



Short Communication

# Hierarchical porous carbon microspheres derived from porous starch for use in high-rate electrochemical double-layer capacitors



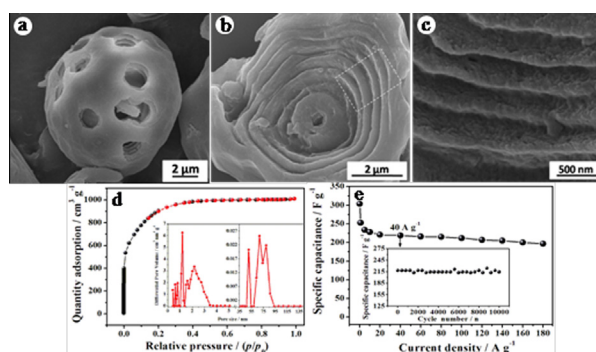
Si-hong Du, Li-qun Wang, Xiao-ting Fu, Ming-ming Chen\*, Cheng-yang Wang

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin, PR China

HIGHLIGHTS

- Biomass waste porous starch was utilized to fabricate hierarchical porous carbon.
- The nanocarbon contains inherent macropores and KOH-creating meso- and micropores.
- The capacitance could be maintained at 197 F g<sup>-1</sup> even at 180 A g<sup>-1</sup>.

GRAPHICAL ABSTRACT



ARTICLE INFO

**Article history:**  
 Received 10 February 2013  
 Received in revised form 21 April 2013  
 Accepted 23 April 2013  
 Available online 30 April 2013

**Keywords:**  
 Porous starch  
 Hierarchical porous carbon microspheres  
 Electric double layer capacitors  
 High rate

ABSTRACT

Porous starch was used as a precursor for hierarchical porous carbon microspheres. The preparation consisted of stabilisation, carbonisation and KOH activation, and the resultant hierarchical porous carbon microspheres had a large BET surface area of 3251 m<sup>2</sup> g<sup>-1</sup>. Due to the large surface area and the hierarchical pore structure, electrodes made of the hierarchical porous carbon microsphere materials had high specific capacitances of 304 F g<sup>-1</sup> at a current density of 0.05 A g<sup>-1</sup> and 197 F g<sup>-1</sup> at a current density of 180 A g<sup>-1</sup> when used in a symmetric capacitor with 6 M KOH as the electrolyte. After 10,000 cycles, the capacitor still exhibited a stable performance with a capacitance retention of 98%. These results indicate that porous starch is an excellent precursor to prepare high performance electrode materials for EDLCs.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

An electric double-layer capacitor, which is sometimes termed a supercapacitor and which relies on the accumulation of charges at the electrodes via purely electrostatic forces (Frackowiak and Beguin, 2001), is a fast energy storage device compared with lithium ion batteries (Choi et al., 2012), which involve Li<sup>+</sup>/Li electrochemical reactions. Hence, unlike batteries, an electric double-layer capacitor has a long charge-cycling life of over several million cycles, a high specific capacitance and a high rate of energy

delivery, which are characteristics that scientists place many emphasis on (Kötz and Carlen, 2000; Sherrill et al., 2011). Currently, the final electrochemical performance of the available electric double-layer capacitors depends on the nanostructure of the carbonaceous electrode material. Ordered mesoporous carbon (Korenblit et al., 2010) and hierarchical porous carbon (Wang et al., 2008) have become hot topics in this research field because these structures enable fast ion diffusion, assuming a high-rate performance, and provide abundant micropores, leading to a high specific capacitance.

In recent years, biomaterials have been shown to be advantageous for fabricating the above-mentioned structures (White et al., 2009). In 2007, Kijima and Kobayashi developed a new way

\* Corresponding author. Tel./fax: +86 22 27890481.  
 E-mail address: [chmm@tju.edu.cn](mailto:chmm@tju.edu.cn) (M.-m. Chen).

to control pore distribution but not pore size, which was highlighted in chemical science of RCS publishing. Recently, his group used the biomaterial alkaline lignin to prepare micropore-based highly porous carbons, which were considered to be commendably applied to EDLC applications (Kijima et al., 2011). In addition, cassava peel waste (Ismanto et al., 2010), *Argania spinosa* seed shells (Elmouwahidi et al., 2012), bamboo (Kim et al., 2006), waste coffee beans (Rufford et al., 2008) and sunflower seed shells (Li et al., 2011) have all been used as precursors for carbon materials. Although these materials were prepared using completely different precursors and were activated by different chemical agents (KOH for cassava peel waste, *Argania spinosa* seed shells and sunflower seed shells, H<sub>2</sub>O for bamboo, ZnCl<sub>2</sub> for waste coffee beans), all of the activated carbons are microporous; this property holds true for all plant-derived carbon. And these types of carbons can be termed group 1. Active carbons in group 1 generally have large micropore surface areas, over 1000 m<sup>2</sup> g<sup>-1</sup>, consequently giving excellent specific capacitances of approximately 150–300 F g<sup>-1</sup> at current densities less than 100 mA g<sup>-1</sup> in an aqueous electrolyte. Due to the dominance of their microporous characteristic, the capacitance retention of these carbons decreases quickly as the current density increases. Additionally, the use of non-aqueous electrolytes greatly reduces the specific capacitance of group 1 materials. For example, Kim et al. (2006) reported that in 1 M Et<sub>4</sub>NBF<sub>4</sub>/PC solution, a specific capacitance of only 60 F g<sup>-1</sup> was achieved at a scan rate of 1 mV s<sup>-1</sup>. For this group of carbon materials, Li et al. (2011) reported that if the precursors are activated directly without pre-carbonisation specific capacitances of 244 F g<sup>-1</sup> at a current density of 0.25 A g<sup>-1</sup> and of 171 F g<sup>-1</sup> at a current density of 10 A g<sup>-1</sup>, which is 70% of the former capacitance, can be achieved. Another group of biomaterial carbons consists of hierarchical structures that contain macro-, meso- and micropores (Chen et al., 2010; Huang et al., 2011). In this group, the nanostructure is hierarchical, i.e. is not micropore-dominated, and the capacitance retention of the carbon electrode is quite good (a specific capacitance of 130 F g<sup>-1</sup> was maintained even at a high current density of 40 A g<sup>-1</sup> in the work of Chen et al. (2010), and a capacitance retention of 70% was obtained by Huang et al. (2011) when the current density was increased from 0.05 to 100 A g<sup>-1</sup>). These results indicate that a carbonaceous hierarchical electrode in an electric double-layer capacitor could produce a high rate of energy delivery.

Porous starch is a type of bio-product that has macropores and a fixed carbon percentage of approximately 41%, which is higher than those of the other biomasses summarised by Ismanto et al. (2010). In this paper, the potential of utilizing porous starch biomass in the field of energy storage is discussed. First, a hierarchical structure based on a porous starch was developed by combining (1) the macropores inherited from the precursor with (2) the micro- and mesopores created by KOH activation. The importance of the macropores and the primary shape of the microspheres are discussed as well as the relationship between the hierarchical structure and the energy storage performance of the EDLC fabricated from the porous carbon microspheres.

## 2. Experiment

### 2.1. Sample preparation

Hierarchical porous carbon microspheres were prepared from porous starch. A commercial porous starch powder (corn starch, 200 mesh, Lida Biotechnology, Liaoning, China) was impregnated with a 10 wt.% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> aqueous solution for 1 h, dried at 40 °C and then stabilised at 210 °C for 3 h in a nitrogen atmosphere. After carbonisation at 600 °C for 2 h and KOH activation

(KOH/starch mass ratio = 4:1) at 800 °C for 2 h, nanoporous carbon microspheres were obtained.

### 2.2. Characterisation

The morphology of the porous carbon material was observed using a scanning electron microscope (SEM, Nano SEM 430, FEI, America). N<sub>2</sub> adsorption–desorption isotherms were measured using a Micromeritics ASAP 2020 instrument at 77 K. The specific surface area ( $S_{\text{BET}}$ ) was calculated from the nitrogen adsorption isotherms using the Brunauer–Emmett–Teller (BET) method, and the micropore surface area ( $S_{\text{micro}}$ ) was determined using the *t*-plot method. The pore size distribution was studied using original density functional theory (DFT). The macropores were measured using the AutoPore IV 9510 mercury porosimetry analyser from the Micromeritics Company.

### 2.3. Electrode preparation and electrochemical measurements

The electrochemical performances were measured using symmetric two-electrode cells in a 6 M KOH aqueous electrolyte. The electrode was fabricated by pressing a mixture of the obtained porous carbon sample (80 wt.%), black carbon (10 wt.%) and polytetrafluoroethylene (10 wt.%) onto a nickel foam current collector. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a Princeton PARSTAT2273 electrochemical workstation. Different scan rates, between 50 and 300 mV s<sup>-1</sup>, were used in the CV tests with the voltage varying from 0 to 1.0 V. Nyquist plots were evaluated at frequencies from 100 kHz to 1 mHz. Galvanostatic charge–discharge cycles were conducted over the range from 0.05 to 180 A g<sup>-1</sup> using an Arbin battery test instrument. The gravimetric capacitance *C* of the symmetric capacitor was calculated from the charge–discharge curves using the formula  $C = \Delta t / m \Delta V$ , where *I* is the set discharge current,  $\Delta t$  is the discharge time, *m* is the total mass of the active materials in the symmetric capacitor and  $\Delta V$  is the voltage drop upon discharge (excluding the IR drop). The single electrode capacitance  $C_g$  is one quarter of the gravimetric capacitance of the symmetric capacitor.

## 3. Results and discussion

The SEM micrographs of the raw material and of the hierarchical porous carbon microspheres are shown in Fig. S1. These show that the granular shape of the precursor was well preserved during the preparation of the microspheres, although there was some shrinkage in the particle sizes (Fig. S1(a) and (c)). In addition, the holes with diameters of 1–2 μm in the precursor were maintained in the hierarchical porous carbon microspheres (Fig. S1(b) and (d)). These macropores are not only on the surface but also go deep inside the granule in a ladder-like manner (Fig. S1(e)). It is suggested that the granule shape can be maintained with the aid of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, although the starch-based material has to undergo a harsh heat treatment of up to 600 °C afterwards. The KOH activation of the carbon microspheres caused a new porous structure to appear on the surface of the ladder-like channel (Fig. S1(f)). The pores created by KOH along with the macropores inherited from the precursor give the porous carbon a 3D hierarchical structure.

To further investigate the structure of the pores in the prepared hierarchical porous carbon microspheres, N<sub>2</sub> adsorption–desorption and mercury porosimetry measurements were conducted, and the results are shown in Fig. S2. According to IUPAC, the isotherm of the hierarchical porous carbon microspheres (Fig. S2(a)) can be classified as a mixture of type I and IV, indicating the existence of both micropores and macropores. In addition, when the

Download English Version:

<https://daneshyari.com/en/article/7082773>

Download Persian Version:

<https://daneshyari.com/article/7082773>

[Daneshyari.com](https://daneshyari.com)