



Influence of surface oxygen functional group on the electrochemical behavior of porous silicon carbide based supercapacitor electrode



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ABSTRACT

Supercapacitors have been attracting considerable interest because of their wide range of applications in electric vehicles, digital devices due to their high power density, short charging time, and long cycling life. For ideal charge/discharge mechanism, the micro and mesoporous silicon carbide flakes (PSF) with a high surface area of $1376 \text{ m}^2 \text{ g}^{-1}$ were obtained by one-step carbonization of Si flakes. The micropores originated from the partial evaporation of Si atoms during the carbonization process, while the mesopores were formed by the integration of neighboring micropores. Subsequently, oxygen-containing functional groups were introduced on the PSF surface to stimulate the faradic redox reaction during the charge/discharge process. The PSF electrode oxidized for 24 h (OPSF–24 h) exhibits a high charge storage capacity, showing a specific capacitance of 243.3 F g^{-1} at a scan rate of 5 mV s^{-1} with 85.6% rate performance from 5 to 500 mV s^{-1} in 1 M KCl aqueous electrolyte. This outstanding capacitive performance of OPSF–24 h electrode can be attributed to the harmonious synergistic effect between the electric double-layer capacitive contribution of the PSF and the pseudocapacitive contribution of the oxygen-containing functional groups.

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1. Introduction

The growing energy demands and worsening global issues demand an urgent development of clean alternative energies as well as advanced energy storage devices. Electrochemical capacitors, also known as supercapacitors, have drawn considerable research attention as ideal energy storage devices owing to their significant advantages, such as high power density, long cycle-life, and safety tolerance to high rate charge and discharge [1–4]. According to the energy storage mechanism, two types of supercapacitors can be identified, namely, electric double-layer capacitors (EDLCs) and pseudocapacitors. The capacitance of the former, of which carbon materials are typical examples, arises from an electric double layer at the interface between electrode and electrolyte. On the other hand, the capacitance of the latter is due to fast and reversible Faradic reactions occurring on the electrode surface; transition metal oxides belong to this category [5–7]. Currently, the most commercially available supercapacitors are symmetric EDLCs based on high-surface-area carbon materials. However, in most practical applications, EDLCs with porous carbon electrodes suffer from limited energy density, which is typically of

the order of $4\text{--}5 \text{ Wh kg}^{-1}$ for fully assembled cells—an order of magnitude lower than that of the batteries [8].

In the attempt to obtain high energy density electrode materials, controlling the structure and morphology of the porous electrode materials is an effective strategy to provide them with high surface areas and efficient paths for ion diffusion [9]. Moreover, the excellent electrical conductivity of the electrode materials can significantly reduce the internal resistance of an electrode, by forming a conductive network, and facilitate the application of electrostatic charges, which favor the accumulation of electric double layers [10]. To obtain a high surface area, porous carbonaceous materials such as activated carbon, carbide-derived carbons, ordered mesoporous carbons, and carbon aerogels have been studied as high-surface-area electrodes for EDLCs [11–16]. However, their low electrical conductivity may hinder the formation of a conductive network (which decreases the internal resistance of the electrode) and the application of electrostatic charges on the surface of the electrode (which form the electric double layer) [17].

Recently, a few new approaches based on the use of semiconductors, or cermet nanowires, as EDLC electrode materials instead of traditional carbon-based materials have been proposed. Various types of EDLC materials such as silicon nanowires, silicon carbide nanowires, titanium nitride nanowires, and titanium dioxide nanotubes and nanowires have attracted considerable

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interest because of their high surface area and excellent electrical conductivity [18–23]. Among these, β -polytype silicon carbide, especially nanowire-type silicon carbide, is considered a promising EDLC material owing to its high electron mobility, low band gap, and high surface area. However, as the working materials are grown directly on the current collector, these nanowire structures are not ideal for the fabrication of hybrid composites consisting of metal oxides, or conductive polymers, and for application as macroscale supercapacitor electrodes. Notably, recent studies have shown that β -polytype silicon carbide microsphere particles have great potential as EDLC materials; however, their porous properties (such as surface area and pore volume) are not satisfactory because of their non-porous structure, which results in a low capacitive performance, e.g., 72.4 F g^{-1} at a scan rate of 10 mV s^{-1} in Na_2SO_4 aqueous electrolyte [24–26]. Thus, to obtain a high surface area, silicon carbide particles with a porous structure need to be developed.

Furthermore, synergetic effects may be achieved when the capacitive charging of the double layer overlaps with a faradic redox (pseudocapacitive) reaction, and the two storage mechanisms work in parallel [27]. Among the pseudocapacitive components, the introduction of oxygen functional groups to EDLC materials is the simplest method to stimulate faradic redox reactions. Recent studies have shown that oxygen-functionalized nanocarbons, including carbon nanotubes and reduced graphene oxides, can enhance the energy density of the carbon electrodes owing to the surface redox reactions between oxygen groups and electrolyte ions [28]. However, in the case of porous materials, physical properties such as the surface area, pore volume, and concentration of oxygen-containing functional groups have a significant impact on both the electric double-layer capacitance and pseudocapacitance. Therefore, it is essential to optimize the degree of oxidation of the porous materials to maximize the supercapacitance [29].

Here, we demonstrate the synthesis of high-surface-area micro and mesoporous silicon carbide flakes (PSF) by one-step carbonization of Si flakes without any chemical or physical activation; furthermore, we introduce oxygen functional groups on the PSF surface to investigate the relationship between the electric double-layer capacitive and pseudocapacitive contributions. In this PSF dual-pore system, the micropores play an essential role in optimizing the electric double-layer surfaces and enhancing the capacitance value, providing also low-resistant pathways for ion diffusion in the pores and good charge propagation, which lead to an improved capacitive activity. In addition, the presence of oxygen groups and SiO_2 layer on the PSF surface can yield faradic charge-transfer reactions, with enhance the surface wettability. The PSF electrode oxidized for 24 h exhibited a high charge storage capacity, showing a specific capacitance of 243.3 F g^{-1} at a scan rate of 5 mV s^{-1} with 85.6% rate performance from 5 to 500 mV s^{-1} in 1 M KCl aqueous electrolyte. These encouraging results indicate that the PSF electrode oxidized for 24 h possesses potential advantages for application as a supercapacitor electrode with high energy and power density.

2. Experimental

2.1. Raw Materials

The Ethanol ($\text{C}_2\text{H}_5\text{OH}$, HPLC grade, Samchun Chemical, Pyungteak, Korea), Argon gas (Ar, purity: 99.999%, Hyeopsin, Seoul), Hydrofluoric acid (HF, HPLC grade, Samchun Chemical, Pyungteak, Korea), Hydrogen peroxide (H_2O_2 , HPLC grade, Samchun Chemical, Pyungteak, Korea), Carbon black (Super-P, MTI Korea) were used as received. Poly(tetrafluoroethylene) (PTFE, Aldrich, Seoul), Potassium chloride (KCl, Aldrich, Seoul), deionized water (DI water, HPLC

grade, Aldrich, Seoul) were purchased from Sigma Chemical. All of the chemicals were used without further purification.

2.2. Synthesis of Oxidized Micro and Mesoporous Silicon Carbide Flakes

Micro and mesoporous silicon carbide flakes (PSF) were synthesized as follows. Si powders (0.8 g) were loaded in a ceramic boat, which was subsequently placed in the hot zone of a horizontal tubular furnace. The system was heated up to 1250°C ($5^\circ\text{C}/\text{min}$) and held at this temperature for 8 h. In our experiment, ethanol was used as the carbon source. Ethanol was ultrasonically sprayed using a home humidifier (60 MHz, 35 W) and carried by Ar gas at a flow rate of 60 sccm. After the reaction terminated and the furnace was cooled to room temperature, the products were exposed to air and heated at 600°C for approximately 4 h to remove superfluous carbon. Finally, both the SiO_2 layer adsorbed on the surface of the PSF particles and the residual Si flakes were removed via treatment with hydrofluoric acid (HF). The obtained powder (10 g) was placed in 300 mL of 10% HF solution and stirred for 24 h. Subsequently, the sample was 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 vacuum. To introduce the oxygen-containing functional groups on the PSF surface, HF-treated PSF powder was dispersed in a 34% hydrogen peroxide (H_2O_2) solution and heated to 85°C for 20, 24, 28, or 32 h with vigorous stirring. The resulting mixture was filtered, washed several times, and dried in a vacuum oven at 60°C for 24 h. The resultant oxidized micro and mesoporous silicon carbide flake (OPSF) materials are denoted as OPSF-*H*, where *H* indicates the oxidation time.

2.3. Characterization Methods

X-ray diffraction (XRD) patterns were collected (New D8-Advance/Bruker-AXS) at a scan rate of 1° s^{-1} within the 2θ range of 10° – 80° using $\text{CuK}\alpha_1$ radiation (0.154056 nm). The morphologies of the samples were analyzed 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 $\text{Mg K}\alpha$ 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 conducted at 77 K using an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with an automated surface area analyzer, using the Brunauer–Emmett–Teller (BET) calculations for the surface area. The pore-size distribution plots were recorded from the desorption branch of the isotherms, based on the nonlocal density functional theory (NLDFT).

2.4. Preparation and Characterization of Supercapacitors

The working electrodes were fabricated as follows. The PSF or OPSF-*H* powder was mixed with poly(tetrafluoroethylene) (60 wt% water suspension) to form an electrode consisting of active materials (85 wt%), carbon black (10 wt%), and binder (5 wt%). The resulting mixture was then coated onto a stainless steel foil substrate ($1 \times 1 \text{ cm}^2$) and dried in a vacuum oven at 60°C for 6 h. The loading mass of each electrode was approximately 6 mg. In a three-electrode cell, the above-loaded stainless steel foil substrate, a platinum foil, and a Ag/AgCl (KCl-saturated) electrode were used as the working, counter, and reference electrodes, respectively. All measurements, including cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS), were performed using a CHI 660C electrochemical

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