



## Potassium chloride templated carbon preparation for supercapacitor

Yuhe Cao<sup>a,\*\*</sup>, Xiaomin Wang<sup>a</sup>, Zhengrong Gu<sup>a,\*</sup>, Qihua Fan<sup>b</sup>, William Gibbons<sup>c</sup>, Venkataramana Gadhamshetty<sup>d</sup>, Ning Ai<sup>e</sup>, Ganning Zeng<sup>f,g</sup>

<sup>a</sup> Agricultural and Biosystems Engineering Department, South Dakota State University, Brookings, SD, USA

<sup>b</sup> Electrical Engineering and Computer Science Department, South Dakota State University, USA

<sup>c</sup> Department of Biology and Microbiology, South Dakota State University, Brookings, SD, USA

<sup>d</sup> Civil and Environmental Engineering Department, South Dakota School of Mines and Technology, Rapid City, SD, USA

<sup>e</sup> College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

<sup>f</sup> College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou, China

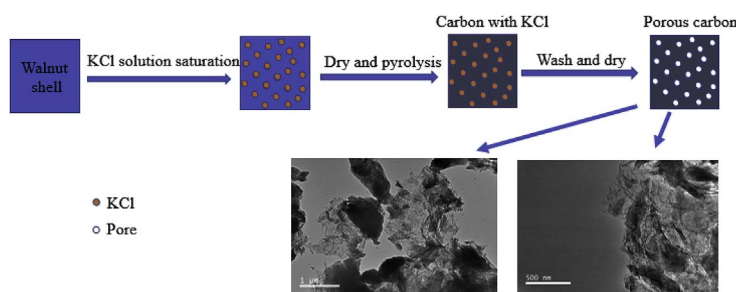
<sup>g</sup> State Key Laboratory of Satellite Ocean Environment Dynamics, Hangzhou, China



### HIGHLIGHTS

- Porous active carbons were prepared from KCl templated walnut shell.
- BET surface area of  $1958 \text{ m}^2 \text{ g}^{-1}$  and a pore volume of  $1.12 \text{ cm}^3 \text{ g}^{-1}$  were obtained.
- Capacitance retention ratio was 95.4% after 4000 cycles at different current density.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

This is the first report of KCl templated carbon preparation from walnut shell. Activated carbon (AC) with high specific surface area ( $1958 \text{ m}^2 \text{ g}^{-1}$ ) was obtained by  $\text{CO}_2$  activation of KCl templated biochar at  $900^\circ\text{C}$ . The electrochemical properties were evaluated by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. WS-90 had relatively low inner resistance of  $1.7 \Omega$ . The specific capacitance was  $245.0 \text{ F g}^{-1}$  in  $6 \text{ mol L}^{-1}$  KOH electrolyte at a current density of  $0.1 \text{ A g}^{-1}$ , and it can maintain very good cyclic stability with capacitance retention ratio of 95.4% (from  $245.0$  to  $233.7 \text{ F g}^{-1}$  at current density of  $0.1 \text{ A g}^{-1}$  after 4000 cycles ( $0.1, 0.5, 1.0$  and  $5.0 \text{ A g}^{-1}$  for 1000 cycles, respectively)).

### 1. Introduction

Wind and solar power are sustainable and renewable electricity resources. It is of great importance to store efficiently electrical energy generated by them with an affordable technology. Supercapacitor could provide great power, faster response times, and long cycle life [1], which can potentially be used as power and memory back-up for

electronic devices [2]. It is a promising potential for the energy storage systems, which could meet the increasing power demands [3]. Many types of electrode materials were used to fabricate supercapacitor, such as conductive polymer [4], transition metal oxide [5]. However, their commercial application was prevented by low surface area, poor conductivity.

Carbon materials have attracted electrochemists for a long time.

\* Corresponding author. Agricultural and Biosystems Engineering, South Dakota State University, North Campus Drive 1400, Brookings, SD, 57007, USA.

\*\* Corresponding author. Agricultural and Biosystems Engineering, South Dakota State University, North Campus Drive 1400, Brookings, SD, 57007, USA.

E-mail addresses: [yuhe.cao@jacks.sdstate.edu](mailto:yuhe.cao@jacks.sdstate.edu) (Y. Cao), [Zhengrong.gu@sdstate.edu](mailto:Zhengrong.gu@sdstate.edu) (Z. Gu).

New carbon-based materials such as carbon monolith [6], graphene [7], carbon nanotubes [8], and carbon nanofibers [9] were used as electrode materials since they have very high electrochemical properties [10]. Activated carbon (AC) has also been widely used in supercapacitor [11] due to their large surface area, relatively good electrical property and low cost, which will be easier to be commercialized. Two activation methods can be used to fabricate AC: chemical and physical process. Chemical agents such as KOH [12],  $K_2CO_3$  [13], NaOH [14],  $ZnCl_2$  [15], and  $H_3PO_4$  [16] were used for chemical activation at a high temperature. These chemicals degrade and dehydrate the cellulosic materials. In the meantime, they also served as support layer to prevent shrinkage during carbonization. Generally physical activation is a two-step process: the bulk of the volatile matter was eliminated firstly at 400–500 °C, then the partial carbonaceous materials was gasified in steam,  $CO_2$ , or a combination of these.

The physical activated carbon generally has a relatively lower specific surface area than the chemical activated carbon. Chemical activation has advantages such as lower operating cost and energy, higher carbon yields and larger surface areas, which can also generate a more microporous structure [17]. However, the post-treatment of the activating agent discharged effluent, which need a complex recovery and treatment [18]. Moreover, these hydroxides are very corrosive and the activating agents are more expensive than  $CO_2$  and  $H_2O$  [19]. Physical activation is simple and can produce good physical strength activated carbons with well-developed micropores, which is widely used for commercial activated carbon production [18]. However, it is difficult to obtain high BET surface area activated carbons. Normally, low BET surface areas were obtained by using  $CO_2$  as an activation reagent, as is shown in Table 1. To obtain higher BET surface area activated carbon, we tried to use salt as an assistant for carbon fabrication. The soluble inert salt could have impregnated into the precursor, which could be the support spots for the polymer (lignin, cellulose, and hemicellulose) in the biomass precursor. The soluble salt can be removed by washing after the carbonization, which would generate porous structure inside the carbon matrix. Based on this hypothesis, agricultural waste walnut shell was used as a precursor, KCl was used as a soluble template to prepare activated carbon. As far as we know, there are very few reports on the preparation of activated carbons by using KCl as soluble inert template.

Walnut shell is an agricultural waste, which is a good precursor for activated carbon production. In this study, relatively well-developed porosity activated carbons from walnut shells were prepared on a laboratory scale. Their performance as supercapacitor electrodes was evaluated.

## 2. Experimental section

### 2.1. Preparation of ACs

Walnut shell, collected from a local source, was dried and ground. The powdered samples (50 g, below mesh No. 50) were impregnated with KCl concentrated solution (50 g salt with 120 g water). Then dried

**Table 1**  
BET surface areas from different carbons.

Carbon resource	Surface area ( $m^2 g^{-1}$ )	Literature
Oil palm stone	1410	[20]
Polyacrylonitrile based activated carbon nanofiber	1320	[21]
Pistachio-nut shells	778.1	[22]
Corn hulls	1010	[23]
Corn stover	712	[23]
Oak	985	[23]
Bituminous Coal	1171	[24]
Oil-palm-stone	320.6	[25]
Walnut shell	1958	This work

in an oven at 120 °C overnight. Impregnated sample was placed on a ceramic boat, inserted in a tubular furnace. The sample was heated to the carbonization temperature 800 °C at the rate of 20 °C/min under gases protection ( $N_2$  flow at the rate of 248 Std. ml/min and  $CO_2$  at the rate of 264 Std. ml/min), and the temperature was maintained for 30 min. After carbonization, the sample was cooled down in  $N_2$  atmosphere, which is named as WS-KCl. The carbonized sample was washed several times sequentially with hot and finally cold distilled water to remove any residual chemicals. The activated carbon product was then dried in an oven at 130 °C, which is named as WS. WS was heated in the tubular furnace of 900 °C under gases protection ( $N_2$  flow at the rate of 248 Std. ml/min and  $CO_2$  at the rate of 264 Std. ml/min), and the temperature was maintained for 70, 90, and 105 min, after carbonization, the sample was cooled down in  $N_2$  atmosphere. And the carbons were named as WS-70, WS-90, and WS-105, respectfully. All the chemical and reagents used were analytical reagent grade obtained from Sigma-Aldrich.

### 2.2. Characterizations of ACs

One ASAP 2020 Micropore analyzer was used to do the isotherm adsorption of  $N_2$  at 77 K. Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area. The total pore volumes were obtained at relative pressure 0.995  $P_0$ , while the density functional theory (DFT) was used to determine the micropore and mesopore volume and the pore size distribution based on the  $N_2$  isotherm adsorption data. Transmission electron microscopy (TEM) (JEM-2100 LaB6, JEOL, Japan, operating at 200 kV) was used to characterize the structure of ACs and Energy Dispersive Spectroscopy (EDS) (OXFORD X-MaxN) was employed to determine their elemental compositions. Raman Spectrum (Horiba LABRam confocal Raman microscope) at room temperature was employed to characterize the structures of ACs, which used an excitation wavelength at 532 nm from a diode pumped solid-state laser.

### 2.3. Supercapacitor fabrication and electrochemical characterization

The supercapacitors were assembled as the we did before [26]. The slurry of AC, carbon black (conducting material from Fisher scientific) and PTFE (binder) with a mass ratio of 8:1:1 were pressed on nickel foam, which formed the electrodes. Masses of WS, WS-75, WS-90 and WS-105 electrodes are 7.2/7.4, 6.8/6.9, 7.1/7.2 and 6.9/7.0 mg, respectively. The geometrical surface area of the AC electrode used was 1  $cm^2$  and the medium thickness was  $\sim 100 \mu m$ . A stainless coin cell (2032) with a microporous PP separator clegard-3501 were used to assemble two-electrode sandwich-type cells. Meanwhile, 6 mol  $L^{-1}$  KOH was used as the electrolyte. Cyclic voltammetry (scan rate from 5 to 200  $mV s^{-1}$ ) and galvanostatic charge/discharge cycling (current density load from 0.1  $A g^{-1}$  to 5  $A g^{-1}$ ) were performed using a SP-150 multichannel potentiostat-galvanostat-EIS (Biologic, France). The electrical conductivity of the carbon materials was also measured through the impedance spectroscopy (i.e. frequency response analysis yields over the frequency ranging from 0.1 Hz to 100,000 Hz with potential amplitude of 5 mV) with a SP-150 multichannel potentiostat-galvanostat-EIS (Biologic, France). Neware battery test systems was employed to perform the galvanostatic charge/discharge cycling. The equation (2) [27] was used to calculate the specific capacitance of the electrode

$$C = \frac{2I\Delta t}{m\Delta V} \quad (1)$$

here,  $I$  is the discharge current density,  $\Delta t$  is the corresponding discharge time,  $m$  is the mass of active materials on single electrode and  $\Delta V$  is the total corresponding potential change.

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