Activated carbon material based on angsana leaves (*Pterocarpus indicus*) prepared by $ZnCl_2$ activation method as electrode for high performance supercapacitor

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Activated Carbon Material based on Angsana Leaves (*Pterocarpus indicus*) Prepared by $ZnCl_2$ Activation Method as Electrode for High Performance Supercapacitor

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Abstract. Biomass-based activated carbon has been synthesized from angsana leaves (*Pterocarpus indicus*) for high capacitive properties of supercapacitor electrodes. To establish the high specific capacitance, the synthesis process of activated carbon from biomass-based chemical activation is established in this study. This study focuses on the chemical activation process using $ZnCl_2$. Single-step carbonization and physical activation processes are chosen as pyrolysis process. $ZnCl_2$ activator agent exhibit excellent capacitive as high as 202 F g^{-1}. This excellent capacitive supported by porosity and chemical content analysis which present high specific surface area as high as 477.513 m^2g^{-1} and high carbon content of 95.75%. The microcrystalline dimension and surface morphology also characterized for support data.

INTRODUCTION

The Angsana (*Pterocarpus indicus*) is one of the many plants that are used as a reducing of pollution in a city. The angsana leaves can absorb and accumulate heavy metals due to air pollution so that the angsana plant is a popular choice for lungs of cities. Angsana plants can be found in Southeast Asia as the lungs of cities such as southern Myanmar, Cambodia, southern China, Vietnam, Philippines, Brunei, Malaysia and Indonesia [1]. Aside from being a protective plant and city lungs, angsana plants are one of the biomass sources that have not been utilized optimally [2]. The angsana leaves wastes only develop organic waste which is burned and causes pollution to the environment. Along with the development of the science of angsana plants have been used as animal feed [3] and as a dye of silk batik [4]. Further utilization, angsana leaves can be used as a raw material for the activated carbon as supercapacitor electrodes because it is composed of cellulose, hemicellulose and lignin reaching of 60 %. Several studies have shown excellent performance of supercapitor electrode made from biomass as raw material such as Willow leave [5], cycas leaves [6], and durian shell [7] which have produced specific capacitances of 216 F g^{-1}, 170 F g^{-1} and 130 F g^{-1}, respectively. Excellent capacitive properties are obtained by variations of modified carbon electrode preparations such as physical and chemical activation. One such modification of carbon electrodes can be carried out through chemical activation. Chemical activators that are often such as $ZnCl_2$. $ZnCl_2$ as an activator agent can produce carbon electrodes which have more micropores at a high temperature and tend to form mesopores. Based on these reasons, the utilization of angsana leaves waste as activated carbon can be applied as a supercapacitor electrode. The optimum specific capacitance in this study was found as high as 202 F g^{-1}.

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MATERIAL AND METHODS

Angsana leaves are collected from the Pekanbaru city, Riau. Cutting, washing and drying angsana leaves are done as a first step. Pre-carbonization is carried out by using an oven from room temperature to 200 ˚C with periodic temperature rises. Pre-carbonized samples were pulverized by using mortar and ball milling for 10 hours to produce powder. Sifting process is carried out to produce powders with sizes <53 μm. 1 M $ZnCl_2$ is used as a chemical activator agent. Chemical activation is carried out by dissolving the sample with the activator agent by using a hot plate at a temperature of 80 ˚C. The chemical activated sample converted into a monolith form by using a hydraulic press at a pressure of 8 tons. The process of carbonization and physical activation is carried out in one stage [7, 8], starting with the flow of nitrogen gas from room temperature to 600 ˚C and then followed by the flow of carbon dioxide gas until a temperature of 850 ˚C. The last step monolith samples are neutralized and it is further arranged into supercapacitor cells [9].

Characterization of carbon electrodes conducted in this study is the electrochemical properties by using the Cyclic Voltammetry method. The data generated in the CV method is used to evaluate the specific capacitance, energy density and power density through the standard equation [10-12]. To support the electrochemical properties, physical characterization was also carried out including thermal resistivity using TG/DTG profile, density was calculated based on the mass and volume of carbon electrodes, the degree of crystallinity evaluated using the X-ray diffraction method, surface morphology and chemical composition were reviewed by using the Scanning electron microscopy method and energy dispersive X-ray, and the specific surface area was evaluated by using the N_2 gas absorption method.

RESULT AND DISCUSSION

The cyclic voltammetry (CV) is a popular method for evaluating the electrochemical properties of a biomass carbon electrode. The CV curve shows the relationship between voltage and current density. The current density is exhibited as a charge current (I_c) and a discharge current (I_d) at a voltage of 0-0.5 V. CV measurements are carried out in a two-electrode system with 1 M H_2SO_4 aqueous as an electrolyte at a relatively low scanning rate (1 mV s^{-1}). The choice of low scanning rate is because the ions will diffuse optimally to the pores on the surface area of the carbon electrode so that the resulting higher capacitance. Figure 1 shows CV curve for supercapacitor electrode made of angsana leaves which according to the rectangular type curve. This type is normal for supercapacitor electrodes which indicate the specific capacitance [13]. The rectangular area of the I_c and I_d currents found in the sample with a specific capacitance of 202 F g^{-1}. The specific capacitance of a cyclic voltammetry analysis can be determined using standard equations. The energy density and the resulting power density are 7.01 Wh kg^{-1} and 50.6 W kg^{-1}, respectively. The capacitive properties obtained in this study are similar to several other studies that use $ZnCl_2$ as a chemical activator agent as shown in Table 1.

TABLE 1. The capacitive properties of supercapacitor cell for different biomass resources

Biomas resources	Specific capacitance	Energy	Power	References
Peanut shell	184	4.94	740	[14]
Cotton	240	12.5	-	[15]
Nori	220	6.1	50	[12]
Durian shell	88	-	-	[16]
Willow leaves	216	-	-	[5]
Angsana leaves	202	7.01	50.6	This study

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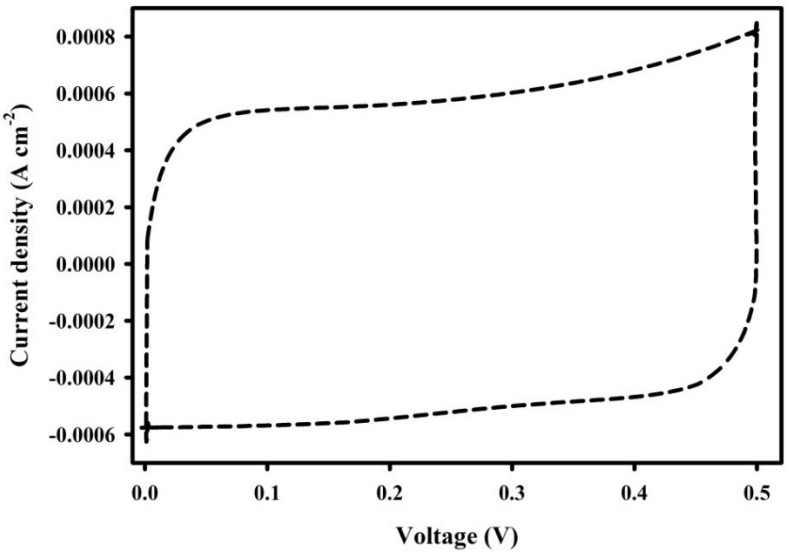

FIGURE 1. The CV curve for angsana leaves carbon electrode

The thermal stability properties of angsana leaves biomass were evaluated by the thermogravimetry analysis (TGA) method which was used as temperature resistant in the carbonization and activation process. The TGA is a curve that shows a reduction in mass against temperature. Figure 2(a) shows the Thermal Gravimetry (TG) curve and the Differential Thermal Termographymetry (DTG) curve. The TG curve shows a decrease in mass to temperature and the DTG curve shows the rate of change in mass against temperature rise. This analysis was carried out by flowing nitrogen at temperature intervals from 25 ˚C to 600 ˚C and the temperature rate increase of 10 ˚C min^{-1} and the mass of the sample tested was 2.230 mg.

The TG curve shows 3 stages of mass degradation to temperature. The first stage occurs at a temperature of 200.2 ˚C with a mass decrease of 5.39%, identifying the occurrence of evaporation of water. The second stage occurs at a temperature of 350 ˚C with a very significant mass reduction of 45.08%. Several previous studies stated that the second stage is the decomposition of complex compounds which including hemicellulose, cellulose and lignin [8, 9]. The third stage was shrinking by 66.81% at a temperature of 550.4 ˚C, which was caused by the ongoing extraction of sample compounds. The DTG curve shows a mass shrinkage peak at a temperature of 313.5 ˚C with a decomposition speed of 0.113 mg min^{-1}. At this point, there is a shrinkage of the compound at the most in time. This analysis is related to the analysis of the TG curve which also experienced a significant decrease in mass so that at a temperature of 313.5 ˚C it was chosen as temperature resistant in the carbonization and activation process.

The density analysis is evaluated based on measurement data of the diameter, thickness and mass of the electrodes before and after the carbonization and physical activation processes. Figure 2(b) shows the change in density of angsana leaves carbon electrodes based on the $ZnCl_2$ activator agent. The sample density experienced a significant decrease after the carbonization and physical activation processes. This phenomenon is caused by the reduction or loss of the contents of the elements present in carbon samples due to high-temperature pyrolysis, resulting in shrinkage of the mass and reducing the carbon electrode density. Heating causes impurities to evaporate and form new pores on carbon electrodes, which can be assumed that the greater the decrease in density, the more pores will be formed.

X-ray diffraction is one of the most common methods used to evaluate the microstructure of material including carbon electrodes from biomass. The XRD pattern for the angsana leaves carbon electrode is shown in Fig. 2(c). the XRD curve shows the peaks at a certain diffraction angle. Figure 2(c) shown two broadening peaks and several sharp peaks. In general, there are two wide peaks at diffraction angles 22˚ and 44˚. Both of these peaks appear to be wide and blunt at diffraction angles of 22˚ and 44˚ indicating that the electrodes of angsana leaves are carbon with amorphous structure [17,18]. The presence of this sharp peak indicates the presence of other elements besides carbon such as pottasium with the crystal structure. This analysis is further supported by chemical composition analysis using the EDX method. Calculation of carbon electrode lattice parameters such as layer height (L_c), layer width (L_a), and interlayer spacing (d) are obtained through Microcal Origin software approach and calculated using standard Equations, complete parameters $2\theta_{002}$, $2\theta_{100}$, d_{002}, d_{100}, L_c and L_a for angsana leaves electrodes were 23.996˚, 44.272˚, 3.7055 Å, 2.0443 Å, 15.5870 Å, and 7.0639 Å, respectively.

The surface morphology of angsana activated carbon leaves was reviewed using the Scanning Electron Microscopy method as shown in Fig. 2(d) at magnifications of 40000 times. Surface morophology presented the irregular shape of particles with dominated pores that are numerous and clear on particle. Many cavities formed in these particle fissures identify that more pores are formed in the $ZnCl_2$ variation. Pore sizes range from 0.153 µm to 0.303 µm. This more pore shape is influenced by the chemical activator agen of the sample. $ZnCl_2$ activator causes further release of oxygen and hydrogen in the sample material [15] so that more pores are formed so that it can affect the specific capacitance to be higher.

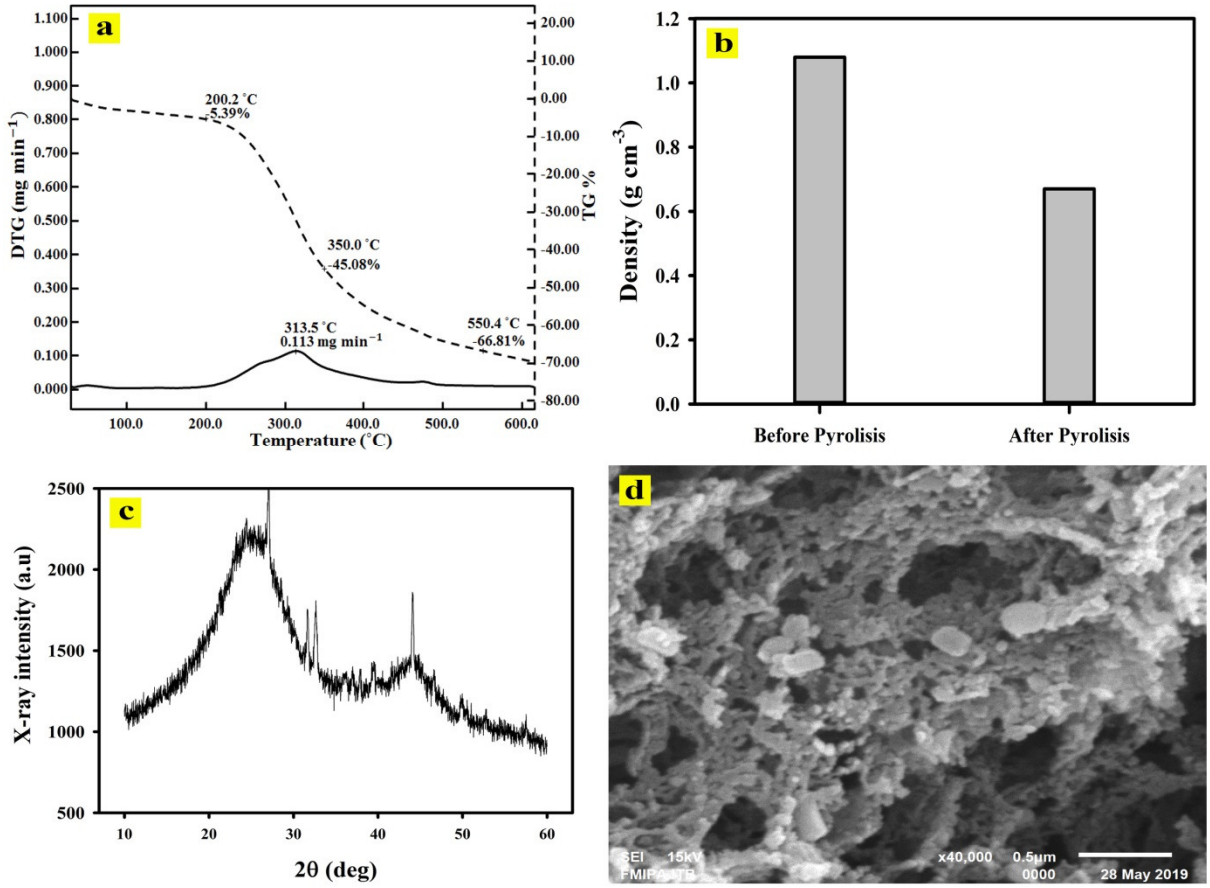

FIGURE 2. (a) TG/DTG curve, (b) density of before and after pyrolysis process, (c) X-ray difraction pattern for angsana leaves carbon electrode, and (d) SEM with micrograph of 40000x

The content of the carbon electrode element from the angsana leaves is characterized using the energy dispersive X-ray (EDX) energy method. Fig. 3(a) shown the elements on the angsana leaves carbon electrode in peaks. In general, electrodes contain elements such as Carbon (C), Oxygen (O) and Pottasium (K). Carbon elements have the highest percentage of 95.75%. The oxygen element is the element that is at the second peak of 4.07%, the oxygen contained in the carbon sample is caused by the carbon bond with oxygen during the CO_2 activation process. The presence of other elements such as Potassium (K) is indicated by the general constituent elements of biomass that have not been biodegradable [19].

N_2 gas absorption method is carried out to determine the pore properties and the magnitude of carbon specific surface area. The surface area of the carbon electrode was evaluated using the Brunauer Emmet Teller (BET) method. This method aims to determine the physical adsorption of gas molecules on a solid surface and serves as a basis for analyzing the surface area of carbon samples. The N_2 gas absorption curve generally exhibits type IV based on the IUPAC classification. Type IV is often found on carbon electrodes made from biomass as raw material, as in cocoa pod husk [20] and waste tea leaves [21]. Type IV is characterized by rapid saturation at relatively low pressures and the presence of hysterical loops at relative pressures of 0.4 to 0.99. The curve shape like this indicates that the electrode

is dominated by mesopores and micropores [22]. The surface area of the sample was found to be 477.513 $m^2 g^{-1}$. The pore size is reviewed using the BJH method. The pore size of activated carbon affects the ability of carbon sequestration. Figure 3(c) shows the pore size of a mesoporous carbon sample in the range of 2.1 nm to 2.5 nm. The size of mesoporous in activated carbon gives a good effect on the ability of carbon to carry out the process of N_2 gas absorption [23].

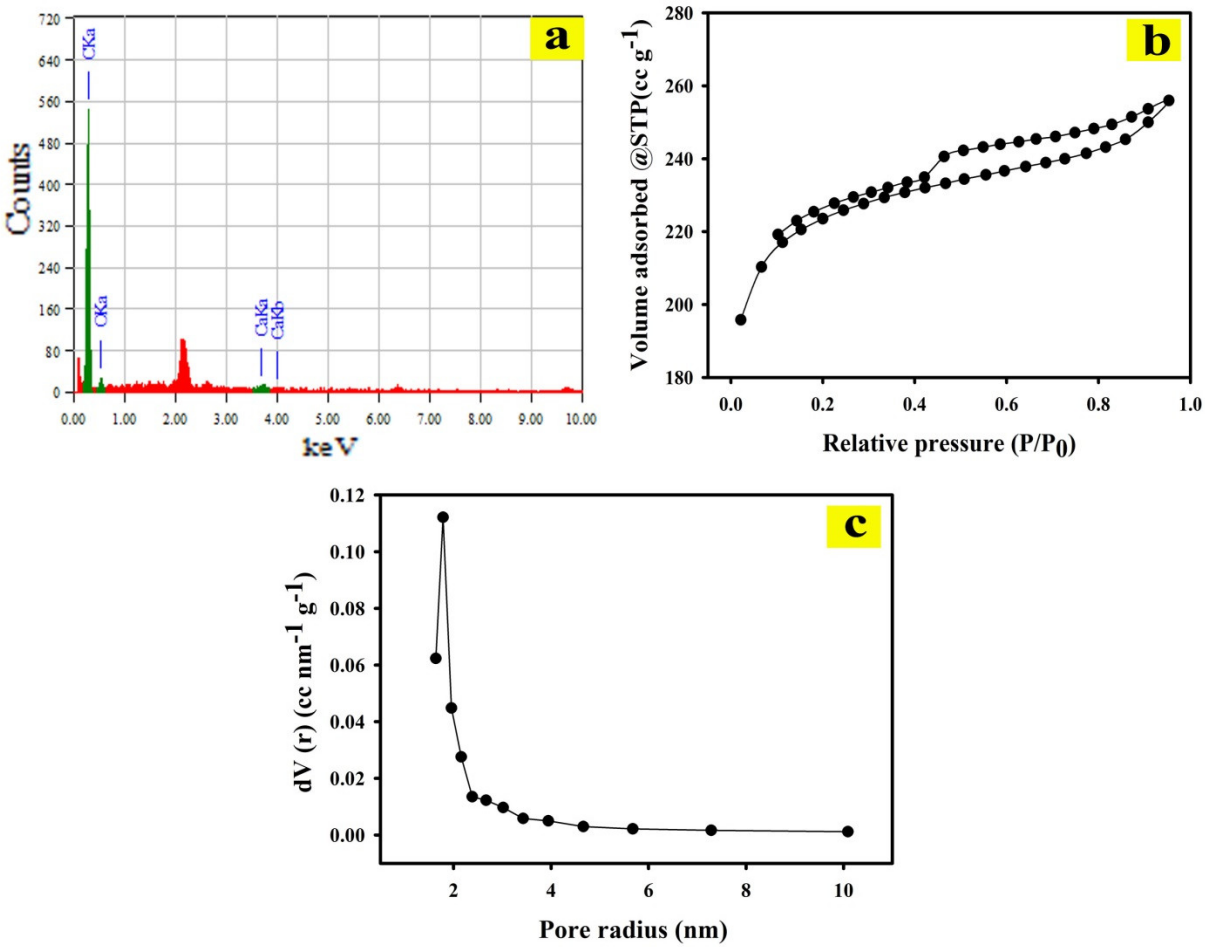

FIGURE 3. (a) EDX curve, (b) Nitrogen adsorption-desorption isotherms, and (c) Pore size distribution curves

CONCLUSIONS

The activated carbon electrodes made from angsana leaves (*Pterocarpus indicus*) for high capacitive properties of supercapacitor electrodes have been successfully synthesized. The carbon monolith is prepared without additional adhesive materials. The pyrolysis process is carried out by using one-step carbonization and physical activation process. The carbon electrode exhibit excellent capacitive properties such as specific capacitance, energy density and power density as high as 202 F g^{-1}, 7.01 Wh kg^{-1} and 50.6 W kg^{-1}, respectively. This excellent capacitive supported by physical properties such as surface morphology, porosity and chemical content analysis. Surface morphology presented the irregular shape of particles with dominated pores that are numerous and clear on particle with size range of 0.153 µm to 0.303 µm. The high carbon content of 95.75% and specific surface area as high as 477.513 $m^2 g^{-1}$ with the pore size range of 1-2.5 nm. Based on this reason, angsana leaves have high potential as raw material to the synthesis of activated carbon electrodes is applied to energy storage.

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