Bottom-up Synthesis of Mesoporous Carbon/Silicon Carbide Composite at Low Temperature for Supercapacitor Electrodes

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Abstract:

Novel mesoporous carbon/silicon carbide (C/SiC) composite was synthesized via self-templating method. The synthesis utilizes salt byproducts as the internal self-forming templates. When using as the supercapacitor electrode, the C/SiC composite exhibits a specific capacitance of 220 F g⁻¹, an outstanding cycling stability, and a good rate capability.

1. Introduction

Due to the high chemical stabilities and excellent mechanical properties, silicon carbide (SiC) has been widely used in catalyst supports and power electronics. SiC and SiC based composites are promising materials for long-lifetime supercapacitors [1]. However, commercial SiC possesses a low specific surface area, which hinders its application [2]. Therefore, the preparations of both SiC and SiC based composites with high surface area are attractive challenges [3]. Recently, many novel methods have been developed to synthesize high surface area SiC and SiC based composites by using templating methods [4]. However, there are few successful fabrications of SiC based composites with high surface areas [5]. The main obstacles are the lack of the proper precursors and the high carbonation temperatures [6].

The utilization of templates is one of the most important approaches for the synthesis of mesoporous materials. The templates could be divided into soft templates and hard templates [7]. The soft templates are supramolecular aggregates, while the hard templates are mesoporous solids [8]. The methods of removing templates base on the types of templates, and this process plays a crucial role in the difficulty and cost [9]. Calcination is the most common method of template removal in the soft-templating approach [10]. Otherwise, organic solvent could also be used as extracting agents to remove the soft templates. In the hard-templating synthesis, the templates have to be removed by physical or chemical methods [11]. Since the most popular hard template is siliceous material, the removal usually requires etching with HF or NaOH solution [12].

Herein, we synthesized a novel mesoporous C/SiC composite via the reduction of SiCl₄ and CCl₄ by sodium potassium (NaK) alloy. The resultant salts are incorporated as the porogen, which could be removed with water. This approach enables synthesis of C/SiC composite at 700 °C.

The characterization results suggest the formation of C/SiC composite with mesoporous structure. When using as the supercapacitor electrode, the mesoporous C/SiC composite exhibits high specific capacitance (220 F g^{-1}), excellent rate capability, and good cycling performance ($>95\%$ for 6000 cycles). Compared to the mesoporous carbon prepared with this method, the mesoporous C/SiC composite has better performance in long-lifetime supercapacitors.

All manipulations were performed in a glovebox filled with Ar. Sodium potassium alloy (NaK) was prepared by mixing sodium (0.35 g, 0.015 mol) and potassium (1.35 g, 0.035 mol). The prepared alloy was dropped into a toluene solution of SiCl_4 (0.90 mL, 0.0078 mol) and CCl_4 (0.75 mL, 0.0078 mol). This mixture was heated at 120 °C for 8 h. After cooling the mixture down to room temperature, diethyl ether solution of HCl was added to remove the excess NaK alloy. The product was carbonated at two different temperatures (600 and 700 °C) for 1 h under Ar atmosphere. The annealed sample was washed with water, collected by filtration, and dried at 80 °C under vacuum. The samples are denoted as C/SiC-X, where X represents the carbonization temperature.

C/SiC-700, and (e) high resolution XPS spectrum of Si 2p region of C/SiC-700, (f) TGA curve of C/SiC-700.

The XRD pattern of the intermediate product shows that the peaks could be corresponded to KCl and NaCl (Fig. 1a), indicating the formation of the salt byproducts [13]. The XRD pattern of C/SiC-700 shows that the SiC peaks are obtained (Fig. 1b). The peaks shown at 36° , 61° , and 72° could be assigned to the (111), (220), and (311) planes of SiC, respectively. Two broad peaks at around 24° and 42° could be attributed to amorphous carbon [14]. However, the XRD patterns of C/SiC-120 and C/SiC-600 show two peaks at 24° and 42° , and there are no peaks that could be assigned to SiC (Fig. 1b). It could be concluded that the annealing temperature is critical for the formation of SiC. The Raman spectra of C/SiC-120 and C/SiC-700 were both investigated (Fig. 1c). The disordered D band around 1350 cm^{-1} and the ordered G band around 1590 cm^{-1} are both observed [14]. Due to the peak intensities, the values of I_G/I_D ratios for C/SiC-120 and C/SiC-700 are 1.33 and 1.45, respectively, indicating these composites possess graphitic and disordered structures. Moreover, the I_G/I_D ratio increased for C/SiC-700, indicating that C/SiC-700 possesses improved electrochemical performance [15]. The high resolution XPS analysis (Fig. 1e) exhibits the Si 2p spectrum could be fitted into two peaks at 100.8 eV and 101.4 eV, respectively, and the former is the characteristic of SiC [16]. The TGA curve of C/SiC-700 was shown in Fig. 2f. The weight loss of 66% between 400°C and 600°C could be ascribed to the combustion of carbon. When the temperature increases further, the curve shows the third weight-change with a slight rising trend, due to the oxidation of SiC [2]. This result indicates the mass ratio of carbon/silicon carbide is around 2: 1.

Fig. 2. Nitrogen physisorption isotherms of (a) C/SiC-120 and (c) C/SiC-700. Pore size distributions of (b) C/SiC-120 and (d) C/SiC-700.

The Nitrogen physisorption isotherms in Figs 2a and 2c are both type-IV isotherm curves, indicating the mesoporous structure. Furthermore, the H1 hysteresis loops indicate that C/SiC-120 and C/SiC-700 possess good pore connectivity [17]. The BET specific surface areas for C/SiC-120 and C/SiC-700 are 501.37 and 1188.96 $\text{m}^2 \text{g}^{-1}$, respectively. The pore volume of C/SiC-120 is 0.34 $\text{cm}^3 \text{g}^{-1}$, while C/SiC-700 possesses much higher pore volume of 1.76 $\text{cm}^3 \text{g}^{-1}$. As shown in Fig. 2b, the pore size distribution of C/SiC-120 is centered on 4 nm. Additionally, there is a fraction of large mesopores in C/SiC-700 (Fig. 2d).

Fig. 3. (a, b) TEM images and (c) HRTEM image of the intermediate product, TEM images of (d) C/SiC-120 and (e) C/SiC-700, (f) HRTEM image of C/SiC-700.

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To confirm the mechanism of this reaction, the intermediate product, C/SiC-120, and C/SiC-700 were characterized by TEM. The TEM image and the HRTEM image of the intermediate product confirm that the KCl nanoparticles act as the templates (Figs 3a-3c). In the intermediate product, the diameters of the KCl nanoparticles are consistent with those of the mesopores in the final products. The TEM images reveal the presence of mesopores in C/SiC-120 and C/SiC-700 (Figs 3d and 3e). As compared to C/SiC-120, large mesopores could be observed in C/SiC-700. The lattice fringes of SiC [200] are observed in HRTEM image (Fig. 3f) [1]. According to the results above, both C/SiC-120 and C/SiC-700 possess porous structure.

Fig. 4. (a) CVs of C/SiC-700 at different scan rates, (b) charge/discharge curves of C/SiC-700 with increasing scan rates, (c) calculated capacitance according to the data in (b), (d) Stability test of C/SiC-700 during 6000 cycles at 1 A g⁻¹.

C/SiC-700 could be anticipated to possess potential application in supercapacitors. Two electrodes were assembled in a CR-2016 coin cell, with a 6 M KOH solution used as the electrolyte. Fig. 4a shows the CV curves of C/SiC-700 over a wide range of scan rates (5-100 mV s⁻¹). The electrodes show the rectangular-like curves, indicating that the capacitive response is from the electric double layer capacitance. As shown in Fig. 4b, the galvanostatic charge/discharge curves are symmetrical and linear. Moreover, all of these curves are consistent with the CVs. As shown in Fig. 4c, the specific capacitances are 220, 202, 197, 193, 166, and 130 F g⁻¹ at current densities of 1, 2, 5, 10, 20, and 50 A g⁻¹, respectively. Furthermore, C/SiC-700 shows high cycling stability at 1 A g⁻¹ (Fig. 4d). Compared to the mesoporous carbon

synthesized with this method, C/SiC-700 shows better performance in long-lifetime supercapacitors [13]. 95% of the original capacitance is retained after 6000 cycles, indicating good cycle stability. All the results above show that C/SiC-700 could be a good candidate for supercapacitor.

4. Conclusions

We developed a novel approach to prepare C/SiC composite via the reduction of silicon tetrachloride and carbon tetrachloride by NaK alloy. The resultant byproducts could be used as the porogen. The characterization results suggest formation of the C/SiC composite with mesoporous structure. When the temperature is 600 °C or lower, the obtained samples are amorphous. When using as the supercapacitor electrode, C/SiC-700 exhibits high specific capacitance (220 F g⁻¹) and excellent cycling performance (>95% for 6000 cycles).

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Figure1

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Figure2

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Figure3
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Figure4

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