

# PREPARATION AND CHARACTERIZATION OF POROUS CARBON FROM RICE HUSK APPLIED FOR ELECTRODE MATERIALS

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## ABSTRACT

Rice husk (RH) was used as the precursor for porous carbon preparation applying as electrode materials. Porous carbon was synthesized by pyrolysis of RH under inert gas atmosphere followed by hydrothermal treatment in NaOH to remove the silica fraction and  $K_2CO_3$  activation to increase porosity of archived carbon. The temperature of RH decomposition was determined by the thermal gravimetric analysis (TGA) method in the nitrogen atmosphere. The performance of porous carbon and C-SiO<sub>x</sub> were examined using Brunauer-Emmett-Teller (BET) measurement and Scanning electron microscopy (SEM). The electrochemical characterizations of the synthesized materials were analyzed using cyclic voltammetry (CV) and chronopotentiometry techniques. The effect of parameters of hydrothermal and activation steps on the capacity of these porous carbons were researched. The activated porous carbon which obtained by  $K_2CO_3$  activation at 900<sup>o</sup>C in 2 hours has high specific surface area ( $S_{BET} = 769.3$  m<sup>2</sup>/g). Specific capacitance of the as-prepare electrode is 116.2 F.g<sup>-1</sup> at scan rate of 5 mV/s. Therefore, as-prepared porous carbon from RH would be proper candidate for application as electrode material.

*Keywords:* rice husk (RH), porous carbon, hydrothermal, electrode materials.

## 1. INTRODUCTION

Vietnam was the world's top rice exporter with an avagrage of 4.88 million tons of rice in the year 2016. Previously, rice husk was considered as waste that caused serious environmental problem. Hence, looking for new applications of husk is fundamental. Recently, rice husk has been studied as precursor for preparation of active carbon [1, 2], silica [1, 3], zeolite [4, 5], concrete [6], etc. With such advantages like porous structure, high surface area and low cost, porous carbon has attracted considerable attention and has been widely studied as catalyst carriers, adsorb materials or as electrode materials for batteries and capacitors [7 - 9].

Since the official commercialization in 1991, lithium-ion batteries can approach almost every energy storage requirement with a power density of 20 ÷ 100 Wh kg<sup>-1</sup>. Furthermore, supercapacitor is a modern and common energy storage device. In the 1990s, supercapacitors

was developed widely, especially in the electric car sector. This type of capacitor has much higher capacity than conventional capacitors and is faster in charge/discharge than conventional batteries. Supercapacitor has very high capacitance up to 5000 F, shorter charging/discharging time (about 10 seconds), and life cycle is also higher than conventional batteries (about 10 times) [8]. The capacity of these two energy storage devices rely much on the characteristics of the electrode material. In order to obtain a remarkable energy density, porous carbon must have larger specific surface area for higher specific capacitance value, low resistivity and well adapted micro-texture so that electrolyte could access into the inner surface of the electrode [9].

The aim of this work is to synthesize a low-cost, high specific surface area porous carbon using rice husk as the raw material. The effects of hydrothermal condition on the elimination of SiO<sub>2</sub>, the K<sub>2</sub>CO<sub>3</sub>/C ratio, impacts of activated time on the specific surface area and electrochemical performance of porous carbon samples have been examined.

## 2. EXPERIMENTAL

### 2.1. Preparation of porous carbon

The process of porous carbon preparation from rice husk is described in Figure 1. Also, the preparation of porous carbon is effected by many factors at different stages.

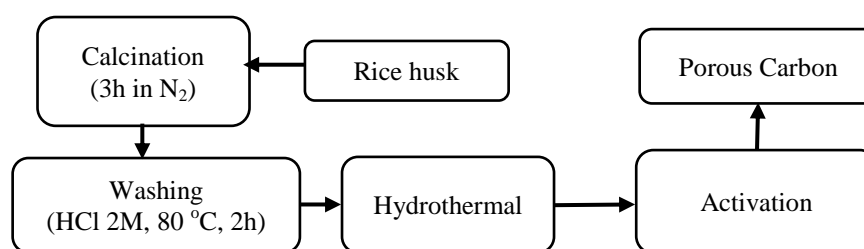


Figure 1. Porous carbon preparation diagram

Table 1. Experimental parameters of porous carbon synthesizing process

No.	Sample No.	Experiment Parameters			
		Hydrothermal		Activation	
		[NaOH] (mol/l)	Time (hours)	Mass ratio K <sub>2</sub> CO <sub>3</sub> /C (%)	Time (hours)
1	C1.1	1	3		
2	C1.2	2			
3	C1.3	4			
4	C2.1 (without hydrothermal)				
5	C2.2	2	2		
6	C2.3		3		
7	C2.4		4		
8	C3.1		3	8	
9	C3.2	2		10	2
10	C3.3			12	
11	C4.1	2	3	10	1
12	C4.2				2
13	C4.3				3

The Rice husk was calcinated in N<sub>2</sub> atmosphere for 3 h. After calcinating process, the Rice Husk Ash (RHA) was washing by HCl 2M solution. The RHA was then put into an autoclave with NaOH solution to perform hydrothermal process. The purified carbon was obtained after the hydrothermal process and activated using K<sub>2</sub>CO<sub>3</sub>. Obtained porous carbon was collected and characterized. The samples will be examined as shown in Table 1.

## 2.2. Characterization of porous carbon

The morphology of the porous carbon was obtained with a Scanning electron microscopy (S4800-Hitachi) analyzer. Thermogravimetric analysis was performed in a Thermogravimetric Analyzer (NETZSCH STA 409 PC/PG). The rice husk sample were heated in N<sub>2</sub> air at 10 °C.min<sup>-1</sup>, and within the temperature range 20 - 900 °C. The specific surface area of the porous carbon sample was measured by nitrogen gas adsorption and the Brunauer - Emmett - Teller (BET) calculation in a Micromeritics TriStar II 3020 surface analyzer.

## 2.3. Electrode preparation and electrochemical measurements

The working electrodes were formed by coating the active material on titan foil current collector. Composite of the active material was prepared by mixing the porous carbons and poly-1,1-difluoroethene (PVDF) with a ratio of 90/10 (by weight). N-methyl-2-pyrrolidone (NMP) was used until the paste achieved a smooth syrupy viscosity. The paste was then spread uniform on titan foil and dried at 80 °C for about 1.5 h. The 1cmx1cm area coated foil was compressed into 110-130 μm.

Electrochemical measurements were carried out by an electrochemical Autolab device using a three electrode system containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. A platinum sheet electrode and a Ag/AgCl electrode served as the counter and reference electrode, respectively. Cyclic voltammetry (CV) measurements were conducted with a potential window from -0.3 V to 0.7 V vs silver chloride electrode at different sweep rates ranging from 5 to 100 mV.s<sup>-1</sup>.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Characteristics of porous carbons

In order to determine the suitable rice husk heating temperature, thermogravimetric analysis was performed. Based on the TGA / dTG result of the rice husks in N<sub>2</sub> atmosphere, it is proposed that the rice husk digestion scheme is shown in Figure 2.

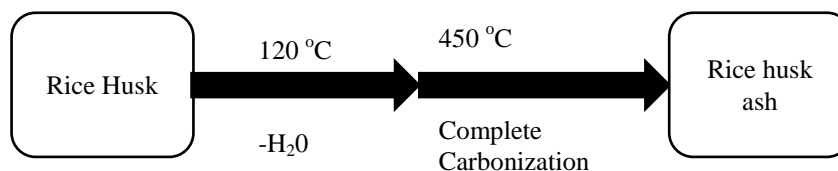


Figure 2. Carbonization process of rice husks in N<sub>2</sub> medium at heating rate of 10 °Cmin<sup>-1</sup>

The most suitable heating mode was selected at 450 °C for 3 hours with an efficiency of 96.83 %. The rice husk ash after washing by the acid to remove the metal impurities, will be performed SiO<sub>2</sub> elimination using hydrothermal method in NaOH solution under various

experimental conditions. The SiO<sub>2</sub> elimination results are shown in Table 2. Mechanism of SiO<sub>2</sub> eliminating process by NaOH is described below:

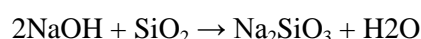


Table 2. SiO<sub>2</sub> elimination efficiency by hydrothermal method in NaOH

Sample No.	[NaOH] (mol/l)	Time (hours)	Sample mass (before hydrothermal) (g)	Sample mass (after hydrothermal) (g)	Sample mass decrease (g)
C1.1	1	3	2,0007	1,5641	0,4366
C1.2	2	3	2,0003	1,5407	0,4596
C1.3	4	3	2,0005	1,5403	0,4602
C2.1 (without hydrothermal)	2		2,0010	1,6157	0,3853
C2.2	2	2	2,0004	1,5603	0,4401
C2.3	2	3	2,0006	1,5401	0,4605
C2.4	2	4	2,0012	1,5398	0,4614

By the results in Table 2, it was considered as the lost weight of sample after hydrothermal process is the SiO<sub>2</sub> content. On the other hand, the sample that did not conduct SiO<sub>2</sub> eliminating process by hydrothermal method but just wash by NaOH at 80 °C giving the lost weight of 0.3853 g. Meanwhile, for samples C2.2, C2.3, C2.4 conducted by hydrothermal method, the SiO<sub>2</sub> content removal was higher than, even above 0.4g. Hence, using hydrothermal methods to remove SiO<sub>2</sub> could give very high efficiency. Moreover, when the NaOH concentration increased, the SiO<sub>2</sub> weight removed was increased, but increased less when the concentration increased from 2 M to 4 M (0.13 %). Additionally, high concentration of NaOH also increase chemical costs and equipment conditions, thus NaOH 2 M is the most suitable condition for this process.

The removed SiO<sub>2</sub> weight increases by the hydrothermal time, however, when hydrothermal time is from 3 hours to 4 hours, the amount of removed SiO<sub>2</sub> is very few only 0.0009 g (0.19 %). After 3 hours of hydrothermal treatment, almost all of the SiO<sub>2</sub> content was removed from the rice husk ash sample.

The porous carbon is synthesized by the activation of the husks after carbonization under different conditions. These porous carbon samples' surface were analyzed by scanning electron microscopy (SEM) and BET method.

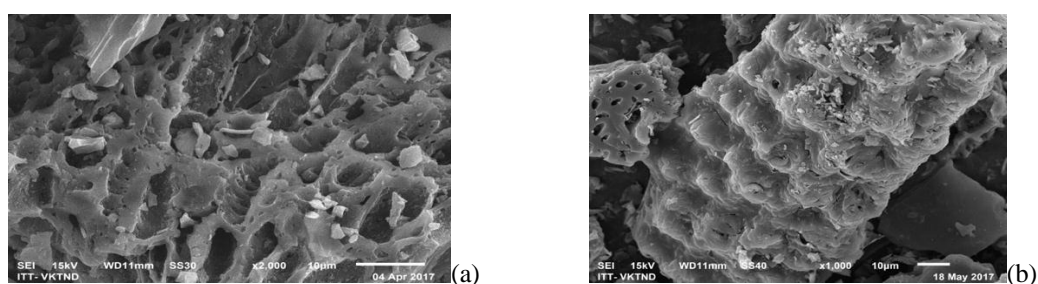
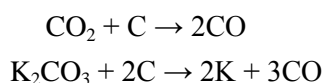


Figure 3. SEM images of porous carbon before activation (a) and after activation (900 °C, 2 h, K<sub>2</sub>CO<sub>3</sub>/C = 10 %)(b)

Obviously, the effect of  $K_2CO_3$  on the surface of the carbon resulting more porous holes. The reactions occur during the activation process are following:



A part of purified carbon was oxidized to form CO and  $CO_2$ . This process drills several small holes and deep into the carbon surface. In addition, the gas abrades the carbon surface created concave on the surface. These effects improved the surface area of the carbon. Thus, the BET result of the porous C after activation enlarged to  $796.3 \text{ m}^2 \text{ g}^{-1}$  comparing to pre-activated carbon only  $156 \text{ m}^2 \text{ g}^{-1}$ .

### **3.2. Electrochemical feature of porous carbons**

Cyclic voltammetry (CV) of porous carbon samples in 0.5 M  $Na_2SO_4$  at scan rate of 5, 10, 50 and  $100 \text{ mV.s}^{-1}$  is shown in Fig. 4. At scan rate of  $5 \text{ mV.s}^{-1}$ , all the porous carbon samples show a symmetric and quasi-rectangular sharp profile typical of electrode materials [10]. With the escalation of scan rate, the CVs which still remain rectangular sharped even at a scan rate up to  $100 \text{ mV.s}^{-1}$  indicated a good capacitor behavior of the material at a high scan rate.

The gravimetric capacitance,  $C_{CV}$  ( $F.g^{-1}$ ), was calculated from CVs using the following equation:

$$C_{CV} = \frac{\sum |I| \Delta t}{2m\Delta V} \quad (1)$$

where  $\sum |I| \Delta t$  is the area of the current (A) against time (s) curve, m is the mass of active material in the electrode (g), and  $\Delta V$  is the potential window (V). The specific capacitances of porous carbon samples electrodes at different scan rates were calculated due to Eq. (1) are reported in Table 3.  $C_{CV}$  gravimetric capacitance decreases when the scan rate increases with all samples. However, porous carbon sample without activation process (C2.3 sample) has not electrochemical feature.

This can be explained as the specific surface area of purified carbon composite is only  $156 \text{ m}^2 \text{ g}^{-1}$ , consequently, there is a small area available to contain sodium ions. After activated, the specific capacity of all samples improved significantly as the expansion of samples' surface area. Sample C3.2 with activation conditions in  $K_2CO_3$  for 2 hours at  $900 \text{ }^\circ\text{C}$  and the mixture of 10 %  $K_2CO_3 / C$  has the highest specific capacity at (Table 3) scanning speed of  $5 \text{ mV.s}^{-1}$ . The results also show that the activated ratio and activated duration affect on the electrochemical behavior of the carbon sample because the mechanism of activation is to oxidize a part of purified carbon into CO and  $CO_2$  and creating the pores. As a result, increasing the activation ratio and activation time may expand the surface area of the material, resulting higher capacitor. However, when this gas is generated massively, it causes the reduction of the specific surface area, reducing the hosting ability of  $Na^+$  ion.

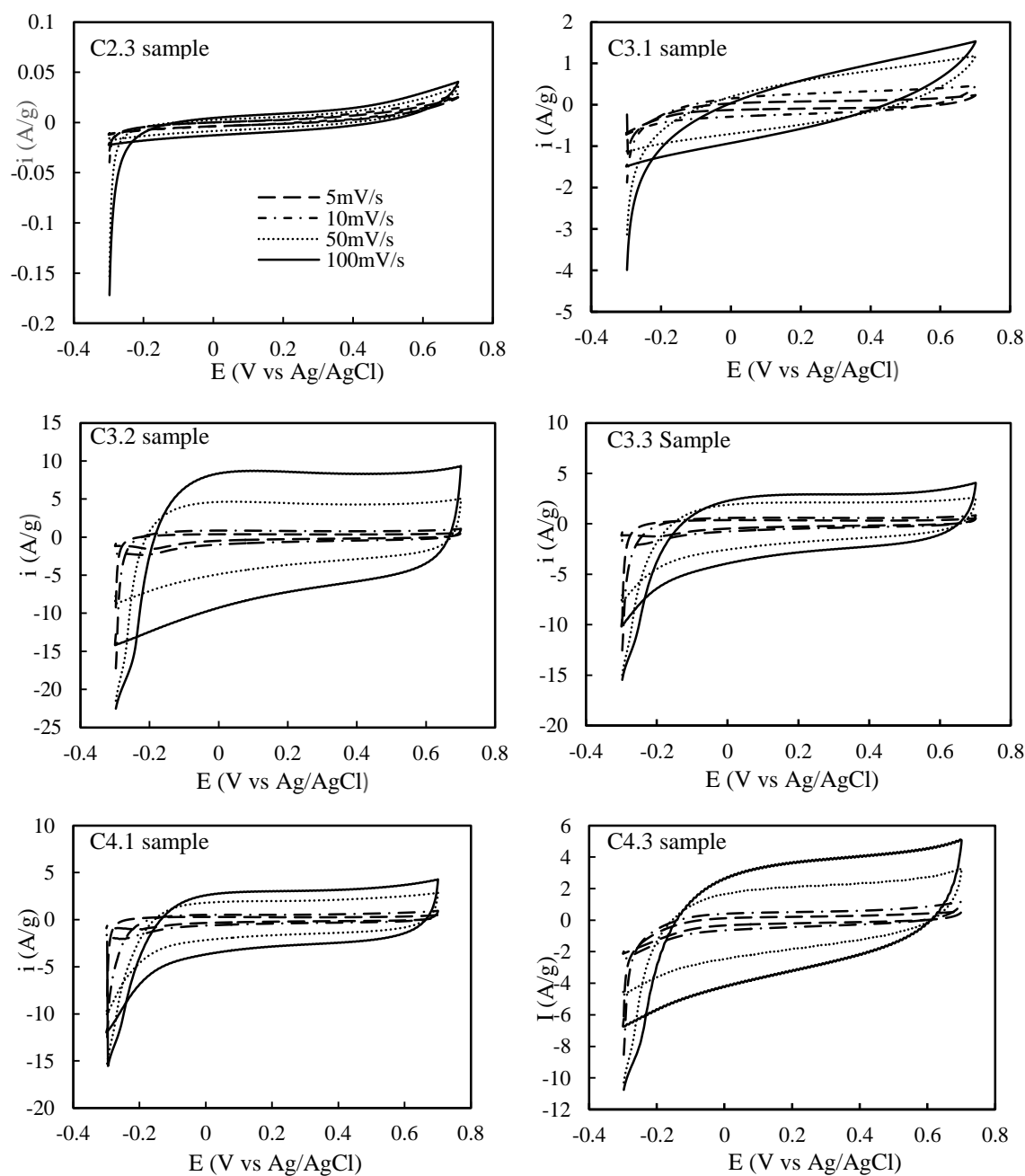


Figure 4. CV curves of porous carbon samples at different scan rate.

Table 3. Gravimetric capacitance  $C_{CV}$  of the porous carbon samples at different scan rate

Scan rate ( $\text{mV}\cdot\text{s}^{-1}$ )	$C_{CV}$ ( $\text{F}\cdot\text{g}^{-1}$ ) of samples					
	C2.3	C3.1	C3.2	C3.3	C4.1	C4.3
5	1.26	43.43	116.22	92.02	67.45	85.60
10	0.72	27.83	93.05	79.19	73.49	67.93
50	0.21	12.57	88.41	51.37	47.99	43.37
100	0.14	8.03	80.95	36.81	35.92	35.47

#### 4. CONCLUSIONS

Porous carbon was successfully synthesized by pyrolysis of RH at 450 °C during 3 hours under N<sub>2</sub> gas atmosphere followed by hydrothermal treatment in NaOH 2M at 150 °C within 3 hours to remove the silica fraction. The activated porous carbon which obtained by K<sub>2</sub>CO<sub>3</sub> activation at 900 °C has high specific surface area ( $S_{\text{BET}} = 796.3 \text{ m}^2/\text{g}$ ). Specific capacitance of the as-prepare electrode reached 116.22 F.g<sup>-1</sup> at scan rate of 5 mV/s. Consequently, porous carbon procedured from RH may be suitable candidate for application as electrode material.

The present result of research is encouraging, however, further research must be carried on to improve the surface area. Moreover, many articles indicate that the doping of metal oxide could improve significantly the electrochemical performance of the porous carbon [10-12]. On our future research, these experiments will be performed to raise the probability of the rice husk application.

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