

# Huge enhancement of energy storage capacity and power density of supercapacitors based on the carbon dioxide activated microporous SiC-CDC



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## ABSTRACT

Nanostructured carbide-derived carbons (CDC) were synthesized from SiC powders (SiC-CDC) via gas phase chlorination within the temperature range from 1000 °C to 1100 °C. Thereafter the CDCs were additionally activated by CO<sub>2</sub> treatment method, resulting in nearly two-fold increase in specific surface area. The results of X-ray diffraction, high-resolution transmission electron microscopy and Raman spectroscopy showed that the synthesized CDC materials are mainly amorphous, however containing small graphitic crystallites. The low-temperature N<sub>2</sub> sorption experiments were performed and the specific micropore surface areas from 1100 m<sup>2</sup> g<sup>-1</sup> up to 2270 m<sup>2</sup> g<sup>-1</sup> were obtained, depending on the extent of CO<sub>2</sub> activation. The energy and power density characteristics of the supercapacitors based on 1 M (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>CH<sub>3</sub>NBF<sub>4</sub> solution in acetonitrile and SiC-CDC as an electrode material were investigated using the cyclic voltammetry, electrochemical impedance spectroscopy, galvanostatic charge/discharge and constant power discharge methods. The electrochemical data indicated two-times increase in specific capacitance. Most importantly, the activation of SiC-CDC with CO<sub>2</sub> significantly increases the performance (energy density, power density, etc.) of the supercapacitors especially at higher potential scan rates and at higher power loads.

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## 1. Introduction

Chlorination of metallic (TiC, Mo<sub>2</sub>C, WC, VC) or nonmetallic (SiC, B<sub>4</sub>C) carbides has been traditionally used for the production of corresponding chlorides, as in 1918 Hutchins patented a method for the production of silicon tetrachloride by reaction of silicon carbide with chlorine [1]. However, only in 1959, the prepared carbon residue attracted the attention of researchers, and Mohun introduced the carbide-derived carbons as a “fourth class of amorphous carbon” [2]. The unique nanoporous structure of carbide-derived carbon (CDC) with the narrow pore size distribution and possibility to fine-tune the pore size, has noticeably forced the development of carbon based devices and systems based on the micro- and mesoporous hierarchical carbon materials [3–6]. CDCs, produced by selective etching of metal carbides in a chlorine-containing environment, offer narrow distribution of micropores (places for adsorption of ions) and very high specific capacitance values have

been reported when CDC were used in supercapacitors containing organic electrolytes [5,7]. Differently from other CDCs prepared from TiC, Mo<sub>2</sub>C and B<sub>4</sub>C, the CDC prepared from SiC demonstrated very low capacitance values within negatively charged potential region (as well as at high potential cyclation rates) [5], because no mesopores and only very limited amount of bigger micropores has been observed in SiC-CDC applicable for quick adsorption of big triethylmethylammonium ((C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>CH<sub>3</sub>N<sup>+</sup>) cations. Yushin and co-workers [11] established that the mesopores in SiC-CDC allowed for a greatly increased specific surface area up to 2430 m<sup>2</sup> g<sup>-1</sup> and peaking specific capacitance 170 F g<sup>-1</sup>, in aqueous electrolytes, thus nearly doubling the previously reported values [12]. Simon and co-workers showed that evaluation of the ordered mesoporous SiC-CDC as an electrode material for supercapacitors terminates as respectable gravimetric capacitance 80 F g<sup>-1</sup> in non-aqueous electrolyte, nearly 40 F g<sup>-1</sup> lower than that established for TiC-CDC or Mo<sub>2</sub>C-CDC based supercapacitors [5,9,14–16]. High capacity retention (up to 1 V s<sup>-1</sup>) at high cyclation rate has been demonstrated compared to other high specific surface area porous carbons, explained by the quick mass-transfer processes in mesopores and bigger micropores [5,9,14–16]. Systematic analysis of electrochemical impedance data showed a low intrinsic

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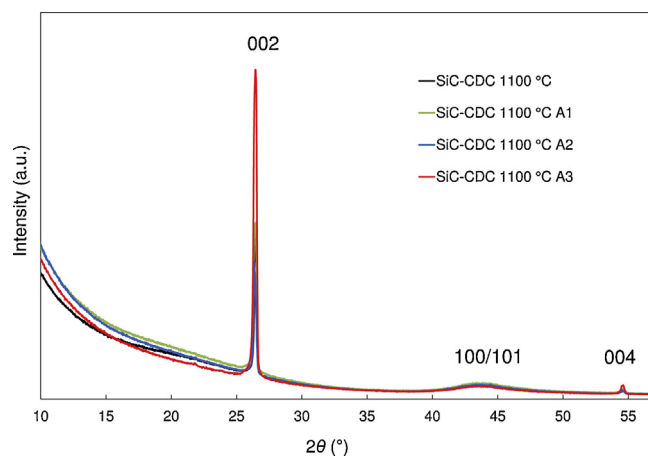
resistance of CDC based systems, high ion accessibility to the microporous-mesoporous hierarchical structure, and thus a remarkably low relaxation time of the system, evidencing that the use of such hierarchical porous carbons for high power supercapacitors is very promising [5,8,13–16].

In the present study, CDC materials were synthesized using silicon carbide as a precursor and thereafter the different raw SiC-CDC materials were activated with carbon dioxide ( $C + CO_2 \rightarrow 2CO$ ), thus reacting out some of the carbon from microporous precursor material. SiC is the most promising carbide for CDC synthesis when taking into account the precursor price and material production cost. However, in previous studies the SiC-CDC based supercapacitors have shown only moderate performance compared to other CDC based supercapacitors [5,14]. Thus, the aim of this work was to increase the specific surface area and average pore sizes of SiC-CDC by activation with  $CO_2$  in order to improve the supercapacitor performance and to establish some dependencies taking into account the pore sizes and distribution influencing the electrochemical characteristics. The structure of CDC has been characterized in detail using the X-ray diffraction (XRD), Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM) and the low-temperature  $N_2$  sorption methods. The energy-related properties of the supercapacitors have been investigated using the cyclic voltammetry, electrochemical impedance spectroscopy, galvanostatic charge/discharge and the constant power discharge methods.

## 2. Experimental results and physical characterization

### 2.1. Preparation and activation of SiC-CDC materials

Silicon Carbide (SiC, 98.5% purity, 320 grit powder, Alfa Aesar), was placed onto a quartz stationary bed reactor and reacted with  $Cl_2$  (AGA, 99.99%) at chosen fixed reaction temperatures,  $T$ , 1000 °C and 1100 °C, respectively, noted as SiC-CDC 1000 °C and SiC-CDC 1100 °C. In our study the flow rate of  $Cl_2$  was fixed at 100 ml/min. More detailed description of the etching technique has been reported previously [15,16]. The by-products were led away by the stream of excess  $Cl_2$  and after reaction the reactor was flushed with a stream of argon to remove the residues of gaseous by-products and  $Cl_2$  from the carbon powder. During heating up and cooling down steps, the reactor was flushed with argon (1000 ml/min). The resulting CDC was thereafter treated with  $H_2$  at 900 °C for 1.5 h to dechlorinate thoroughly the CDC powders as well as to remove the residual chlorides, chlorine and oxygen-containing functional groups from the surface of the porous carbon under study. For the fine tuning of pores the obtained SiC-CDC materials were additionally activated by  $CO_2$  at selected temperatures,  $T$ , 900 °C and 950 °C. During heating up and cooling down steps the reactor was flushed with argon. The reaction (activation) times were varied between 3 to 16 hours while keeping the flow of  $CO_2$  fixed at 50 ml/min. After activation the CDC powders were once again



**Fig. 1.** Characteristic XRD patterns for initial SiC-CDC 1100 °C and corresponding data for  $CO_2$  activated materials at 900 °C and 950 °C for different activation times, given in Table 1.

treated with  $H_2$  at 900 °C for 1 h to remove oxygen-containing functional groups from the surface of the porous carbon under study. All synthesized materials with their abbreviations are given in Table 1.

### 2.2. Powder XRD and Raman spectroscopy analysis of the SiC-CDC materials

XRD analysis of the CDC powder samples has been carried out to investigate the structural changes in CDC that occurred at different activation temperatures. The XRD measurements were performed using  $CuK\alpha$  radiation (45 kV, 35 mA,  $\lambda = 0.154056$  nm) with a step size  $0.01^\circ$  of glancing angle  $\theta$  and with the holding time of 2 s at fixed  $\theta$  on Bruker D8 Advance diffractometer (Bruker Corporation). The diffraction spectra for initial SiC-CDC 1100 °C and corresponding  $CO_2$  activated materials were recorded at 25 °C and treated by the Topaz 4.0 software (Fig. 1). Quite similar diffraction spectra for initial SiC-CDC 1000 °C and corresponding  $CO_2$  activated materials were recorded and presented in Supplementary Information, Fig. S1.

The XRD patterns (Fig. 1 and in Supplementary Information Fig. S1) for synthesized CDCs showed reflections corresponding to the graphitic areas, thus 002 at  $2\theta \sim 26^\circ$  and 100/101 planes at  $\sim 43^\circ$ , respectively. The 002 diffraction peak at  $2\theta \sim 26^\circ$  characterizes the parallel graphene layers, while the 100/101 diffraction peak at  $2\theta \sim 43^\circ$  can be associated with the 2D in-plane symmetry along the graphite layers [17].

The Raman spectra for the synthesized CDCs were recorded using a Renishaw inVia micro-Raman spectrometer using Ar laser excitation ( $\lambda_L = 514$  nm) (Fig. 2 and in Supplementary Information Fig. S2).

**Table 1**

The synthesized materials with their abbreviations.

Abbreviation	Synthesis temperature (°C)	$CO_2$ activation temperature (°C)	Activation time (h)	Activation burn-off (%)
SiC-CDC 1000 °C	1000	–	–	–
SiC-CDC 1000 °C A1	1000	900	6	15
SiC-CDC 1000 °C A2	1000	950	3	30
SiC-CDC 1000 °C A3	1000	950	8	48
SiC-CDC 1100 °C	1100	–	–	–
SiC-CDC 1100 °C A1	1100	900	6	19
SiC-CDC 1100 °C A2	1100	950	3	29
SiC-CDC 1100 °C A3	1100	950	16	68

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