The physical and electrochemical properties of activated carbon electrode made from Terminalia Catappa leaf (TCL) for supercapacitor cell application

E Taer1, A Afrianda1, R Taslim2, Krisman1, Minarni1, A Agustino1, A Apriwandi1 and U Malik1

1Department of Physics, University Riau, 28293 Simpang Baru, Riau, Indonesia
2Department of Industrial Engineering, State Islamic University of Sultan Syarif Kasim, 28293 Simpang Baru, Riau, Indonesia.

Email : erman.taer@yahoo.com

Abstract. In this study, the utilization of TCL as raw material in production of carbon supercapacitor electrodes are focused on variations in carbonization temperature. Carbonization temperatures were varied by 500 °C, 600 °C, 700 °C, and 800 °C marked with the code TCL500, TCL600, TCL700 and TCL800 corresponding to the selection of carbonization temperature. All samples were activated using CO2 gas at 850 °C for 2 hours and 30 minutes. The density of the resulting carbon electrode was 0.776 g cm⁻³, 0.754 g cm⁻³, 0.738 g cm⁻³ and 0.762 g cm⁻³ for electrodes TCL500, TCL600, TCL700 and TCL800, respectively. The crystalline nature of the resulting carbon sample was found to be amorphous with 2θ scattering angle 23.880°, 44.192° and stacking high (Lc) 8.482 Å for TCL700 samples. Lc data has been used to obtain a sample surface area and it was found as high as 1160.497 m² g⁻¹. The morphology of the electrode surface has been tested using a SEM instrument. The elements content of the electrode have also been analyzed based on the EDS data. The optimum specific capacitance of carbon electrodes from TCL is obtained at a carbonization temperature of 700 °C as high as 54 F g⁻¹.

1. Introduction
The supercapacitor is an energy storage device that has a high capacitance and low internal resistance. The mechanism in a supercapacitor storage is charge separation at a porous electrode and electrolyte interface[1,2]. The supercapacitor consists of two electrodes, a separator, an electrolyte and two current collectors. The widely used supercapacitor electrodes are carbon materials because of their lower cost, material availability, and high surface area. Carbon material commonly used as an electrode material is activated carbon. Activated carbon was prepared by carbonization and activation, sample a variety of biomass used a raw material for production of activated carbon electrode such as dregs of sago [3], rubberwood sawdust [4], bamboo [5], banana fibers [6] and others. Selection of leaves as the raw material in this study because most of the basic elements of the leaves are carbon so it is potential to converted to be an activated carbon.

Research on leaf utilization raw material in production of supercapacitor electrode has been widely performed, such as pineapple leaves, lotus leaves, green onion, tea leaves with high specific
capacitance, each of 202 \( \text{F g}^{-1} \) [7], 379 \( \text{F g}^{-1} \) [8], 158.6 \( \text{F g}^{-1} \) [9] and 330 \( \text{F g}^{-1} \) [10] indicating that this leaf has a high potential as an electrode material for supercapacitor cell.

Terminalia Catappa is a combretaceous plant often found in tropical and subtropical regions [11], such as Indonesia, Philippines, Malaysia. The characteristics of Terminalia Catappa plants are stems that have long and flat branches, the leaves are round, flowers with white color and small size, not have the crown and its fruit is oval. The TCL many uses as an ingredient of various drugs such as antioxidants [12], anti-inflammatory [13], anticancer [14], and antidiarrheal [15], while the utilization as a supercapacitor cell electrode material has never been reported.

Plant of Terminalia Catappa is very much grown in Indonesia, where Terminalia Catappa plants can grow in lowland and highlands, in primary and secondary forests, along the river or in the coastal areas. Plants of Terminalia Catappa are found in the Riau University area that fell its leaves twice time in a year. The leaves that fall will produce waste in the environment that can affect the quality of the environment so that it needs to be processed, one of them can be used as a raw material for supercapacitor electrode. This study will be demonstrated the application of TCL as the raw material in the production of carbon electrode for supercapacitor cell. The activation of carbon electrode samples is carried out by the carbonization process and physical activation. Carbonization was performed in the \( \text{N}_2 \) gas environmental with varying temperatures of 500 °C, 600 °C, 700 °C and 800 °C. While physics activation using \( \text{CO}_2 \) gas at 850 °C for 2 hours and 30 minutes.

2. Experimental Methods
The raw material used in this research is TCL collected from Riau University area. The TCL first dried under the sun for 2 days, then dried using an oven at a 110 °C for 2 days. Pre-carbonization was carried out on samples at a temperature of 200 °C for 2 hours. The pre-carbonized sample was milled with mortar and ball milling then sieved to found a particle size less than 38 µm. Chemical activation using a 0.4 M KOH activator agent. The powder form was transformed to a pellet form by applying an 8 tons pressing force by using a hydraulic press machine. The carbonization process starts at room temperature to 323.4 °C with a temperature scan rate of 1 °C/min, then at 323.4 °C maintained for 1 hours and then continued to reach the desired temperature with an increasing rate temperature of 3 °C/min. The carbonization temperature various of 500 °C, 600 °C, 700 °C and 800 °C. The samples were labeled based on the different carbonization temperature, for example, the sample was carbonized at a temperature of 500 was labeled as TCL500, TCL mean Terminalia Catappa Leaf and 500 is referred carbonization temperature. so all samples were labeled TCL500, TCL600, TCL700, and TCL800. The physical activation process using \( \text{CO}_2 \) at a temperature of 850 °C which is maintained at this temperature for 2 hours and 30 minutes. Characterization of Terminalia Catappa leaf based carbon electrodes such as density, surface morphology, element content, the degree of crystallinity and specific capacitance. The specific capacitance is calculated using the following formula [16]:

\[
C_{sp} = \frac{(I_e-I_d)}{s \times m}
\]

3. Results and Discussion
3.1. Density Measurement Analysis
The carbon electrode densities before and after pyrolysis process shown in Figure 1. The density for TCL500, TCL600, TCL700 and TCL800 electrodes before pyrolysis were 0.9620 g cm\(^{-3}\), 0.9463 g cm\(^{-3}\), 0.9503 g cm\(^{-3}\) and 0.9737 g cm\(^{-3}\), respectively, while after pyrolysis were 0.776 g cm\(^{-3}\), 0.754 g cm\(^{-3}\), 0.738 g cm\(^{-3}\) and 0.762 g cm\(^{-3}\). Sample density before the carbonization-activation process looks relatively same because until this stage there were no differences in treatment on each sample. while the density after carbonization-activation process looks to decrease at samples of TCL500 to TCL700 and increase at TCL800. The smallest density was found in the TCL700 sample, it indicates impurities on the carbon electrode sample are more and more unraveled so it can be concluded that the temperature of 700 °C is the optimal carbonization temperature in the production of TCL carbon electrodes to
found the maximum porosity properties. The difference in density shows that the carbonization temperature has a very important influence on the density of the resulting carbon electrode. Electrode samples from other biomass materials that have been studied also resulted in smaller densities after pyrolysis processes such as durian shell carbon electrodes yielding densities of 0.716 g/cm$^3$ to 0.862 g/cm$^3$ [17] and rubber wood sawdust based carbon electrodes has a density of 0.849 g/cm$^3$ to 1.034 g/cm$^3$ [18].

![Figure 1. Comparison of density value of electrodes.](image)

3.2. Thermogravimetry analysis

Thermogravimetry (TG) of TCL is shown by a dashed line, while differential thermogravimetry (DTG) of TCL is shown by a solid line shown in Figure 2. The TG curve shows a decrease in the sample mass as high as 6.56 % that starting at a temperature of 30 °C to 242.1 °C indicating the water content in the sample has evaporated with the lignin and hemicellulose began decomposed. Significant mass reduction occurs at a temperature of 242.1 °C to 405 °C as high as 40.8 % indicating that at these temperatures complex compounds such as lignin, cellulose and hemicellulose decompose simultaneously. The decreasing in mass still occurred at a temperature of 405 °C to 553.6 °C as high as 19.13 % indicating the lignin compound was still being decomposed and increase carbon content in the sample. Decomposition of hemicellulose, cellulose and lignin occurred at a temperatures range of 200 °C to 300 °C, 260 °C to 390 °C [19] and 160 °C to 900 °C [20], respectively. The decreasing in the TG curve still occurs at a temperature of higher than 553.6 °C which indicates that there is lignin which is still decomposed.
Figure 2. DTG and TG curve of TCL sample.

DTG curve shows there are three peaks, the peak indicates the occurrence of mass shrinkage in units of time. The first peak at a temperature of 61 °C indicates the highest speed water evaporate appear in the sample. The second peak at a temperature of 323.2 °C has significant mass shrinkage with a speed of 0.341 mg min\(^{-1}\). This peak shows the highest peak its mean a higher decomposed of lignin, hemicellulose, and cellulose occur at the same time. This temperature in the carbonization process maintained for 1 hour to found the higher carbon contained in the sample. The third peak appears at a temperature of 487.027 °C there was a lower peak than second one which indicated that there was still a chemical complex compound i.e lignin that still decomposed in the sample. Similar DTG trend also found in other biomass samples such as sago and coconut leaves, where the highest DTG peaks occur at a temperature of 311 °C and 343 °C for dregs of sago [21] and coconut leaf [22], respectively.

3.3. Scanning Electron Microscopy Analysis

The TCL electrode morphology form analysed using SEM testing shown in Figure 3. Figure 3a and 3b show TCL500 and TCL700 samples with 40000 times magnification. Figure 3a shows that the nano fibers formed was found in sample with a diameter range of 0.113 µm to 0.220 µm and Figure 3b shows that the resulting nano fiber with a smaller diameter range of 0.032 µm to 0.108 µm. The increasing carbonization temperatures the smaller nanofibers diameter in the sample. This fiber serves as a connector between the particles with one another. The fibers can also increase the conductivity of the carbon electrode. The nanofiber form cause easier for the ions to diffuse into the pores of the carbon electrode and finally increase the specific capacitance [23].
3.4. Energy Dispersive X-ray Analysis
The element contained in the TCL electrode obtained from EDX test and its shown in Table 1. Carbon element (C) is the most dominant element contained in the electrode sample. Similar results are also found in previous studies of banana stems based electrode with carbon element varied from 81% to 87% [24]. In addition, the other elements such as oxygen (O$_2$), silicon (Si), magnesium (Mg), potassium (K) and Calcium (Ca) are also found in the electrode sample. The O$_2$ element caused by the imperfect carbonization process and can also occur bonding on the activation process [25]. The Si element is commonly encountered in carbon samples derived from biomass materials [26]. The K element may be caused by a less clean washing in the electrode preparation process. The element of Mg and Ca comes from the constituent elements of the Terminalia Catappa leaf i.e. tannin [27], where the tannin element will produce metal ions such as Mg and Ca elements.

| Table 1. Percentage of element content of activated carbon TCL samples. |
|------------------|-------|---------|
| Element          | TCL500 (%) | TCL700 (%) |
| C                | 69.78  | 74.49   |
| O$_2$            | 21.53  | 13.49   |
| Si               | -      | 1.32    |
| Mg               | 0.21   | -       |
| K                | 0.85   | 1.34    |
| Ca               | 7.64   | 9.36    |
| Total            | 100    |         |

3.5. X-Ray Diffraction Analysis
Figure 4 shown curve of XRD results. XRD curve shows the TCL electrode is an amorphous structure, which is marked by a broadening peak appear in the XRD curve. The sharp peak also found in the XRD data its mean there is crystal structure in the electrode samples such as CaCO$_3$. The CaCO$_3$ compounds are indicated to originate from the basic elements of TCL, that come from Ca elements. Table 2 shows the diffraction angle for plane 002 (2θ$_{002}$), the diffraction angle for plane 100 (2θ$_{100}$), the inter layer spacing for plane 002 (d$_{002}$), the inter layer spacing for plane 100 (d$_{100}$), the stack height (L$_c$), and the stack width (L$_a$) for the TCL500 and TCL700 electrode sample. The increasing carbonization temperature causes a shift in 2θ angle and modifies d$_{002}$, d$_{100}$, L$_c$, and L$_a$. The 2θ angle indicates the peak coverage of good carbon material possessed by TCL carbon electrodes [28]. The L$_c$ values for TCL500 and TCL700 samples are 14.048 Å and 8.482 Å and then use to calculate the surface area of the carbon electrode. The smaller L$_c$ values will result in the larger surface area.
The relationship of the stack height of the graphitic microcrystallite ($L_c$) and the SSA of the material is given by formula [2].

$$SSA_{xrd} = \frac{2}{(\rho_{xrd} L_c)}$$

Where $\rho_{xrd}$ is X-ray density given by the formula $\rho_{xrd} = \left\{ \frac{d_{002(\text{graf})}}{d_{002}} \right\} \rho_{(\text{graf})}$, the values of $d_{002(\text{graf})} = 0.33354$ nm and $\rho_{(\text{graf})} = 2.268$ g cm$^{-3}$. Based on the formula (2), the surface area of the TCL500 and TCL700 electrode are 725.374 m$^2$ g$^{-1}$ and 1160.497 m$^2$ g$^{-1}$, respectively.

### Specific Capacitance Analysis using the Cyclic Voltammetry Method

The curve of current density (A cm$^{-2}$) vs voltage (V) at a 1 mV s$^{-1}$ scan rate was measured using the cyclic voltammetry method in 1 M H$_2$SO$_4$ solution shown in Figure 5. Figure 5 shows the curve of the charging-discharging current for all samples. The TCL500 electrode shows the supercapacitor cell with the smallest I-V curve indicated a smallest specific capacitance. The TCL700 electrode has the largest I-V curve. It shows the highest specific capacitance. The highest specific capacitance is obtained at a 700 °C carbonization temperature. It is indicating that this temperature is the optimum temperature for the carbonization process. The specific capacitance of the supercapacitor cell has a decreasing at the TCL800. This may be indicated at too high a carbonization temperature will cause the pores that have been formed will be damaged so that specific capacitance produced is smaller.
Based on the equation (1), the specific capacitance for supercapacitor cell with various electrodes shown in Table 3. Where the TCL700 electrode with the highest specific capacitance supported by the smallest density and stack height, the highest surface area and carbon content. Previously reported studies with different biomass produced specific capacitances that are almost the same as this study, i.e. biomass of banana stem [16] and bamboo [30] with a specific capacitance of 68 F g\(^{-1}\) and 60 F g\(^{-1}\), respectively.

**Table 3. Specific capacitance values of supercapacitor electrode at a scan rate of 1 mVs\(^{-1}\).**

| Samples | Mass (g) | s (mVs\(^{-1}\)) | Ic (A) | Id (A) | Csp (F g\(^{-1}\)) |
|---------|----------|-----------------|--------|--------|-------------------|
| TCL500  | 0.0088   | 0.001           | 0.000159 | 0.000068 | 25                |
| TCL600  | 0.0082   | 0.001           | 0.000222 | 0.000136 | 44                |
| TCL700  | 0.0084   | 0.001           | 0.000388 | 0.000070 | 54                |
| TCL800  | 0.0100   | 0.001           | 0.000249 | 0.000100 | 35                |

4. Conclusions
Based on all results and discussion carried out it can be concluded that the 700 °C is the best carbonization temperature in production of carbon electrode made from Terminalia Catappa Leaf. This temperature carbonization produced the carbon electrode with the optimum physical properties such as smallest density, higher carbon content, and the largest surface area with particles in the form of nanofibers with a diameter range of 32 nm to 108 nm. The optimum physical properties supported to found the best supercapacitor electrochemical properties.

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