Journal of Power Sources 359 (2017) 88-96

Contents lists available at ScienceDirect

Journal of Power Sources

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

Flute type micropores activated carbon from cotton stalk for high performance supercapacitors



Xun Tian ^{a, b}, Hongru Ma ^a, Zhe Li ^a, Shaocun Yan ^a, Lei Ma ^{b, **}, Feng Yu ^a, Gang Wang ^a, Xuhong Guo ^{a, c}, Yanqing Ma ^{a, b, *}, Chingping Wong ^{d, e}

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

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

^d Department of Electronic Engineering, The Chinese University of HongKong, Shatian, NewTerritories, Hong Kong, China

^e School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, United States

HIGHLIGHTS

• FTMAC material has been successfully obtained from cotton stalk.

• FTMAC material exhibits on ordered flute type pores structure.

• The FTMAC-based electrode could deliver a high specific capacitance of 254 F g⁻¹.

• Symmetric supercapacitor can deliver a high energy density of 18.14 Wh kg⁻¹.

ARTICLE INFO

Article history: Received 18 November 2016 Received in revised form 5 May 2017 Accepted 17 May 2017 Available online 24 May 2017

Keywords: Flute type micropores activated carbon Supercapacitors Cotton stalk

ABSTRACT

Flute type micropores activated carbon (FTMAC) has been successfully obtained from cotton stalk via KOH-chemical activation method. The synthesized carbon material exhibits an ordered pore structure with high specific surface area of 1964.46 m² g⁻¹ and pore volume of 1.03 m³ g⁻¹. The assembled FTMAC-based electrode delivers a high specific capacitance of 254 F g⁻¹ at a current density of 0.2 A g⁻¹ in 1 M H₂SO₄ aqueous electrolyte. It still can maintain 221 F g⁻¹at a current density of 10 A g⁻¹, demonstrating a good rate capacity (87% retention), as well as long cyclic stability of 96% capacitance retention after 10000 charging and discharging cycles at current density of 1 A g⁻¹. Moreover, the symmetric supercapacitor can deliver a high energy density of 18.14 W h kg⁻¹ and a power density of 450.37 W kg⁻¹ which is operated in the voltage range of 0–1.8 V.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Mobile electrical device and vehicle have attracted more attention in energy storage and conversion [1,2], due to the scarcity of fossil fuels and its environmental issues. Supercapacitors are known as the most promising energy storage systems due to their fast charge and discharge time, long life cycle and higher specific

** Corresponding author.

power density than the most widely commercial application lithium ion batteries [3–5]. At the same time, the disadvantages of supercapacitors including much lower energy density and higher production cost than lithium ion batteries [6,7], which need to be addressed. Thus, a number of studies have been actuated to exploring new advanced electrode materials for supercapacitors [8].

Carbon-based supercapacitor storage mechanism has fast physical absorption and desorption [9]. Therefore, the development of porous carbon materials can effectively overcome the obstacle of low energy density of supercapacitor [8,10]. Carbon materials, ranging from activated carbon [11], carbon nanotubes [12], carbon aerogel [13], graphene [14–17], carbon foam [18] and biomass-derived porous carbons [9,19–21], have been reported for



^{*} Corresponding author. 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.

E-mail addresses: lei.ma@tju.edu.cn (L. Ma), mayanqing@shzu.edu.cn (Y. Ma).

electrode materials. Biomass-derived activated carbon has been regarded as a promising electrode material for supercapacitors due to their sustainable development characteristics, low cost, high specific surface area and good conductivity [22]. In general, KOH activation can generate micropores and small mesopores of various carbon frameworks [23]. The mechanism of KOH activation carbon materials is as the following equation (1):

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \tag{1}$$

The Xinjiang Production and Construction Corps is an agricultural province in China, and its cotton annual production is up to 1.5 million tons [11]. Cotton stalk as a waste byproduct has become a big issue. Generally, cotton stalk is dumped or burned in the field which resulting with ash and hazardous gaseous that pollutes the environment. However, cotton stalk contains a lot of cellulose, hemicelluloses and lignin. In this work, we demonstrate a green route to fabricated flute type micropores activated carbon by the chemical activation method for supercapacitors electrode from cotton stalk as raw material. Meanwhile, the ordered pore structure on the carbon particle surface prepared by using KOH as activating agent can improve its apparently surface area of activated carbon. This unique structure can be beneficial to enhance the electrochemistry performance of supercapacitors.

2. Experimental

2.1. Materials

The cotton straw used in this work was from local cotton fields. All chemicals in the present work were analytical reagent grades and were used as received without further purifications.

2.2. Pretreatment of cotton stalk

Firstly, the cotton stalk was sheared into small pieces and subsequently washed with distilled water and then dried at 100 °C overnight. Cotton stalk was crushed and screened with a 200 mesh. This material was first treated with an alkaline hydrolysis, according to the reported method [24]. The lignin and hemicelluloses was removed. The cotton stalk was kept at 80 °C in 4% mass fraction of sodium hydroxide solution and acetic acid for 4 h, respectively. Then, the cotton stalk was immersed into sodium chlorite solution again for one week until the color of sample became white [13]. The obtained white samples were washed thoroughly with deionized water until almost neutral (pH 6.5) and finally dried at 50 °C overnight.

2.3. Preparation of flute typed micropore activated carbon

The obtained white samples (16.55 g) were then carbonized in a tube furnace under a N₂ flow and with a heating rate of 5 °C min⁻¹ at 800 °C for 1 h. Then, samples were cooled down to room temperature at the rate of 5 °C min⁻¹. The carbonized samples (3.12 g) were washed several times with deionized water and dried at 50 °C for 12 h. The obtained carbon samples (0.5 g) were mixed with solid KOH under various weight ratios and the mixture sample was heated to 800 °C for 2 h under a continuous N₂ flow. The obtained samples were washed thoroughly with deionized water and 10 wt% HCl solution under vigorous stirring for 24 h to remove the residual chemicals thoroughly. Then the samples were further washed thoroughly with a lot of deionized water and dried at 50 °C for 12 h. These samples are referred to as FTMAC-2 (0.24 g), FTMAC-3 (0.25 g), FTMAC-4 (0.17 g), FTMAC-5 (0.21 g) and FTMAC-6 (0.15 g) (2–6 are KOH and carbonized cotton stalk weight ratios).

2.4. Characterization

The morphology and microstructure of the flute typed activated carbon was observed by a Scanning Electron Microscope (JSM 6490-LV from JEOL), and a High Resolution Transmission Electron Microscopy (HRTEM) from a FEI Tecnai G20. The Raman spectroscopy of porous carbon was carried out using a Laser confocal MicroSpectroscopy (LabRAM HR800) with the 512 nm line of a He-Ne laser as 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 ($\lambda = 1.5406$ 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 isotherm with Micromeritics ASAP 2020 instrument at 77 K.

2.5. Electrochemical measurements

The electrode thin sheets were prepared by porous carbon materials (80 wt%), acetylene black (10 wt%) and polytetrafluoroethylene (PTFE, 10 wt%) binder. Then the mixture was homogenized in a mortar, adding a few drops of absolute alcohol and the resultant paste was rolled into uniform thin sheets electrode of 8 mm diameter using tablet press and dried at 110 °C for 4 h. The mass loading of the active materials in each electrode was around 1.6 mg. Symmetrical supercapacitor was made of two quality similar electrodes on the hydrophilic carbon paper and separated by a piece of polypropylene membrane in a stainless steel plate. 1 M H₂SO₄ was used as the electrolyte. Electrochemical performance measurements were carried out in a two-electrode system by a cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) on a CHI 604E electrochemical workstation. The charge-discharge performance of supercapacitors was studied on a CHI 760E electrochemical workstation. CV test of the two-electrode cell and three-electrode test were investigated between 0.8 V and 0 V. Saturated calomel electrode (SCE) reference electrode and Pt counter electrode were used in the three-electrode testing systems. 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. The tests of cycle life 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:

$$C_m = \frac{I_d \times \Delta t}{\Delta V \times m} \tag{2}$$

Where C_m (F g⁻¹) is specific capacitance, I_d (mA) is the discharge current, Δt (s) is the discharge time and ΔV (V) is the discharge voltage range, 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:

$$E = \frac{1}{2}C_m \times \Delta V^2 \times \frac{1}{3.6} \tag{3}$$

$$P = \frac{E}{\Delta t} \times 3600 \tag{4}$$

Where as C_m (F g⁻¹) is specific capacitance based on mass loading of active materials in both electrodes, ΔV (V) is the discharge voltage range that is exclusive of the IR drop, Δt (s) is the discharge time.

3. Results and discussion

Scheme 1 shows the main process of preparing flute typed micropores activation carbon derived from cotton stalk. The first step is the pretreatment of cotton stalk from a local farm, which the cotton stalk was kept in sodium hydroxide solution and acetic acid, respectively. Subsequently, cotton stalk was again immersed into a sodium chlorite solution until the sample becomes white to obtain the cellulose. And then, carbonizing process in a tube furnace was treated at 800 °C for 1 h to obtain layered carbon sheet by the following SEM image and further activation with KOH activating agent. The ordered flute typed pore structure can be obtained. The change amount of KOH can be to further optimize the pore size distribution.

3.1. Material characterization

Fig. 1 (b-f) shows the typical SEM images of six FTMAC samples after activation. It can be seen clearly that all FTMAC samples reveal the uniform arrange ordered pore structure on the carbon particle surface, due to the carbon matrix during the activation, resulting in the expansion of the carbon lattices. All samples show the presence of open pores structure, forming a flute-like structure. However, when the amount of KOH was increased, the average distance between pores decreased from 4.18 μ m to 3.51 μ m. This probably attributes to the more KOH can react with the more graphitized area in the carbon particle. Interestingly, the average diameter of the pore size of FTMAC-4 samples (Fig. 1d) is the largest and it reaches 1.67 μ m. The samples of FTMAC-2 (Fig. 1b) and FTMAC-3 (Fig. 1c) increase only a little, corresponding to an average diameter of pore size is 1.13 μ m and 1.16 μ m, respectively. The carbonized cotton stalk presents a bulk carbon particle (Fig. 1a).

The morphology and structure of FTMAC samples were examined by transmission electron microscopy (TEM). Fig. 2a clearly revealed that the graphitized monolith has a high sponge-like porous network morphology. It is revealed to be in the form of slight inhomogeneous macropore pores (exceed 50 nm). The high resolution TEM micrographs of FTMAC-4 show the primarily heterogeneous mesoporous (20–50 nm) in Fig. 2b. The materials have defective microporous morphology with highly disordered flute hole-like porous structure. The pore sizes are in the range of about 2 nm as shown in Fig. 2c. The white arrow is an amorphous carbon layer allows the storage of large amount of electros in the electrode to increase the capacitance [25]. The square frame regions in Fig. 2c also show that there are little part ordered carbon structure, which is from the graphitization of the flute-like activated carbon to some extent. The reason of this result was probably due to the etching of



Fig. 1. The representative SEM images of all samples at the different magnifications: carbonized cotton stalk (a); FTMAC-2 (b); FTMAC-3 (c); FTMAC-4 (d); FTMAC-5 (e); FTMAC-6 (f).

KOH to obtain the graphitized carbon. This renders good conductivity and facilitates ion transport during the fast chargingdischarging process.

In order to analysis essential structural characteristic of five samples, XRD and Raman were carried out to analysis intrinsic properties of FTMAC samples. Fig. 3a shows the XRD patterns of five activated carbon samples, a typical diffraction peak at approximately 22° and 43° were observed, corresponding to amorphous carbon. Increasing the amount of KOH, the intensity of the 002 diffraction peak at 22° of FTMAC-4 sample significantly reduces and broadens. This probably forms graphitic crystalline structures of the FTMAC samples [26]. It is consistent with the high magnification transmission electron microscopy. The same results can be get from the Raman spectra, two typical carbon characteristic diffraction peaks appeared in 1360 cm⁻¹ (D peak) and 1586 cm⁻¹ (G peak) in Fig. 3b. D peak with a double-resonance represents the degree of disordered structure or structural defects. G peak corresponding to graphite in-plane vibrations is an ordered carbon. The intensity



Scheme 1. Schematic of flute typed micropore activated carbon.



Fig. 2. The representative TEM images of FTMAC-4 sample at the different magnifications.



Fig. 3. (a) XRD patterns of five samples; (b) Raman spectra of five samples; (c) Nitrogen adsorption-desorption isotherms of five samples and (d) pore size distribution of five samples, calculated from the adsorption isotherms using DFT method.

ratio between D and G bands I_D/I_G was calculated could exactly reflect the graphitic degree of five samples. When the amount of KOH was increased, the value of I_D/I_G decreased from 0.95 to 0.85, this probably due to the more KOH can react with the more graphitized area in the carbon particle [27,28]. Furthermore, the five activated carbon also exhibit slight second order 2D and D + G peak at 2680 and 2890 cm⁻¹, which are attributed to the existence of ordered carbon structure [27].

The porous texture of five samples was characterized by N₂

adsorption-desorption at 77 K. As illustrated in Fig. 3c, the type I/IV isotherms could be found for all FTMAC specimens, which all possess considerable porosity and high surface areas [29], indicating major adsorption of the samples occurs at a low relative pressure of less than 0.1 and the existence of significant amount of micropores [13]. Moreover, it is obvious that there appeared an ambiguous hysteresis loop between the adsorption and desorption branches (at $0.4-1.0 P/P_0$) in all samples. It demonstrates the poor pore openness and rough pore wall during the process of activation

Table 1 Textural characteristic properties of the cellulose derived porous carbon.

	1 1	1
Sample	$S_{BET} (m^2 g^{-1})$	$V_{total}(cm^3~g^{-1})$
FTMAC-2	1347.85	0.71
FTMAC-3	1778.82	0.93
FTMAC-4	1964.46	1.03
FTMAC-5	2250.55	1.21
FTMAC-6	2525.36	1.23

[9]. Fig. 3d shows the pore distributions calculated by density functional theory (DFT) model. The FTMAC samples have both mesopores and micropores. The sizes of the micropores were predominantly in the range of 0.25–0.88 nm, which is suitable for the diffusion of electrolyte ions [14]. The sizes of mesopores are typically centered at 14 nm of the five samples.

Table 1 provides the porous textural details of FTMAC samples. The surface area and the pore volume depend on the amount of activating agent of KOH. It can be observed that the specific surface area and total pores volume straight increases due to excessive addition of KOH. The specific surface area and total pore volume of FTMAC-6 are 2525.36 m² g⁻¹ and 1.23 cm³ g⁻¹ respectively. While the specific capacitance of FTMAC-6 electrode not continue to increase, indicating that the increase the specific surface area cannot improve categorically specific capacitance of supercapacitors.

3.2. Electrochemical properties

In order to evaluate the electrochemical performance of FTMAC electrode using 1 M Na₂SO₄ as the aqueous electrolyte was investigated in a three-electrode system with a potential window of 0.8 V. Fig. 4 (a-e) depicted present the CV curves of the five electrodes at different scanning rates ranging from 2 mV s⁻¹ to

100 mV s⁻¹. The detailed information of gravimetric specific capacitance of FTMAC electrodes (FTMAC-2, FTMAC-3, FTMAC-4, FTMAC-5 and FTMAC-6) at the scan rate of 20 mV s⁻¹ are shown in Fig. 4f. It can be seen that there is no pseudocapacitive behavior of all electrodes.

In order to evaluate the electrochemical performance of FTMAC electrode using 1 M H₂SO₄ as the aqueous electrolyte was investigated in a two-electrode system with a potential window of 0.8 V. Fig. 5 (a-e) depicted present the CV curves of the five electrodes at different scanning rates ranging from 2 mV s⁻¹ to 100 mV s⁻¹. As shown in Fig. 5, all the curves of FTMAC electrode exhibited a good rectangular shape, indicating an ideal electrical double-layer capacitive behavior. And the rectangular CV curve of FTMAC electrode is slightly distorted at a high scanning rate of 100 mV s^{-1} , which indicates the low contact resistance. The specific capacitance was calculated from the integrated area of CV curves. The detailed of gravimetric specific capacitance of FTMAC electrode (FTMAC-2, FTMAC-3, FTMAC-4, FTMAC-5 and FTMAC-6) at the scan rate of 2 mV s⁻¹ as shown in Fig. 5f, which were 199, 232, 251, 223 and 230 F g^{-1} , respectively. It worth noting that the specific capacitance of FTMAC-4 electrode has the highest compared with the other electrode and it still retains 172 F g^{-1} at high scan rate of 100 mV s^{-1} (69% retention) confirmed the rate capability of the FTMAC-4 electrode. The FTMAC-2 electrode displayed the lowest specific capacitance of only 199 F g⁻¹ even at the scan rate of 2 mV s⁻¹, due to the less amount of KOH in activation process of carbon materials. When the amount of KOH was increased, the specific capacitance of FTMAC electrodes was enlarged. We compared the specific capacitance of all FTMAC electrodes through the cyclic voltammetry test. The specific capacitance of all FTMAC electrodes shows a trend of increasing at first (FTMAC-2 and FTMAC-3) and then decreasing slightly (FTMAC-5 and FTMAC-6). The FTMAC-4 electrode has the highest specific capacitance. When the ratio of KOH and carbon cotton stalk was 7, the specific



Fig. 4. Three-electrode system: the CV curves of five electrodes at various scan ranging from 2 to 100 mV s⁻¹: FTMAC-2 (a); FTMAC-3 (b); FTMAC-4 (c); FTMAC-5 (d); FTMAC-6 (e); The CV curves of five electrodes at scanning rates of 20 mV s⁻¹ (f).



Fig. 5. Two electrode system: the CV curves of five electrodes at various scan ranging from 2 to 100 mV s⁻¹: FTMAC-2 (a); FTMAC-3 (b); FTMAC-4 (c); FTMAC-5 (d); FTMAC-6 (e); Specific capacitances of five electrodes as a function at various scan ranging from 2 to 100 mV s⁻¹ (f).



Fig. 6. (a) Specific capacitances of five electrodes as a function at various current density ranging from 0.2 to 10 A g^{-1} ; (b) charge-discharge curves of the FTMAC-4 electrode at different current densities; (c) Cycle stability performance of the FTMAC-4 electrode at current density of 1 A g^{-1} over 10000 cycles; (d) Nyquist plots of FTMAC-4 electrodes (The inset shows the magnified view of the high-frequency region and the electrical equivalent circuit used for fitting impedance spectra).



Fig. 7. (a) CV curves of the symmetric supercapacitor at different voltage windows in 1 M Na_2SO_4 aqueous electrolytes at 20 mV s⁻¹; (b) CV curves of symmetric supercapacitor at various scan rates; (c) GCD curves of symmetric supercapacitor at different current densities; (d) Ragone plots of symmetric supercapacitor.

Table 2

Summary of electrochemical parameters of biomass derived carbon electrodes.

Carbon type	$C(a) (F g^{-1})$	T(b)	E(c)	Ref
Hierarchical porous carbon aerogel derived from bagasse	142	0.5 A g^{-1}	6 M KOH	[13]
Triethanolamine functionalized graphene	210	2 mV s^{-1}	1 M TEABF ₄ /AN	[16]
Coal tar pitch mesoporous carbons	224	0.1 A g^{-1}	6 M KOH	[20]
Activated carbon fibers	100	$0.5 \ A \ g^{-1}$	1 M H ₂ SO ₄	[32]
Micro-mesoporous carbon spheres derived from carrageenan	230	1 A g^{-1}	6 M KOH	[33]
Activated carbon from nanocellulose	84	0.1 A g^{-1}	BMPY TFSI ionic liquid electrolyte	[34]
Activated carbon derived from melaleuca barks	233	2 mV s ⁻¹	1 M H ₂ SO ₄	[35]
Cherry stones derived activated carbons	230	1 A cm ⁻²	2 M H ₂ SO ₄	[36]
Prolific chitosan derived porous carbons	220	0.1 A g^{-1}	1 M H ₂ SO ₄	[37]
Deoiled asphalt derived porous carbons	235	$0.05 \ A \ g^{-1}$	7 M KOH	[38]
FTMAC	254	0.2 A g^{-1}	1 M H ₂ SO ₄	This work

^(a) Specific capacitance, ^(b) Current density or scan rate, ^(c) Electrolyte type.

capacitance just changed a little bit and characterization is not optimized. So, the all experimental data of FTMAC-7 sample has added in the supporting information.

In order to confirmation the electrochemical property of FTMAC electrodes, galvanostatic charge-discharge tests were performed at various current densities from ranging from 0.2 A g⁻¹ to 10 A g⁻¹. Fig. 6a shows that the specific capacitance of FTMAC-4 electrode exhibited a better capacitance performance than other electrode up to 254 F g⁻¹ at current densities of 0.2 A g⁻¹, even at a current density as high as 10 A g⁻¹, a specific capacitance of 9.25 F). As still retention (Carbon paper provides capacitance of 9.25 F).

shown in Fig. 6b, there have the approximate linear lines with obvious symmetric triangular shape of the different current density curves. The negligible IR value of 0.01 V can be obtained at 0.2 A g⁻¹, due to the good electric conductivity [22]. The high specific capacitance and good rate capability of FTMAC-4 electrode was attributed to arrange ordered pore structure of the synthesis of flute micropores activated carbon. In addition, this particular structure of FTMAC samples provides a shorten ion diffusion pathway on a large electrode/electrolyte interface and facilitates rapid ion transfer. As the most important parameter to evaluate for practical application, the cycle stability experiment was carried out.

Fig. 6c shows the FTMAC-4 electrode was investigated at current density of 1 A g^{-1} . The specific capacitance could retain 96% of the initial capacitance after 10000 cycling. It shows that symmetry supercapacitor have a very good cycle stability. Electrochemical impedance spectroscopy (EIS) further is analyzed the electrochemical behavior of supercapacitors, with the frequency range of 0.01 Hz-100 kHz and at open circuit potential of 5 mV. Fig. 6d shows that there is apparent semicircle in the high-frequency range in the EIS spectrogram of FTMAC-4 electrodes, which is caused by the electric double-layer capacitance, corresponding to the charge transfer resistance. The Re and Rct resistance value of FTMAC-4 electrode were 4.72 Ω and 0.76 Ω , indicting a low system resistance and good charge-transfer rate. The oblique line of the lowfrequency region represents the ion diffusion resistance and the degree of ideal supercapacitors is 90°. It can be seen that there is an almost vertical line of FTMAC-4 electrode in the low frequency region, demonstrating that FTMAC-4 electrode had ideal capacitive behaviors [30,31]. Equivalent circuit diagram include 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.

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. 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 FTMAC-4 electrodes in 1 M Na₂SO₄ aqueous electrolyte. which possesses a higher operation voltage than acid solution. Fig. 7a show the CV curves of FTMAC-4//FTMAC-4 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-like shape and no obvious increase of anodic current at 1.8 V and rapid increase of anodic current at 2.0 V, indicating that the symmetric supercapacitor can be reversibly cycled within the voltage window up to 1.8 V. The CV curves of the FTMAC-4//FTMAC-4 symmetric supercapacitor under different scanning rates from 10 mV s⁻¹ to 100 mV s⁻¹ are shown in Fig. 7b. It can be seen that the CV curve still maintains quasi-rectangular shape at an extremely high scanning rate of 100 mV s⁻¹, indicated an ideal rate performance. Fig. 7c show 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. Because of the low internal resistance, it shows good rate capability and electrochemical capacitance for FTMAC-4// FTMAC-4 symmetric supercapacitor. Energy density and power density of symmetric supercapacitor was shown in the Ragone plot from Fig. 7d. The specific capacitance and the operating voltage is 160 F g^{-1} (0.5 A g^{-1} current density) and 1.8 V, respectively. The energy density of symmetry supercapacitor is calculated 18.14 W h kg^{-1} when the power density is 450.37 W kg^{-1} . These results indicate that flute type micropores activated carbon with ordered pore structure could deliver a high energy density.

Thus, the FTMAC samples were a promising material for advanced electrodes for supercapacitors. In compares with the other similar carbon electrodes previously reported in Table 2 [13,16,20,32–38]. The FTMAC electrodes show the highest specific capacitance. This demonstrates that FTMAC materials with uniform arrange ordered pore structure and high surface area is promising candidates for electrode materials in the economy of synthetic strategy and the application of products.

4. Conclusion

In summary, flute type micropore activated carbon has been successfully synthesized by carbonizing and chemical activating from cotton stalk. The obtained materials present a high surface area up to 1964.46 m² g⁻¹ and with a pore volume of 1.03 m³ g⁻¹. Additionally, the FTMAC-4 electrode displays a comparable specific capacitance of 254 F g⁻¹ at current density of 0.2 A g⁻¹ and with an excellent cycling stability of specific capacitance retention of 96% after 10000 cycles at the current density of 1 A g⁻¹. Cotton stalk as one of raw materials is renewable and it is a green and sustainable electrode materials for supercapacitor application.

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).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.05.054.

References

- [1] C. Xu, Z. Li, C. Yang, P. Zou, B. Xie, Z. Lin, Z. Zhang, B. Li, F. Kang, C.P. Wong, Adv. Mater. 28 (2016) 4105–4110.
- [2] J. Chen, J. Xu, S. Zhou, N. Zhao, C.-P. Wong, Nano Energy 15 (2015) 719–728.
- [3] R. Wang, C. Xu, J.-M. Lee, Nano Energy 19 (2016) 210–221.
- [4] K. Qin, J. Kang, J. Li, E. Liu, C. Shi, Z. Zhang, X. Zhang, N. Zhao, Nano Energy 24 (2016) 158–164.
- [5] Y. Zuo, G. Wang, J. Peng, G. Li, Y. Ma, F. Yu, B. Dai, X. Guo, C.P. Wong, J. Mater. Chem. A 4 (2016) 2453–2460.
- [6] R.R. Gaddam, D. Yang, R. Narayan, K. Raju, N.A. Kumar, X.S. Zhao, Nano Energy 26 (2016) 346–352.
- [7] Y. Yang, Z. Peng, G. Wang, G. Ruan, X. Fan, L. Li, H. Fei, R.H. Hauge, J.M. Tour, ACS Nano 8 (2014) 7279–7287.
- [8] G. Wang, L. Zhang, J. Zhang, Chem. Soc. Rev. 41 (2012) 797–828.
- [9] Y. Li, G. Wang, T. Wei, Z. Fan, P. Yan, Nano Energy 19 (2016) 165–175.
- [10] G. Jung, T. Kim, S. Yoo, K.S. Suh, R.S. Ruoff, ACS Nano 7 (2013) 6899–6905.
- [11] M. Chen, X. Kang, T. Wumaier, J. Dou, B. Gao, Y. Han, G. Xu, Z. Liu, L. Zhang, J. Solid State Electrochem. 17 (2012) 1005–1012.
- [12] Y. Hu, Y. Zhao, Y. Li, H. Li, H. Shao, L. Qu, Electrochimica Acta 66 (2012) 279-286.
- [13] P. Hao, Z. Zhao, J. Tian, H. Li, Y. Sang, G. Yu, H. Cai, H. Liu, C.P. Wong, A. Umar, Nanoscale 6 (2014) 12120–12129.
- [14] G. Sun, B. Li, J. Ran, X. Shen, H. Tong, Electrochimica Acta 171 (2015) 13-22.
- [15] Z. Peng, J. Lin, R. Ye, E.L. Samuel, J.M. Tour, ACS Appl. Mater. interfaces 7 (2015) 3414–3419.
- [16] B. Song, C. Sizemore, L. Li, X. Huang, Z. Lin, K.-s Moon, C.-P. Wong, J. Mater. Chem. A 3 (2015) 21789–21796.
- [17] L. Zhang, D. Huang, N. Hu, C. Yang, M. Li, H. Wei, Z. Yang, Y. Su, Y. Zhang, J. Power Sources 342 (2017) 1–8.
- [18] Z. Qi, A. Younis, D. Chu, S. Li, Nano-Micro Lett. 8 (2015) 165–173.
- [19] T. Wei, X. Wei, Y. Gao, H. Li, Electrochimica Acta 169 (2015) 186-194.
- [20] X. He, R. Li, J. Qiu, K. Xie, P. Ling, M. Yu, X. Zhang, M. Zheng, Carbon 50 (2012) 4911–4921.
- [21] B. Xu, S. Hou, G. Cao, F. Wu, Y. Yang, J. Mater. Chem. 22 (2012) 19088.
- [22] B. Li, F. Dai, Q. Xiao, L. Yang, J. Shen, C. Zhang, M. Cai, Adv. Energy Mater. (2016) 1600802.
- [23] J. Wang, S. Kaskel, J. Mater. Chem. 22 (2012) 23710.
- [24] D. Bhattacharya, L.T. Germinario, W.T. Winter, Carbohydr. Polym. 73 (2008) 371–377.
- [25] K. Qin, E. Liu, J. Li, J. Kang, C. Shi, C. He, F. He, N. Zhao, Adv. Energy Mater. 6 (2016) 1600755.
- [26] Y. Gao, L. Li, Y. Jin, Y. Wang, C. Yuan, Y. Wei, G. Chen, J. Ge, H. Lu, Appl. Energy 153 (2015) 41–47.
- [27] X. Liu, D. Chao, Y. Li, J. Hao, X. Liu, J. Zhao, J. Lin, H. Jin Fan, Z. Xiang Shen, Nano Energy 17 (2015) 43–51.
- [28] C. Yang, W. Li, Z. Yang, L. Gu, Y. Yu, Nano Energy 18 (2015) 12-19.
- [29] J. Ding, H. Wang, Z. Li, K. Cui, D. Karpuzov, X. Tan, A. Kohandehghan, D. Mitlin, Energy Environ. Sci. 8 (2015) 941–955.
- [30] Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, Adv. Funct. Mater. 21 (2011)

2366-2375.

- [31] L. Li, A.R. Raji, H. Fei, Y. Yang, E.L. Samuel, J.M. Tour, ACS Appl. Mater. interfaces 5 (2013) 6622–6627.
 [32] N. Diez, P. Díaz, P. Álvarez, Z. González, M. Granda, C. Blanco, R. Santamaría,
- R. Menéndez, Mater. Lett. 136 (2014) 214–217.
- [33] Y. Fan, X. Yang, B. Zhu, P.-F. Liu, H.-T. Lu, J. Power Sources 268 (2014) 584–590.
- [34] Z. Li, J. Liu, K. Jiang, T. Thundat, Nano Energy 25 (2016) 161–169.
 [35] Q.P. Luo, L. Huang, X. Gao, Y. Cheng, B. Yao, Z. Hu, J. Wan, X. Xiao, J. Zhou,

- Nanotechnology 26 (2015) 304004.
 [36] M. Olivares-Marín, J.A. Fernández, M.J. Lázaro, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, F. Stoeckli, T.A. Centeno, Mater. Chem. Phys. 114 (2009) 323–327.
- [37] Y.-Y. Wang, B.-H. Hou, H.-Y. Lü, F. Wan, J. Wang, X.-L. Wu, RSC Adv. 5 (2015) 97427–97434.
- [38] W. Zhang, Z.-H. Huang, Z. Guo, C. Li, F. Kang, Mater. Lett. 64 (2010) 1868-1870.