Carbonization temperature dependence of pore structure of silicon carbide spheres and their electrochemical capacitive properties as supercapacitors

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Abstract

Three-dimensional silicon carbide-based frameworks with hierarchical micro- and mesoporous structures (2MSiC) are prepared by employing the template method and carbonization reaction using aerosol-spray drying. The mesopores are generated by the self-assembly of a structure-directing agent, whereas the micropores originate from the partial evaporation of Si atoms during the carbonization process. During the carbonization process, the proportion of micro- and mesopores in 2MSiC can be controlled by the carbonization temperature by controlling the amount of partial evaporation of Si atoms. The 2MSiC electrode prepared using a Brij56 structure-directing agent as the mesopore template and carbonized at 1250 °C exhibits a high charge storage capacity with a specific capacitance of 259.9 F g^{-1} at a scan rate of 5 mV s^{-1} with 88.1% rate performance from 5 to 500 mV s^{-1} in 1 M KCl aqueous electrolyte. This outstanding electrochemical performance can be attributed to the synergistic effect of both the enhanced electric double layer properties caused by micropores and reduced resistant pathways for ion diffusion in the pores as well as a large accessible surface area for ion transport/charge storage caused by mesopores. These encouraging results demonstrate that the 2MSiC electrode prepared with Brij56 and carbonized at 1250 °C is a promising candidate for high-performance electrode materials for supercapacitors.
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1. Introduction

Compared with Li-ion batteries and traditional dielectric capacitors, supercapacitors have received worldwide attention because of their fast charging and discharging, long cycle life, high power density, safety, and environmental friendliness [1–3]. Supercapacitors can be classified into two types according to the energy storage mechanism, namely electric double-layer capacitors (EDLCs) and pseudocapacitors. The capacitance of the former arises from an EDL at the interface between the electrode and electrolyte; carbon materials are typical examples [4]. The capacitance of the latter results from the fast and reversible Faradic reactions at the surface of electrodes, such as transition metal oxides. Currently, most commercial supercapacitors are

symmetric EDLCs based on high-surface-area carbon materials [5]. However, in most practical applications, EDLC with porous carbon electrodes suffer from a limited energy density, which is typically on the order of 4–5 Wh kg^{-1} for fully assembled cells —an order of magnitude lower than that of batteries [6]. Therefore, to solve these problems, scientists have attempted to increase the capacitance with high-surface-area electrode materials.

To obtain a high surface area, porous carbonaceous materials such as activated carbon, carbide-derived carbon, ordered mesoporous carbon, and carbon aerogels have been studied as high-surface-area electrodes for EDLCs. These porous carbon electrode materials are prepared using various synthetic routes, such as carbonization of organic/polymeric precursors [7,8], chemical vapor deposition [9,10], excimer laser ablation of graphitic targets [11,12], and sputtering/plasma-based synthesis [13,14]. However, the low electrical conductivities of

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these materials are not favorable to construct a conductive network because it can decrease the internal resistance of an electrode and generate electrostatic charges on the surface of the electrode, forming the electric double layer [15].

Several approaches have proposed the application of semiconductors or cermet nanowires as EDLC electrode materials instead of traditional carbon-based materials. Various types of EDLC materials such as silicon (Si) nanowires, silicon carbide (SiC) nanowires, titanium nitride (TiN) nanowires, titanium dioxide (TiO_2) nanotubes, and nanowires have attracted considerable interest because of their high surface area and excellent electrical conductivity [16–21]. Among these, SiC, nanowire type SiC in particular, shows potential as an EDLC material because of its high electron mobility, small band gap, and high surface area. However, because the working materials are grown directly on the current collector, these nanowire structures are ill suited for the fabrication of hybrid composites combined with metal-oxide or conductive polymers or their application as macroscale supercapacitor electrodes. Recently, the use of SiC microsphere particles as EDLC materials has been reported, demonstrating their potential. However, the porous properties of these SiC microsphere particles, such as their surface area and pore volume, are not impressive because of the nonporous structure, which results in low capacitive performance (72.4 F g^{-1} at a scan rate of 10 mV s^{-1} in Na_2SO_4 aqueous electrolyte) [22–24]. Consequently, to obtain a high surface area, it is crucial to develop SiC particles with porous structures.

Most porous carbon EDLC materials consist of an abundant proportion of micropores (pore diameters < 2 nm). These micropores play an essential role in optimizing the electric double layer surfaces and strengthening the capacitance. However, because of the small pore size, these micropores are not always fully accessible to ions. The small micropores are not easily wetted by the electrolyte, and the exposed surface in the micropores may not be utilized for charge storage. Moreover, even when the micropores are wetted by the electrolyte, the ionic motion in such small pores may be so slow that a high rate capability cannot be achieved [25,26]. Therefore, mesopores that can provide low-resistant pathways for ion diffusion in the pores with good charge propagation are needed to improve the capacitive activity, resulting in a harmonious electrochemical environment for the complete realization of fast ion transport and high charge storage capability.

In this study, we developed a novel micro- and mesoporous SiC sphere (2MSiC) using the template method and carbonization with aerosol spray drying. The mesopores were generated by the self-assembly of the structure-directing agents, whereas the micropores were generated from the partial evaporation of Si atoms during the carbonization. To achieve fundamental insight into the electrode kinetic mechanisms and correlation between the porous structure and electrolyte ions, the relationship between the porosity of micro- and mesopores and electrochemical performance must be investigated. Therefore, the micro- and mesopores in 2MSiC were controlled by the carbonization temperature, and their electrochemical performance was investigated. The 2MSiC electrode prepared using

Brij56 as the structure-directing agent and carbonized at 1250 °C exhibited a high charge storage capacity with a specific capacitance of 259.9 F g^{-1} at a scan rate of 5 mV s^{-1} with 88.1% rate performance from 5 to 500 mV s^{-1} in 1 M KCl aqueous electrolyte. These encouraging results indicate that the 2MSiC electrode prepared with Brij56 for the mesopore template possesses potential advantages for applications as supercapacitor electrodes with high energy and power density.

2. Experimental

2.1. Synthesis of micro- and mesoporous silicon carbide sphere

In a typical synthesis, 0.917 g of Si nanoparticles (of approximately 5 nm) was dispersed in 33 mL of D.I. water. Subsequently, 0.014 mL of hydrogen chloride (HCl), 43.3 mL of ethanol (C_2H_5OH), and 1.9742 g of $C_{16}H_{33}(EO)_{20}H$ (Brij56) were added and stirred for 1 h. The resulting solution mixtures were ultrasonically sprayed with a home humidifier (60 MHz and 35 W). The droplets were carried by Ar gas (purity: 99.999%) at a flow rate of 100 sccm (standard cubic centimeter per minute) into a tubular reactor. The tubular reactor was separated into two segments, namely, the drying zone and heating zone. The drying-zone tubular reactor (30 mm in diameter and 700 mm in length) was heated up to 150 °C; the heating-zone tubular reactor (30 mm in diameter and 1000 mm in length) was heated up to 1150, 1250, or 1350 °C. At the entrance of the heating zone, C_2H_5OH was ultrasonically mixed and carried by Ar gas at a flow rate of 60 sccm. The particles were recovered by filtration at the outlet of the heating-zone tubular reactor. After the reaction was terminated and the reactor was cooled to room temperature, the resulting products were exposed to air and heated to 600 °C for 4 h to eliminate the superfluous C. Finally, the SiO_2 layer adsorbed on the surface of the 2MSiC particles was removed by treatment with hydrofluoric acid (HF). 2MSiC powder (10 g) was placed in 300 mL of 10% HF solution and stirred for 24 h. The sample was then leached with distilled water until the pH of the leaching water reached a value of 7–8. The resulting powder was collected and dried at 100 °C in a vacuum. The resultant 2MSiC sphere materials are denoted as 2MSiC-*T*, where *T* indicates the carbonization temperature.

2.2. Characterization methods

X-ray diffraction (XRD) patterns were collected using a New D8-Advance/Bruker-AXS diffractometer at a scan rate of 1° s^{-1} within the 2θ range of 10–80° using CuK$_{\alpha 1}$ radiation (0.154056 nm). The morphologies of the samples were examined using high-resolution transmission electron microscopy (HR-TEM, JEM-3010). X-ray photoelectron spectroscopy (XPS) analysis was performed on a VGMicrotech ESCA2000 system using a spectrometer with a Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer. During the curve fitting, the Gaussian peak widths were constant in each spectrum. Nitrogen sorption analysis was performed using an