



Porous silicon carbide flakes derived from waste silicon wafer for electrochemical supercapacitor



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HIGHLIGHTS

- Porous SiC flakes are derived by waste Si wafer via carbonization process.
- Micropores are derived by partial evaporation of Si atoms during the carbonization.
- Mesopores are formed by the integration of neighboring micropores.
- The material has specific capacitance of 49.2 F g^{-1} in 1 M KCl electrolyte.
- The material shows energy density of $65.84 \text{ W h kg}^{-1}$ in 1 M BMIM BF_4/AN electrolyte.

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ABSTRACT

Supercapacitors have been attracting significant research interest because of their wide range of applications in electric vehicles, digital devices, pulsing techniques due to their high power density, short charging time, and long cycling life. For ideal charge/discharge mechanism, the micro/mesoporous silicon carbide flakes (SiCFs) with a high surface area of about $1376 \text{ m}^2 \text{ g}^{-1}$ were obtained by one-step carbonization of waste Si wafer without any chemical or physical activation. The micropores are derived from the partial evaporation of Si atoms during the carbonization process and mesopores are formed by the integration of neighboring micropores. Two-electrode supercapacitor cells constructed with this silicon carbide yielded high values of gravimetric capacitance and energy density with aqueous and organic electrolytes. SiCF electrode carbonized at $1250 \text{ }^\circ\text{C}$ shows a high-charge storage capacity, with a specific capacitance of 49.2 F g^{-1} in 1 M KCl aqueous electrolyte at a scan rate of 5 mV s^{-1} (specific capacitance for the single electrode : 196.8 F g^{-1}). In addition, a specific capacitance of 38.7 F g^{-1} is measured in 1 M 1-butyl-3-methyl-imidazolium tetrafluoroborate in acetonitrile (BMIM BF_4/AN) organic electrolyte at a scan rate of 5 mV s^{-1} (specific capacitance for the single electrode: 154.8 F g^{-1}), with an energy density of $65.84 \text{ W h kg}^{-1}$; and $\sim 98.65\%$ specific capacitance being retained over 20,000 cycles.

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1. Introduction

Supercapacitors (also called electrical double layer capacitors (EDLC)) are energy-storage devices that accumulate energy in the form of electrical charge and have drawn intensive research attention due to their significant advantages of high power density, long cycle-life and safety tolerance to high rate charge and discharge [1–3]. However, they suffer from limited energy density, which is typically on the order of $4\text{--}5 \text{ W h/kg}$ for fully-assembled cells, an order of magnitude lower than in batteries [4]. Therefore, extensive work has been focused on ways to enhance their energy densities by (i) increasing capacitance using high-surface area with high

electrical conductivity electrode materials and (ii) broadening the operational voltage with electrolytes with high-potential windows [5,6].

Traditionally, porous carbonaceous materials have been widely used as EDLCs materials in order to obtain a high surface area. Mostly, activated porous carbon materials having high surface area ($2000\text{--}3000 \text{ m}^2 \text{ g}^{-1}$) are used as electrode materials in supercapacitors with a specific capacitance around $250\text{--}350 \text{ F g}^{-1}$ [7–9]. Scientists have tried several interesting synthetic routes to obtain high quality carbon. These include carbonization of organic/polymeric precursors [10,11], chemical vapor deposition [12,13], excimer laser ablation of graphitic targets [14,15], and sputtering/plasma based synthesis [16,17]. Recently, many researchers have started utilizing organic waste materials, such as food, agricultural wastes, and even

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insects, for the synthesis of carbon for specific absorbants or charge storage application [18–23].

Unfortunately, these carbonaceous materials suffer from limited electrical conductivity, resulting in the unfavorable decrease of electrode internal resistance [24]. To overcome these low electrical conductivity, a few new approaches have been proposed that make use of semiconductors or cermet nanowires as EDLC electrode materials instead of traditional carbon-based materials [25–29]. Recently, we successfully developed the micro and mesoporous β -SiC spheres as promising EDLC materials owing to high electron mobility and low band gap with high surface area [30]. The excellent electrical conductivity of β -SiC can significantly decrease the internal resistance of an electrode by the formation of a conductive network and can facilitate the application of electrostatic charges, which favor the accumulation of the electric double layers [31]. In addition, micro and mesoporous feature of SiC effectively gives them high surface area and efficient paths for ion diffusion, resulting in the ideal capacitive behavior [30]. The micro and mesoporous β -SiC spheres show a high-charge storage capacity, with a specific capacitance of 253.7 F g^{-1} in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte at a scan rate of 5 mV s^{-1} [30]. Therefore, the high surface area contributed by micro and mesoporous feature and excellent electrical conductivity contributed by β -polytype SiC is a promising electrode material for EDLC.

Therefore, we took note of the ideal charge/discharge properties of porous β -SiC and the silicon (Si) wafer fragments are created in ton quantities during sawing process of Si wafer in semiconductor manufacturing companies. As a result, it was motivated that the strategy for conversion waste Si wafer fragments to porous β -polytype SiC to fabricate the EDLC electrode materials would contribute to enhance cost competitiveness in energy supply markets, explore novel materials for long-term sustainable energy storage, reduce environmental impacts, and meet the urgent need for green and sustainable development strategies [18]. Here, we demonstrate the synthesis of high surface area micro and mesoporous silicon carbide flakes (SiCFs) by one-step carbonization of waste Si wafer without any chemical or physical activation and examine its properties for supercapacitor application. The prepared SiCF exhibits a large specific surface area of $1376 \text{ m}^2 \text{ g}^{-1}$ with excellent electrical conductivity (48.6 S cm^{-1}), which is a desirable property for EDLC electrode materials. Finally, for practical application of SiCF, we successfully assembled a two-electrode symmetrical supercapacitor with four kinds of organic electrolytes. Electrochemical characterizations indicated that the supercapacitor with the all organic electrolytes can be operated between 0 and 3.5 V, showing a specific capacitance of 38.7 F g^{-1} (BMIM BF_4/AN), 36.4 F g^{-1} (BMIM BF_4/PC), 32.6 F g^{-1} (TEA BF_4/AN), and 30.3 F g^{-1} (TEA BF_4/PC) at a scan rate of 5 mV s^{-1} . These encouraging results showed that the obtained SiCF materials have a great potential as supercapacitor electrodes ensuring a high energy and power density.

2. Experimental

2.1. Raw materials

The waste Si (100) wafer used in this study were supplied by LG Innotek (Ansan, Korea). Ethanol ($\text{C}_2\text{H}_5\text{OH}$, HPLC grade, Samchun Chemical, Pyungteak, Korea), nitrogen gas (N_2 , purity: 99.999%, Hyeopsin, Seoul), argon gas (Ar, purity: 99.999%, Hyeopsin, Seoul), hydrofluoric acid (HF, 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), 1-butyl-3-methyl-imidazolium tetrafluoroborate

in acetonitrile (BMIM BF_4/AN , Aldrich, Seoul), 1-butyl-3-methyl-imidazolium tetrafluoroborate in propylene carbonate (BMIM BF_4/PC , Aldrich, Seoul), tetraethylammonium tetrafluoroborate in acetonitrile (TEABF₄/AN, Aldrich, Seoul), tetraethylammonium tetrafluoroborate in propylene carbonate (TEABF₄/PC, Aldrich, Seoul) were purchased from Sigma Chemical. All of the chemicals were used without further purification.

2.2. Synthesis of micro and mesoporous silicon carbide flake (SiCF-T)

The waste Si (100) wafer fragments, as starting material, were pulverized to powder by ball milling process. The waste Si wafer fragments (3 g) were loaded in a steel milling vial with 20 zirconia balls (10 mm in diameter). The vial was sealed and filled with pure nitrogen gas at a pressure of 200 kPa above atmospheric pressure to avoid environmental contamination. The rotation speed of the planetary mill was set at 150 rpm to generate rolling actions of the balls which apply shearing forces on the materials. The as-prepared Si flake (0.8 g) were loaded in a ceramic boat and put into the hot zone of a horizontal tubular furnace. The system was heated up to 1150, 1250, or 1350 °C ($5 \text{ }^\circ\text{C}/\text{min}$) and held at this temperature for 8 h. Ethanol was used as carbon source in our experiment. Ethanol was ultrasonically sprayed using a home humidifier (60 MHz and 35 W) and carried by Ar gas at a flow rate of 60 sccm (standard cubic centimeter per minute). After the reaction was terminated and the furnace was cooled to room temperature, the products were exposed to air and heat at 600 °C for about 4 h to remove superfluous carbon. Finally, the both adsorbed SiO_2 layer on the surface of the SiCF particles and residual Si flakes was 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 7–8. The resulting powder was collected and dried at 100 °C in a vacuum. The resultant micro and mesoporous silicon carbide flakes (SiCFs) materials are denoted as SiCF-T, where T indicates the carbonization temperature.

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 $5\text{--}80^\circ$ using $\text{CuK}\alpha_1$ radiation (0.154056 nm). The morphologies of the samples were observed 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 $\text{K}\alpha$ 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 carried out using an ASAP 2020 accelerated surface area and porosimetry instrument (Micromeritics), equipped with an automated surface area at 77 K, using 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 the supercapacitors

The working electrodes were fabricated as follows. The SiCF-T powder was mixed with poly(tetrafluoroethylene) (60 wt% water suspension) to form an electrode consisting of 85 wt% active SiCFs materials, 10 wt% carbon black, and 5 wt% binder. The resulting mixture was then coated onto a stainless steel foil substrate (1 cm \times 1 cm) and dried in a vacuum oven at 60 °C for 6 h. The loading mass of each electrode was approximately 6 mg. The

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