



High-power supercapacitors based on hierarchical porous nanometer-sized silicon carbide-derived carbon



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ABSTRACT

The nanoscale microporous carbide-derived carbon (nano-CDC) is synthesized by chlorination of silicon carbide nano-powder with a particle diameter around 60 nm and further pore-tuned by KOH activation with different KOH/nano-CDC ratios. Based on the higher specific surface area (SSA), a hierarchical micro- and meso-pore structure (especially for the greatly produced mesopores), and the shorter inherent ion transport distance within porous nano-carbons, the KOH-activated nano-CDC exhibits superior supercapacitive performances. Its specific capacitance is up to 141 F g⁻¹, 156% increase compared with that of pristine nano-CDC (54 F g⁻¹). Most interestingly, the cyclic voltammogram curve of the activated nano-CDC can keep a rectangular-like shape even at a scan rate of 5000 mV s⁻¹, exhibiting significantly better power performance. This work confirms that constructing favorable pore structure in nanometer-sized porous carbons is an effective strategy for fabricating high-power supercapacitors.

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1. Introduction

Due to the rapid charge/discharge performance, high-power supercapacitor has been considered to a promising high power energy source for consumer electronics, medical electronics, electric transportation technology and electric utility industry, etc. [1–5]. Various carbon materials have been studied as the electrode material for high power supercapacitors, e.g., carbon nanotube (CNT) and carbon nano-onions (OLC) [6–8]. Though CNT and OLC behave excellent rate performance, the poor energy density, which is ascribed to the relatively low specific surface area (SSA) and undeveloped pore structure, limits their further application.

One of the potential strategies to enhance the power performance of supercapacitors involves minimizing the ion paths within the porous channels of porous carbons, since the minimal ion paths can provide both shorter transport distance of ions and lower resistance [9–13]. This strategy can be realized by decreasing the size of the carbon particles to the nanoscale. However, it is generally difficult to produce porous activated carbons with

nanometer-size [11]. High energy ball milling has been known to be an effective method to minimize particle size to the nanoscale [14]. However, the pristine microstructure as well as pores in carbon particles will be destroyed during the ball milling [15].

Carbide derived carbon (CDC), a porous carbon material, is produced by selective removal of non-carbon atoms from carbide lattice layer by layer [16–18]. Because both shape and size of carbide as precursor can be maintained during carbide-carbon transformation [19,20], the nanoscale porous carbons can be obtained from the nanometer-sized carbides. Unfortunately, up to now, few work concerns the nanoscale CDC used in the energy storage field. Pérez et al. [21] synthesized a nanoscale carbon from the nano-TiC. However, the as-prepared nano-CDC shows a limited improvement in the power performance due to its micropore characteristic.

In this work, the nanoscale porous CDC is synthesized by chlorination of the nanometer-sized SiC powder and followed by KOH activation. The obtained nanoscale CDC possesses both high SSA (2265 m²g⁻¹) and a hierarchical porous structure, and, therefore, shows excellent supercapacitive performances (especially for the rate performance). Even at a scan rate of 5000 mV s⁻¹, the cyclic voltammogram curves can keep a rectangular-like shape.

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2. Experimental

2.1. Sample preparation

Nanometer-sized β -SiC powder (2.5 g, 99%, ~60 nm, Hefei Kaier Nanometer Energy & Technology Co., Ltd) was placed in a horizontal quartz tube furnace and heated to 800 °C under argon (high purity argon, 99.999%) at atmospheric pressure. The argon flow was stopped when the temperature reached 800 °C and the pure chlorine (99.9%, Tianjin Summit Specialty Gases Co., Ltd) was passed through the quartz tube at a flow rate of 20 ml min⁻¹. The chlorination was lasted for 3.5 h. The produced chloride gases were blown away by the chlorine flow immediately during the chlorination. At last, the quartz tube was purged with argon for 10 min at a rate of 1.5 L min⁻¹ and cooled down to room temperature. The waste chlorine and chloride gases were absorbed by 1 mol L⁻¹ NaOH aqueous solution. The resulting nano-powders (denoted as nano-CDC) were thereafter treated with H₂ at 600 °C for 1 h to remove the trapped chlorine in the pores. The final yield of nano-CDC is about 98% of the theoretical.

The hierarchical porous nano-CDC was obtained by the KOH activation. The nano-CDC was mixed with KOH (analytical reagent, Tianjin Kemiou Chemical Reagent Co., Ltd) at a designed weight ratio of KOH to nano-CDC in mortar. Then the mixture was placed in a horizontal tube furnace and heated to the activation temperature (800 °C) at a rate of 5 °C min⁻¹ and held for 1 h under a constant of argon flow (200 ml min⁻¹). Thereafter, the furnace was cooled to room temperature under argon. The as-prepared sample was washed with 1 mol L⁻¹ HCl and then repeatedly washed by deionized water until pH=7. The weight ratios of KOH to nano-CDC were chosen as 3:1, 6:1, 7:1 and 8:1, and the corresponding KOH-activated nano-CDCs were denoted as CDC-K3, CDC-K6, CDC-K7 and CDC-K8, respectively. After the KOH activation, the final weight losses for CDC-K3, CDC-K6, CDC-K7 and CDC-K8 are 12, 45, 50 and 60%, respectively.

2.2. Characterization

The microstructure of the samples was observed by transmission electron microscopy (TEM, JEOL JEM-2010, Japan). X-ray diffraction (XRD) patterns between 10 and 70 (2 θ) degrees were collected by Rigaku D/MAX-2500 powder diffractometer with Cu-K α radiation ($\lambda = 0.154$ nm) operated at 40 kV and 200 mA. The N₂ adsorption and desorption analysis was performed at 77 K using the ASAP 2020 system (Micromeritics). Prior to analysis, all the samples were degassed in vacuum at 200 °C for 8 h. The SSA and micropore volume were calculated by Brunauer-Emmett-Teller (BET) method and t-plot method, respectively. The pore size distribution was determined by density functional theory (DFT).

2.3. Preparation of electrode and electrochemical measurement

The electrochemical investigations were carried out in a symmetrical two-electrode cell with a cellulose separator (TF4030, NKK). The working electrodes were prepared as follows: A slurry consisting of 80 wt.% active materials, 10 wt.% carbon black and 10 wt.% PTFE (60 wt.% suspension in water) binder was smeared into nickel foam and dried in vacuum at 120 °C for 10 h. Thereafter, the electrode was pressed at a pressure of 10 MPa. The active area of the electrode is 1 cm². 6 mol L⁻¹ KOH solution was used as electrolyte. The electrochemical performances of all samples were characterized by cyclic voltammograms (CV) in a potential range of 0 ~ 0.9 V at different scan rates of 5 ~ 5000 mV s⁻¹, galvanostatic charge/discharge tests with cutoff voltage of 0 ~ 0.9 V and electrochemical impedance spectroscopy (EIS) in the frequency range between 10 mHz and 100 kHz with amplitude of

5 mV. The CV and EIS measurements were performed on CHI650D electrochemical workstation. The galvanostatic charge/discharge and long life tests were carried out on potentiostat/galvanostat (CT2001A, Land, Wuhan, China).

3. Results and discussion

Fig. 1 shows the XRD patterns of the pristine nano-CDC and the KOH-activated nano-CDCs. In the XRD patterns of all the CDC samples are observed a broad peak at around 24°, corresponding to the diffuse scattering from disordered amorphous carbon, indicating the amorphous nature of nano-CDC [21,22]. Moreover, an increased background signal between 10 and 15° in the XRD patterns of activated nano-CDCs demonstrates that these samples have higher density of pores than pristine nano-CDC, since the increase in the density of pores eventually scatter the X-ray beam and hence result in the elevated background signal [23].

The microstructures of the pristine nano-CDC and CDC-K7 are examined by high-resolution TEM, as shown in Fig. 2. It can be seen that the pristine nano-CDC is composed of large amounts of amorphous carbons and some short single-layer graphene flakes (marked by arrows). After KOH activation, more short single-layer graphene flakes with random orientation can be observed due to the preferential etching of the amorphous carbon by KOH. This is beneficial to the formation of pores, especially for the mesopores.

To disclose the effect of activation on the pore structure, the low-temperature N₂ adsorption/desorption isotherms and pore size distributions of nano-CDC and CDC-K7 are shown in Fig. 3. It can be observed from Fig. 3a that both nano-CDC and CDC-K7 adsorb N₂ at low relative pressure (P/P_0) largely, indicating the existence of large amount of micropores in these two samples. However, the CDC-K7 continuously adsorb N₂ at $P/P_0 = 0.1 \sim 0.8$ and shows a notable hysteresis loop at $P/P_0 = 0.4$, suggesting a high mesopore content. In addition, these two samples both have a vertical tail at P/P_0 close to 1.0 in the N₂ adsorption/desorption isotherms, corresponding to the presence of macropores (inset Fig. 3b) which may be contributed by the space among the irregular agglomerate nano-CDC particles [24,25]. The more detailed porosity characteristics of pristine nano-CDC and KOH-activated CDCs are listed in Table 1. With the increasing of the KOH/nano-CDC ratio, the SSA value of nano-CDC first increases, reaching the maximal value of 2265 m² g⁻¹ at the 7:1 weight ratio of KOH to nano-CDC, and then trends to decrease. However, in any case, all the KOH-activated nano-CDCs behave higher SSA values compared with the pristine nano-CDC, indicating that KOH activation results in a significant increase in the SSA of nano-CDC. Obviously, higher SSA will be beneficial to offer more accessible surface for electrolyte ions and thus obtain higher capacitance. In addition,

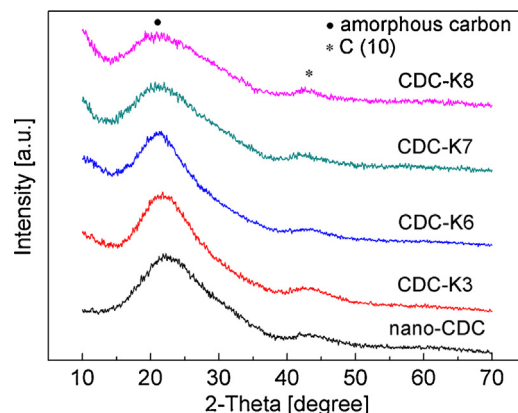


Fig. 1. XRD patterns of nano-CDC and KOH-activated nano-CDCs.

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