Bagasse-based Nanoporous Carbon for Supercapacitor Application

SI Wei-Jiang, WU Xiao-Zhong, XING Wei, ZHOU Jin, ZHUO Shu-Ping
(School of Chemical Engineering, Shandong University of Technology, Zibo255049, China)

Abstract: A kind of nanoporous carbon has been successfully prepared from sugarcane bagasse through a facile microwave-induced ZnCl₂ activation and tested as electrode material in ionic liquid supercapacitor. The as-prepared nanoporous carbons are systematically characterized by a variety of means such as N₂ adsorption, SEM (scanning electron microscope) and TEM (transmission electron microscope). Characterization results reveal that the pore size of nanoporous carbons can be tuned from 2.5 nm to 7 nm by simply adjusting the concentration of ZnCl₂ solution from 20 wt% to 60 wt%. The nanoporous carbons are tested as electrode materials in ionic liquid using different electrochemical means such as cyclic voltammetry, constant current charge-discharge and electrochemical impedance spectroscopy. As evidenced by electrochemical measurements, the capacitive performances of the carbons are closely related to their pore sizes. It has been demonstrated that large pore size benefits the good capacitive performance of nanoporous carbon in ionic liquid electrolyte.

Key words: biomass; nanoporous carbon; N₂ adsorption; supercapacitor; energy density

In recent years, supercapacitors are considered as promising high power energy sources for digital communication devices, high power suppliers, memory backup systems and advanced vehicles[1-2]. Electrode material is one of the dominating factors influencing the performance of supercapacitor. Up to date, carbon electrode materials are still considered as the most promising materials for future capacitors with superior performances due to their low price and stable physicochemical properties. Various carbonaceous materials, including carbon aerogels[3], carbon nanotubes[4], microporous carbon[5], hard-templated ordered mesoporous carbons (OMCs)[6-7] and hierarchical porous carbons[8-9] have been investigated as electrode materials of supercapacitor. However, the preparation processes for these carbons require expensive raw materials, a lot of time and energy, and tedious preparation procedures. By contrast, biomass wastes are very cheap and easily available, which are potential raw materials for the preparation of porous carbons with good electrochemical capacitive performance. Recently, much attention[10-15] has been drawn to utilization of biomass wastes to prepare porous carbons for EDLCs. Yang et al[10] used walnut shells as precursors to prepare nanoporous carbon by means of simultaneous physical-chemical activation. The results demonstrate that pore structure, especially pore size distribution of the resulted carbons, had a significant influence on the performance of the EDLC. Raymundo-Piñero et al[11] prepared a high-performance carbonaceous material for EDLCs by one-step carbonization of an oxygen-rich biopolymer. Although the carbon developed has a low specific surface area, the capacitance values per mass of active material are comparable to the best activated carbons, due to the oxygen present in the carbon network participating in pseudofaradic charge-transfer reactions. Guo et al[12] prepared porous carbon by chemical activation of rice husk. The specific capacitance of the resulted carbons is not linearly proportional to the surface area and strongly depends on the pore structure and the functional groups of the carbons. Wu et al[13] used firewood to prepare activated carbons by means of steam activation. The carbon shows specific capacitance as high as 120 F/g measured at high sweep rate of 200 mV/s, which is also ascribed to the mesopores formed in the texture. Kim et al[14] prepared activated carbons from bamboo waste by chemical activation. The results demonstrated that the carbon with higher mesopore fraction shows higher capacitance in organic electrolyte and desirable rate capability in aqueous electrolyte. Rufford et al[15] prepared nanoporous carbon from sugarcane bagasse by chemical activation and studied its capacitive performance in H₂SO₄ electrolyte. Herein, we present a facile strategy to synthesize nanoporous carbon from sugarcane bagasse via mi-
crowave irradiation that has such merits as very short activation duration, energy-saving and low cost. The pore-structure, especially pore size, of the carbon can be easily tuned only by adjusting the activation agents used. Electrochemical capacitive behaviors of the as-prepared carbons have also been tested in ionic liquid (IL) electrolyte which is a very promising electrolyte for supercapacitor due to its unique physicochemical properties such as low vapor pressure, high thermal stability, and wide electrochemical windows\textsuperscript{16}.

1 Experimental

1.1 Preparation of nanoporous carbon

The raw material (bagasse pith), a waste product from local sugar mill was used as a precursor for preparing nanoporous carbons. Bagasse pith was washed with distilled water and then dried. The pretreated bagasse pith was sieved and resized until all particle fractions had length of 5–10 mm. The obtained particle fractions were immersed in ZnCl\textsubscript{2} solution with different concentrations for 24 h, followed by filtration and drying at 100 \degree C overnight. The ZnCl\textsubscript{2} loaded bagasse pith was subject to microwave irradiation for 15 min under N\textsubscript{2} atmosphere in microwave oven (2.45 GHz, 700 W). The resultant was washed with 10 wt\% HCl solution to remove Zinc derivatives and ash content and then washed with deionized water intensively. The dried samples are designated as AC-XX, where XX represents the weight percent of ZnCl\textsubscript{2} in the solution.

1.2 Structure characterizations and electrochemical tests

Micromeritics ASAP 2020 instrument was used to characterize the surface area and pore structure of nanoporous carbons using N\textsubscript{2} sorption at 77 K. Before the measurements, all samples were degassed at 350 \degree C under vacuum for 5 h. Surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The total pore volume (V\textsubscript{t}) was obtained at \(P/P_0 = 0.995\), and the pore size distribution was calculated by the BJH (Barrett, Joyner, Halender) method using the desorption branch of the isotherm. Scanning electron microscopy (SEM) images were obtained on a Sirion 200 electron microscope (FEI, Holand). Transmitting electron microscopy (TEM) images were obtained on a JEM 2000FX electron microscope (JEOL, Japan).

Carbon samples were grounded with 5wt\% of polytetrafluoroethylene binder and pressed between two pieces of nickel foam under 300 kg/cm\textsuperscript{2}. [EMIM]BF\textsubscript{4} (1-ethyl-3-methylimidazolium tetrafluoroborate, Shanghai Chengjie Chemical Co. LTD) was used as electrolyte in this work. Cyclic voltammetry, galvanostatic charge-discharge and impedance analysis were recorded in two-electrode supercapacitor using a CHI 660C electrochemical testing system. The specific capacitances of the materials are calculated according to the following equation:

\[
C = \frac{2\times I\times t}{\Delta V \times m}
\]

where \(C\) is the single-electrode specific capacitance of electrode material, \(I\) is discharge current, \(t\) is discharge time, \(\Delta V\) is voltage drop during discharge and \(m\) is the mass of electrode material in one electrode.

2 Results and discussion

The N\textsubscript{2} adsorption-desorption isotherms of nanoporous carbons shown in Fig.1 are of different types. The isotherm of AC-20 can be basically classified as type I isotherm with a broad knee within low relative pressure range, indicating that AC-20 mainly comprises micropores and small mesopores, which also can be validated by its pore size distribution curves shown in Fig.1 inset. As for AC-30 and AC-40, obvious hysteresis loops can be observed at high relative pressures ranging from 0.5 to 1.0, demonstrating the existence of substantial mesopores with larger pore size. As reflected by their pore size distribution curves, small mesopores (<3 nm) decrease sharply and larger increase, which can be explained by the evolvement of micropores into mesopores through pore-size enlargement due to activation. When it comes to AC-50 and AC-60, adsorption uptakes increase sharply at relative pressures ranging from 0.8 to 1.0, indicating very large mesopores and macropores were formed when using

![Fig. 1 N\textsubscript{2} sorption isotherms of nanoporous carbons and their pore size distribution (inset)](image-url)

Pore size distribution was calculated by BJH method using desorption branch. The isotherms of AC-30, AC-40, AC-50 and AC-60 were offset vertically by 200, 400, 600 and 800 cm\textsuperscript{3}/g, respectively.
ZnCl₂ solution with higher concentration to soak the bagasse. The above description outlines the trend of pore-structure evolvement. This is, micropores and small mesopores were formed when small amount of ZnCl₂ (e.g. using 20wt% ZnCl₂ solution to soak bagasse) was used for activation, while large mesopores or even macropores were produced as the increase of concentration of ZnCl₂ solution. The results of N₂ adsorption/desorption also confirm that the pore-structure of the nanoporous carbon can be easily controlled by simply adjusting the concentration of ZnCl₂ solution.

The surface area and pore-structure parameters of nanoporous carbons are tabulated in Table 1. The BET surface area of all nanoporous carbons ranges from 1348 m²/g to 1489 m²/g, demonstrating that microwave irradiation is a highly efficient means to make the bagasse deeply activated. AC-20 possesses apparently more micropore surface and volume than the other nanoporous carbons. Mesopore volume rises monotonously from 0.85 cm³/g to 2.07 cm³/g and average pore diameter rises from 2.5 nm to 7.0 nm with the increase of the concentration of ZnCl₂ solution from 20wt% to 60wt%. The pore size of the nanoporous carbons can be tuned easily in a wide range by adjusting the concentration of ZnCl₂ solution, capable of meeting different application scenarios where nanoporous carbons with varying pore size are required.

The morphology of the nanoporous carbons was observed by scanning electron microscope. As shown in Fig. 2 (a), there are some round holes of about 2 µm in diameter on the surface of AC-20, which may be formed from the pyrolysis of bagasse. The edge of the holes was heavily etched for AC-40 after moderate activation, as was shown in Fig.2 (b). Those holes completely disappeared on the surface of AC-60 after severe activation, which can be observed from Fig.2 (c). SEM images shown in Fig.2 (d), (e) and (f) vividly illustrate the pore-structure evolvement of the nanoporous carbons with more and more ZnCl₂ used to activate the bagasse. Only small mesopores indicated by white arrow in Fig.2 (d) can be found on the surface of AC-20, while large mesopores and macropores were observed on the surface of AC-40 and AC-60, respectively, which coincides with the results derived from N₂ adsorption analysis. The large mesopores in AC-40 were evolved from small micropores through pore-widening effects during activation. Very large

Table 1  Surface area and pore-structure parameters of nanoporous carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}})(^a) (m²/g(^{-1}))</th>
<th>(S_{\text{meso}})(^b) (m²/g(^{-1}))</th>
<th>(S_{\text{micro}})(^c) (m²/g(^{-1}))</th>
<th>(V_{\text{micro}})(^d) (cm³/g(^{-1}))</th>
<th>(V_{\text{meso}})(^e) (cm³/g(^{-1}))</th>
<th>(V_{\text{t}})(^f) (cm³/g(^{-1}))</th>
<th>(D)(^g) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-20</td>
<td>1465</td>
<td>1139</td>
<td>636</td>
<td>0.30</td>
<td>0.85</td>
<td>0.92</td>
<td>2.5</td>
</tr>
<tr>
<td>AC-30</td>
<td>1489</td>
<td>1326</td>
<td>229</td>
<td>0.11</td>
<td>1.24</td>
<td>1.30</td>
<td>3.5</td>
</tr>
<tr>
<td>AC-40</td>
<td>1416</td>
<td>1323</td>
<td>205</td>
<td>0.09</td>
<td>1.59</td>
<td>1.63</td>
<td>4.6</td>
</tr>
<tr>
<td>AC-50</td>
<td>1365</td>
<td>1197</td>
<td>276</td>
<td>0.13</td>
<td>1.95</td>
<td>2.19</td>
<td>6.4</td>
</tr>
<tr>
<td>AC-60</td>
<td>1348</td>
<td>1179</td>
<td>273</td>
<td>0.13</td>
<td>2.07</td>
<td>2.36</td>
<td>7.0</td>
</tr>
</tbody>
</table>

\(^a\)BET surface area; \(^b\) Mesopore surface area, calculated using BJH method from desorption curve; \(^c\) Micropore surface area, derived from t-plot method; \(^d\) Micropore volume derived from t-plot method; \(^e\) Mesopore volume, calculated using BJH method; \(^f\) Total pore volume, measured at \(P/P_0=0.995\); \(^g\) Average pore diameter, calculated by \(4V_{\text{t}}/S_{\text{BET}}\).
mesopores or macropores in AC-60 were formed in the same way, which can be clearly observed and indicated by black arrows in TEM image shown in Fig. 3.

It should be pointed out that ZnCl₂ plays an important role in the evolvement of pore structure. The degradation of cellulose material and the aromatization of the carbon skeleton upon ZnCl₂ treatment result in the creation of the porous structure. Caturla [17] showed that ZnCl₂ acts as dehydrating agent that promotes the decomposition of carbonaceous material during the pyrolysis process, restricts the formation of tar, and increases the carbon yield. At high ZnCl₂ concentrations, some ZnCl₂ remains in the external part of the carbon particles and widens the porosity by a localized decomposition of the organic matter. This process results in the enhancement of the mesopore and macropore formation.

The cyclic voltammograms shown in Fig.4 (a) maintain distorted rectangular shapes for all the carbons investigated, indicating a reasonably good capacitive behavior in IL electrolyte. As denoted by the arrow in Fig.4 (a), the distortion degrees of voltammograms are in the order of AC-60<AC50<AC40<AC-30<AC-20, which coincides with the decreasing sequence of pore sizes for those carbons as tabulated in Table 1. AC-20 mainly comprises micropores and small mesopores, while AC-60 mainly contains larger mesopores. The larger pore size is expected to favor fast electrolyte transport in the pore-channel of AC-60 as compare to AC-20. It has been demonstrated that larger pore size secures better capacitive performance in IL (such as EMImBF₄ in this case), which is composed entirely of large ions and ion-pairs and therefore is hard to move in or out of micropores or small mesopores.

The formation of electric double layer (EDL) involves the ion transport in porous texture and the electric static adsorption of ions on the electrode/electrolyte interface region. The ion-accessible electrode/electrolyte interface area determines the EDL capacitance. As shown in Fig.4 (b), the minimized capacitance at high current density originates from the decreased ion accessible electrode/electrolyte interface areas due to the reduced inner-pore ion transport capability. At low current density of 200mA/g, AC-40 presents the highest specific capacitance of 138 F/g, indicating AC-40 possesses the largest accessible electrode/electrolyte interface area for EMImBF₄ electrolyte at this low current density. In contrast, at high current density of 2 A/g, AC-60 shows the highest specific capacitance. The capacitance retention ratio is used to evaluate the specific ion transport behavior of the carbons investigated (Fig.4 (b) inset), and the bigger the retention ratio, the better the ion transport behavior. This result shows the rank of ion transport behavior of the carbons, AC-60>AC-50>AC-40>AC-30>AC-20, at all current densities applied, which is also closely related to the pore size of those carbons. It has been revealed that the bigger the pore size, the better the ion transport behavior in IL electrolyte.

Figure 5 shows the dependence of normalized capacitance per unit surface area on the average pore size diameter of the carbons investigated. It can be seen that the normalized capacitance basically increases with the average pore size. AC-40, AC-50 and AC-60 possess obvi-
Fig. 5 Dependence of normalized capacitance on average pore size diameter

Fig. 6 (a) Normalized real capacitance vs alternative current frequency for the investigated carbons in EMImBF$_4$ (Inset is Nyquist plot); (b) Ragone plot
甘蔗渣基纳米孔碳在超级电容器中的应用

司维江，吴小中，邢伟，周晋，禚淑萍

(山东理工大学 化学工程学院，淄博 255049)

摘 要：以甘蔗渣为原料，采用微波化学活化法制备了一类纳米孔碳，并将其用作离子液体超级电容器的电极材料。采用氮气吸附、扫描电子显微镜和透射电子显微镜等手段对制备的纳米孔碳进行系统的结构表征。结果表明，当氯化锌溶液的浓度从20%增加到60%时，制备的纳米孔碳的孔径从2.5nm增加到7.0nm。这说明纳米孔碳的孔径可以简单地通过控制氯化锌溶液的浓度来调节。通过循环伏安、恒流充放电和电化学阻抗等方法测试纳米孔碳作为离子液体超级电容器电极材料时的电化学性能。研究结果表明，在离子液体中纳米孔碳的电容性能与其孔径紧密相关，纳米孔碳的孔尺寸越大，电容性能越好。

关 键 词：生物质；纳米孔碳；氮气吸附；超级电容器；能量密度

中图分类号：TQ424

文献标识码：A