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Application of Water Lettuce (Pistia S.) as Conductive Carbon in Electrochemical Capacitor

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A conductive carbon material from Water Lettuce (Pistia S.) powder has been prepared for use in Electrochemical Capacitor (EC) device. The features on surface functionality, morphology, and crystallography were analysed based on Boehm titration / FTIR, SEM and XRD instrumentations. The performance of ECs was studied by using impedance spectroscopy method, in which capacitances were calculated from the data. The surface features measurement showed that surface area (S), volume (V_m), and total volume (V_t) were 1238 $m^2\ g^{-1}$, 5.98 $cm^2\ g^{-1}$ and 1.99 $cm^3\ g^{-1}$. FTIR spectrogram shows the functionality on the surface of carbon, -OH (3,800 – 4,000 cm^{-1}), C–C, C–O, C–N (500 – 1,500 cm^{-1}) and C=C, C=O, C=N (1,050, 1,500, 2,300 – 2,400 cm^{-1}). XRD analysis showed that carbon sample has sharp peaks indicating crystallite of carbon and sylvite. SEM analyses indicated the existence of micro pores in the carbon samples. The higher impedances were come from electrodes with high content (70 %) of WL carbon, range from 100 to 120 ohm. Low content carbon (30 %) electrode has impedance range from 80 to 100 ohm. Critical point to capacitance – resistance character of EC for the asymmetric and symmetric ECs was 5 and 114 Hz. Capacitance analysis plots of ECs showed convergence of the values and reached minimum in frequency near 500 Hz. The maximum value of capacitance is about 0.401 F.

1. Introduction

Aquatic plants, such as Water Lettuce (WL) were very fast in breeding, it required serious attention in order not to cause environmental problems (Gupta et al., 2012). Water lettuce covering the river surface causes a reduction of river capacity volume and resulted in flooding. One alternative way to overcome the problem was making WL into porous carbon. The porous carbon may be used as an absorbent (Strelko et al., 2002) or as a base material for the manufacture of porous electrodes (Kim and Pyun, 2003). Porous carbon electrodes were used in electronics widely - electrical energy storage devices, namely batteries, fuel cells and electrochemical capacitors. Energy storage devices are a solution to overcome the fluctualisation on energy supply of many renewable energy source (Hanna and Chakib, 2013). Biomass-based porous electrodes have been studied previously (Syarif and Prasagi, 2016). It can be said that biomass-based has some advantages as compared to non-biomass porous carbon, for example, cheaper production costs, abundant, non-toxic materials and good performance. The biomass-based EC can store relatively large amounts of energy, rapid charging process, longer life cycles and easy constructions (Ruan et al., 2014).
This paper reports the characteristic of porous carbon c made from water lettuce (WL) plants by hydrothermal coupled with microwave pyrolysis methods. Hydrothermal process allows the homogeneous distribution of temperature within the whole volume of the reactor (Fiori et al., 2014) in order to obtain homogeneous pre-treatment product. The research on the preparation of electrode from WL has not been reported by other authors. The EC performance constructed from WL's carbon electrodes was studied by using impedance

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spectroscopy. We emphasise that technologically, the success in the carbon preparation from WL will give an economic value to WL. This study provides knowledge about the use of carbon WL in energy storage devices. Both have an impact on the widespread use of biomass-based carbon, especially WL.

2. Methods

2.1 Carbon Preparation

The whole plant of WL was washed with clean water and dried in oven at 100 °C. Dried WL was cut to obtain the leaves. The leaves of WL are washed and cut into small pieces, then dried under sunlight for about 2 - 3 days. The dried WL was put into the blender and smoothed into powder. 40 g WL powder was mixed with 0.08 g of KOH in 100 mL aqueous solutions, and then stirred for 3 min. The mixture was introduced into a hydrothermal reactor and heated in an oven at temperature of 200 °C and the pressure can be rose in about 1.6 MPa. After 16 h, the reactor was removed from the oven and cooled in order to obtain torrefaction material. The material was then fed into a microwave oven to pyrolyse. The microwave furnace was then heated in microwave oven with full power (1,000 watts) and removed from the microwave oven after 25 min and then placed in fume hood for a pyrolysis process. The temperature reached in the oven just after removal was about 800 °C. The pyrolysis process conducted in isolative system for 2 - 3 h and then was completed when the temperature reached a room temperature. Porous carbon was obtained through this process. The carbon was sieved with 200 mesh sieve.

2.2 Characterisation

Pore characterisation can be determined by using iodine (IN) and methylene blue numbers (MBN). Both methods can be found elsewhere (Nunes and Guerreiro, 2011). The value of the iodine number (IN) and methylene blue number (MBN) of WL were calculated by using the following Eq(1) and Eq(2).

$$\mathrm{IN} = \frac{\mathrm{EqI_2 \, x \, V_{Na_2S_2O_3} \, x \, N_{Na_2S_2O_3} \, x \, 100 \, x \, 10^{-3}}}{\mathrm{w}} \quad (1)$$

$$\mathrm{MBN} = \frac{(\mathrm{C_o - C_e}) \, \mathrm{x \, V}}{\mathrm{M}} \quad (2)$$

Where, EqI_2 is equivalent weight of iodine, $V_{Na2S2O3}$ is volume of $Na_2S_2O_3$ (mL), $N_{Na2S2O3}$ is normality of $Na_2S_2O_3$, w is weight carbon sample (g), C_o is initial concentration of methylene blue solution (mg/L), C_e is equilibria concentration of methylene blue (mg/L), V is volume of solution (L) and M is weight of carbon sample (g).

The surface area (S), volume of micropores (V_m) and volume of total pores (V_t) were calculated by using iodine number (IN) and metylene blue number (MBN) as formulated in Eq(3), Eq(4) and Eq(5):

$$\mathrm{S\ (m^2\ g^{-1})} = 2.28 \, \mathrm{x} \, 10^{2} - 1.01 \, \mathrm{x} \, 10^{-1} \, \mathrm{MBN} + 3.00 \, \mathrm{x} \, 10^{-1} \, \mathrm{IN} + 1.05 \, \mathrm{x} \, 10^{-4} \, \mathrm{MBN^2} + 2.00 \, \mathrm{x} \, 10^{-4} \, \mathrm{IN^2} + 9.38 \, \mathrm{x} \, 10^{-4} \, \mathrm{MBN \, . IN} \quad (3)$$

$$\mathrm{Vm\ (cm^3\ g^{-1})} = 5.60 \, \mathrm{x} \, 10^{-2} - 1.00 \, \mathrm{x} \, 10^{-3} \, \mathrm{MBN} + 1.55 \, \mathrm{x} \, 10^{-4} \, \mathrm{IN} + 7.00 \, \mathrm{x} \, 10^{-6} \, \mathrm{MBN^2} + 1.00 \, \mathrm{x} \, 10^{-7} \, \mathrm{IN^2} + 1.18 \, \mathrm{x} \, 10^{-7} \, \mathrm{MBN \, . IN} \quad (4)$$

$$\mathrm{Vt\ (cm^3\ g^{-1})} = 1.37 \, \mathrm{x} \, 10^{-1} + 1.90 \, \mathrm{x} \, 10^{-3} \, \mathrm{MBN} + 1.00 \, \mathrm{x} \, 10^{-4} \quad (5)$$

2.3 Electrochemical Capacitor Preparation

Electrodes were made by mixing carbon (30 % and 70 %) and graphite with 10 wt% mixture of gelatine and acetic acid as binder. This mixture was spreaded homogeneously on the glass of 35.71 mm x 14.72 mm, thickness of 1.95 mm, which was then allowed to dry and adhere. The spatula was used to disperse the mixture onto the glass. The electrode was ready to be used when its resistance reached a minimum. Solid electrolyte was made from PVA, $BaCO_3$ or $CaCO_3$ and water and then placed on top of the anode. A cathode of Al or Ti foil with size 21 x 10 mm and 1 mm thick was placed on top of the electrolyte.

Two wires of 2 mm in diameter were attached at both tip of the electrode and the metal plate. These wires acted as the applicators or the probes for the connectors. In the application of asymmetric EC, the electrode acted as the anode. The circuitry of the anode – separator – cathode was ready to be used as the asymmetric EC. The asymmetric EC was tested for its performance in the electrochemical impedance instrumentation. The same method was also conducted for symmetric the EC. Both electrodes were consisted of the WL carbon.

2.4 Performance Test

The EC performance test was done by the electrochemical impedance technique. Direct measurement of electrochemical impedance can be done by using oscilloscope and function generator (Barsoukov and Macdonald, 2005), i.e., by measuring the applied AC voltage and the response voltage across the reference resistor, R_e. Channel 1 was used to measure the applied voltage, V_1, and channel 2 to measure the voltage response by EC, V_2. The load was a resistor (Re), where the current passes through EC. The required times to form the wave for signals V_1 and V_2 were recorded as T1 and T2. The impedance (Z) and capacitance (C) of the EC are calculated by Eq(6), and Eq(7):

$$Z = V_2/V_1 \times R \quad (6)$$

$$C = 1/\log(Z)2\pi f \quad (7)$$

Where is impedance in ohm, V is potential in Volt, R is resistance in ohm, C is capacitance (Farad) and f is frequency (Hz).

3. Results and Discussions

3.1 Carbon Preparation

The carbonaceous material can be obtained from higher temperature pyrolysis. The pores can be characterised by the surface features of carbon. The results (Table 1) shows that iodine number (IN) is 705.48 mg/g, this value represented the ability of carbon pores to absorb small molecule, i.e. iodine that can be calculated using Eq(1). In the other hand, methylene blue number (MBN) in Eq(2) determines the ability of carbon in absorbing meso-sized molecule in carbon pores (Hsieh and Teng, 2000). The MBN of carbon derived from the WL is 975.846 mg/g. The surface area (S) of the WL carbon was calculated from iodine and methylene blue numbers Eq(3). The results for volume (V_m), and total volume (V_t) were calculated by using Eq(4) and Eq(5) and are shown in Table 1. The surface area of WL carbon (1,238.1 $m^2 g^{-1}$) was higher than the carbon produced from other aquatic i.e., from water hyacinth (904.57 $m^2 g^{-1}$) previously done by Syarif and Pardede (2014). Many carbons from biomasses generally have a surface area of 600 – 2,500 m^2/g (Zhang et al., 2016). Knowledge of carbon pore structure is needed to assess pore size, pore volume and carbon surface area. There is a relationship between these parameters with the capacitance of EC.

Table 1: Pore characteristic of water lettuce carbon

IN (mg/g)	MBN (mg/g)	S (m^2/g)	V_m (cm^2/g)	V_t (cm^3/g)
705.48	975.846	1,238.1	5.98	1.99

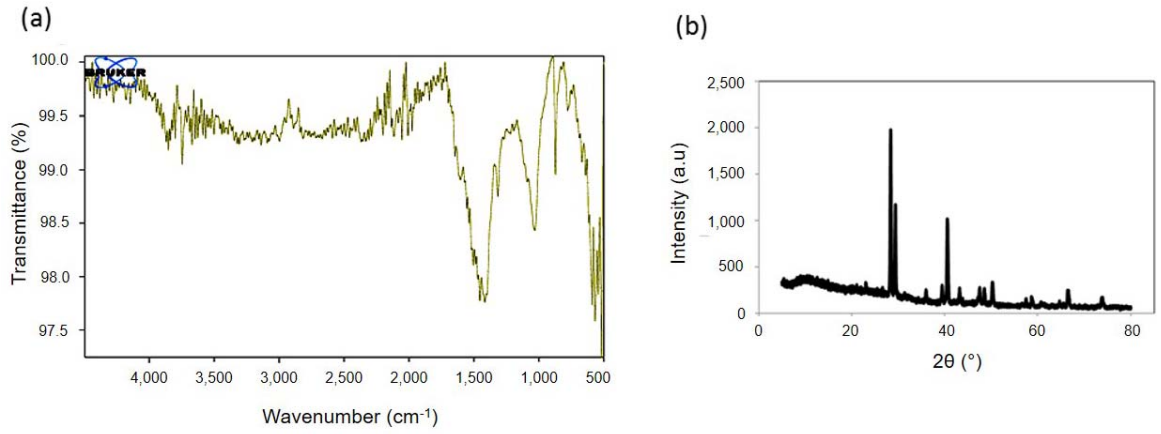

Figure 1: (a) FTIR spectra and (b) XRD diffractogram of water lettuce carbon

FTIR spectrogram (Figure 1a) shows the functionality on the surface of carbon, especially the functionality that accommodate ionic absorption. It can be shown that the carbon was dominated with OH (3,800 – 4,000 cm^{-1}). This functionality is necessary for the formation of double layer formation. It also can be shown that the carbon featured with single bond of C–C, C–O, or C–N (500 – 1,500 /cm) that coming from amorphous part of carbon. The existation of sharp peak on 1,050, 1,500, 2,300 – 2,400 /cm indicates C=C, C=O, C=N bond. The presence of O-H indicated that the carbon can be made into electrode for EC. The result of XRD diffraction

(Figure 1b) shows the presence of three distictive peaks in 2θ, i.e 28.36°, 29.39°, and 40.56°. Those peaks indicated the presence of crystal (graphite) in carbon. Low intensity suggest that the crystal is relatively small compare to other crystals, i.e KCl (sylvite) in 28.39° and 29.36° (JCPDS no. 01-073-0380) or CaCO3 (Calcite) in 40.56°. Diffractive angle 2θ = 23.03° does not clear on the XRD because it was covered by the diffractive angle of KCl crystal. SEM analysis of water lettuce (WL) carbon can be shown in Figure 2a and 2b with 10,000 and 20,000 times magnification. It is clearly shown that the carbon has some micropores about 123 - 710 µm. These pores were originated from the blokage the cavity in the material that formed after the impurities were decomposed in carbonisation process.

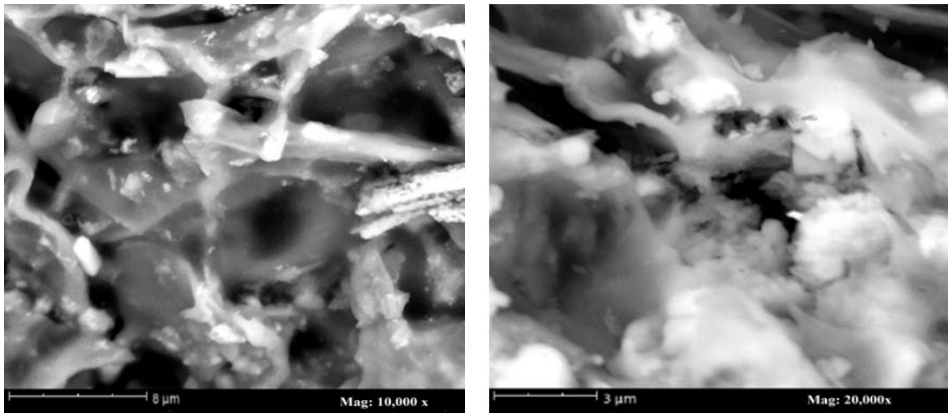

Figure 2: Micrographs for water lettuce carbon with magnification of (a) 10,000 and (b) 20,000 times

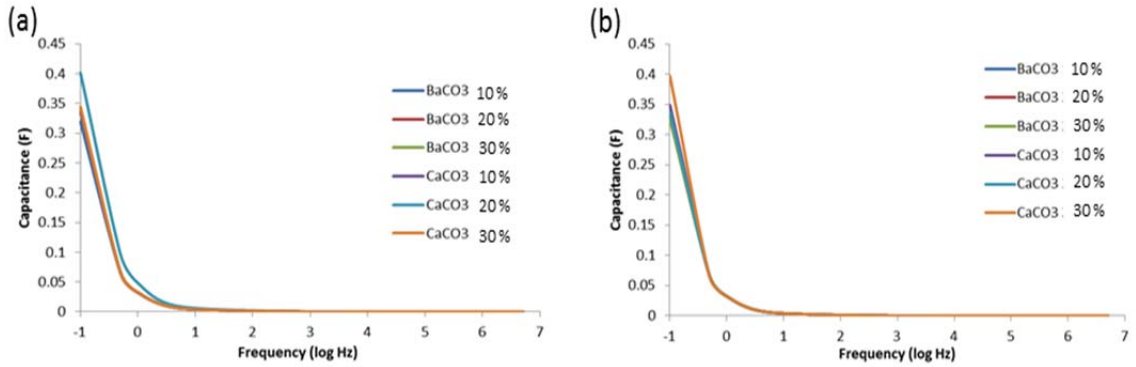

Figure 3: Capacitance plot of (a) asymmetric and (b) symmetrical EC with 30 % WL carbon

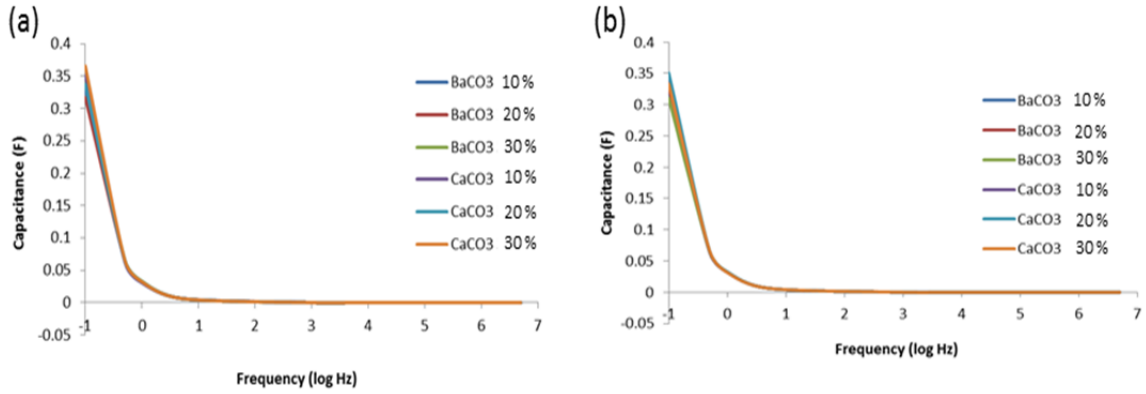

Figure 4: Capacitance plot of (a) asymmetric and (b) symmetrical EC with 70 % of WL carbon

3.2 Electrochemical Capacitor

Carbon electrodes from water hyacinth (Eichhornia R.) have a capacitance of 11.8 mF/g (Syarif et al., 2012). Some variations have been made in order to study electrochemical properties of WL electrode in ECs. The ECs were built in both asymmteric and symmetric electrode systems. The impedance spectroscopy instrumentation has been used to measure and calculate two parameters, i.e impedance, i.e Eq(6) and capacitance, i.e Eq(7) . The analysis of capacitance asymmetric and symmetrical EC can be seen in Figure 3 and 4. It can be shown that the convergence of capacitance values that reach minimum in frequency near 500 Hz. It also can be seen that the EC has maximum value about 0.401 F by using 30 % WL carbon in electrode and $CaCO_3$ as electrolyte. This results inferred that the higher capacitance can be obtained in lower frequency, the same situation can be obtained from lower scan rate in voltammetry. It happens because kinetics energy of ion is transfered from electrical field and applied for the movement. Low frequency of electrical field affects the ion to move slower. As the ion moves slower, its penetrates more deeper and reach micropore region. However, penetration of ion into pores is affected by the size of the ion, vise versa (Lee and Pyun, 2007). If the minimum requirement of pore size to the ion penentration is fulfilled and the concentration does not block ion movement it formed more electrical double layer formation. More double layer was formed, higher capacitance was got.

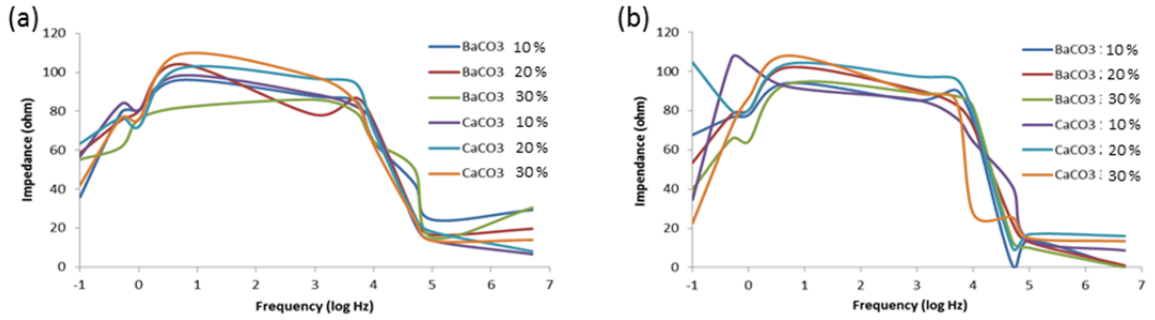

Figure 5: Impedance spectrogram of (a) asymmetric and (b) symmetric EC using 30 % of WL carbon

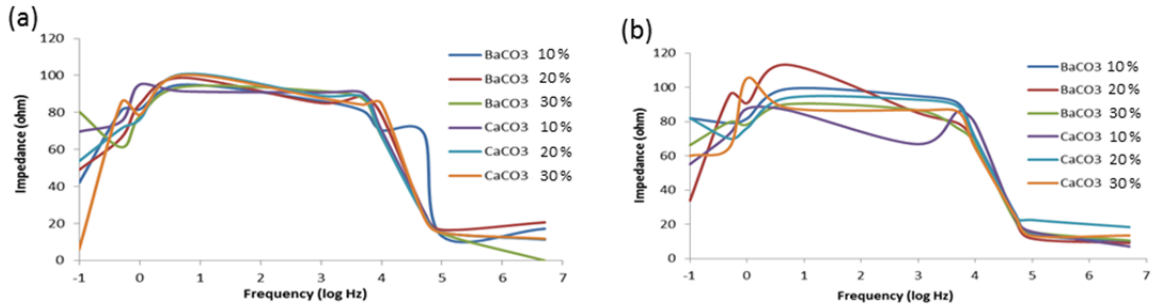

Figure 6: Impedance spectrogram of (a) asymmetric and (b) symmetric EC using 70 % WL carbon

The analysis of impedance spectroscopy for asymmetric and symmetrical EC can be seen in Figure 5 and 6. It can be seen that the lowest impedance in low frequency (< 10 Hz) was obtained in EC with $CaCO_3$ electrolyte in asymmetric system, i.e, ~ 10 ohm (Figure 5a and 6a). The lowest impedance in low frequency for symmetrical EC was impedance that was also obtained in $CaCO_3$ electrolytes, i.e. approximate 20 ohm (Figure 5b and 6b). It also can be seen the higher impedance that were come from the electrodes with low content (30 %) of WL carbon, range from 100 to 120 ohm (Figure 5a and 5b). While high content carbon (70 %) electrode have impedance range from 80 to 100 ohm (Figure 6a). It can be accepted since the WL carbon has low specific conductivity (100 – 1,000 S/cm). The diffractogram (Figure 1b) confirmed that WL carbon has relatively low crystalinity. Since the main advantage of using this carbon which is its high surface area that affects the phase shift (strength of capacitive character) of EC (Ahmed and Reifsnider, 2011).

4. Conclusions

The surface features measurement showed that surface area (S), volume (V_m), and total volume (V_t) are 1,238 m^2/g, 5.98 cm2/g and 1.99 cm3/g. The surface area of WL carbon (1,238.1 m2/g) was higher than the

carbon produced from other aquatic i.e., from water hyacinth (904.57 m^2/g). FTIR spectrogram shows the functionality on the surface of carbon, i.e., the carbon was dominated with OH (3,800 – 4,000 /cm). This functionality is necessary for the formation of double layer formation of EC. It is also can be shown that the carbon featured with single bond of C–C, C–O, or C–N (500 – 1,500 /cm) and C=C (1,050 /cm), C=O (1,500 /cm), C=N (2,300 – 2,400 /cm) bond. XRD analysis showed that carbon sample had sharp peaks indicating crystallite carbon and sylvite. SEM analyses indicated that the existence of micropores in the carbon samples. The higher impedances were come from the electrodes with low content (30 %) of WL carbon, range from 100 to 120 ohm. The high content carbon (70 %) electrode has impedance range from 80 to 100 ohm. The higher impedances were come from electrodes with high content (70 %) of WL carbon, range from 100 to 120 ohm. The low content carbon (30 %) electrode has impedance range from 80 to 100 ohm. Capacitance analysis plots of ECs show convergence of the values. They reached a minimum value in frequency near 500 Hz with the maximum about 0.401 F.

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