Contents lists available at ScienceDirect





Electrochimica Acta

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

Synthesis of micro- and meso-porous carbon derived from cellulose as an electrode material for supercapacitors



Xun Tian^a, Shan Zhu^b, Jun Peng^a, Yongtao Zuo^a, Gang Wang^a, Xuhong Guo^{a,c}, Naiqin Zhao^b, Yanqing Ma^{a,b,*}, Lei Ma^d

^a School of Chemistry and Chemical Engineering, Shihezi University/Key Laboratory for Green Processing of Chemical Engineering of XinJiang Bingtuan/ Engineering Research Center of Materials–Oriented Chemical Engineering of XinJiang Bingtuan, Shihezi 832003, China

^b School of Materials Science and Engineering, Tianjin Key Laboratory of Composites and Functional Materials, Tianjin University, 300350, China

^c State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

^d Tianjin International Center for Nanoparticles and Nanosystems, Tianjin University, 300072, PR China

ARTICLE INFO

Article history: Received 19 January 2017 Received in revised form 6 April 2017 Accepted 7 April 2017 Available online 8 April 2017

ABSTRACT

Cellulose has been explored as a tentative renewable carbon source to convert into micro- and mesoporous carbon (MMC) via carbonizing cellulose aerogel at a temperature of 700 °C without further activation. The obtained MMC materials based on cellulose possess a specific surface area of 646 m² g⁻¹, a pore volume of 0.4403 m³ g⁻¹, with an optimal pore structure that consists of the micropores in average size of 1.49 nm and the mesopores in the range of 2.25 ~ 3.32 nm. A two-electrode symmetric supercapacitor based on the MMC materials exhibits a comparable high electrochemical performance with a large capacitance (up to 160 F g⁻¹ at 0.2 A g⁻¹), an high energy density of 17.81 Wh kg⁻¹ at a power density of 180.11W kg⁻¹ in the voltage range of 0 V to 1.8 V. The mesoporous can provide a good channel to further facilitate the electrolyte ion penetrating inner pores, while the microporous can store more electrolyte ions. The above cooperative effect of MMC is the key to the high-performance of the supercapacitors.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

With the depletion of fossil fuels and the gradual increase in the greenhouse effect, the development of renewable energy-storage and conversion devices has become more and more pertinent. In the application of portable electronic devices and electric vehicles, the most effective and practical electrochemical energy conversion and storage device includes both a lithium ion battery [1] and supercapacitors [2]. So far, electrochemical supercapacitors have drawn much attention, owned mainly to their high power density [3–5], excellent rate capability, fast charge and discharge rates, low maintenance costs, and long-term cyclability (more than 10,000) [6–8]. The energy density of most commercial supercapacitors (less than 10 Wh kg^{-1}) [9] is higher than that of traditional electrolytic capacitors. While, it is still significantly lower than that of lithium ion battery $(100 \text{ Wh} \text{ kg}^{-1})$ [10]. Thus, a multitude of researches are working on improving the energy density of supercapacitors without sacrificing their high power density [11].

http://dx.doi.org/10.1016/j.electacta.2017.04.038 0013-4686/© 2017 Elsevier Ltd. All rights reserved.

Supercapacitor has a higher power density and higher cycle stability than lithium-ion batteries due to the fast physical absorption and desorption of ions at the electrode and electrolyte interface of the electric double layer capacitor [12]. The energy density of modern supercapacitors can be increased via the introduction of new and advanced electrode materials designed with the goal of increasing their specific capacitance [13]. In recent years, carbon materials have attracted great interest due to their large specific surface areas, good conductivity, and low-cost in addition to being environmentally friendly. Most of researchers put the focus on the specific area of carbon materials to enhance the capacitance. However, the increase of the specific surface area cannot always categorically improve the specific capacitance of supercapacitors [14]. Thus, a reasonable pore size distribution is very important for high rate supercapacitors. There are many ways to control the size and morphology of carbon materials including heat treatment [15], alkali treatment [16], template methods [17], physical or chemical activation [18], etc. Among the many reagents for chemical activation, KOH, NaOH, H₃PO₄, and ZnCl₂ are the most commonly used. A carbon precursor is firstly exposed to pyrolysis in inert atmosphere, followed by introducing the activation agent [19]. In principle, activation agent and carbon precursor are both

^{*} Corresponding author. E-mail address: mayanqing@shzu.edu.cn (Y. Ma).

solid phase. In this process, it is very difficult to form homogeneous phase between the activation agent and the carbon precursor. This immensely limits the development of the size of pores during the pyrolysis process. That is to say, the development of a porous carbon electrode material via chemical activation is still a pressing challenge.

Biomass porous carbon, due to its good electrical conductivity, stable physical and chemical characteristics, as well as low cost, is the most widely studied as a prospective electrode material [16]. In light of this, the usage of biomass materials in preparing porous carbon electrode materials is in line with current developmental trends, and many of them, such as cigarette filters [20], leaves [21], chicken eggshell membranes [22], gelatin [23], paulownia sawdust [24], cotton T-shirts [25], wood [26], bagasse [27], willow catkins [28,29], pitch [30–32] have been widely reported. However, porous carbons derived from natural precursors usually require pre-carbonization at moderate temperatures (generally at 400–600 °C) [19] and chemical activation (in KOH or NaOH) at high temperature. Therefore, developing simple route and eco-friendly synthesis strategy for porous carbon materials from available biomass is still a herculean task with far reaching and significance repercussions [33].

Cellulose is a widely present and renewable resource in nature. It possesses high carbon content. However, As far as we know, there is few systematic reports have been concern about the formation of porous carbon from cellulose aerogel. Thus it is of great interest to explore the value of carbon materials of various sizes formed from cellulose. In this work, a simple strategy was designed to synthesize cellulose aerogels after carbonization to obtain porous carbon. Quite unlike the previously well-developed standard pre-carbonization followed by KOH activation process, the sodium hydroxide was used for the cellulose aerogels dissolve and activation to obtain micro- and meso-porous carbon (MMC) materials [34,35]. Accordingly, supercapacitors involved the obtained MMC materials exhibit an excellent capacitive performance.

2. Experimental

2.1. Materials

The microcrystalline cellulose used in this work was purchased from Aladdin. All chemicals in the present work were analytical reagent grade and were used as received without further purification.

2.2. Preparation of cellulose aerogel

First, the microcrystalline cellulose was dissolved in a mixed solution consisted of sodium hydroxide, urea and water

(7.5:12:82 wt%) [36]. Then, the solution was stirred strongly for 4 h at $-8 \degree$ C to obtain cellulose sol. The sol was dried in an oven at 50 °C for 12 h to ensure thorough gelation, and frozen for 24 h in a refrigerator and then dried for 12 h in freeze dryer.

2.3. Preparation of MMC

The obtained cellulose aerogels were carbonized in a tube furnace at temperatures of 600 °C, 700 °C, 800 °C, respectively, with a heating rate of 5 °C min⁻¹ in a nitrogen atmosphere. The samples were held for 2 h at each temperature and then cooled down to room temperature at a rate of 2 °C min⁻¹. The carbonized samples were washed thoroughly several times with deionized water to remove any residual chemicals. The as-carbonized samples were dried at 50 °C for 12 h. These samples are referred to as C-600, C-700, and C-800.

2.4. Characterization

The morphology and microstructure of the as-carbonized porous carbon were observed by a field emission scanning electron microscope (FESEM) from Hitachi Ltd, and high resolution transmission electron microscopy (HRTEM) on a FEI Tecnai G20. Raman spectroscopy of the porous carbon was carried out using laser confocal microspectroscopy (LabRAM HR800) with the 512 nm line of a He-Ne laser as the excitation source. The X-ray diffraction spectra (XRD) measurements were measured using a Bruker D8 advance X-ray diffractometer with Cu K α radiation source (λ = 1.5406 Å) in the scanning angle range of 10-90° at scanning rate of 10° min⁻¹ at 40 mA and 40 kV. The BET surface area analysis was conducted by obtaining nitrogen adsorption iso-therms with Micromeritics ASAP 2020 instrument at 77 K.

2.5. Electrochemical measurements

The electrode thin sheets were prepared by the obtained porous carbon materials (80 wt%), acetylene black (10 wt%) and polytetrafluoroethylene (PTFE, 10 wt%) binder. The mixture was then homogenized in a mortar, during which a few drops of absolute alcohol were added. The resultant paste was rolled into thin, uniform sheets electrodes of 8 mm diameter using a tablet press and then dried at 110 °C for 4 h. The mass loading of the active materials (C-600, C-700, C-800 samples) in each electrode was around 1.6 mg. Symmetric supercapacitors were constructed from two similar electrodes on hydrophilic carbon paper and separated by a piece of polypropylene membrane on a stainless-steel plate; $1 \text{ M } \text{ H}_2\text{SO}_4$ and $1 \text{ M } \text{ Na}_2\text{SO}_4$ were used as the electrolyte. Electrochemical performance measurements were carried out in a two-electrode system by cyclic voltammetry (CV) and



Scheme 1. Schematic of highly porous cellulous-derived carbon with hierarchical pore structure.

electrochemical impedance spectroscopy (EIS) on a CHI 604E electrochemical workstation. The charge-discharge performance of the supercapacitors was measured on a CHI 760E electrochemical workstation. CV tests of the two-electrode cell were investigated and EIS measurements were performed by an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at the open circuit potential. Cycle life tests were performed on a land cell taster (Land, CT-2001A).

According to the charge/discharge curves, the specific capacitance of electrodes can be calculated based on the following equation:

$$C_m = \frac{I_d \times \Delta t}{\Delta V \times m} \tag{1}$$

Where C_m (Fg⁻¹) is specific capacitance, I_d (mA) is the discharge current, Δt (s) is the discharge time, ΔV (V) is the discharge voltage range, and m (mg) is the mass loading of active materials based on both electrodes.

Energy density E (Wh kg⁻¹) and power density P (W kg⁻¹) were calculated according to the following equations:

$$E = \frac{1}{2}C_m \times \Delta V^2 \times \frac{1}{3.6} \tag{2}$$

$$P = \frac{E}{\Delta t} \times 3600 \tag{3}$$

Here $C_m(Fg^{-1})$ is specific capacitance based on the mass loading of the active materials in both electrodes, ΔV (V) is the discharge voltage range that is exclusive of the IR drop, and Δt (s) is the discharge time.

Scheme 1 shows a schematic illustration of the main process for preparing a hierarchically porous carbon derived from cellulose. The commonly preparation methods of cellulose aerogels is that microcrystalline was mixing into urea and sodium hydroxide aqueous solution under the low temperature condition. In the process, urea and sodium hydroxide play the role of dissolution of cellulose. The first step is the dissolution of the cellulose fibers, which consist of sodium hydroxide, urea, and water. This solution was stirring strongly for a few hours to form the gel and then dried in an oven to ensure thorough gelation. After the freeze-drying and carbonization processes, porous carbon can be obtained. To further optimize the pore size distribution and prepare hierarchical porous structures, the obtained porous carbon was then carbonized in a tube furnace under different temperatures. In carbonization

Fig. 1. The FESEM images of the samples at different magnifications: C-600 (A) and (B); C-700 (C) and (D); C-800 (E) and (F).



process, the sodium hydroxide plays as an activator to obtain microporous and mesoporous carbon materials.

3. Results and discussion

3.1. Material Characterization

Fig. 1 shows the FESEM images of porous carbon samples at three different temperatures. The C-600 sample formed a porous structure (shows in Fig. 1A), but did not have a clear pore channel and had few openings to the pore structure (Fig. 1B). As can be seen from Fig. 1C and Fig. 1D, the C-700 sample formed very clearly connected and open pore channels with a more uniform distribution of pore size compared with the C-600 sample. When the temperature was raised to 800°C, the continuous pore structure was destroyed (Fig. 1E and 1F). HRTEM is used to further investigate the microstructure of porous carbon. The open and interconnected pores are not formed in the C-600 sample and the structure is disorderly (Fig. 2A), which is consistent with the FESEM results. This structure is not conductive to the transmission of electrolyte during periods of high charge and discharge rate (Fig. 2B). It can be seen clearly that there are large number of microporous structures with diameters less than 2 nm, which can store electrolyte ion and increase specific capacitance. Fig. 2E and Fig. 2F demonstrate that high temperatures can cause significant damage to the pore channel and microporous structure of the porous carbon.

The XRD patterns of the C-600, C-700 and C-800 samples are shown in Fig. **3A**. The porous carbon has two diffraction peaks which are consistent with graphitic carbon. The peak was broad in

width and low in intensity at 23-25°, suggesting amorphous characteristics of the carbon materials. The XRD pattern of samples have broad diffraction peak at 24.5°, 25.5° and 23.2°, corresponding to interlayer spacing of 0.36 nm, 0.34 nm and 0.38 nm, respectively. This result suggests that the C-700 sample has the smallest interlayer spacing and the lowest degree of graphitization of all samples [37]. Another peaks were weak at 43°, implying graphitic structure was developed to a slight extent [38].

The supporting evidence of the Raman spectroscopy in Fig. 3Bshows that all three samples possess two typical carbon characteristic diffraction peaks at 1360 cm^{-1} (peak D) and 1586 cm⁻¹ (peak G). Peak D, with a double-resonance, represents the degree of disorder in the structure or any structural defects [39,40]. The intensity ratio, I_D/I_G , of the porous carbon is increased from 0.97 for the C-600 sample to 1.02 for the C-700 sample, demonstrating that the C-700 sample has a lower degree of graphitization than the C-600 sample. The value of I_D/I_G of the C-800 sample [34] decreased a little to 0.98, indicating a graphitization effect at high temperatures, which results in increased amounts of sp² carbon atoms in the structure of the C-800 sample. The MMC also exhibits a slight second order peak 2D and D+G at 2670 and 2910 cm⁻¹, which are attributed to the existence of ordered carbon structure. This shows that the C-700 sample with a porous structure possesses a high degree of disorder, a large amount of edges, and great number of defects. This suggests that the porous carbon with micro- and meso-porous structures was obtained by carbonization treatment from the Raman spectra and XRD analysis. The porosity of the C-700 sample was very developed, although the degree of graphitization was lower. This is beneficial for the transmission and diffusion of electrolyte ions.



Fig. 2. The HRTEM images of the samples at different magnifications: C-600 (A) and (B); C-700 (C) and (D); C-800 (E) and (F).



Fig. 3. (A) XRD patterns of three porous carbon samples; (B) Raman spectra of three porous carbon samples; (C) N_2 adsorption-desorption isotherms and (D) pore size distribution of three porous carbon samples, calculated from the adsorption isotherms using DFT method; (E) The inset shows the magnified view of (C); C-600 (a); C-700 (b); C-800 (c).

Nitrogen adsorption/desorption isotherms are shown in Fig. 3C and pore properties parameters are summarized in Table 1. Three porous carbon samples exhibit Type IV isotherm in Fig. 3C, and adsorption capacity increased rapidly at the initial stages (inset in Fig. 3E) and the obvious convex curve at low relative pressure (less than 0.2), with adsorption-desorption coincidence. At an intermediate relative pressure from 0.2-0.8, the adsorption amount gradually rises with increasing relative pressure. A type H4 Type hysteresis loop can also be seen, indicating that a large number of mesoporous volume [37,41,42] and clogging phenomena does not occur [36]. There are no obvious platforms implying that all samples contain a small number of macroporous structures or few pore accumulation phenomena at high relative pressure. As we have seen, Fig. 3D shows that the pore structure of all samples was composed of mesopores and micropores. The sizes of the micropores of all the samples are typically centered at 1.49 nm, consistent with electrolyte ions and micropores. Moreover, the C-600 and C-700 samples have few mesopores that are predominantly in the range from $2.25 \sim 3.32$ nm. The specific surface area and volume of the micropores were calculated by the BET and tplot methods, respectively. Table 1 shows detailed BET and pore volumes information for all three samples and the average pore sizes for C-600, C-700 and C-800 samples which are 2.9 nm, 2.7 nm and 3.3 nm, respectively. The C-700 sample has the highest pore

Table 1				
Textural	parameters	of the	porous	carbons.

volume and greatest specific surface area at $0.4403 \text{ m}^3 \text{g}^{-1}$ and $646 \text{ m}^2 \text{g}^{-1}$, respectively.

3.2. Electrochemical Behavior

Cyclic voltammetry test was performed at different scan rate. In addition, charge-discharge tests were performed at different current densities. These two tests were used to assess the electrochemical performance of the supercapacitors. Symmetric supercapacitors were assembled in 1 M H₂SO₄ electrolyte, with voltages ranging from 0 to 0.8 V. The CV curve of the C-600, C-700 and C-800 electrodes at a scanning rate of 5 mV s^{-1} are shown in Fig. 4A. The CV curves of the three electrodes exhibit a symmetric and approximately rectangular shape [43], which indicates that the formation of an electric double layer electrode [44] and further indicates that the three electrodes have good electrochemical performance [45]. The CV curves of the C-700 electrode under different scanning rates from 2 mV s⁻¹ to 200 mV s⁻¹ are shown in Fig. 4B. It can be seen that the CV curve maintains approximate rectangular shape at an extremely high scanning rate of 200 mV s⁻¹, indicating the electrolyte ion transports efficiently inside the C-700 electrode. That is to say, more of the microporous structure is utilized predominantly to store more electrolyte ions. During charging and during the formation of the double electrode layer,

Sample	$S_{BET}(m^2g^{-1})$	V_{total} (cm ³ g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	Daverage (nm)
C-600	417	0.2978	0.1733	0.1245	2.9
C-700	646	0.4403	0.1361	0.3042	2.7
C-800	126	0.1042	0.0539	0.0503	3.3



Fig. 4. (A) CV curves of the three electrodes at potential scan rates of 5 mV s⁻¹ and (B) C-700 at various scan ranging from 2 to 200 mV s⁻¹; (C) Specific capacitances of three electrodes at varied potential scan rates in 1 M H₂SO₄.

which can be attributed to the cooperative effects between the microporous and mesoporous structures, indicating a superior ion diffusion in the micro-mesoporous structure and leading to the maxim specific capacitance in the C-700 electrode. Rate performance, of great import in supercapacitors, can be benefited by allowing the electrolyte ions to more easily enter the pores. When the scanning rate increases, the specific capacitance with the C-700 electrode decreases clearly more than that with the C-600 and C-800 electrodes. The specific capacitance of the C-600 electrode decreased from 108 Fg^{-1} to 37 Fg^{-1} when the scanning rate was increased from 2 to 200 mV s⁻¹. The C-600 electrode presents a low specific capacitance retention ratio of 34% due to the fact that the connected pore channels and opening structures are not formed. This in turn hinders the transfer of the electrolyte ion. It was unexpected that the C-700 electrode would have the maximum specific capacitance of 190 F g⁻¹ at 2 mV s⁻¹ resulting from its large specific surface area and pore volume. A reasonable match with micropores can be used to store more electrolyte ion. And mesoporous pores can provide a good channel to further facilitate the electrolyte ion penetrating inner pores. However, the specific capacitance of C-800 electrode is only 88 Fg⁻¹ at 2 mV s⁻¹. This is due to the structure of both the microporous and mesoporous is destroyed resulting in reduced specific capacitance after carbonation at 800°C.

In order to further verify the electrochemical properties of the C-700 electrode, the galvanostatic charge-discharge rate was tested at different current densities. The approximate linear lines with obvious symmetric triangular shapes are shown in Fig. 5A. This reveals that the C-700 electrode has very good capacitive behavior [46], and a slight IR drop can be seen, resulting from the low internal resistance [47,48]. From Fig. 5B, it can be seen that the specific capacitance of C-700 electrode at 0.1 Ag^{-1} can reach 195 Fg⁻¹. Although the current density reaches 20 Ag^{-1} , the

specific capacitance of the C-700 electrode was also maintained at 126 Fg^{-1} and a retention ratio of 83%, indicating that the symmetric supercapacitor has good rate performance. Since the C-700 electrode has a large number of mesoporous structures, the electrolyte ions can be transferred easily at a high charge and discharge rate, reducing the diffusion time of the electrolyte ions. Thus the supercapacitor retains a high capacity at a high current density. Porous carbon with micro- and mesoporous structure not only improves the specific capacitance of supercapacitors but also enhances the rate performance of supercapacitors. Cycle stability experiment was carried out to assess the application of symmetric supercapacitor. Fig. 5C shows that the specific capacitance of C-700 electrode at current density of 1 Ag^{-1} was decreased from 186 Fg^{-1} to 167 Fg^{-1} after 10000 cycling test with specific capacitance retention rate of 90%. It shows that symmetry supercapacitor have a very excellent cycle stability.

As mentioned above in Fig. 1, this structure hinders the transmission and the diffusion rates of the electrolyte, leading to the lowest electrochemical performance of the tested supercapacitors. This unique structure of the C-700 sample is beneficial to both the transmission and diffusion of electrolyte and improving the electrochemical performance of supercapacitors [37].

It is well known to us that the energy density and power density are not only relevant to the specific capacitance of the supercapacitor but also closely interrelated to the high stability operating voltage [27,29]. Moreover, high window operating of supercapacitor can be attained in neutral solution. In order to further improve the energy density, we assembled symmetric supercapacitors by using two same C-700 electrode in 1 M Na₂SO₄ aqueous electrolyte, which possesses a higher operation voltage than acid solution. Fig. 6A show the CV curves of C-700//C-700 symmetric supercapacitor at a scan rate of 20 mV s⁻¹ in different voltage windows. It is clear that the CV curves keep a rectangular-



Fig. 5. (A) Galvanostatic charge-discharge curves of C-700 at different current densities ranging from 0.1 Ag^{-1} to 20 Ag^{-1} ; (B) Specific capacitance of the C-700 sample at current density derived from (A); (C) Cycle stability of C-700 electrode at current density of 1 Ag^{-1} over 10000 cycles.



Fig. 6. (A) CV curves of the symmetric supercapacitor at different voltage windows in 1 M Na₂SO₄ aqueous electrolytes at 20 mV s^{-1} ; (B) CV curves of the C-700//C-700 symmetric supercapacitor at various scan rates; (C) GCD curves of the C-700//C-700 symmetric supercapacitor at different current densities; (D) Ragone plots of the C-700//C-700 symmetric supercapacitor.

like shape and no obvious increase of anodic current at 1.8 V and rapid increase of anodic current at 2.0 V. It indicates that the symmetric supercapacitor can be reversibly cycled within the voltage window up to 1.8 V. The CV curves of the C-700//C-700 symmetric supercapacitor under different scanning rates from 10 mV s⁻¹ to 100 mV s⁻¹ are shown in Fig. 6**B**. It can be seen that the CV curve still maintains quasi-rectangular shape at an extremely high scanning rate of 100 mV s⁻¹. This proves that it is an ideal rate performance. Fig. 6C shows the galvanostatic charge-discharge rate was tested at different current densities. The approximate linear lines with obvious symmetric triangular shapes are shown and a slight IR drop can be seen, resulting from the low internal resistance, indicting good rate capability and electrochemical capacitance for C-700//C-700 symmetric supercapacitor. Energy density and power density of symmetric supercapacitor were shown in the Ragone plot from Fig. 6D. The specific capacitance and the operating voltage is 160 Fg^{-1} (0.2 A g⁻¹ current density) and 1.8 V, respectively. The energy density of symmetry supercapacitor is calculated 17.81 Wh kg⁻¹ when the power density is 180.11 W kg⁻¹. Even when the power density is as high as 17829.47 W kg⁻¹, the energy density of the symmetry supercapacitor remains at 9.41 Wh kg⁻¹. Thus, we have obtained a high performance supercapacitor which was used cellulose as a carbon source for preparing porous carbon electrode material.

Electrochemical impedance spectroscopy (EIS) helps to further analyze the electrochemical behavior of the supercapacitors. It is performed with a frequency range of 0.01 Hz to 100 kHz at an open circuit potential of 5 mV. Fig. 7**A** shows that there is an apparent semicircle in the high-frequency range in the EIS spectrogram of three electrodes, which is caused by the electric double-layer capacitance, which itself corresponds to the charge transfer resistance [49]. The resistance values of the C-600, C-700 and C-



Fig. 7. (A) Nyquist plots of three electrodes. The inset shows the magnified view of the high-frequency region and the electrical equivalent circuit used for fitting impedance spectra; (B) the bode phase diagrams.

Table 2

Summary of electrochemical properties of porous carbon electrodes derived biomass for supercapacitor reported in recent papers.

Carbon type	C^{a} (Fg ⁻¹)	T ^b	Ec	Ref
Starch-derived mesoporous carbons	144	$0.05 \mathrm{A g^{-1}}$	6 M KOH	[40]
Enteromorpha based porous carbons	206	$0.5 \mathrm{Ag}^{-1}$	6 M KOH	[46]
(N-doped) meso-microporous	153	$1 \mathrm{A g^{-1}}$	6 M KOH	[20]
hybrid carbon				
coffee grounds-derived carbon	57	$0.05{A}{g}^{-1}$	1 M H ₂ SO ₄	[56]
Wood-based activated carbons	160	$0.01 \mathrm{Ag}^{-1}$	1 M TEABF4	[55]
Hierarchical porous carbon aerogels	142	$0.5 \mathrm{A}\mathrm{g}^{-1}$	6 M KOH	[36]
Rice husk-derived activated carbon	172	$5 { m mV}{ m s}^{-1}$	0.5 M K ₂ SO ₄	[54]
Peanut shell-derived activated carbon	242	$0.05{ m Ag^{-1}}$	6 M KOH	[43]
Rice husk-derived mesoporous carbon	176	$0.5 \mathrm{A}\mathrm{g}^{-1}$	6 M KOH	[44]
MMC	195	$0.1 \mathrm{Ag}^{-1}$	1 M H ₂ SO ₄	This work

^a Specific capacitance.

^b Current density or scan rate.

^c Electrolyte type.

800 electrodes were 0.82, 0.45 and 0.96 Ω , respectively, indicting a good charge-transfer rate [50]. It is observed that the charge transfer resistance of the C-700 electrode is minimal. The oblique line in the low-frequency region represents the ion diffusion resistance [51] and the degree of ideal supercapacitors is 90 degrees [29]. It can be seen that there is an almost vertical line for the C-700 electrode in the low frequency region, demonstrating that the C-700 electrode has ideal capacitive behavior [52]. An equivalent circuit diagram inset in Fig. 7A includes Re express resistivity system consist of intrinsic resistance, electrolyte ions resistance, the contact resistance between active material and current collector. Rct is the charge transfer resistance, CdI represents double layer capacitor, Zw is Weber resistance [53]. Fig. 7B shows that the phase angle of the C-700 electrode is 78.27° from the Bode plot, which is the closest to the ideal diffusion slope of supercapacitors. It shows that the impact of diffusion is minimal in the electrode.

In comparison with the published reported porous carbons electrode materials which were commonly synthesized by chemical activation methods (Table 2) [20,36,40,43,44,46,54–56], the MMC electrode shows the competitive specific capacitance of 195 Fg^{-1} at a discharge current density of 0.1 Ag^{-1} . This result shows the formation uniform system of cellulose aerogels. It plays an important role for optimizing the pore size of MMC in carbonization process. And the electrochemical properties of the MMC electrode obtained by using cellulose as carbon source are better than other biomass materials.

4. Conclusion

In summary, porous carbons with mesopore/micropore hybrid structures were prepared by carbonizing a cellulose aerogel without in addition activating reagent. The porous carbon electrode has a comparably high specific capacitance of $195 \,\mathrm{Fg}^{-1}$ at a discharge current density of 0.1 Ag⁻¹, and good cycling stability (90% capacity retention after 10000 cycles at current density of 1 Ag^{-1}). This is a simple and rote prime candidate for a renewable and environmentally friendly electrode material for use in the manufacture of supercapacitors. The reasonable match between micropores and mesoporous can supply high energy density and power-energy synergetic characteristics. To the best of our knowledge, such a phenomenon has yet to be reported and very little research has been performed that is concerned with utilizing cellulose as a precursor to produce porous carbon for applications in supercapacitors with superior performance. This study shows that cellulose based porous carbon is an ideal candidate electrode materials for supercapacitors. Indeed, this free-activating agent synthesis strategy holds great promise for preparing novel porous carbons from cellulose biomass resources for application in state-of-art energy storage devices.

Acknowledgments

This work was financially supported by Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT, No. IRT1161); Program of Science and Technology Innovation Team in Bingtuan (No. 2011CC001); and the National Natural Science Foundation of China (No. 21263021, U1303291).

References

- [1] Y. Zuo, G. Wang, J. Peng, G. Li, Y. Ma, F. Yu, B. Dai, X. Guo, C.P. Wong, Hybridization of graphene nanosheets and carbon-coated hollow Fe3O4 nanoparticles as a high-performance anode material for lithium-ion batteries, Journal of Materials Chemistry A 4 (2016) 2453–2460.
- [2] Z. Peng, J. Lin, R. Ye, E.L.G. Samuel, J.M. Tour, Flexible and Stackable Laser-Induced Graphene Supercapacitors, ACS Applied Materials & Interfaces 7 (2015) 3414–3419.
- [3] J. Chen, J. Xu, S. Zhou, N. Zhao, C.P. Wong, Template-grown graphene/porous Fe2O3 nanocomposite: A high-performance anode material for pseudocapacitors, Nano Energy 15 (2015) 719–728.
- [4] B. Song, C. Sizemore, L. Li, X. Huang, Z. Lin, K.-s. Moon, C.P. Wong, Triethanolamine functionalized graphene-based composites for high performance supercapacitors, Journal of Materials Chemistry A 3 (2015) 21789–21796.
- [5] X. Zhao, L. Zhang, S. Murali, M.D. Stoller, Q. Zhang, Y. Zhu, R.S. Ruoff, Incorporation of Manganese Dioxide within Ultraporous Activated Graphene for High-Performance Electrochemical Capacitors, ACS NANO 6 (2012) 5404– 5412.
- [6] Y. Yang, Z. Peng, G. Wang, G. Ruan, X. Fan, L. Li, H. Fei, R.H. Hauge, J.M. Tour, Three-Dimensional Thin Film for Lithium-Ion Batteries and Supercapacitors, ACS NANO 8 (2014) 7279–7287.
- [7] X. Lu, L. Li, B. Song, K.-s. Moon, N. Hu, G. Liao, T. Shi, C. Wong, Mechanistic investigation of the graphene functionalization using p-phenylenediamine and its application for supercapacitors, Nano Energy 17 (2015) 160–170.
- [8] B. Song, L. Li, Z. Lin, Z.K. Wu, K.S. Moon, C.P. Wong, Water-dispersible graphene/polyaniline composites for flexible micro-supercapacitors with high energy densities, Nano Energy 16 (2015) 470–478.
 [9] T. Kim, G. Jung, S. Yoo, K.S. Suh, R.S. Ruoff, Activated Graphene-Based Carbons
- [9] T. Kim, G. Jung, S. Yoo, K.S. Suh, R.S. Ruoff, Activated Graphene-Based Carbons as Supercapacitor Electrodes with Macro- and Mesopores, ACS NANO 7 (2013) 6899–6905.
- [10] F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A.C. Ferrari, R.S. Ruoff, V. Pellegrini, Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage, Science 347 (2015) 1246501.
- [11] Y. Yang, L. Li, G. Ruan, H. Fei, C. Xiang, X. Fan, J.M. Tour, Hydrothermally Formed Three-Dimensional Nanoporous Ni(OH)2 Thin-Film Supercapacitors, ACS NANO 8 (2014) 9622–9628.
- [12] J. Yan, Q. Wang, T. Wei, Z. Fan, Recent Advances in Design and Fabrication of Electrochemical Supercapacitors with High Energy Densities, Advanced Energy Materials 4 (2014) 1300816.
- [13] R. Wang, J. Lang, P. Zhang, Z. Lin, X. Yan, Fast and Large Lithium Storage in 3D Porous VN Nanowires-Graphene Composite as a Superior Anode Toward High-Performance Hybrid Supercapacitors, Advanced Functional Materials 25 (2015) 2270–2278.
- [14] T. Wei, X. Wei, Y. Gao, H. Li, Large scale production of biomass-derived nitrogen-doped porous carbon materials for supercapacitors, Electrochimica Acta 169 (2015) 186–194.

- [15] Y. Fan, X. Yang, B. Zhu, P.-F. Liu, H.-T. Lu, Micro-mesoporous carbon spheres derived from carrageenan as electrode material for supercapacitors, Journal of Power Sources 268 (2014) 584–590.
- [16] L. Wei, G. Yushin, Electrical double layer capacitors with activated sucrosederived carbon electrodes, Carbon 49 (2011) 4830–4838.
- [17] G. Sun, B. Li, J. Ran, X. Shen, H. Tong, Three-dimensional hierarchical porous carbon/graphene composites derived from graphene oxide-chitosan hydrogels for high performance supercapacitors, Electrochimica Acta 171 (2015) 13–22.
- [18] F.K. Bo You, Peiqun Yin, Qian Zhang, Hydrogel-derived heteroatom-doped porous carbon networks for supercapacitor and electrocatalytic oxygen reduction, Carbon 103 (2016) 9–15.
- [19] M. Sevilla, R. Mokaya, Energy storage applications of activated carbons: supercapacitors and hydrogen storage, Energy & Environmental Science 7 (2014) 1250.
- [20] M. Lee, G.-P. Kim, H. Don Song, S. Park, J. Yi, Preparation of energy storage material derived from a used cigarette filter for a supercapacitor electrode, Nanotechnology 25 (2014) 345601.
- [21] M. Biswal, A. Banerjee, M. Deo, S. Ogale, From dead leaves to high energy density supercapacitors, Energy & Environmental Science 6 (2013) 1249.
- [22] Z. Li, L. Zhang, B.S. Amirkhiz, X. Tan, Z. Xu, H. Wang, B.C. Olsen, C.M.B. Holt, D. Mitlin, Carbonized Chicken Eggshell Membranes with 3D Architectures as High-Performance Electrode Materials for Supercapacitors, Advanced Energy Materials 2 (2012) 431–437.
- [23] B. Xu, S. Hou, G. Cao, F. Wu, Y. Yang, Sustainable nitrogen-doped porous carbon with high surface areas prepared from gelatin for supercapacitors, Journal of Materials Chemistry 22 (2012) 19088.
- [24] X. Liu, M. Zheng, Y. Xiao, Y. Yang, L. Yang, Y. Liu, B. Lei, H. Dong, H. Zhang, H. Fu, Microtube Bundle Carbon Derived from Paulownia Sawdust for Hybrid Supercapacitor Electrodes, ACS Applied Materials & Interfaces 5 (2013) 4667– 4677.
- [25] L. Bao, X. Li, Towards Textile Energy Storage from Cotton T-Shirts, Advanced Materials 24 (2012) 3246–3252.
- [26] L. Wei, M. Sevilla, A.B. Fuertes, R. Mokaya, G. Yushin, Hydrothermal Carbonization of Abundant Renewable Natural Organic Chemicals for High-Performance Supercapacitor Electrodes, Advanced Energy Materials 1 (2011) 356–361.
- [27] H. Feng, H. Hu, H. Dong, Y. Xiao, Y. Cai, B. Lei, Y. Liu, M. Zheng, Hierarchical structured carbon derived from bagasse wastes: A simple and efficient synthesis route and its improved electrochemical properties for highperformance supercapacitors, Journal of Power Sources 302 (2016) 164–173.
- [28] K. Wang, R. Yan, N. Zhao, X. Tian, X. Li, S. Lei, Y. Song, Q. Guo, L. Liu, Bio-inspired hollow activated carbon microtubes derived from willow catkins for supercapacitors with high volumetric performance, Materials Letters 174 (2016) 249–252.
- [29] Y. Li, G. Wang, T. Wei, Z. Fan, P. Yan, Nitrogen and sulfur co-doped porous carbon nanosheets derived from willow catkin for supercapacitors, Nano Energy 19 (2016) 165–175.
- [30] X. He, R. Li, J. Qiu, K. Xie, P. Ling, M. Yu, X. Zhang, M. Zheng, Synthesis of mesoporous carbons for supercapacitors from coal tar pitch by coupling microwave-assisted KOH activation with a MgO template, Carbon 50 (2012) 4911–4921.
- [31] W. Zhang, Z.-H. Huang, Z. Guo, C. Li, F. Kang, Porous carbons prepared from deoiled asphalt and their electrochemical properties for supercapacitors, Materials Letters 64 (2010) 1868–1870.
- [32] C. Zhong, S. Gong, L.e. Jin, P. Li, Q. Cao, Preparation of nitrogen-doped pitchbased carbon materials for supercapacitors, Materials Letters 156 (2015) 1–6.
- [33] D. Wang, S. Liu, G. Fang, G. Geng, J. Ma, From Trash to Treasure: Direct Transformation of Onion Husks into Three-Dimensional Interconnected Porous Carbon Frameworks for High-Performance Supercapacitors in Organic Electrolyte. Electrochimica Acta 216 (2016) 405–411.
- [34] S. Rolda'n, I. Villar, V. Rui'z, C. Blanco, M. Granda, R. Mene'ndez, R. Santamari'a, Comparison between Electrochemical Capacitors Based on NaOH- and KOH-Activated Carbons, Energy & Fuels 24 (2010) 3422–3428.
- [35] B. Xu, F. Wu, D. Mu, L. Dai, G. Cao, H. Zhang, S. Chen, Y. Yang, Activated carbon prepared from PVDC by NaOH activation as electrode materials for high performance EDLCs with non-aqueous electrolyte, International Journal of Hydrogen Energy 35 (2010) 632–637.

- [36] P. Hao, Z. Zhao, J. Tian, H. Li, Y. Sang, G. Yu, H. Cai, H. Liu, C.P. Wong, A. Umar, Hierarchical porous carbon aerogel derived from bagasse for high performance supercapacitor electrode, Nanoscale 6 (2014) 12120–12129.
- [37] S.L. Candelaria, B.B. Garcia, D. Liu, G. Cao, Nitrogen modification of highly porous carbon for improved supercapacitor performance, Journal of Materials Chemistry 22 (2012) 9884.
- [38] L. Zhu, Q. Gao, Y. Tan, W. Tian, J. Xu, K. Yang, C. Yang, Nitrogen and oxygen codoped microporous carbons derived from the leaves of Euonymus japonicas as high performance supercapacitor electrode material, Microporous and Mesoporous Materials 210 (2015) 1–9.
- [39] Y. Lv, F. Zhang, Y. Dou, Y. Zhai, J. Wang, H. Liu, Y. Xia, B. Tu, D. Zhao, A comprehensive study on KOH activation of ordered mesoporous carbons and their supercapacitor application, Journal of Materials Chemistry 22 (2012) 93– 99
- [40] M. Wu, P. Ai, M. Tan, B. Jiang, Y. Li, J. Zheng, W. Wu, Z. Li, Q. Zhang, X. He, Synthesis of starch-derived mesoporous carbon for electric double layer capacitor, Chemical Engineering Journal 245 (2014) 166–172.
- [41] Y. Huang, L. Peng, Y. Liu, G. Zhao, J. Chen, G. Yu, Biobased Nano Porous Active Carbon Fibers for High-Performance Supercapacitors, ACS Applied Materials & Interfaces 8 (2016) 15205–15215.
- [42] X. He, Z. Liu, H. Ma, N. Zhang, M. Yu, M. Wu, Shell-like hierarchical porous carbons for high-rate performance supercapacitors, Microporous and Mesoporous Materials 236 (2016) 134–140.
- [43] M. Wu, R. Li, X. He, H. Zhang, W. Sui, M. Tan, Microwave-assisted preparation of peanut shell-based activated carbons and their use in electrochemical capacitors, New Carbon Materials 30 (2015) 86–91.
- [44] M. Wu, L. Li, J. Liu, Y. Li, P. Ai, W. Wu, J. Zheng, Template-free preparation of mesoporous carbon from rice husks for use in supercapacitors, New Carbon Materials 30 (2015) 471–475.
- [45] X. He, J. Lei, Y. Geng, X. Zhang, M. Wu, M. Zheng, Preparation of microporous activated carbon and its electrochemical performance for electric double layer capacitor, Journal of Physics and Chemistry of Solids 70 (2009) 738–744.
- [46] M. Wu, P. Li, Y. Li, J. Liu, Y. Wang, Enteromorpha based porous carbons activated by zinc chloride for supercapacitors with high capacity retention, RSC Adv. 5 (2015) 16575–16581.
- [47] Y. Wang, H. Xuan, G. Lin, F. Wang, Z. Chen, X. Dong, A melamine-assisted chemical blowing synthesis of N-doped activated carbon sheets for supercapacitor application, Journal of Power Sources 319 (2016) 262–270.
- [48] H. Mi, J. Zhou, Q. Cui, Z. Zhao, C. Yu, X. Wang, J. Qiu, Chemically patterned polyaniline arrays located on pyrolytic graphene for supercapacitors, Carbon 80 (2014) 799–807.
- [49] J. Ji, L. Zhang, H. Ji, Y. Li, X. Zhao, X. Bai, X. Fan, F. Zhang, R.S. Ruoff, Nanoporous Ni(OH)2 Thin Film on 3D Ultrathin-Graphite Foam for Asymmetric Supercapacitor, ACS nano 7 (2013) 6237–6243.
- [50] F. Gao, G. Shao, J. Qu, S. Lv, Y. Li, M. Wu, Tailoring of porous and nitrogen-rich carbons derived from hydrochar for high-performance supercapacitor electrodes, Electrochimica Acta 155 (2015) 201–208.
- [51] Z. Ling, Z. Wang, M. Zhang, C. Yu, G. Wang, Y. Dong, S. Liu, Y. Wang, J. Qiu, Sustainable Synthesis and Assembly of Biomass-Derived B/N Co-Doped Carbon Nanosheets with Ultrahigh Aspect Ratio for High-Performance Supercapacitors, Advanced Functional Materials 26 (2016) 111–119.
- [52] L. Li, A.-R.O. Raji, H. Fei, Y. Yang, E.L.G. Samuel, J.M. Tour, Nanocomposite of Polyaniline Nanorods Grown on Graphene Nanoribbons for Highly Capacitive Pseudocapacitors, ACS Applied Materials & Interfaces 5 (2013) 6622–6627.
- [53] Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, Asymmetric Supercapacitors Based on Graphene/MnO2 and Activated Carbon Nanofiber Electrodes with High Power and Energy Density, Advanced Functional Materials 21 (2011) 2366–2375.
- [54] K. Le Van, T.T. Luong Thi, Activated carbon derived from rice husk by NaOH activation and its application in supercapacitor, Progress in Natural Science: Materials International 24 (2014) 191–198.
- [55] G. Dobele, A. Volperts, G. Telysheva, A. Zhurinsh, D. Vervikishko, A. Sametov, E. Shkolnikov, J. Ozolinsh, Wood-based activated carbons for supercapacitors with organic electrolyte, Holzforschung 69 (2015).
- [56] T.E. Rufford, D. Hulicova-Jurcakova, Z. Zhu, G. Lu, A comparative study of chemical treatment by FeCl3, MgCl2, and ZnCl2 on microstructure surface chemistry, and double-layercapacitance of carbons from waste biomass, Journal of Materials Research 25 (2011) 1451–1459.