Journal of Power Sources 246 (2014) 132–140

Contents lists available at ScienceDirect

Journal of Power Sources

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

Effects of adding ethanol to KOH electrolyte on electrochemical performance of titanium carbide-derived carbon

Jiang Xu [a], Ruijun Zhang [a,*], Peng Chen [a], Shanhai Ge [b,**]

[a] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
[b] Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

- Wettability and contact angle of carbide-derived carbons (CDCs) are investigated.
- Hydrophilicity and specific capacitance of CDC depend on its microstructure.
- Well-ordered graphite ribbons have lower hydrophilicity and capacitance.
- A strategy that improving the surface wettability and capacitive behavior of CDC.

ARTICLE INFO

Article history:
Received 24 June 2013
Received in revised form
13 July 2013
Accepted 16 July 2013
Available online 31 July 2013

Keywords:
Carbide-derived carbon
Supercapacitor
Hydrophilicity
Potassium hydroxide electrolyte

ABSTRACT

Porous carbide-derived carbons (CDCs) are synthesized from TiC at different chlorination temperatures as electrode materials for electrochemical capacitors. It is found that the microstructure of the produced CDCs has significant influence on both the hydrophilicity in aqueous KOH electrolyte and the resultant electrochemical performance. Because the TiC-CDC synthesized at higher temperature (e.g. 1000 °C) contains well-ordered graphite ribbons, it shows lower hydrophilicity and specific capacitance. It is also found that addition of a small amount of ethanol to KOH electrolyte effectively improves the wettability of the CDCs synthesized at higher temperature and the corresponding specific capacitance. Compared with the CDC synthesized at 600 °C, the CDC synthesized at 1000 °C shows fast ion transport and excellent capacitive behavior in KOH electrolyte with addition of ethanol because of the existences of mesopores and high specific surface area.

1. Introduction

Capacitors and batteries are the most common electrical energy-storage devices. Batteries can provide high energy density but relatively low power density, which restricts their use in a number of applications. Electrochemical capacitors, also known as supercapacitors or ultracapacitors, can provide high specific power (10 kW kg^{-1}), long cycle life ($>10^5$), and fast charge/discharge processes (within seconds), and therefore have become an alternative or supplement to batteries in the field of energy storage [1–5]. Recent supercapacitor research and development aim to increase power, energy density, lower fabrication costs and environmentally friendly materials. The electrode materials for supercapacitors include carbons, conductive polymers, metal oxides, and their composites [6].

Porous carbons as electrode materials for electric double-layer capacitors (EDLCs) have attracted more interest than other materials due to the high specific surface area (SSA), high electrical conductivity, low cost and various forms such as powders, fibers, tubes, and composites etc. [7]. More importantly, carbon materials exhibit high stability in different solutions (from strongly acidic to alkali) in a wide range of temperatures [7]. The electrochemical behavior of the carbon-based supercapacitors is dependent on the SSA. Average pore size and pore size distribution of porous carbon is a key to its capacitance. The capacitance of a carbon-based supercapacitor can be improved significantly by matching the size of solvated electrolyte ions with the pore size distribution of carbon electrode [8–11]. To date, major efforts in the field of carbon-based supercapacitor are to optimize pore size, pore structure and surface properties of the electrode materials.

Carbide derived carbon (CDC) technique is one of the most promising and economic ways to produce carbons with desired

---

* Corresponding author. Fax: +86 335 8514884.
** Corresponding author.
E-mail addresses: zhangrj@ysu.edu.cn (R. Zhang), sug13@psu.edu (S. Ge).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.07.069

porosity. CDC is produced by selective removal of metal or metalloid atoms from carbide lattices layer by layer. Atomic-level control can be achieved in the synthesis process, which may produce carbons with pores matching with the size of solvated electrolyte ions [8,12]. Chlorination temperature has a significant influence on the structure of the produced CDC. The pores in CDC can be tuned with subangstrom accuracy in a wide range by controlling the chlorination temperature [12]. The width of the produced pores increases as the chlorination temperature increases [13–16]. In addition, it is notable that the degree of order of the produced CDC increases with increasing chlorination temperature and the microstructure changes from amorphous carbon to graphite ribbons [17–19]. The microstructure of carbon has much influence on both surface properties and conductivity of the carbon-based electrode materials, which greatly affects the resultant electrochemical performance [7,11,20,21]. Although a few efforts have been done on the compatibility of electrolytes with electrodes [8,12,22,23], very few studies in the literature have focused on the microstructure dependence of CDC wettability.

For carbon-based supercapacitors, both organic and aqueous solutions can be used as electrolytes [7,24]. The supercapacitor using organic-based electrolyte can show high performance, but safety, environmental pollution and fabrication cost are big challenges for this kind of supercapacitor. For these reasons, many researches used aqueous electrolytes to improve the performance of hybrid system [25–27]. An eco-friendly and efficient aqueous electrolyte is a key to high performance supercapacitor. Wu et al. [22] reported that carbon electrode in aqueous KOH electrolyte exhibits higher capacitance than neutral aqueous electrolytes because of the fast mobility of OH^- ions.

In our previous work, a microstructure control strategy for CDC by ball-milling metal carbide precursor prior to CDC synthesis was investigated [28]. In this work, the electrochemical performance of the produced CDC is further investigated in aqueous KOH electrolyte. A small amount of ethanol is added to the electrolyte to investigate the effect of wettability of the produced CDC on its electrochemical behaviors.

2. Experimental

2.1. Sample preparation

Commercial available TiC powder (99.5%, ~2 μm, Changsha Xinlan Cemented Carbide Co. Ltd, P.R. China) was used as precursor. The experimental device has been shown in our previous work [28]. In brief, CDC powder was prepared as follows: TiC powder (approximately 4 g) was placed in a horizontal quartz tube furnace and heated to a desired temperature under argon at atmospheric pressure. Once it reached the desired temperature, the argon flow was stopped and the pure chlorine was passed through the quartz tube at a rate of ~30 ml min^{-1}. Chlorination lasted for 2 h at the desired temperature (e.g. 600, 800, 1000 and 1200 °C). In the last step of the experiment, the quartz tube was purged with argon for 30 min to blow away the residual chlorine and chlorides gases, and then cooled down to room temperature under argon flow. The waste gases were adsorbed by NaOH solution.

2.2. Material characterization

Transmission electron microscopy (TEM) was performed using a JEM 2010 TEM equipped with an image filter (Gatan GIF) at 200 kV. A slurry composed of CDC and ethanol was coated on a copper grid with a lacey carbon film to prepare samples for TEM testing. Gas sorption analysis was done by using V-Sorb 2800TP specific surface area and pore size analyzer (Beijing Gold APP Instruments Co. Ltd, P.R. China) with N_2 as adsorbent at 77 K. Specific surface area – according to BET (Brunauer, Emmet and Teller) theory and nanopore volume – was calculated by using *t*-plots based on the N_2 sorption isotherm. The FTIR measurements were performed on a Fourier transform infrared (FTIR) spectrometer (E55Xfra106, BRUKER, Germany) in the wave range of 1000–4000 cm^{-1}, using KBr disk method.

2.3. Preparation of electrode and electrochemical measurement

The electrochemical investigation was carried out in a three-electrode system using platinum as counter electrode and Hg/HgO as reference electrode. The working electrodes were prepared as follows: A slurry consisting of 80 wt.% CDC, 10 wt.% carbon black powder and 10 wt.% polytetrafluoroethylene (PTFE, 60 wt.% suspension in water) binder was smeared into nickel foam. Then it was dried in vacuum at 120 °C for 12 h. Thereafter, the electrode was pressed at a pressure of 10 Mpa. KOH solutions with/without addition of ethanol were used as electrolyte. The active area of the electrode is 1 cm^2. Before each measurement, the working electrode was soaked in electrolyte to ensure thoroughly wet.

The electrochemical performances of the produced CDCs were characterized by cyclic voltammetry (CV) in the potential range of −1.0–0 or −0.8–0 V at different scan rates of 20–500 mV s^{-1}, galvanostatic charge/discharge tests at 500 mA g^{-1} with cutoff voltage of −1–0 V and electrochemical impedance spectroscopy (EIS) in the frequency range from 10^5 Hz to 10^{-2} Hz with amplitude of 5 mV. The CV and EIS measurements were performed on CHI650D electrochemical workstation. The galvanostatic charge/discharge tests were carried out on potentiostat/galvanostat (CT2001A, Land, Wuhan, China).

3. Results and discussion

Fig. 1a and b shows the CVs and galvanostatic charge/discharge curves of TiC-CDCs in 6 M KOH electrolyte, respectively. The CDCs are synthesized at different temperatures. It can be seen from Fig. 1a that all samples exhibit double layer capacitive behavior (rectangular shape) and no faradic reaction can be found within the voltage window. Moreover, the specific capacitance decreases with increasing chlorination temperature. The specific capacitance of CDC synthesized at chlorination temperature of 1000 °C (denote as TiC-CDC-1000) decreases to almost zero. The chlorination temperature dependence of specific capacitance of the produced CDC is further confirmed by charge/discharge curves shown in Fig. 1b. It can be found that both curves of the CDCs synthesized at 600 and 800 °C (denote as TiC-CDC-600 and TiC-CDC-800) are almost symmetrical isosceles lines, demonstrating that the produced CDCs have typical porous carbon capacitive behavior in 6 M KOH aqueous electrolyte [29]. Whereas for the sample TiC-CDC-1000, both the short charge/discharge time and a sudden potential drop (IR drop) at the beginning of discharge indicate a poor capacitive behavior.

Fig. 2 shows nitrogen adsorption/desorption isotherms of TiC-CDCs synthesized at different temperatures. SSA, average pore size and pore volume is calculated. It shows that TiC-CDC-600 adsorbed N_2 only at low relative pressure (P/P_0), which means that nearly no mesopore exists in this sample (Fig. 2a) [30]. Whereas for TiC-CDC-1000, the uptake of N_2 increases with increasing P/P_0, indicating a broad pore size distribution in the CDC. Further, a notable hysteresis between N_2 adsorption and desorption isotherms indicates the existence of mesopores in TiC-CDC-1000. Fig. 2b shows that both values of the SSA and pore size increase with increasing chlorination temperature. Large SSA is only a necessary condition for high specific capacitance because the pore size also plays an important role in the achievement of high specific