**A strategy for constructing the compact carbon structure with high
volumetric performance for supercapacitors from porous carbons**

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Abstract

In this paper, we present an approach to construct the compact carbon structure with high volumetric capacitive performance by means of the porous carbon structural collapse and the introduction of oxygen-containing functional groups, which is exemplarily realized by oxidizing the porous titanium carbide-derived carbon (CDC) via a modified Hummers method. Electrochemical investigations demonstrate that the oxidized CDC exhibits simultaneously outstanding volumetric capacitance (216.6 F cm⁻³) and high gravimetric capacitance (228 F g⁻¹) in 6 M KOH aqueous electrolyte, almost 23 and 16 times improvement in comparison to those of the pristine CDC (9.4 F cm⁻³ and 14 F g⁻¹), respectively. Furthermore, the oxidized CDC also exhibits an excellent cycling stability (almost 92 % specific capacitance being retained even after 10000 cycles). The results of this work suggests that the strategy for constructing the compact carbon structure from the porous carbon by means of the structural collapse and the introduction of oxygen-containing functional groups will be promising for the

development of the electrode material with high volumetric performance for supercapacitors.

Keywords: Carbide-derived carbon; Hummers oxidation; Compact carbon structure; Volumetric performance; Supercapacitors

1. Introduction

Supercapacitors or electrochemical double-layer capacitors (EDLCs), bridge the gap between batteries and conventional capacitors, have been attracting considerable interest in the energy storage field [1, 2]. The relatively low capacitive performance has evoked numerous efforts on development of porous carbon with high specific surface area (SSA) and developed pore structure as the electrode materials [3-5], since for EDLCs, charge storage mechanism is based on the electrostatic adsorption of charge separated ions on the surface of an electrode material [6], and, therefore, large surface area and porosity of electrode active materials are beneficial to achieve high specific capacitance [7].

Recently, with the increasing demand for consumer electronics, medical electronics and electric vehicles, miniaturized portable energy storage devices show more promising for practical application [8, 9]. In this case, the volumetric performance becomes a crucial parameter for practical applications especially those in highly limited space. Unfortunately, for the porous carbon materials having high SSA and large pore volumes, their volumetric performance is less competitive although they can show excellent gravimetric performance [8, 10].

Up to now, many efforts have been made to achieve superior volumetric performance, including the use of carbon nanotubes and graphene materials as substrates [11, 12], or the introduction of certain types of heteroatoms such as nitrogen into carbon frameworks [13, 14], et al. Here, we propose a different strategy that constructs the compact carbon structure with low pore volume but high volumetric performance from porous carbon materials, which is exemplarily realized by oxidizing a porous carbon, i.e., titanium carbide-derived carbon (Pr-CDC), through using a modified Hummers method. In 6 M KOH aqueous electrolyte, the oxidized CDC (Ox-CDC) exhibits an outstanding volumetric capacitance (216.6 F cm^{-3}), and, furthermore, its gravimetric capacitance is also up to 228 F g^{-1} . This work demonstrates that the collapse of the pore structure and the introduction of oxygen-containing functional groups can be considered as an effective route to construct the compact carbon structure having high volumetric capacitance from porous carbon materials.

2. Experimental

2.1. Sample preparation

Commercial available TiC powder (99.5 %, $\sim 2 \text{ }\mu\text{m}$, Changsha Xinlan Cemented Carbide Co. Ltd, P.R. China) was used as precursor. The pristine CDC (Pr-CDC) was synthesized as follows: TiC powder ($\sim 4 \text{ g}$) was placed in a horizontal quartz tube furnace and heated to $1000 \text{ }^{\circ}\text{C}$ under argon atmosphere. Once it reached the desired temperature, argon flow was stopped and pure chlorine was passed through the quartz tube at a rate of $\sim 30 \text{ ml min}^{-1}$. Chlorination lasted for 2 h at the temperature of $1000 \text{ }^{\circ}\text{C}$.

At last, the quartz tube was purged with argon for 30 min to blow away the residual chlorine and chlorides gas, and then cooled down to room temperature under argon flow. The waste gases were absorbed by sodium hydroxide solution.

The resultant Pr-CDC was oxidized by the modified Hummers method [15]. In brief, 2 g Pr-CDC and 1 g NaNO_3 were added into a 250 ml flask filled with 46 ml H_2SO_4 (98 %) in ice bath under magnetic stirring. Next, 6 g KMnO_4 was slowly added to the solution, meanwhile, the ice bath was used to keep the temperature of the solution below 10 °C. After adding KMnO_4 , the ice bath was removed and the solution was heated to 50 °C, followed by a slowly addition of 80 ml deionized water. Thereafter temperature of the solution was raised to 90 °C and maintained for 30 min. And then, 60 ml deionized water and 30 ml H_2O_2 was added to the solution until the reaction was terminated. The resultant solution was centrifuged by 10 wt. % HCl to remove the impurities and then washed by deionized water until to neutral, and dried at 80 °C for 12 h. Finally, the dried product was heat-treated at 1000 °C for 30 s, thus obtaining the oxidized CDC (Ox-CDC).

2.2. Characterization

The microstructures of the samples were observed using a JEM-2010 transmission electron microscopy (TEM) at 200 kV. X-ray diffraction (XRD) patterns between 10~70 ° (2 θ) 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. Raman spectra was measured by a Renishaw in Via Raman microscope instrument equipped with an Ar⁺

laser ($\lambda=514$ nm) at 50 $\times$ magnification and 10 % power. Gas adsorption/desorption analysis was done in the V-Sorb 2800TP surface area and pore distribution analyzer (Gold APP Instruments Corporation, China) with N₂ as adsorbent at 77 K. The SSA was calculated by the BET (Brunauer-Emmet-Teller) theory and nanopore volume was obtained by the t-plots based on N₂ sorption isotherm. Pore size distributions were calculated using the Horvath-Kawazoe method. Existence of oxygen functional groups was examined by Fourier transform infrared spectroscopy (FTIR, BrukerOptiks E55+FRA106, Germany). Electrical conductivity measurement was conducted by ST-2722 four-point probe resistivity of the powder tester (Suzhou Jingge Electronic Co. Ltd).

2.3. Preparation of electrode and electrochemical measurement

The electrochemical investigations were carried out in a three electrode system using Platinum as the counter electrode, Hg/HgO as the reference electrode, and 6 M KOH as electrolyte. The working electrodes were prepared by mixing the active substance, carbon black and polytetrafluoroethylene (PTFE) with a mass ratio of 8:1:1 to form a homogeneous slurry. The slurry was smeared into nickel foam and dried in vacuum at 120 °C for 10 h, and then pressed at a pressure of 10 Mpa. The loading mass of the electrode is around 3 mg with an area of 1 $\times$ 1 cm². The symmetric two-electrode cells with two nearly identical electrodes and a cellulose separator. Cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) were collected on CHI650D electrochemical workstation in a potential range of -1~0 V and

0~1 V, respectively. The scan speeds for all CV tests were in range of 10~500 mV s⁻¹. The galvanostatic charge/discharge tests were carried on potentiostat/galvanostat (CT2001A, Land, Wuhan, China). The energy density (E) was calculated according to the following equations: $E = 1/2 C (\Delta V)^2$, Where I is the current density, C is the specific capacitance of the cell, ΔV is the potential change within the discharge time Δt .

3. Results and discussion

Fig. 1a and **b** shows the high-resolution TEM micrographs of Pr-CDC and Ox-CDC, respectively. It can be seen that there exists well-ordered graphite ribbons of graphite structure in Pr-CDC (Fig. 1a). As for Ox-CDC, the graphite ribbons become evidently shorter and more disordered (Fig. 1b). This result indicates that, after the oxidation, the well-ordered graphitic structure existing in Pr-CDC has been seriously destroyed.

Fig. 1. HRTEM images of Pr-CDC (a) and Ox-CDC (b), respectively

Fig. 2a shows the XRD patterns of Pr-CDC and Ox-CDC. A sharp (002) peak at

$2\theta = 26^\circ$ can be distinctly observed on the XRD pattern of Pr-CDC (Fig. 2), which corresponds to the graphite like structure. In addition, the broader peak at around $2\theta = 23^\circ$ illustrates that there also exists the disordered carbon structure in Pr-CDC [16]. However, the (002) peak on the diffraction pattern of Ox-CDC becomes invisible, suggesting the structural amorphization, which can be ascribed to the serious damage of the well-ordered graphite ribbons in Pr-CDC caused by the Hummers oxidation. The structures of Pr-CDC and Ox-CDC were further verified by Raman measurement, as shown in Fig. 2b. Both the spectra of Pr-CDC and Ox-CDC display two peaks at approximately 1340 and 1580 cm^{-1} , which assigned to the D- and G- bands, respectively. In addition, on the spectrum of Pr-CDC, there also appears the 2D peak at around 2670 cm^{-1} . However, the 2D peak becomes invisible for Ox-CDC. The 2D peak correlates with the ordered graphite structure [17, 18], therefore, the disappearance of 2D peak further confirms the severe damage of the ordered graphite structure in Ox-CDC, which is in well accordance with the XRD and TEM analysis.

Fig. 2. XRD patterns (a) and Raman spectra (b) of Pr-CDC and Ox-CDC, respectively

The nitrogen adsorption/desorption isotherms and pore size distributions are

shown in **Fig. 3**, and more detailed porosity characteristics about the two samples are listed in **Table 1**. It can be calculated according to the BET method from N₂ adsorption, the SSA values of Pr-CDC and Ox-CDC are 1923 m² g⁻¹ and 600 m² g⁻¹, respectively. The significant drop in SSA value indicates that the oxidation by the modified Hummers method leads to the collapse of the pore structure in Pr-CDC. As for the pore size distributions, both of the two samples show a micro- and meso- porous hierarchical porous structure (Fig. 3b). Comparatively, Ox-CDC possesses lower total pore volume but larger mesopore volume. The difference in the porosity characteristics may suggest that these two samples will behave quite different electrochemical performances.

Fig. 3. Low-temperature Nitrogen adsorption/desorption isotherms (a) and pore size distribution (b) curves of Pr-CDC and Ox-CDC. The inset in (b) is the mesopore size distribution

Table 1. Porosity characteristics of Pr-CDC and Ox-CDC

Samples	S_{BET}	V_{micro}	V_{meso}	P_{micro}	P_{meso}
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	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(nm)	(nm)
Pr-CDC	1923	0.82	0.20	0.83	3.2
Ox-CDC	600	0.23	0.26	0.81	3.8

$P_{\text{micro}}, P_{\text{meso}}$: Micropore and Mesopore average value obtained from BJH desorption dV/dD pore volume plot.

FTIR spectroscopy is used to examine the surface functional groups on the CDCs before and after Hummers oxidation, and the corresponding FTIR spectra are shown in **Fig. 4**. Several weak adsorption peaks at about 1236, 1634 and 3430 cm⁻¹, assigned to -C-O, -C=C and -OH groups, respectively, can be observed on the Pr-CDC sample. As for Ox-CDC, the intensities of peaks at about 1634 and 3430 cm⁻¹ are increased, and, meanwhile, there occurs two adsorption peaks at about 1054 and 1728 cm⁻¹, which are assigned to -C-O and -C=O groups, respectively. It indicates that the oxygen-containing functional groups are introduced onto the graphitized CDC by the Hummers oxidation. Obviously, the introduction of oxygen-containing functional groups will affect the electrochemical performance of the graphitized CDC.

Fig. 4. FTIR spectra of Pr-CDC and Ox-CDC

The gravimetric capacitances of Pr-CDC and Ox-CDC, calculated from CV curves, are 14 F g^{-1} and 228 F g^{-1} at a scan rate of 10 mV s^{-1} (**Fig. 5a**), respectively, indicating that the Hummers oxidation results in a surprisingly 16 times improvement in the gravimetric capacitance. This gravimetric capacitance of Ox-CDC is much higher than those of the graphenes obtained from Hummers oxidation via thermal or chemical reduction process [15, 19]. More interestingly, the volumetric capacitance of Ox-CDC is up to 216.6 F cm^{-3} , an almost 23 times higher than that of Pr-CDC (9.4 F cm^{-3}). This result indicates that more surfaces become accessible for electrolyte ions due to the improvement in wettability contributed by the introduction of the oxygen-containing functional groups [20], despite causing the decrease in electrical conductivity (Table S1). Moreover, there can also be observed an obvious redox peak on the CV curve of Ox-CDC, implying that the introduced oxygen-containing functional groups also contribute the faradaic pseudocapacitance by reacting with the electrolyte. As for the surprisingly improvement in the volumetric capacitance of Ox-CDC, it can be attributable to the low pore volume resulting from structural collapse and the introduction of oxygen-containing functional groups caused by the Hummers oxidization. In addition, the specific capacitances of the two samples show a decrease trend as the scan rate increases (Fig. 5b), which is due to the fact that the charge diffusion cannot match the rapid increase in the scan rates [21]. However, Ox-CDC can always exhibit markedly higher capacitance at the same scan rates. Even at a scan rate of 500 mV s^{-1} , the gravimetric and volumetric capacitances of Ox-CDC

are approximately 29 and 41 times higher than those of Pr-CDC, showing a superior rate capability. This can be ascribed to the existence of more mesopores in Ox-CDC. The larger pore size can still provide unblocked pathways for solvated ions though a large number of the surface functional groups are introduced.

In order to further investigate the superior electrochemical performance of Ox-CDC, a two-electrode symmetrical supercapacitor electrode was assembled with 6 M KOH electrolyte. Figure S1 displays the CV curves of Pr-CDC and Ox-CDC at a scan rate of 10 mV s^{-1} . And the relative gravimetric and volumetric capacitance of Ox-CDC is 229 F g^{-1} and 217.6 F cm^{-3} , respectively. Additionally, we also calculated the energy density (E) of the Ox-CDC sample, and the corresponding volumetric and gravimetric energy densities are 7.55 Wh L^{-1} and 7.95 Wh kg^{-1} , respectively.

Fig. 5. The CV curves of Pr-CDC and Ox-CDC at 10 mV s^{-1} in a three electrode system with Hg/HgO as the reference electrode (a) and the plots of both gravimetric (C_g) and volumetric (C_v) capacitance versus scan rates ranging from 10 to 500 mV s^{-1} of Pr-CDC and Ox-CDC (b)

Galvanostatic charge/discharge curves, recorded at a current density of 0.5 A g^{-1} ,

of Pr-CDC and Ox-CDC are presented in **Fig. 6**. It can be seen that the curve of Pr-CDC is almost symmetrical isosceles lines and near linear shape (Fig. 6a). While, for the Ox-CDC, it shows a distorted linear shape and not linear with time, further indicating the presence of pseudocapacitance [22], which is consistent with the CV results. Furthermore, Ox-CDC shows much longer charge/discharge time than Pr-CDC, suggesting a higher specific capacitance value. In addition, it can be obviously observed in Fig. 6b that there occurs a sudden potential drop (IR drop) at the beginning of discharge. This phenomenon primarily originates from the resistance of the electrolyte and the inner resistance related to the migration of ions in the carbon materials [23]. Therefore, the surprisingly much lower IR drop of Ox-CDC suggests that these resistances with regard to the electrolyte diffusion and the ions migration are markedly decreased, which can be attributed to the improvement in the wettability of the graphitized CDC surface due to the introduction of the oxygen-containing functional groups, thereby leading to the excellent electrochemical reversibility and charge-discharge properties of Ox-CDC.

Fig. 6. Galvanostatic charging-discharging profiles of Pr-CDC and Ox-CDC at current

density of 0.5 A g^{-1} (a) and the IR drop of Pr-CDC and Ox-CDC (b)

To further investigate the dynamic behavior of Pr-CDC and Ox-CDC, Nyquist plots are obtained as shown in **Fig. 7**. Clearly, the Nyquist plot of Ox-CDC leans more towards to the imaginary axis than that of Pr-CDC, suggesting a superior capacitive behavior. On the other hand, the dramatically shorter length of the Nyquist plot in the low frequency region also means that Ox-CDC possesses higher specific capacitance [24], which is consistent with the measurement results of CV and galvanostatic charge/discharge. In addition, the semicircle in the high frequency is a mirror of the electron transfer process at the electrode-electrolyte interface, and, larger semicircle represents higher charge transfer resistance [25]. From the inset of Fig. 7, it can be deduced that Ox-CDC can provide a lower interfacial charge transfer resistance, thereby it being easier for the electrolyte to enter the electrode surface. This means that the introduction of oxygen-containing functional groups makes it much easier for the electrolyte to run across the electrical double layer and facilitates charge accumulation on the current collector due to the improvement of wettability.

Fig. 7. The Nyquist plots of Pr-CDC and Ox-CDC in 6M KOH electrolyte (the inset

shows expanded high-frequency region of Nyquist plots)

Long-term cycling stability is a crucial factor required for supercapacitor electrodes. The long-term cycling stability of Ox-CDC has been performed at a current density of 1 A g^{-1} in 6 M KOH electrolyte, and the related results are displayed in **Fig. 8**. It is observed that, the specific capacitance of Ox-CDC is quite stable over the entire cycle numbers, almost 92 % specific capacitance being remained even after 10000 cycles. The excellent cycling stability suggests that the oxygen-containing functional groups, which are introduced by Hummers oxidation, bond strongly with Ox-CDC and keep stable during the long-term cycling, which is important for the practical application.

Fig. 8. Cycling stability of Ox-CDC at a density of 1 A g^{-1} in 6 M KOH electrolyte

4. Conclusion

We have demonstrated a strategy that constructs the compact carbon structure with high volumetric capacitance from porous carbons by means of the structural collapse and the introduction of oxygen-containing functional groups. Oxidizing the porous

titanium carbide-derived carbon (CDC) via a modified Hummers method leads to the dramatic drop in SSA and pore volume, suggesting the collapse of porous CDC structure and the formation of the compact carbon structure. Meanwhile, there occur lots of oxygen-containing functional groups on the oxidized CDC. Electrochemical investigations demonstrate that the oxidized CDC behaves an enormous enhancement in capacitive performance. The volumetric and gravimetric capacitance of Ox-CDC in alkaline electrolyte is 216.6 F cm^{-3} and 228 F g^{-1} , respectively, almost 23 and 16 times higher than those of Pr-CDC, respectively. Besides, for the oxidized CDC, almost 92 % specific capacitance can be retained even after 10000 cycles, indicating an excellent cycling stability. The huge improvement in volumetric capacitive performance of the oxidized CDC, contributed by the collapse of porous structure and the introduction of the oxygen-containing functional groups, suggests that the present strategy will be potential for the construction of the compact carbon structure with outstanding volumetric capacitance from other porous carbons.

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