profiles of the $SiO_x@C$ composites synthesized at different pyrolysis temperatures for 3 h at 100 mA g⁻¹ (a, b) and rate capability profiles of the $SiO_x@C$ composites pyrolyzed at 600, 700 and 1000 °C for 3 h (c)

Fig.6 Cycle performance profiles of the SiO_x@C nanocomposites pyrolyzed at 1000 $^{\circ}$ C for different time at 100 mA g⁻¹ (a) and XRD patterns of the SiO_x@C nanocomposites pyrolyzed at 1000 $^{\circ}$ C for 2, 3 and 5 h (b)

Fig.7 Nyquist plots of SiO_x@C electrodes pyrolyzed at 600, 800 and 1000 $^{\circ}$ C for 3 h after 15 cycles (a) and fitting equivalent circuit for these Nyquist plots (b)



Fig.1











Fig.2



Fig.3



Fig.4



Fig.5



Fig.6





Fig.7

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