

PROPERTIES OF COCONUT SHELL ACTIVATED CARBON

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MOHD IQBALDIN MN, KHUDZIR I, MOHD AZLAN MI, ZAIDI AG, SURANI B & ZUBRI Z. 2013. Properties of coconut shell activated carbon. Microwave-induced potassium hydroxide activation was used to produce coconut shell-based activated carbon. Surface area, pore size and specific capacitance value of the carbon produced were analysed to investigate its potential as an electrode material for supercapacitor. The activation process was carried out at 600 W with various irradiation times (10 to 30 min). The activated carbon produced had high surface area ranging from 1244.0–1768.8 m² g⁻¹ compared with the inactivated carbon, 36.5 m² g⁻¹. These results were in good agreement with scanning electron micrographs revealing highly porous surface structure. In addition, the specific capacitance value of the material increased from 94.8 to 156.3 F g⁻¹ compared with the inactivated biomass, 6.4 F g⁻¹. The material produced was found to be suitable as an electrode for supercapacitor.

Keywords: Chemical activation, electrode, microwave system, supercapacitor

MOHD IQBALDIN MN, KHUDZIR I, MOHD AZLAN MI, ZAIDI AG, SURANI B & ZUBRI Z. 2013. Ciri-ciri karbon teraktif tempurung kelapa. Gelombang mikro digunakan untuk menghasilkan karbon teraktif tempurung kelapa dengan kalium hidroksida sebagai agen pengaktif. Luas permukaan, saiz liang dan nilai kapasiti spesifik karbon yang dihasilkan dianalisis untuk mengkaji potensinya sebagai elektrod kapasitor lampau. Proses pengaktifan dijalankan pada 600 W dengan masa radiasi yang berbeza (10 min hingga 30 min). Karbon teraktif yang dihasilkan mempunyai luas permukaan yang tinggi iaitu antara 1244.0 m² g⁻¹ dengan 1768.8 m² g⁻¹ berbanding dengan karbon tak teraktif iaitu 36.5 m² g⁻¹. Keputusan ini berpadanan dengan keputusan mikrograf imbasan elektron yang menunjukkan struktur permukaan yang porous. Tambahan lagi, nilai kapasiti spesifik bahan teraktif juga meningkat daripada 94.8 F g⁻¹ menjadi 156.3 F g⁻¹ berbanding dengan karbon tak teraktif iaitu 6.4 F g⁻¹. Karbon teraktif yang dihasilkan didapati sesuai sebagai elektrod kapasitor lampau.

INTRODUCTION

Nowadays, the environmental issue of biomass waste is of top concern. Several researches have been conducted including the production of activated carbon from waste biomass such as date stone (Bouchelta et al. 2008), durian shell (Chandra et al. 2009), soybean oil cake (Tay et al. 2009), cherry stone (Marin et al. 2009), palm shell and coconut shell (Daud & Ali 2004).

Activated carbon is a crude form of graphite having porous structure and high surface area (Li et al. 2008). For these reasons, activated carbon is also well suited as an electrode for supercapacitor. The porous structure of activated carbon is important for ion to migrate and occupy the pores of carbon repetitively to form layers at the interface of electrode–electrolyte in

electrochemical energy-storage devices (Pandolfo & Hollenkamp 2005).

There are two types of activation processes to produce activated carbon from carbonaceous materials, i.e. chemical and physical activation processes. Physical activation procedure involves a two-step process, i.e. carbonisation, followed by activation using steam, oxygen or carbon dioxide as an activating agent (Yuen & Hameed 2009). However, in the chemical activation procedure, carbonisation and activation processes occur in a single stage using chemicals as an activating agent such as potassium hydroxide (KOH), phosphoric acid and zinc chloride (Ncibi et al. 2009).

The production of activated carbon from coconut shell using microwave was done by Li

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et al. (2009) and Yang et al. (2010). However, there were differences between their study and this study because they used a physical activation process which provided different activating agent and longer time. Our study focused on the application of activated carbon for supercapacitor electrode. However, the activated carbon obtained from their study had high specific surface area with pore structure falling in the range of micropores, rendering it unsuitable as supercapacitor electrode.

Supercapacitor is attracting attention nowadays owing to its capability in storing more energy, high power discharge ability and longer life cycle compared with other available energy-storage devices (Yuan et al. 2005). Supercapacitor electrode is one of the activated carbon used in electronic industry. Supercapacitor can provide high power capability (60–120 s), excellent reversibility (90–95% or higher) and long life cycle (> 10⁵) (Zhang et al. 2009). In a supercapacitor, the activated carbon used must have porous texture which is the main criterion of a double electric layer with high capacity and charge exchange. The pore structure of the activated carbon used is important for optimal performance of carbon materials as an electrode for supercapacitor (Babel & Jurewicz 2004).

In this study, the microwave carbonisation irradiation system was used to produce coconut shell activated carbon (CSAC) using KOH as an activating agent. The properties of the activated material such as surface area, pore size and specific capacitance value were analysed to study the potential of the material for supercapacitor electrode.

MATERIALS AND METHODS

Preparation of activated carbon

The coconut shells were collected, washed with distilled water and dried overnight

in an oven at 80 °C. The raw material was ground and sieved into sizes of less than 2 mm to ensure that they were thoroughly mixed with activating agent during the impregnation process. The proximate and ultimate analyses of raw materials were measured using thermal gravimetric analyser and elemental analyser respectively. The particles of coconut shell were then added to 50% KOH (85% purity in a ratio of 1 g of precursor per 0.75 mL of solution) (Deng et al. 2010). The impregnated sample was heated using a microwave oven at 600 W at various irradiation times (10, 15, 20, 25 and 30 min) (Li et al. 2008). The heated process occurred in the presence of nitrogen gas (100 ml min⁻¹) (Marin et al. 2009). The nitrogen gas used was 98% pure. Figure 1 shows the microwave irradiation system used. A modified probe was used to monitor the activation temperature of the activation process. The irradiated sample that became lumpy was washed using 50% hydrochloric acid and water with pH 6.5–7.0 to remove excess KOH. The sample was then dried in an oven at 100 °C for 2 hours.

Characterisation of the activated carbon

The pore size and structure of the activated carbon were determined using N₂ adsorption Brunauer-Emmett-Teller (BET) and scanning electron microscope (SEM) respectively. Samples for the SEM were prepared by cutting the dried samples to fit the specimen stub. The sample surface was sputter coated with a thin film of platinum before being viewed using SEM (Chandra et al. 2009).

Adsorption was performed at -196.2 °C using an automatic volumetric sorption analyser and by immersion calorimetry at 19.9 °C (Marin et al. 2009). The surface area and pore size of CSAC produced were determined using the BET analysis software. The BET surface area was

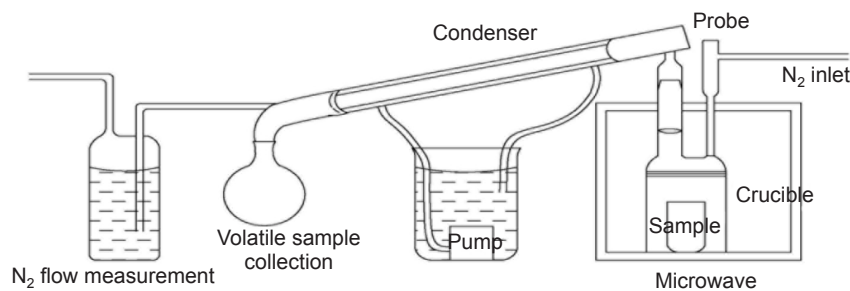


Figure 1 Illustration of the operational system for this study

measured by means of standard BET equation applied with relative pressure (P/P_0) ranging from 0.06 to 0.30.

Electrochemical measurements

The cyclic voltammetry test was used to estimate specific capacitance value. The unit was expressed in Farads per mass ($F\ g^{-1}$) of carbon material. The CSAC electrodes were soaked in 10 M KOH of electrolyte for 2 hours and these symmetric electrodes were sandwiched with separators using Teflon cell before undergoing cyclic voltammetry test. The symmetric electrodes of CSAC were tested at 0–1 V with scan rate of $2\ mV\ s^{-1}$ in aqueous electrolyte (10 M KOH).

RESULTS AND DISCUSSION

Table 1 shows that waste coconut shell material is a carbonaceous material that has high composition of carbon and high potential to become activated carbon. The percentage of carbon significantly increased after carbonisation and activation process to become CSAC.

Textural characteristics of the coconut shell-based activated carbon

The SEM micrographs of coconut shell carbon (CSC) and CSAC showed large differences in surface morphology (Figure 2). During carbonisation, most volatile matter was released. However, no pores developed due to the absence of an activating agent. In CSAC, however, hollow pits were observed and these were due to the

loss of volatile matter and the effect of KOH activating agent on the carbon material (Wang et al. 2009).

According to the International Union of Pure and Applied Chemistry, the pore development of an activated carbon is classified into three groups which are micropores (size $< 2\ nm$), mesopores (2–50 nm) and macropores (size $> 50\ nm$) (Pandolfo & Hollenkamp 2005). Apparently, the detected activation temperature of the process increased significantly with increasing irradiation time (Table 2). The surface area of the CSAC was higher than CSC. Chemical activation had increased the porosity of the surface area of CSAC up to $1768.8\ m^2\ g^{-1}$ compared with CSC at only $36.5\ m^2\ g^{-1}$. This indicates that the activation process has successfully increased the surface area and porosity of char derivative from carbonised organic precursor (Marin et al. 2009).

Table 2 also reveals that time has significant influence on the activation process. The surface area of CSAC increased from 1244.0 to a maximum of $1768.8\ m^2\ g^{-1}$. The pore size of CSAC slightly increased from 2.3 to 2.7 nm with increasing irradiation time from 10 to 20 min. As the irradiation time increased to 30 min, the detected activation temperature also increased, resulting in decreasing surface area of CSAC from 1768.8 to $1399.8\ m^2\ g^{-1}$. However, the pore size of CSAC slightly increased from 2.7 to 2.9 nm due to the sintering process which destroyed and widened the pore during the process (Yuen & Hameed 2012). This observation can be explained by two factors that affect the pore development of the carbon material.

Table 1 Proximate and ultimate analyses of coconut shell (CS), coconut shell carbon (CSC) and coconut shell activated carbon (CSAC)

Analysis	CS	CSC	CSAC
Proximate			
Volatile matter	77.82	48.25	28.46
Fixed carbon	21.38	50.55	69.49
Ash content	0.8	1.20	2.05
Ultimate			
Carbon	49.62	64.87	80.13
Hydrogen	7.31	4.66	2.36
Nitrogen	0.22	0.84	1.10
Sulphur	0.10	0.09	0.06
Oxygen ^a	42.75	29.54	16.35

^aCalculated by difference after all elements were determined

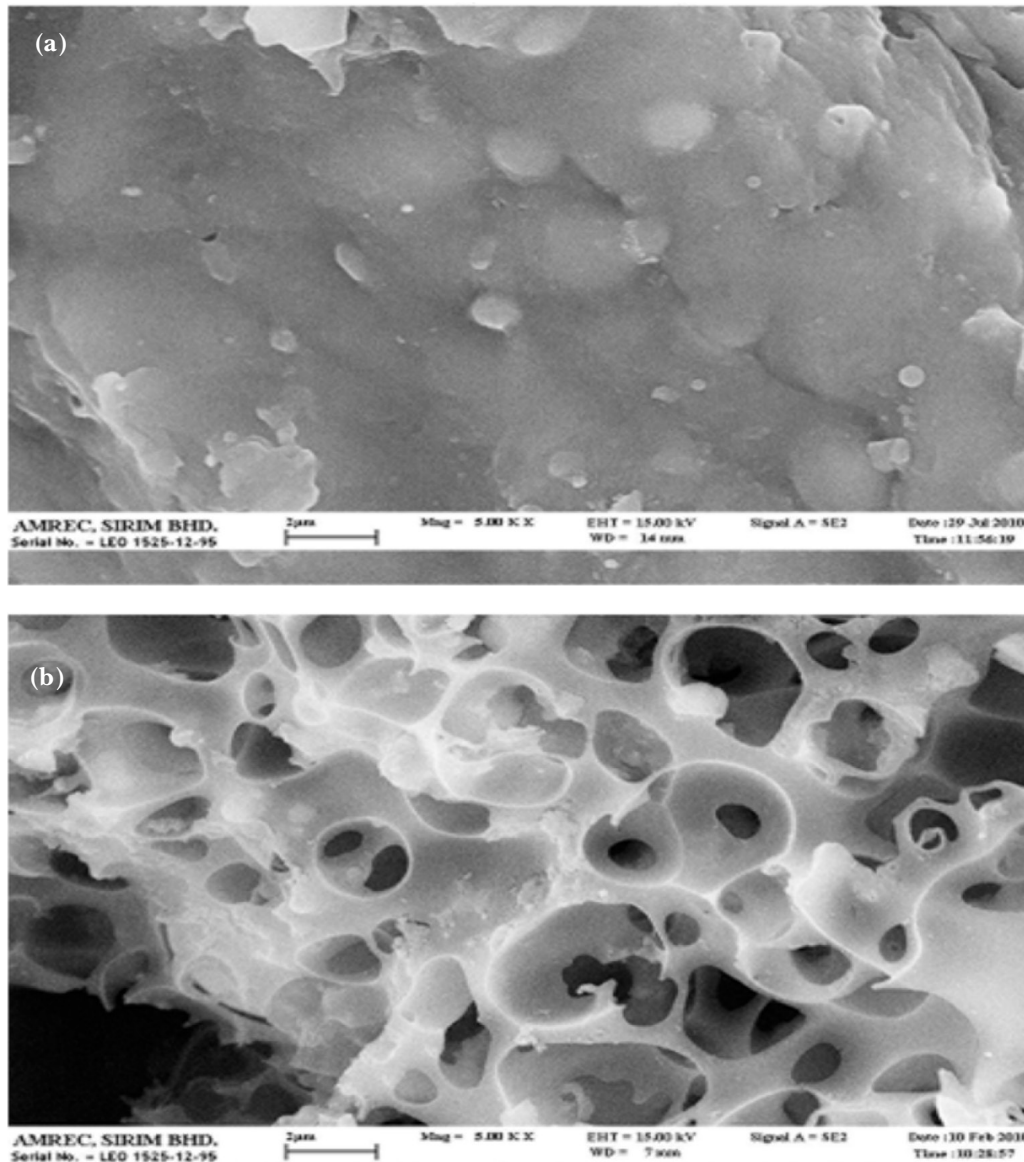


Figure 2 SEM micrographs of (a) coconut shell carbon and (b) coconut shell activated carbon

- (1) When the irradiation time is above 20 min, the activation reaction is over because the activating agent is used up. This means that the ratio of KOH used also has an influence on pore development during the activation process. This phenomenon of the activation process is found similar to a previous study (Yongbin et al. 2007).
- (2) The increasing irradiation time causes the activation temperature to increase significantly. Pores are formed and destructed simultaneously during the activating period (Liu et al. 2010). At certain activation temperature, activation reaction between KOH and carbon within

the sample increases which promotes more pore formation, hence increasing the surface area of CSAC. However, when the activation temperature reaches its limit, the destruction of the pore formation becomes dominant and consequently decreases the surface area. Hence, pore size becomes wider from micropores to mesopores (Yongbin et al. 2007).

Specific capacitance determination

Highly porous electrodes with very high surface area are important for a supercapacitor. Increasing surface area of carbon material

Table 2 Surface area and pore size of coconut shell carbon (CSC) and coconut shell activated carbon (CSAC) with different microwave radiation times

Sample (Time)	Detected temperature (°C)	Surface area (m ² g ⁻¹)	Pore size (nm)
CSAC 10 min	530	1244.0	2.3
CSAC 15 min	577	1311.1	2.5
CSAC 20 min	635	1768.8	2.7
CSAC 25 min	702	1536.2	2.8
CSAC 30 min	744	1399.8	2.9
CSC 20 min	399	36.5	3.7

generally leads to increasing specific capacitance value of the material. The specific capacitance (C_{sp}) of electrodes can be measured using the equation (Yuan et al. 2005) below.

$$C_{sp} = (|Ia| + |Ic|) / (2W \, dv/dt)$$

where the average of anodic (Ia) and cathodic (Ic) currents is divided by scan rate (dv/dt) and mass of active material (W).

Table 3 shows the C_{sp} values of CSAC (at different irradiation times) and CSC which indicate a large difference in specific capacitance of the former (156.33 F g⁻¹) and the latter (6.42 F g⁻¹). Large difference in C_{sp} between the two materials showed that high surface area gave positive impact on C_{sp} (Yuan et al. 2005). The pore formation is very important for ion migration. It is also important for ions to occupy all pores of the carbon repetitively forming layers at the interface of electrode–electrolyte. Hence, accumulation of ions during charging will increase, thus, the increase in specific capacitance of the material (Pandolfo & Hollenkamp 2005).

Figure 3 shows cyclic voltammogram curves for CSAC and CSC, indicating the difference in specific capacitance of the two materials as electrode materials. The CSAC exhibited higher charge–discharge curve profile than the CSC. The curve profile occurred reversibly without having any influence from Faradic scans. This indicates that the charge separation occurs electrostatically at the interface of electrode–electrolyte.

Table 3 indicates the difference in specific capacitance with different irradiation times. The specific capacitance of CSAC increased from 94.77 to 156.33 F g⁻¹ with increasing irradiation time from 10 to 20 min. However, beyond 20 min of irradiation time, the specific capacitance

Table 3 C_{sp} of coconut shell carbon (CSC) and coconut shell activated carbon (CSAC) with different microwave radiation times

Sample (Time)	Specific capacitance, C_{sp} (F g ⁻¹)
CSAC (10 min)	94.77
CSAC (15 min)	101.01
CSAC (20 min)	156.33
CSAC (25 min)	136.18
CSAC (30 min)	113.53
CSC (20 min)	6.42

decreased for CSAC 25 min and CSAC 30 min samples with values of 136.18 and 113.53 F g⁻¹ respectively.

The cyclic voltammogram curves of CSAC at different irradiation times (Figure 4) indicated that the sample of CSAC 20 min had the largest rectangular shape behaviour while the sample of CSAC 10 min, the smallest. This shows that by increasing the irradiation time, the specific capacitance of the activated carbon increases (up to certain irradiation time) because of the increasing surface area and pore size. In fact, this phenomenon happens because of the effect of the surface area and pore size of the materials. These are important for ions to migrate and occupy all pores of carbon repetitively. This process will form layers at the interface of electrode–electrolyte (Pandolfo & Hollenkamp 2005). The higher the specific capacitance, the larger the amount of electric charge stored in carbon, resulting in high energy density. It could be deduced that CSAC had higher specific capacitance due to increasing ion accumulation at the interface of electrode–electrolyte compared with the raw and CSC materials.

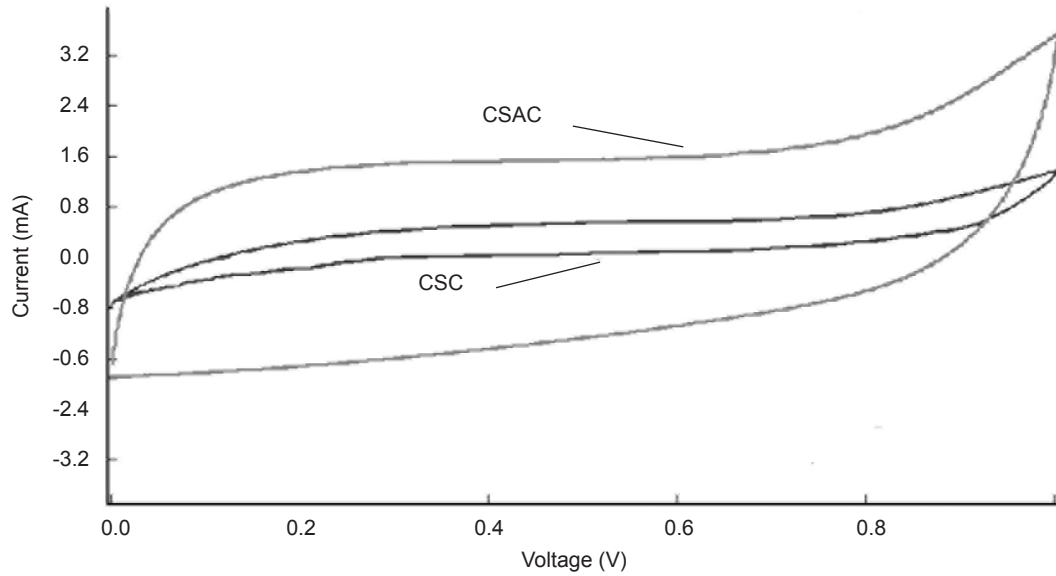


Figure 3 Cyclic voltammogram curves of coconut shell activated carbon (CSAC) and coconut shell carbon (CSC)

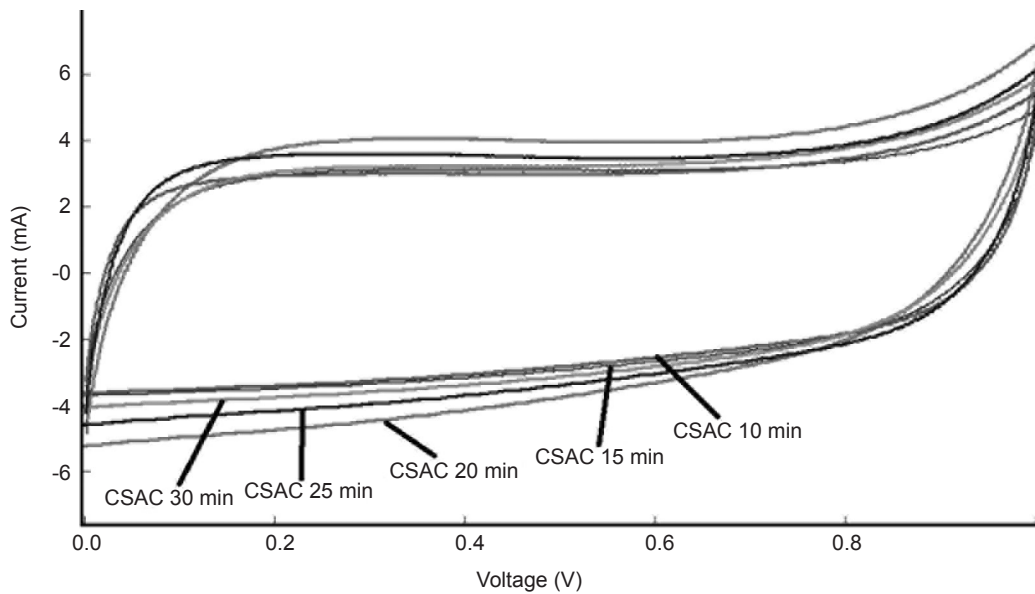


Figure 4 Cyclic voltammogram curves of the coconut shell activated carbon (CSAC) with different activation times of 10 to 30 min

Interestingly, the specific capacitance of the CSAC that was produced using microwave irradiation carbonisation system seemed to be comparable with others. Fuertes et al. (2009) prepared activated carbon from mesostructured SBA-16 silica materials using polyfurfuryl alcohol as a carbon precursor. The surface area of the activated carbon ranged from 1500 to 1800 m² g⁻¹ and pore size ranged from 2 to 8 nm. Specific capacitance of the activated carbon ranged from 100 to 150 F g⁻¹. The

activated carbon showed similar characteristics to CSAC. However, Zhang et al. (2009) reported that activated carbon had specific capacitance of 40 F g⁻¹. Merino et al. (2005) reported that industrial activated carbon nanofibres produced by Grupo Antolin Ingenieria SA at an industrial scale had specific capacitance ranging from 50 to 60 F g⁻¹. Thus, it is proven that specific capacitance of CSAC produced within the microwave system is comparable with and has potential to be an electrode material for supercapacitor.

CONCLUSIONS

KOH activation of coconut shell via microwave at 600 W and 20 min activation time seemed to be effective in producing carbon material with large surface area ($1768.8 \text{ m}^2 \text{ g}^{-1}$) and porosity (2.7 nm) accessible to electrolyte ions. The activation process produced the largest surface area of CSAC, which led to the highest specific capacitance at low current density (156.33 F g^{-1} in 10 M KOH).

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