Fabrication and electrochemical performance of nanoporous carbon derived from silicon oxycarbide

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ABSTRACT

Microporous and mesoporous silicon oxycarbide derived carbons (SiOC-DCs) were obtained by chlorination with post treatment in ammonia (NH_3) using a commercially available polymethyl(phenyl)siloxane resin. In this paper, attentions were focused on the structural evolution and electrochemical performance of SiOC-DCs as a function of pyrolysis temperature. Results showed that the geometry and macrostructure of SiOC-DCs, as well as the carbon ribbons were finely inherited from SiOC. The SiOC-DCs porosity and crystallinity depends mainly on the pyrolysis temperature. Post treatment by NH_3 could further increase the sample porosity, and had little affection on the carbon crystallinity. The final SiOC-DCs samples exhibit excellent electrochemical performance as electrodes for supercapacitors, with a relatively high specific capacitance value up to 148.7 F g^{-1} and good capacitance retention ratio up to 94.3% after 2000 charge–discharge cycles at a current density of 1 A g^{-1} with KOH aqueous solutions as electrolyte. Increasing pyrolysis temperature would lead to a continual decline of specific capacitance.

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1. Introduction

In recent years, nanoporous carbon has attracted much attention for its widespread applications as electrode for supercapacitors or batteries, support for metal nanopaticles, effective adsorbent for separation processes or gas storage, water/air filters, and biomedical devices owing to its typically biocompatible characteristic, low density, high thermal conductivity, quite chemically stable under nonoxidizing conditions, and good electrical conductivity [1–4]. To date, many efforts have been made to fabricate nanoporous carbon, including template techniques (using hard or soft templates) [5–8], activation techniques (including physical or chemical activation) [9,10], carbide derived carbon (CDC) techniques [11–16], etc. And it is well demonstrated that CDC techniques own many advantages on controlling over the porosity (specific surface area, pore volume) and structure (amorphous, turbostratic, onion-like, etc.) at the atomic level by changing etching temperature and carbide species (e.g., SiC, TiC, WC) in comparison with other techniques [11].

Polymer derived ceramics (PDCs), such as SiCN, SiC, and SiOC, have also been adopted as the CDC precursor. As it is expected

the method from PDCs to CDCs can further optimize the CDCs properties by adjusting pyrolysis conditions (e.g., temperature, precursor kind, particle size, and dwelling time) [17–20]. Gogotsi et al. [17] have reported CDCs with hierarchical porosity by employing preceramic polymer-derived SiCN precursors. Their specific surface area in the range of 800–2400 m^2/g and crystallinity could be adjusted by changing the pyrolysis temperature (600–1400 °C) prior to chlorination process. Subsequently, they employed SiOC ceramics as CDC precursors, and found that the specific surface areas (SSA) and pore size distributions (PSDs) depended on the final characteristics of SiOC ceramics. SiOC derived carbons (SiOC-DCs) exhibited a high SSA reaching 2700 m^2/g, and a large pore volume (1.72 cc/g), and showed excellent performance in gas storage (H_2 or CH_4) [18]. Kaskel et al. [21] also prepared SiOC-DCs via pyrolysis and chlorination of a xerogel precursor, found the SiOC-DCs owned large microporosity and exhibited good long term stabilities with an organic electrolyte. Nevertheless, the electrochemical performance of SiOC-DCs with an aqueous electrolyte has hitherto not been discussed.

Herein, this article aims at exploring the structural evolution of SiOC-DCs from polysiloxane and its electrochemical performance with KOH aqueous solutions as electrolyte as a function of pyrolysis temperature. As we all know, the pyrolysis temperature has a significant impact on the structure evolution of SiOC, especially during its phase separation and carbothermal reduction process,

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which may consequently affect its chlorination and performance. However, this has not been explored very well. In addition, the influence of post treatment in NH_3 atmosphere on the porosity and structure of SiOC-DCs was investigated for the first time.

2. Experimental

2.1. Sample preparation

SiOC-DCs powders (<50 µm particle size) were produced by chlorination followed with NH_3 post treatment. SiOC ceramics were produced using a commercially available polymethyl(phenyl)siloxane resin (Dow Corning 249 flake resin). Firstly, the polysiloxane precursor was cross-linked at 250 °C in air for 4 h, and crushed into powders by using disintegrator. The powders, with particle size ranging from 150 to 250 µm were placed in a graphite crucible and heated to appointed pyrolysis temperature for 2 h under nitrogen (99.999% pure) with a heating rate of 5 °C/min and then allowed to cool naturally. Secondly, the SiOC powders which have been ball-milled for 10 h were placed in a horizontal tube furnace (diameter 6 cm), purged in nitrogen flow, heated to 900 °C with the rate of 5 °C/min and exposed to dry chlorine gas (15–20 cm³/min) for 3 h. After chlorination, the etched samples were treated at 600 °C for 2 h under flowing ammonia (NH_3) in order to remove residual chlorine and volatile chlorides trapped in pores. For the sake of briefness, pyrolysis temperature in tables or figures is abbreviated to 'Py'. The samples in this paper are named 'Py1200°C-SiOC', 'Py1600°C-SiOC', 'Py1200°C-SiOC-DCs', etc.

2.2. Characterization methods

2.2.1. Structural analysis

Raman spectra were recorded with a LABRAM-HR (JOBIN YVON) microspectrometer using an argon-ion laser (514.5 nm, ~1 µm lateral spot size). X-ray diffraction (XRD) analysis was managed using a Rigaku diffractometer with CuKa radiation ($k = 0.154$ nm) operated at 30 mA and 40 kV. XRD patterns were collected using step scans, with a step size of 0.01° (2θ) and a count time of 2 s per step between 10 (2θ) and 90 (2θ) degrees. Scanning electron microscopy (SEM) was performed on samples with no sputter coating using a HITACHI FEG S4800 scanning electron microscope operating at 10 kV equipped with an energy dispersive X-ray spectrometer (EDS). All SEM samples were analyzed without the application of any sputter coating. Transmission electron microscopy (TEM) samples were prepared by dispersing powders in ethanol and placing the solution over a copper grid. TEM measurements were performed using a JEOL JEM2100F microscope operating at 200 kV.

2.2.2. Gas sorption measurement

N_2 adsorption–desorption isotherms were obtained using Quantachrome instruments at 77 K. Brunauer–Emmertt–Teller (BET) analyses (estimated at $P/P_0 = 0.05$–0.25) were used to determine the total specific surface area (S_{BET}). The quenched solid density functional theory (QSDFT) method was used to analyze the CDC pore size distributions (PSDs) and pore volume. The total pore volume (V_t) was calculated at $P/P_0 = 0.99$. The micropore volume (V_{micro}, $d < 2$ nm) and mesopore volume (V_{meso}, $2 < d < 50$ nm) were
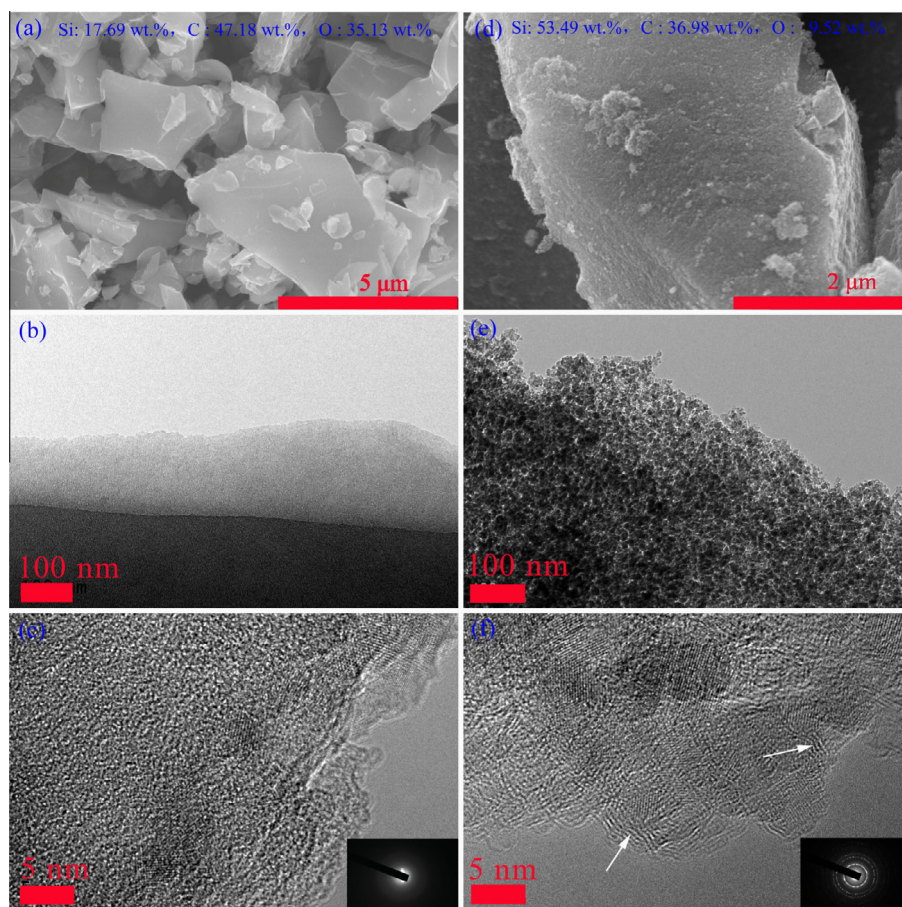
Fig. 1. Structure images of Py1200°C-SiOC (a–c) and Py1600°C-SiOC (d–f), including SEM images and Si, C, O content obtained by EDS (a,d), TEM images (b,e), HRTEM and SAED images (c,f). White arrows symbol carbon ribbons in SiOC ceramics.