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Determination of specific capacitance of modified candlenut shell based carbon as electrode material for supercapacitor

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Abstract. Surface modification of candlenut shell carbon (CSC) using three chemicals: nitric acid (HNO₃), hydrogen peroxide (H_2O_2), and sulfuric acid (H_2SO_4) has been carried out. Activation of CSC was performed using H₃PO₄ solution with different ratio between CSC and activator. Carbon surface area was determined by methylene blue adsorption method. Surface characterization was performed using FTIR spectroscopy and Boehm titration method. Specific capacitance of electrode prepared from CSAC (candlenuts shell activated carbon) materials was quantified by Cyclic Voltammetry (CV) measurement. The surface area before and after activation are 105,127 m²/g, 112,488 m²/g, 124,190 m²/g, and 135,167 m²/g, respectively. Surface modification of CSAC showed the improvement in the chemical functionality of CSAC surface. Analyses using FTIR spectroscopy and Boehm titration showed that modifications with HNO₃, H_2SO_4 and H_2O_2 on the surface of the CSAC increased the number of oxygen functional groups. As a consequence, the specific capacitance of CSAC modified with 65% HNO₃ attained the highest value (127 μ F/g). There is an incredible increase by a factor of 298% from electrode which was constructed with un-modified CSAC material. This increase correlates to the largest number of oxygen functional groups of CSAC modified with nitric acid (HNO₃).

1. Introduction

Capabus or Capacitor Bus that today are operating in developed countries, is one example of supercapacitor applications which are used for storing and generating energy to drive the bus. This example is an answer for the needs of alternative energy other than fuel [1,2].

Supercapacitor is utilizing the principle of EDL (electric double layer) formed between the electrode material and electrolyte interface [3,4,5]. Therefore, electrode materials and electrolyte types are important parts that determine the performance of supercapacitors [6,7]. Commercial carbons are widely used as a supercapacitor electrode active material, but due to the preparation of those materials which are quite expensive and environmentally unfriendly, biomass based carbon is an attractive alternative because it is cheap, plentiful and environmentally friendly [8].

Biomass wastes in Indonesia are in large quantities from plantations, households, agriculture and industry which can be a potential pollutant if they are not managed properly. During this time, the biomass wastes are usually dumped or burned away and not used optimally. In fact, biomass wastes

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such as candlenut shell are potentially producing chemicals and materials of economic value for fuel and electrode material in battery or supercapacitor [9].

The main problems encountered in the preparation of biomass based material for energy storage application are variations of pore size ranging from micropores (<2 nm), mesoporous (2-50 nm) and macropores (> 50 nm). Ion transport for electrolytes in biomass based material with such pore characteristics will be very slow, so it will limit the formation of electric double layer, which in turn will lower the capacitance of electrodes for application in supercapacitors [10,11]. This phenomenon is also found by other researchers in the utilization of biomass based activated carbon for energy storage application [12,13].

Surface chemistry modification of biomass based porous carbons might be a practical and promising way to improve their chemical properties toward many utilizations of these materials. A modified porous carbon comprising various functional groups could be used for many applications such as heavy metals extractions from aqueous and non-aqueous solutions, in catalysis, toxic and radiolytic effluents treatment from industrial processes, and energy storage [14,15]. It was found that chemical modification using nitric acid introduced various oxygen functional groups [16] which have a significant effect on the capacitive properties of carbon material [17].

In this study, the surface of CSAC was modified using oxidizing agents: HNO_3 , H_2SO_4 and H_2O_2 to improve the chemical functionalities of CSAC surface and to apply these materials for supercapacitor electrode. The effect of modification conditions on the electrochemical properties of CSAC electrode-based supercapacitor was studied. The relationship between specific capacitance and the number of oxygen functional groups was discussed.

2. Materials and Methods

2.1. Materials

Candlenut shell, an agricultural based waste was collected from nearby farming as solid wastes. The collected materials were cleaned with distilled water for three times to pull out all the dirt particles. The washed materials were cut into smaller pieces (1-3 cm) and treated with sun-drying for 6 hours and then put into a hot air oven at 110°C for 1h. Carbonization was undertaken in furnace at 380°C for 1h. Carbonization products (CSC) were cooled, crushed, and sieved into 100mesh particles. All chemicals used are of pro analyst (p.a.) grade.

2.2. Methods

Candlenut Shell based Activated Carbon (CSAC) were prepared by immersing the precursor CSC with H_3PO_4 solution (85 vol.%) for 24 hours. The cooled activated carbon was sieved through Buchner funnel and washed with hot distilled water so as removing extra acid and to attain pH values = 6.5 in the washing solution, and finally dried at 110 °C for 1 hour and stored in a desiccator. Surface modification of CSAC was carried out with chemical agents, 98 wt.% H_2SO_4 , 65 wt.% HNO₃, and 30 wt.% H_2O_2 solutions.

Determination of carbon surface area was carried out based on the ability of carbon in methylene blue adsorption. The amount of adsorbed methylene blue is proportional to the surface area of adsorbent as shown in the following formula:

$$S = \frac{X_m \cdot N \cdot a}{M} \tag{1}$$

where S is surface are (m^2/g) , N is Avogadro's number (6.02 x 10^{23} mol⁻¹), Xm is fractional coverage (g/g), a is coverage by 1 molecule MB (197 x 10^{-20} m²), and M is molecular weight of MB (320.5 g/mole).

Characterization of surface chemistry of CSAC was conducted with Boehm titration method (BTM, [18,19]) and FTIR (Fourier Transform Infra-Red) spectroscopy. The BTM can be illustrated as follows: 0.5 g of CSAC were put into a series of flask containing 50mL of 0.05N NaHCO₃, Na₂CO₃,

NaOH and HCl. The flasks were sealed and shaken for 24h. The solutions were, then, filtered and 10mL of each solution was placed to a flask. The solution was titrated with 0.05N NaOH or HCl, depending on the original solution employed. Calculations of Boehm titration results are based on the following assumptions: (i) NaHCO₃ neutralizes carboxyl groups, (ii) Na₂CO₃ neutralizes carboxyl groups and lactones, (iii) NaOH neutralizes carboxyl groups, lactones and phenol groups; and (iv) HCl neutralizes the total base groups. FTIR spectroscopy was performed by Shimadzu 8400S FTIR instrument in wavenumbers range of 4000-500 cm⁻¹.

The electrode body was prepared by connecting copper and platinum wires using a steam solder. The electrode body was then inserted into a tulip pipette and glued together using parafilm. CSAC sample was mixed with parafilm wax with a mass ratio of 1: 1 and stirred until homogeneous by using a spatula in a petri dish. The carbon paste was inserted into the electrode body by being pressed using a spatula for solidifying and flattening.

Specific capacitance (Cs) of the carbon paste electrode was measured using Cyclic Voltammetry (CV) technique. This measurement employed three electrodes system i.e. Pt electrode, Ag/AgCl electrode and carbon paste electrode. Electrode testing was performed with scan rate of 50mV/s using electrolyte solution of H_2SO_4 0.1M to obtain voltage-current voltammogram. Based on that data, specific capacitance (Cs) was calculated.

3. Results and Discussions

3.1. Carbonization of Candlenut Shell

Carbonization of candlenut shell was carried out in furnace at 380°C for 1h. This temperature is the optimum temperature for candlenut shell carbonization. Ash product was observed beyond this temperature. Figure (1-a) is the carbonization product of candlenut shell.

3.2. Activation of Candlenut Shell based Carbon (CSC)

Activation is the process of removing hydrocarbons layer from the carbon surface thereby increasing the carbon porosity. Figure (1-b) is activated carbon prepared from candlenut shell.



(a) (b) **Figure 1.** (a) Carbonization product of candlenut shell, and (b) 100mesh size of Candlenut Shell based Activated Carbon (CSAC).

3.3. Determination of surface area of CSAC

Specific surface area of CSAC (Candlenut Shell Activated Carbon) is determined using Methylene Blue (MB) method. This method is a very simple method compared to commonly used BET method. In addition, the MB method is easier to carry out in the laboratory especially when no sophisticated equipment is available, such as N_2 adsorption instruments. The surface area is calculated based on the amount of MB absorbed by the CSAC as shown in Equation (1). It was found that the surface area increased by 30% after activation of candlenut shell based carbon.

3.4. Surface modification of CSAC

Acid treatment of activated carbon was generally used to oxidize the surface of porous carbon. The treatment will increase the acidic properties, pull off mineral contents and enhance the hydrophilic properties of surface of activated carbon. In addition, surface modification of CSAC will create new functional groups on the carbon surface which is reported to have an effect in increasing the value of specific capacitance of activated carbon as electrode material in supercapacitor [13, 14, 17, 20].

Surface modification of CSAC in this study was carried out using HNO_3 , H_2SO_4 , and H_2O_2 solutions, respectively. The addition of this solution will fabricate new functional groups, especially oxygen-containing functional groups (or surface oxides) that are widely known and the most common species formed on the surface of CSAC, which notably effects their performance in energy storage application [17, 20].

The functional groups generated from this modification are characterized using Boehm titration (back titration). The results of the Boehm titration were further compared with the results of functional group analysis using FTIR (Fourier Transform Infra-Red) spectroscopy.

Concentration of acid- and base-groups of CSAC determined by Boehm titration method is shown in the following figure.



Figure 2. Comparison of functional groups concentration of CSAC before and after modification with HNO_3 , H_2SO_4 , and H_2O_2 solutions. Note NT = Non-Treatment (before modification).

FTIR results of candlenut shell based activated carbon showed absorption of functional groups on the surface which are identified as functional groups for -C-O, -C=O, and -OH. Those groups are oxygen-containing functional groups. Modification with nitric acid (HNO₃), hydrogen peroxide (H₂O₂), and sulfuric acid (H₂SO₄) all give OH-carboxylate, C-O carboxylate, and C=O either in lactone or quinone. This is consistent with the previous study results [14, 16, 17, 20]. Acidic oxygen-containing functional groups were incorporated into CSAC surface by acid oxidation. Carboxylic acid groups were the main species found on the surface. The oxidation process also presented quinone and lactone groups.

Peak analysis performed before modification showed that there is an -O-H group in the region of 3616 cm^{-1} . The regional absorption band at 1166 cm^{-1} indicates the existence of a tertiary C-O group. In addition, the area of 1691 cm^{-1} indicates the presence of a typical -C=O group of carboxylic acids. The absorption band in the area of 1591 cm^{-1} shows the presence of an -C=C bond of aromatic group.

FTIR results on HNO₃ modified activated carbon showed the presence of carbonyl groups in 1716 and 1606cm⁻¹. Absorption at 1716 cm⁻¹ indicates the presence of -C=O groups of lactones, while 1606 cm⁻¹ is usually identified as C=O groups of quinone, and an absorption band at 1529cm⁻¹ indicates the presence of a C=C group. Absorption at 3415cm⁻¹ indicates the presence of OH groups of carboxylates which is reinforced by C-O groups at 1217cm⁻¹ wave numbers. FTIR results of H₂SO₄- and H₂O₂- modified CSAC almost showed the similar pattern with HNO₃-modified CSAC (Table 1).

CSAC treatment	Wave number (cm-1)	Functional groups	Notes
NT	3616	-OH	weakest
	1691	C=O carboxylic acid	weakest
	1591	C=C aromatic	
	1166	C-O tertier	
HNO3	3415	-OH carboxylate	
	1217	-C-O carboxylate	
	1716	C=O lactone	
	1606	C=O quinone	
	1529	C=C	
H ₂ SO ₄	3385	-OH carboxylate	
	1028	-C-O carboxylate	
	1168	C-O tertier	
	1701	C=O lactone	
	1587	C=O quinone	
	1429	C=C	
H ₂ O ₂	3435	-OH carboxylate	widest
	1278, 1037	-C-O carboxylate	
	1705	C=O lactone	
	1597	C=O quinone	

Table 1. FTIR data of CSAC

Both data, Boehm titration and FTIR spectroscopy, demonstrated that HNO₃-modified CSAC increases the oxygen-containing functional groups greater than other CSACs (H₂SO₄-, H₂O₂-modified CSAC and un-modified carbon).

3.5. Relationship between surface modification and specific capacitance of CSAC

We would like to discuss the effect of modification on specific capacitance changes of CSAC. Specific capacitance values were 40.2μ F/g, 124μ F/g and 127μ F/g after modification with H₂O₂, H₂SO₄, and HNO₃, respectively. Surface oxidation with H₂O₂ only led to slightly increase in capacitance of CSAC from the unmodified CSAC (31.9μ F/g). Incredible increase ($\pm 300\%$), however, was observed when using HNO₃ and H₂SO₄ as oxidizing agents. The order of these capacitance values is consistent with the changing of total number of basic functional groups after modification where H₂O₂ < H₂SO₄ < HNO₃ (Table 2). This fact showed that HNO₃ modification increased the number of oxygen oxygen-containing functional groups more than the other chemical agents and gave positive effects on the performance of CSAC-based electrodes [13, 17, 20].

On the contrary, the order of total number of acid functional groups is as follows HNO₃> H₂O₂> H₂SO₄. Even though sulfuric acid is a stronger acid than nitric acid, but nitrate ion is a stronger oxidant than sulphate ion. Nitric acid, for example, can oxidize Cl⁻ to Cl₂, but sulfuric acid cannot. In a nitrate ion, the molecular structure is inherently not very stable, as the nitrogen atom has to bear a positive charge to maintain the molecular structure. Besides, nitrogen itself is a very electronegative element, so that makes the nitrate ion even more unstable, hence its oxygen atom readily reacts with other atoms or molecules that oxygen can oxidize, including chloride ions [5]. On the other hand, hydrogen peroxide (H₂O₂) is a weak acid. H₂O₂ has an interesting chemistry because of its ability to function as oxidant as well as a reductant in both acid and basic solutions. On the whole, H₂O₂ is a

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very powerful oxidizing agent and a poor reducing agent. From this explanation, it might be understood that the order of total number of acid products will be $HNO_3 > H_2O_2 > H_2SO_4$, but quantitative order of the products chemical properties might be $HNO_3 > H_2SO_4 > H_2O_2$ [11, 14]. This assumption is supported by the diversity of chemical functional groups observed by FTIR in Table 1, where H_2SO_4 -modified CSAC produced 6 types of functional groups compared to H_2O_2 -modified CSAC. It was reported that specific surface area (physical properties) is not the only factor which affects the value of specific capacitance. The chemical properties of activated carbon also have an important role in the performance of biomass based-activated carbon electrode. Of course, the formation of new chemical functional groups after modification also contributed to the increase of capacitance value of carbon electrodes. That is why the capacitance of H_2SO_4 -modified CSAC is higher than H_2O_2 -modified CSAC [4, 13, 14].

Sample modification	Scan rate (mV/s)	Mass (g)	Ic (µA)	Ic (µA)	Cs (µF/g)
Unmodified	50	0.0189	3.63	3.33	31.9
HNO ₃	50	0.0164	3.26	2.93	127
H_2SO_4	50	0.0075	3.31	2.83	124
H_2O_2	50	0.01755	3.44	2.34	40.2

Table 2. The specific capacitances of CSAC-electrodes

The capacitance values obtained in this study are still in the order of milli-Farad and are much smaller when compared to the capacitance values obtained in the literature [20]. This may be due to the use of carbon paste electrodes in the determination of capacitance by cyclic voltammetry. In the future research, it will be examined the construction of electrodes as widely used in the literature [17, 20]. However, changes in capacitance values before and after CSAC modification suggested that, at least, biomass carbon modification is necessary to increase the capacitances value of biomass-based carbon for electrode material, especially biomass from agricultural wastes.

4. Conclusions

It has been shown that activation of candlenut shell based carbon increased the surface area of the carbon material. The increase of surface area is supposed by the formation of new pores after activation. The surface area of the candlenuts shell carbons before and after modification are 105,127 m^2/g , 112,488 m^2/g , 124,190 m^2/g , and 135,167 m^2/g , respectively. Surface modification of candlenuts shell based activated carbon with HNO₃, H₂SO₄, and H₂O₂ solutions has produced new functional groups as observed by Boehm titration and FTIR analyses. The formation of these functional groups is attributed to the increase of specific capacitance value of candlenut shell based carbon are 127; 124; and 40,2 μ F/g, respectively. All modification treatment shows an increase compared to untreated candlenut shell activated carbon.

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