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Mesoporous carbide-derived carbons prepared from different chromium carbides

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ABSTRACT

Mesoporous carbide-derived carbons were synthesised from different chromium carbides (Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6) powder via gas phase chlorination within the temperature range from 800 to 1100 °C. Analysis of XRD results show that chromium carbide-derived carbons ($\text{C}(\text{Cr}_x\text{C}_y)$) consist mainly on graphitic crystallites and the apparent crystallite size along the *a*- and *c*-directions of graphite structure $L_a \approx 9$ nm and $L_c \approx 6$ nm were calculated, respectively. The first-order Raman spectra showed the graphite-like absorption peak at ~ 1586 cm^{-1} and the disorder-induced peak at ~ 1355 cm^{-1} . The low-temperature N_2 sorption experiments were performed and a specific surface area up to 285 $\text{m}^2 \text{g}^{-1}$ and total pore volume up to 0.796 $\text{cm}^3 \text{g}^{-1}$ were obtained for $\text{C}(\text{Cr}_7\text{C}_3)$ synthesised at $T = 1100$ °C. For materials prepared at $T > 800$ °C the sorption measurements determined only the presence of mesopores at/inside of the porous carbon powders. Differently from other carbide-derived carbon powders studied previously the bimodal pore size distribution function has been established with the first maxima in the region from 2.5 to 3.5 nm and the second maximum from 6 to 8 nm, respectively. Taking into account the high mesoporosity values in the mesoporous region these $\text{C}(\text{Cr}_x\text{C}_y)$ materials can be attractive for the development of the high power density non-aqueous tetraalkylammonium cation salt based supercapacitors.

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1. Introduction

Atomic-level porosity control in carbide-derived carbons (CDC) is achieved by exploiting the host carbide lattice as a template, permitting controlled layer-by-layer metal extraction by optimizing the chlorination process parameters [1–7]. Various carbides have been chlorinated, including binary and ternary carbides and these studies show that the porous structure of CDCs produced depends especially on the origin and uniformity of the precursor carbide selected as a raw material [1–12]. Based on the crystallographic characteristics of binary metal carbides and previous studies [1,6,7,11,12], Cr_3C_2 , Cr_7C_3 and Cr_{23}C_6 powders seem to be attractive raw materials for synthesis of CDC with medium pore diameter higher than 1 nm. The unique micro/mesoporous structure of carbide-derived carbon with the narrow pore size distribution and possibility to fine-tune the pore size, confirmed recently [2,3,8–12], has noticeably forced the development of applications requiring the CDC materials [3,5]. Previously it was found that the micropore formation is strongly influenced by initial carbide density however the mesopore formation is influenced mainly the carbide structure and chemical properties and the raw carbide density has only minor influence [5].

Systematic analysis of capacitance data in non-aqueous electrolytes and the gas phase characteristics show that the capacitance of

positively charged microporous carbon electrode (C_+) is usually somewhat higher than that of negatively charged (C_-) electrode [7]. However, for the higher total capacitance as well as extreme power and energy density values of the supercapacitors, C_+ and C_- should be equal, which is possible only for materials having higher adsorption capacitance values for negatively charged electrode [1,7,10–15]. It was demonstrated that for CDC with half pore width lower than 0.76 nm there are noticeable capacitive limitations in non-aqueous electrolytes caused by the mismatch of solvated or partially desolvated ion radii and porous structure characteristics [1,7]. The normalised series capacitance values, i.e. electrode capacitance divided by the specific surface area, increase strongly with the decrease of pore radius of the CDC, prepared from the binary titanium carbide at lower synthesis temperatures [9]. Different dependence of electrochemical characteristics for various CDCs can be explained by the various shape of small micropores in the micro/mesoporous carbons, synthesised at different temperatures and using various raw materials, i.e. binary and ternary carbides under study [5,16]. Big progress in micro/mesopore size control in CDC has been made using a mesoporous silicon carbide precursor approach [17]. Mesoporous carbon material with the very high specific surface area (2430 $\text{m}^2 \text{g}^{-1}$) has been synthesised and gravimetric capacitance up to 170 F g^{-1} in 1 M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ in acetonitrile has been calculated. Additionally a novel class of carbons with ordered and uniform small pores (pore width smaller than 2 nm) has been synthesised using zeolite template, demonstrating importance of the pore tortuosity to the high rate capability in supercapacitors [18].

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This paper describes a systematic study designed to determine the effect of initial carbide stoichiometry and chlorination temperature on the porosity, specific surface area and pore size distribution for the CDC, prepared from Cr_3C_2 , Cr_7C_3 and Cr_{23}C_6 within the temperature range from 800 to 1100 °C, applicable for high power density supercapacitors.

2. Experimental results

2.1. Preparation of mesoporous carbide-derived carbon materials

Chromium carbides Cr_3C_2 (99.5% purity, –325 mesh powder, Sigma–Aldrich), Cr_7C_3 (99.5% purity, –325 mesh powder, Alfa Aesar) and Cr_{23}C_6 (99.5% purity, –325 mesh powder, Alfa Aesar) were placed into a quartz stationary bed reactor and reacted with a flow of Cl_2 (AGA, 99.99%) at chosen fixed reaction temperatures from 800 to 1100 °C. The comparatively low chlorination temperature (800 °C) has been used to avoid the formation of mainly microporous material (Table 1) and thus to prepare the mixed micro/mesoporous carbon for electrochemical studies. However, at $T=800$ °C the prolonged chlorination process is needed (2.5 times longer than calculated theoretically) to produce the carbon powder free from the residuals of raw material. The CDC material was synthesised from various chromium carbides according to the following simplified reaction scheme, Eq. (1)



Details of the chlorination technique have been reported previously [1,11,12] and in our study the flow rate of Cl_2 was fixed at 50 ml/min. The by-product CrCl_3 was led away by the stream of excess chlorine and after reaction the reactor was flushed with a slow stream of argon to remove the excess of chlorine and residues of gaseous by-products from carbon. During heating and cooling, the reactor was flushed with argon (500 ml/min). The vapour pressure of CrCl_3 is low and the long-lasting cleaning process with H_2/Ar (1:4) mixture at 800 °C during 1.5 h is inevitable to remove the residual chlorine, chlorides and oxygen-containing functional groups from the surface of porous CDC under study.

2.2. Powder XRD and Raman spectroscopy analysis of carbon materials

The X-ray diffraction (XRD) analysis (Fig. 1) [19–21] of the powder samples was carried out to investigate the structural changes in $\text{C}(\text{Cr}_x\text{C}_y)$ that occurred at different chlorination temperatures. The XRD measurements were performed by using $\text{CuK}\alpha$ radiation (45 kV, 35 mA, $\lambda = 0.154056$ nm) with a step size of 0.02° glancing

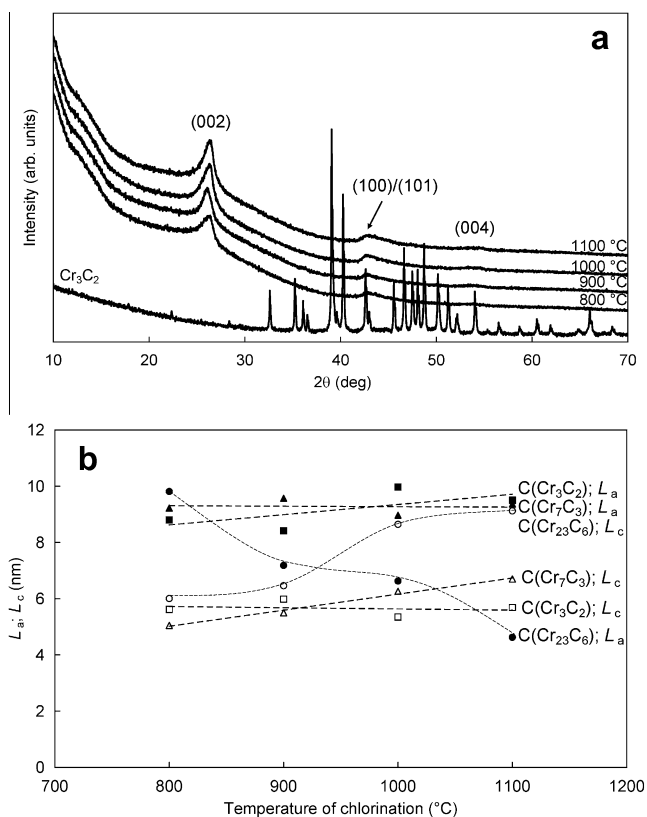


Fig. 1. Characteristic XRD patterns for initial Cr_3C_2 and for porous $\text{C}(\text{Cr}_3\text{C}_2)$ prepared at various chlorination temperatures (a) and apparent crystallite size L_a (L_c) along the a (c)-directions of the graphite structure within the chlorination temperature range from 800 to 1100 °C for $\text{C}(\text{Cr}_x\text{C}_y)$ (b); L_a – filled marks, L_c – open marks, squares – $\text{C}(\text{Cr}_3\text{C}_2)$, triangles – $\text{C}(\text{Cr}_7\text{C}_3)$, circles – $\text{C}(\text{Cr}_{23}\text{C}_6)$.

angle θ and with the holding time of 5 s at fixed θ on Bruker D8 Advance diffractometer (Bruker Corporation). The diffraction spectra were recorded at 25 °C and treated by the AXES 3.0 computer software. The XRD patterns (Fig. 1a) of CDCs synthesised showed reflections corresponding to the graphite (0 0 2), (1 0 0)/(1 0 1) and (0 0 4) planes at $2\theta \sim 26^\circ$, $\sim 43^\circ$ and $\sim 54^\circ$, respectively. Comparison of the XRD data for raw binary carbide (Fig. 1a) and prepared CDCs demonstrate that the reaction time used was sufficient to prepare the micro/mesoporous carbon free from the binary carbide and CrCl_3 residuals. The 002 and 004 diffraction peaks at $2\theta \sim 26^\circ$ and $\sim 54^\circ$, corresponding to parallel graphene layers can be observed in Fig 1a. The (1 0 0)/(1 0 1) diffraction peaks at 2θ

Table 1
Results of sorption measurements of CDCs prepared from different chromium carbides.

CDC	Chlorination temperature (°C)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	APS (nm)
$\text{C}(\text{Cr}_3\text{C}_2)$	800	270	102	0.0565	0.318	4.71
	900	269	–	–	0.338	5.03
	1000	273	–	–	0.517	7.56
	1100	212	–	–	0.706	13.31
$\text{C}(\text{Cr}_7\text{C}_3)$	800	204	66	0.0353	0.336	6.60
	900	211	–	–	0.451	8.55
	1000	270	–	–	0.574	8.51
	1100	285	–	–	0.717	10.1
$\text{C}(\text{Cr}_{23}\text{C}_6)$	800	225	–	–	0.370	6.58
	900	198	–	–	0.384	7.76
	1000	171	–	–	0.558	13.1
	1100	164	–	–	0.796	19.4

S_{BET} – BET specific surface area; S_{micro} – micropore area; calculated using t -plot method; V_{micro} – micropore volume; V_{tot} – total pore volume; APS – weighted average pore size (pore width).

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