Microporous and Mesoporous Materials 131 (2010) 89–96

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Preparation of porous doped carbons and the high performance in electrochemical capacitors

Huanlei Wang, Qiuming Gao *, Juan Hu

State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences,
1295 Dingxi Road, Shanghai 200050, PR China

ARTICLE INFO

Article history:
Received 15 September 2009
Received in revised form 8 December 2009
Accepted 10 December 2009
Available online 13 December 2009

Keywords:
Porous doped carbon
Activation
Electrochemical capacitance
Aqueous electrolyte
Organic electrolyte

ABSTRACT

Porous doped carbons were synthesized by casting technique using zeolite 13X as the template through a polymerization reaction between ethylenediamine and carbon tetrachloride. The nitrogen contents and pore structures were further tailored by carbon dioxide and potassium hydroxide activations. These parameters played important roles in the electrochemical capacitors. The nitrogen- and oxygen-containing functional groups can make pseudocapacitance contribution to the overall capacitance, but face the disadvantage of blocking the electrolyte ions into pores. The investigation of relationship between the capacitance and the surface area or volume of the micropores indicated that high capacitance can be obtained for the carbon with large surface area and volume of micropores. Moreover, the mesopores in the carbons can be favor for smooth ion transfer. The porous doped carbon material with large specific surface area up to 2970 $m^2 g^{-1}$ and volume of the micropores up to 1.04 $cm^3 g^{-1}$ was achieved after the KOH activation, which exhibits the optimized electrochemical behavior with the gravimetric capacitances of 259 $F g^{-1}$ in 6 M potassium hydroxide electrolyte and 176 $F g^{-1}$ in acetonitrile solution containing 1.5 M tetraethylammonium tetrafluoroborate electrolyte at the current density of 0.25 $A g^{-1}$.

1. Introduction

Supercapacitors can be used in the field of portable electronic devices, back-up power storage and hybrid transportation systems to complement or replace batteries and fuel cells because of their unique characteristics of short time for recharge, long cycling time, higher energy density than conventional capacitors, and larger power density than rechargeable batteries [1–4]. Porous carbons are the essential electrode materials for supercapacitors due to their stable physical and chemical properties, large specific surface area, controlled pore structure, high conductivity, low cost, and availability [5]. The capacitances of carbon-based supercapacitors are closely related to their intrinsic pore characteristics, functionalization of the materials as well as selection of the electrolytes [6–11]. Theoretically, the higher the surface area is, the larger the capacitance should be. Moreover, the small and interconnected mesopores in the carbons are beneficial for providing quick pathways for the electrolyte transportation [6,12–15], which are helpful for maintaining high capacitance retention. Thus, tailoring the pore structures for the most effective utilization of the surface area is the key to optimize their electrochemical properties. Recently, researchers have found the anomalous capacitance increase at pore sizes less than 1 nm in organic electrolyte [16] and micropores with the diameter of about 0.5 nm could be accessible for aqueous electrolyte [17,18], which indicated that the effect of pore size depends closely on the used electrolytes. And the pore size which can lead to the maximum capacitance should be close to the electrolyte ion size [18,19].

Energy storage in carbon-based supercapacitors depends on the charge uptake in the electrolyte/electrode interfacial regions. The foreign atoms modified the electron donor/acceptor characteristic of the graphene layers and the surface chemical functional groups at the edge of layers can be consequently expected to affect the charging of the electric double-layer and to give a pseudocapacitive contribution [20,21]. Recent work showed that surface modification to introduce functional groups with the elements of N, O, B and P could enhance the electric double-layer capacitances and further introduce pseudocapacitances to the electrodes [18,20–26]. Moreover, the heteroatoms in the carbon materials could also improve the wettability of the electrode and increase the operation voltage window [9,26,27]. Briefly, the feasible synthesis of carbon materials with suitable porosities that allows the electrolyte to access all the inner pore surface and functionalization of the porous carbons that enhances the electrochemical capacitance are still of great challenges.

Previous work showed that physical or chemical activation could be used to control the pore structures and compositions of

---

* Corresponding author. Tel.: +86 21 52412513; fax: +86 21 52413122.
E-mail address: qmgao@mail.sic.ac.cn (Q. Gao).

1387-1811/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2009.12.007

the mesoporous carbon and/or carbon nitride [28,29], which had significant effects on their electrochemical capacitive behaviors. In this work, porous doped carbon was synthesized by using the template route and we attempted to control of the pore structure and nitrogen content of porous carbon using the activation to optimize the electrochemical performance. The relationships among porous structures and textures, nitrogen and oxygen contents, as well as electrochemical properties both in alkaline and organic electrolytes are discussed in detail.

2. Experimental section

2.1. Material synthesis

Porous doped carbon was synthesized by adding 4 g of zeolite 13X into a mixture of ethylenediamine (5 mL) and carbon tetrachloride (7.5 mL), and then the obtained mixture was refluxed at 363 K for 6 h and followed by drying in an oven overnight. The resultant dark brown zeolite/carbon composite was heated to 873 K with a heating rate of 3 K min^{-1} under nitrogen atmosphere and kept at 873 K for 5 h to carbonize the polymer. The carbon material was liberated from the zeolite framework by washing with 10 wt% hydrofluoric acid at room temperature and then 3 M hydrochloric acid at 333 K. The template-free carbon material was filtered, washed with deionized water, and dried in an oven at 373 K. The resultant porous carbon material was denoted as Mic-CNX.

The CO_2 activation was performed by gasifying Mic-CNX at 1223 K under CO_2 flow. The resultant samples were denoted as Mic-CNX-Cm, in which C stands for the CO_2 activation and m indicates the gasifying time (h) at 1223 K. The yields were 43% for Mic-CNX-C3 and 16% for Mic-CNX-C5. The KOH activation was performed by heating a physical mixture of Mic-CNX and KOH at 1023 K for 1 h under argon flow. Finally, the mixture was washed with 3 M hydrochloric acid at room temperature and then thoroughly with deionized water. The resultant samples were dried at 373 K in air. The obtained samples were denoted as Mic-CNX-K*n*, in which K stands for the KOH activation and *n* indicates the mass ratio of KOH/Mic-CNX. The yields were 24% for Mic-CNX-K1 and 36% for Mic-CNX-K3.

2.2. Material characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-2200 diffraction operating at 40 kV and 40 mA and using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). High resolution transmission electron microscopy (HRTEM) images were performed on JEOL (JEM-2100F) microscope operating at 200 kV. Elemental analyses (C, H and N) were performed with a Vario EL III elemental analyzer. Nitrogen adsorption–desorption isotherms were measured at 77 K on a Micrometrics ASAP 2020 system. The packing density was determined by pressing a given amount of sample into a glass tube with a cylindrical rod. The measurement of the height of the rod with the tube empty and with the sample allows the evaluation of the volume of the sample and then the packing density [30].

2.3. Electrochemical measurements

Cyclic voltammogram (CV) curves were recorded using a CHI440 electrochemical workstation. Galvanostatic charge/discharge cycling was performed using CT2001A (Land, China) at different current densities. The electrodes were fabricated by mixing the carbon material, polytetrafluoroethylene and carbon black powder in a mass ratio of 80:10:10. The button cell was fabricated using the same material as positive and negative electrodes. Both aqueous electrolyte of 6 M KOH and organic electrolyte of 1.5 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in acetonitrile solution were used to evaluate the electrochemical capacitive behaviors. The specific gravimetric capacitance (C_{gc}) per single electrode was calculated according to the following equation:

$$C_{gc} = \frac{2I \bullet \Delta t}{\Delta V \bullet m}$$

where, I is the constant discharging current, Δt is the discharge time, ΔV is the voltage window from the end of the ohmic drop to the end of the discharge process, and m is the mass of carbon material on a single electrode. All the electrochemical experiments were carried out at room temperature.

3. Results and discussion

3.1. Structure and porosity analyses

XRD pattern of the porous nitrogen-doped carbon Mic-CNX is shown in Fig. 1. A broad and weak diffraction peak at 2θ of around 25° corresponding to the (0 0 2) diffraction with d spacing of 0.356 nm can be observed, which indicates that there exists turbostatic stacking of the carbon and nitrogen atoms. The widen diffraction peak shows that the crystallinity of the porous carbon material is low. There is no diffraction peak at 2θ of around 6° in the XRD pattern for Mic-CNX, indicating that the zeolitic regularity can not be kept for the carbon material obtained after the removal of zeolite 13X [31]. XRD patterns of the carbon materials after the CO_2 and KOH activations are also shown in Fig. 1. The (0 0 2) diffraction peaks of Mic-CNX-C3 and Mic-CNX-C5 are similar to that of Mic-CNX, which demonstrates that no pronounced graphitization occurred at the activation temperature of 1223 K. However, the (0 0 2) diffraction peaks of Mic-CNX-K1 and Mic-CNX-K3 are less apparent than that of Mic-CNX, which suggests a breakdown of aligned structural domains in the carbon matrix after the KOH treatment [32].

HRTEM images of the obtained carbon materials are given in Fig. 2. The particles of Mic-CNX tangled together (Fig. 2a), indicating that the carbon precursors not only infiltrated into the pores but also deposited outside the particle surface. After CO_2 activation, it is clear to see that the carbon pieces of Mic-CNX-C5 become thinner than Mic-CNX (Fig. 2c). The TEM image of Mic-CNX-K3 showed that the carbon among particles was etched during KOH activation (Fig. 2e). Moreover, the carbon pieces with uniformly

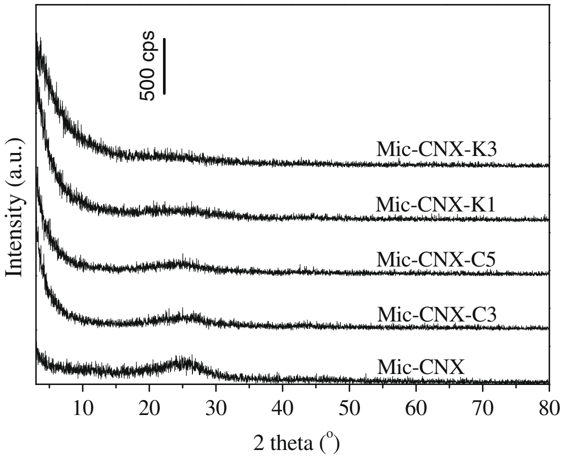

Fig. 1. XRD patterns of the porous doped carbons before and after the CO_2 and KOH activations.