



# Mesoporous carbon microspheres with high capacitive performances for supercapacitors



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## ABSTRACT

Novel small-mesopores-enriched porous carbon microspheres have been synthesized from carbonaceous polysaccharide microspheres, by using the associated lithium acetate treating and heat treating strategies. X-ray diffraction, scanning electron microscope, transmission electron microscopy and nitrogen adsorption-desorption techniques have been employed to investigate the as-prepared samples. The analysis results indicate that the porous carbon microspheres has a high specific surface area of  $1163 \text{ m}^2 \text{ g}^{-1}$  and a satisfactory small mesoporous texture (2~5 nm), with the mean pore size of 3.24 nm and the pore volume ratio of 2~5 nm pores up to 92%. The capacitive performances of the samples in  $6 \text{ mol L}^{-1}$  KOH aqueous electrolyte, have been tested by cyclic voltammetry, electrochemical impedance spectroscopy and charge-discharge techniques. A specific capacitance of  $171.5 \text{ F/g}$  is obtained for the porous carbon microspheres via charge-discharge at a current density of  $1000 \text{ mA/g}$ . It also displayed a very high cycle stability of 97.8%, compared with the initial capacitance, after 1000 cycles at the high current density of  $1000 \text{ mA/g}$ .

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## 1. Introduction

Supercapacitors (SCs) have attracted intense interest as efficient and durable energy storage devices, which are promising to meet the requirements of emerging portable electronic devices and hybrid electric vehicles, in virtue of their advantages including high power density, long cycle life-time and low maintenance cost [1–3]. The commercially available SCs are mainly based on porous carbon electrodes, such as activated carbons and mesoporous carbons, on which the ion-adsorption electric double layer capacitance (EDLC) is essentially depended [4–6]. Currently, the design and synthesis of porous carbon electrode materials in favourable morphologies and pore structures have become central issues in the development of high-performance SCs [7,8].

Among various porous carbon materials, spherical porous carbon has been recently proved to be one of advantageous architectures, which provides great opportunity for improving volume energy density due to their high packing density, excellent dispersivity and fluidity [9–11]. On the other hand, it is generally accepted that, porous carbon with appropriate small mesopores

(2~5 nm) can endow with really large pore volume and highly accessible surface area, which affords considerably high EDLC owing to their fast ion transportation and efficient ion adsorption of electrolytes [12–15]. Therefore, it seems one of attractive strategies to develop high-performance SCs by using spherical and small mesopores-enriched porous carbon as electrode materials.

Carbonaceous polysaccharide microspheres (CPMs) are considered as a class of unique spherical carbon materials with carbonaceous inner core and polysaccharide outer layer, which can be easily prepared from inexpensive raw material of glucose via the moderate hydrothermal synthesis [16]. Generally, the CPMs can be used as sacrificial templates for the synthesis of various metal oxide hollow microspheres [17,18], or as precursors for the synthesis of solid carbon microspheres (SCMs) [19,20]. However, it is still a challenge to prepare porous carbon materials with spherical morphology and mesoporous structures by using CPMs as precursors, since the polysaccharide component of CPMs are often vulnerable to strong chemical activating agent.

In this study, we report novel spherical porous carbon materials, small mesopores-enriched porous carbon microspheres (PCMs), as advanced electrode materials for high-performance SC applications. The PCMs are directly fabricated from CPMs via a facile and scalable sintering synthesis route with  $\text{CH}_3\text{COOLi}$  as pre-treatment agent. As mild chemical agent, the  $\text{CH}_3\text{COOLi}$  can

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react with the  $\text{OH}^-$  of CPMs and the generated LiOH can slowly but surely embed into the CPMs. After the sintering, the LiOH in the CPMs can convert in situ into the  $\text{Li}_2\text{CO}_3$  and the mesopores of PCMs can be formed by dilute acid washing. The  $\text{Li}_2\text{CO}_3$  component plays a highly-efficient “site-occupying” role (or “post-templating” role) for the formation of mesopores. Because the “LiOH-embedding” is induced by a gently esterification reaction in room temperature and the “ $\text{Li}_2\text{CO}_3$ -converting” is realized in the high temperature carbonization, the spherical morphology of CPMs can be well preserved for PCMs. Altogether, three features become apparent for the present product: (i) good spherical distributions (sphere diameter: 100~300 nm), (ii) small mesoporous structures (average pore diameter: 3.24 nm) and (iii) desirable specific surface area (BET specific surface area:  $1163 \text{ m}^2 \text{ g}^{-1}$ ). With these merits, we investigated that high-performance SC can be designed on the basis of such porous carbon materials.

## 2. Experimental

### 2.1. Materials synthesis

For the synthesis of CPMs, 5 g glucose was dissolved in 40 mL deionized water and then transferred into a Teflon-lined stainless steel autoclave with 50 mL capacity. The autoclave was sealed and maintained at  $180^\circ\text{C}$  for 4 h. Then the CPMs products were isolated by filtration, cleaned in water and alcohol, and oven-dried at  $80^\circ\text{C}$  for 12 h. For the synthesis of PCMs,  $\text{CH}_3\text{COOLi}$  treating, heat treating and acid washing three steps are included. (i)  $\text{CH}_3\text{COOLi}$  treating: 0.5 g of as-prepared CPMs was dispersed in 100 mL absolute alcohol under ultrasonic treatment for 15 min. Next, 1.0 g of  $\text{CH}_3\text{COOLi}$  was added into above mixture, ultrasonically treated sequentially for 30 min, and then 10 mL of deionized water was added and sonicated for another 30 min. At last, the treated CPMs were isolated by filtration (this semi-finished product is named as  $\text{CH}_3\text{COOLi}$ -treated CPMs). (ii) Heat treating: the  $\text{CH}_3\text{COOLi}$ -treated CPMs were further sintered under Ar flow at  $800^\circ\text{C}$  for 1 h with a rate of  $5^\circ\text{C}/\text{min}$ . The “Ar flow” plays a protective atmosphere role preventing the oxidation of CPMs at high temperature. The “ $800^\circ\text{C}$  for 1 h” is a required condition for assuring the hundred-percent carbonization of CPMs [21,22]. The “ $5^\circ\text{C}/\text{min}$ ” is a moderate heating rate for attaining a steady carbonization progress [23,24]. (iii) Acid washing: the PCMs products were finally achieved by washing with 5% HCl and water, and oven-dried at  $80^\circ\text{C}$  for 12 h. For comparison, the solid carbon microspheres (SCMs) are prepared by directly sintering CPMs at  $800^\circ\text{C}$  for 1 h under Ar flow without the  $\text{CH}_3\text{COOLi}$ -treated procedure. In addition, activated carbon microspheres (ACMs) are also prepared from CPMs precursor by direct lithium hydroxide (LiOH) (0.5 g CPMs + 1.0 g of LiOH) activation under Ar flow at  $800^\circ\text{C}$  for 1 h

with a rate of  $5^\circ\text{C}/\text{min}$ , washed with 5% HCl and water, and oven-dried at  $80^\circ\text{C}$  for 12 h.

### 2.2. Material characterization

The structures of the samples were analyzed by X-ray diffraction (XRD) (Rigaku, D/max 2500v/pc), Fourier transform infrared (FT-IR) spectrum (AVATAR370) and Raman spectrum (Jobin Yvon HR 800) techniques. The morphologies of the samples were observed using a field emission scanning electron microscope (SEM) (FEI Quanta 200 FEG) and transmission electron microscopy (TEM) (JEOL-2010). The specific surface area and pore-structural properties of material were investigated using physical adsorption of nitrogen at the liquid nitrogen temperature (77 K) on an automatic volumetric sorption analyzer (ASAP 2010).

### 2.3. Electrochemical measurements

Electrochemical measurements were performed in conventional three-electrode system. In a typical process of working electrode fabrication, the active material was mixed with acetylene black and polytetrafluoroethylene (PTFE) (90:5:5, w/w/w) in ethanol to form a slurry, then the slurry was pressed onto Ni foam ( $1 \text{ cm}^2$ ) and dried under the vacuum at  $80^\circ\text{C}$  for 12 h. The mass loading of the active material was  $10 \text{ mg cm}^{-2}$  on Ni foam. The three-electrode system was tested in a  $6 \text{ mol L}^{-1}$  KOH aqueous solution, with a Pt foil as the counter electrode, a reversible hydrogen electrode (RHE) as the reference electrode. The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) measurements and the charge-discharge (CD) for the aqueous system were recorded by an electrochemical work station (CHI 660).

## 3. Results and discussion

### 3.1. Morphology and structure

The crystal structure of the as-obtained PCMs sample was identified by XRD and Raman spectra analyses (see Fig. 1). From the XRD pattern in Fig. 1(A), the two peaks at  $2\theta \approx 24^\circ$  and  $43^\circ$ , corresponding to the (002) and (101) face peaks of carbon, are very wide and clear, which suggests that the PCMs sample have a typical local-order structure of the carbon materials [25]. Expressly, the obvious presence of increasing intensity when  $2\theta$  less than  $15^\circ$  is highly indicative of good nanoporous structures of the PCMs sample [26]. From the Raman spectrum in Fig. 1(B), there are two intense broad peaks appeared at  $1342$  and  $1585 \text{ cm}^{-1}$ , which can be ascribed to the D (disordered structure) and G (graphite-like structure) bands of the carbon materials [27]. The slightly high and sharp intensity of G band for the PCMs

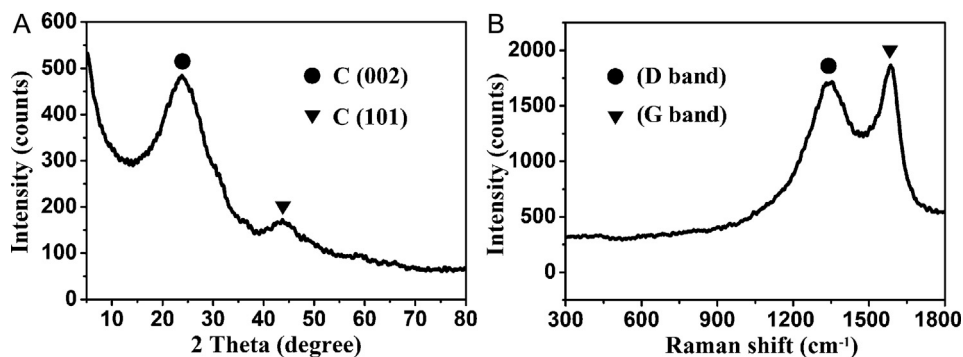


Fig. 1. XRD pattern (A) and Raman spectrum (B) of PCMs sample.

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