Materials Letters 174 (2016) 249–252

Contents lists available at ScienceDirect

Materials Letters

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

Bio-inspired hollow activated carbon microtubes derived from willow catkins for supercapacitors with high volumetric performance

Kai Wang [a,b], Rui Yan [a,b], Ning Zhao [a], Xiaodong Tian [a,b], Xiao Li [a,b], Shiwen Lei [a], Yan Song [a,*], Quangui Guo [a], Lang Liu [a]

[a] Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:
Received 18 August 2015
Received in revised form
7 March 2016
Accepted 12 March 2016
Available online 14 March 2016

Keywords:
Carbon materials
Porous materials
Willow catkins
Supercapacitor
High volumetric performance

ABSTRACT

A novel bio-inspired hollow activated carbon microtubes (HACMs) was prepared from low-cost, renewable biomass willow catkins by low temperature pre-carbonization combined with KOH chemical activation and used as supercapacitor electrode materials. The as-prepared HACMs exhibit hollow fiber-like structure with thin wall thickness of less than 1 μm, high microporosity surface area (997 $m^2 g^{-1}$) and concentrated pore size distribution (1–2 nm). The electrochemical measurement results demonstrate that the HACMs electrode materials have high gravimetric capacitance of 306 F g^{-1} superior to most of the previously reported activated carbons and outstanding volumetric capacitance of 303 F cm^{-3}.

1. Introduction

Considering the ever-growing demands in energy storage systems, miniaturized portable electric devices with high volumetric performances, it is urgently needed to minimize the volume of devices [1,2]. Among energy storage systems, supercapacitors have attracted considerable attention due to their fast charge-discharge characteristics, high power density and long cycling stability. Activated carbons (ACs) are widely used as electrode materials for supercapacitors based on their high specific surface area (SSA), low-cost and environmental compatibility. Generally, ACs with well-developed porosity and high SSA often lead to high gravimetric capacitance. However, the volumetric capacitance of ACs is rather low due to the high porosity [3].

Activated carbon fibers (ACFs) have many advantages over the ACs such as micropores-dominated characteristic and micropores open directly to the exterior. Among the ACFs, a kind of specific carbon fibers with hollow structure has attracted researchers' attention greatly [4]. Due to the unique structure, hollow activated carbon fibers (HACFs) possess larger surface area and higher ion adsorption-desorption rate, which is more preferable for energy storage application. Herein, we used willow catkins as precursor to prepare HACMs. The as-synthesized HACMs possessed hollow fiber-like structure, high microporosity surface area, concentrated pore size distribution (PSD) but low porosity that results in high volumetric capacitance. The HACMs were proved to be a promising candidate for supercapacitors electrode materials.

2. Experimental

2.1. Preparation of HACMs

In a typical process, a certain amounts of feed willow catkins (WCs) was washed with deionized water repeatedly to remove adherent soil and impurities, dried at 100 °C overnight. Then, the WCs was pre-carbonized at 500 °C for 2 h, fully mixed with KOH at the mass ratio of 1:1 and followed by evaporating water at 80 °C. The mixture was pyrolyzed in a nickel crucible at 700 °C for 1 h under nitrogen flow. After being cooled to room temperature, the annealed samples were washed with 1 M HCl and deionized water until the pH value reached to 7.0. The final products were obtained after drying in vacuum at 80 °C for 10 h and labeled as HACMs. Besides, the commercial activated carbon (Nanjing XFNANO Materials Tech Co., Ltd.) labeled as C-ACs were used for comparison.

2.2. Characterization of the samples

SEM images of the carbonized and activated samples were taken by a JEOL JSM-7001F microscope. The porous texture was

* Corresponding author.
E-mail address: yansong1026@126.com (Y. Song).

http://dx.doi.org/10.1016/j.matlet.2016.03.063
0167-577X/

conducted by physical adsorption of N_2 at 77 K using physisorption apparatus (ASAP 2020, Micromeritics).

2.3. Electrochemical measurements

The capacitive performance of HACMs was performed with three-electrode configuration on a CHI 660C electrochemical workstation (Shanghai ChenHua Instruments Co., China). The working electrode was prepared by mixing the HACMs, acetylene black, conducting graphite, and polytetrafluoethylene (PTFE) binder at a mass ratio of 75:10:10:5. The mixture was pestled by mortar and coated onto a nickel foam current collector. A platinum foil and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The electrochemical performance was studied in 6 M KOH electrolyte by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques with a frequency range of 10 mHz to 100 kHz.

3. Results and discussion

Fig. 1a and b shows the SEM images of the carbonized WCs, the samples are exhibited long hollow tubular-like structure with coarse surface and covered by large amounts of spherical granules. The wall thicknesses are less than 1 μm while the outer diameters are less than 10 μm. The morphology of the samples was derivative from the pristine biomass (inset in Fig. 1a and Fig. S1). Fig. 1c and d show that the HACMs still retain original hollow configuration while small amounts of the samples collapse into fragments. The surface of the samples show distinct stripe texture with less granules. This specific morphological structure of HACMs makes the sample with high ions and electrons transport rate along the hollow microtubes.

In order to understand the pore structure properties, the HACMs were characterized by nitrogen adsorption-desorption analyses. The nitrogen adsorption-desorption isotherms are shown in Fig. 2a, the HACMs show a steep gas uptake at very low pressure and a fairly flat plateau in the high pressure with inconspicuous hysteresis loop that is the characteristic of a microporous-predominant structure with small amounts of mesopores. However, the C-ACs are incorporated by both a broader knee and more obvious hysteresis loop, which is a combination of type I and IV isotherm according to IUPAC classification, indicating the coexistence of both micropores and mesopores. The PSD curves of the samples in Fig. 2b show that the samples have greatly different pores. For the HACMs, the especially high microporosity (90.2 vol%) and concentrated PSD (1 to 2 nm) that is normally associated with high capacitance values [5]. While the C-ACs show bimodel PSD centered at 1.1 nm and 2.3 nm that results in low microporosity (37.7 vol%). Besides, the HACMs and C-ACs have similar micropore surface (997 *vs.* 913 $m^2 g^{-1}$) and average pore size (1.8 *vs.* 2.0 nm) that make them comparable on the electrochemical properties (Table 1).

Fig. 3 shows the electrochemical performance of the HACMs and C-ACs. CV testing (Fig. 3a) shows nearly rectangular curves at low scan rate of 5 mV s^{-1}, exhibiting typical characteristics of electrochemical double layer capacitors (EDLCs). Noticeably, the CV curve shows broad pseudopeaks at low potential region, indicating the existence of pseudocapacitive behavior due to its high heteroatoms content of the HACMs [6]. The CV curves still maintain a less rectangular shape (Fig. 3b) at high scan rate of 100 mV s^{-1}, implying good rate performance. Moreover, The GCD curves (Fig. 3c) exhibit almost symmetrical and linear geometry at

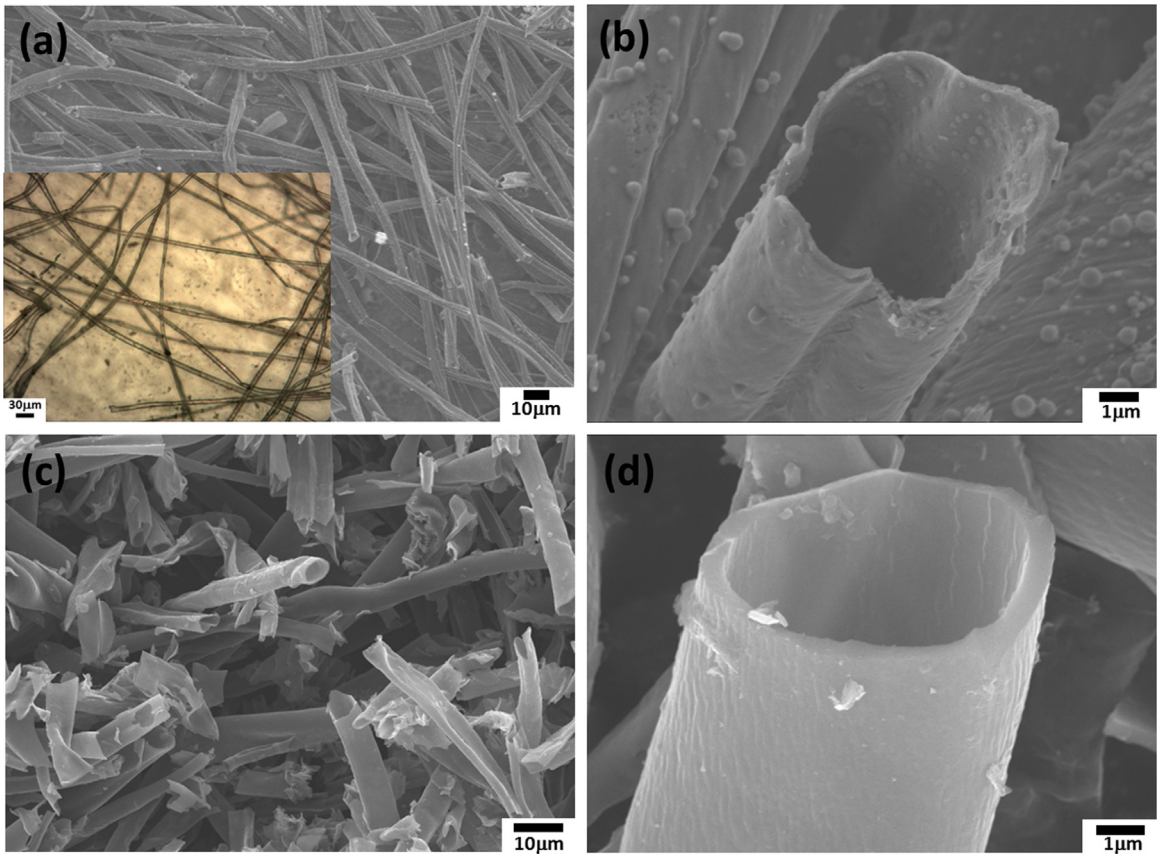

Fig. 1. SEM images of the carbonized WCs (a), (inset: the metallo-graph of pristine WCs) (b); SEM images of the HACMs (c), (d).

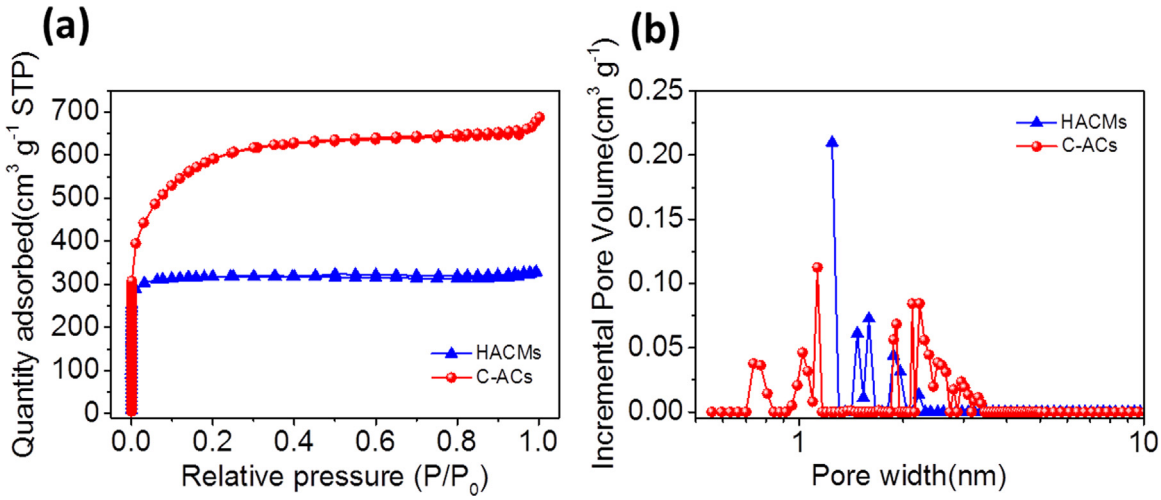

Fig. 2. (a) Nitrogen adsorption-desorption isotherms; and (b) PSD curves.

Table 1
The pore structure properties of samples.

Sample	S_{BET} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	V_{micro}/V_{total} (%)	D_{ave} (nm)
HACMs	1107	997	0.51	0.46	90.2	1.8
C-ACs	2054	913	1.06	0.40	37.7	2.0

increased current densities (0.1–10 A g^{-1}), indicating an ideal capacitor with good electrochemical reversibility. The relationships between the capacitances and current densities were presented in Fig. 3d. The gravimetric capacitance of HACMs and C-ACs are 306 and 292 F g^{-1} at 0.1 A g^{-1}, respectively. Corresponding to the volumetric capacitance of 303 F cm^{-3} for the HACMs that is far above the C-ACs (187 F cm^{-3}). The high volumetric capacitance of the HACMs greatly depends on the concentrated PSD but low pore volume that is suitable for the high-efficiency charges storage of EDLCs and rich heteroatoms that induce extra pseudo-capacitance [6]. The gravimetric capacitance of HACMs electrode still remains 200 F g^{-1} at 10 A g^{-1}, also exhibiting good rate capability. Besides, the volumetric capacitances of the HACMs are much higher than other alternative of biomass-based ACs (Table S1), further implying excellent electrochemical performance.

Nyquist plots of the samples are shown in Fig. 3e, the HACMs display good capacitive behavior with nearly vertical slope at the low frequency region. At high frequency region, the intercept of plot with real axis represents the equivalent series resistance (ESR). The low ESR of 0.78 Ω (inset in Fig. 3e) indicates good conductivity of the test device. The 0.39 Ω semicircle shows good ionic conductivity at the interface of electrolytes and electrode.

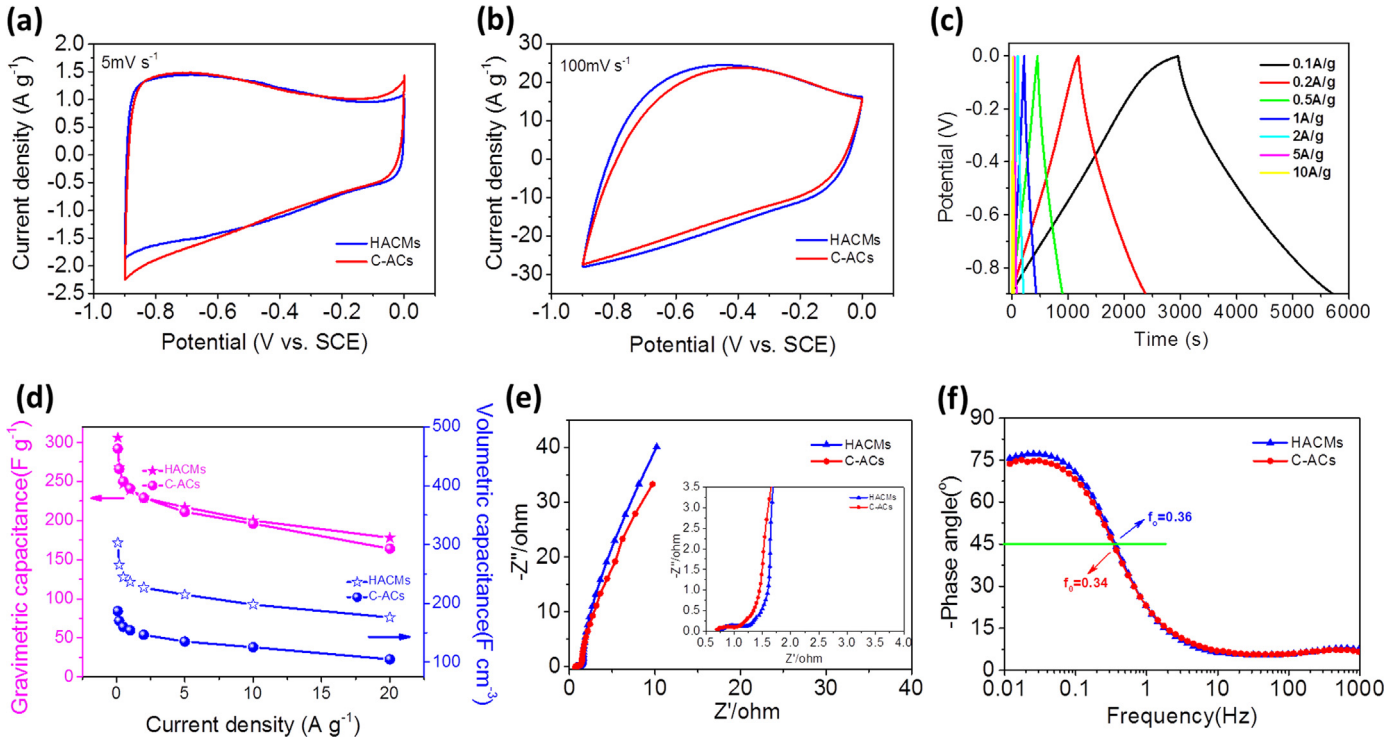

Fig. 3. (a) CV curves of HACMs and C-ACs at 5 mV s^{-1}; (b) at 100 mV s^{-1}; (c) GCD curves of HACMs under different constant currents; (d) the dependence of gravimetric and volumetric capacitance as a function of current density; (e) nyquist plots of the samples, the inset shows the magnified view of the high-frequency region; and (f) plot of Bode phase angle with frequency.

Fig. 3f shows the plot of Bode phase angle with frequency. The near 90° phase angle at low frequencies indicates good capacitive behavior. The characteristic frequency f_o for a phase angle of −45° is 0.36 Hz. The corresponding relaxation time constant τ_0 ($1/f_o$) is 2.78 s, which obviously lower than that of the C-ACs (2.94 s) and some reported AC (10–100 s) [7] and advanced microporous carbon [8], indicating the high discharge rate and good capacitance retention due to the specific hollow structure that facilitates fast ions and electrons transport within the microtubes.

4. Conclusions

In summary, bio-inspired HACMs has been fabricated by pre-carbonization and KOH activation of biomass willow catkins. The obtained HACMs exhibit hollow fiber-like structure with thin wall thickness, resulting in high microporosity surface area ($997\ m^2\ g^{-1}$) and concentrated PSD (1–2 nm) but low pore volume. HACMs are proved to be a promising candidate for supercapacitors with high gravimetric capacitance of $306\ F\ g^{-1}$ and superb volumetric capacitance of $303\ F\ cm^{-3}$.

Acknowledgments

This work was financially supported by the Natural Science Foundation of Shanxi Province (No. 2012011219-3).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2016.03.063.

References

[1] M. Sevilla, R. Mokaya, Energy Environ. Sci. 7 (2014) 1250–1280.
[2] Y. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, et al., Science 332 (2011) 1537–1541.
[3] C. Long, L. Jiang, X. Wu, Y. Jiang, D. Yang, C. Wang, et al., Carbon 93 (2015) 412–420.
[4] X. Du, W. Zhao, Y. Wang, C. Wang, M. Chen, T. Qi, et al., Bioresour. Technol. 149 (2013) 31–37.
[5] C.O. Ania, Khomenko V, E. Raymundo-Piñero, J.B. Parra, F. Béguin, Adv. Funct. Mater. (17) 1828-36.
[6] K. Wang, N. Zhao, S. Lei, R. Yan, X. Tian, J. Wang, et al., Electrochim. Acta 166 (2015) 1–11.
[7] L. Wei, M. Sevilla, A.B. Fuertes, R. Mokaya, G. Yushin, Adv. Energy Mater. 1 (2011) 356–361.
[8] D. Puthusseri, V. Aravindan, S. Madhavi, S. Ogale, Energy Environ. Sci. 7 (2014) 728–735.