The relationship of surface area to cell capacitance for monolith carbon electrode from biomass materials for supercapacitor application

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Abstract: In this paper, the activated carbon monolith (ACM) for the supercapacitor electrode is produced from different raw materials and methods. Carbon electrodes made from several materials such as rubberwood sawdust (RWSD), mission grass flower (MGF) and banana peel (BP). Preparation of the carbon electrode begins with a pre-carbonization process at a temperature of 250 °C and followed by grinding the sample, then chemically activated using several activator agents such as KOH, ZnCl₂, and NaOH. The sample is then formed into a pellet form with a pressure of 8 tons using a Hydraulic press and followed by carbonization and physical activation using a furnace in the temperature range of 600-900 °C. The difference in the electrode production process was intended to obtain the difference in samples specific surface area. The specific surface area was carried out by N₂ gas adsorption-desorption method while the specific capacitance was performed by using Cyclic Voltammetry method. The surface area and capacitance are obtained by multiplying the mass on the data of specific surface area and specific capacitance. Based on the results it has been found that the capacitance of the supercapacitor cell increases linearly with the increase of the electrode surface area.

1. Introduction
Supercapacitor or electrochemical double layer capacitor (EDLC) is an energy storage device having a high power density, high cycle efficiency and long life cycle [1]. The EDLC energy storage mechanism is different from the batteries. The batteries stores energy based on chemical reaction, while the EDLC stores system based on pure electrical mechanism, its involve the ion-electron pair that exist at the interface of electrode and electrolyte [2,3,4]. The supercapacitor consists of several parts such as carbon electrode, current collector, electrolyte and separator.

The surface area of electrode (A) is one of the major factors determining the performance of a supercapacitor [5]. The surface area of carbon electrode is determined based on the total surface area of the micropore, mesoporous and macropore. The surface area relate to the ability of the ion to
Diffusion into the pores of the carbon electrode to form an ion-electron double layer [6]. The double layer capacitance is known to be directly proportional to $A$ and inversely proportional to the distance from the surface of the electrode to the center of the ionic layer ($\delta$), so the higher surface area of electrode or the lower the distance from the surface of the electrode to the center of the ionic layer produce the higher cell capacitance [7]. The surface area of the carbon material can be improved by using the activation method. The activation method can be divided into two type that is chemical activation and physical activation method [8]. Chemical activation is performed by mixed the raw material with chemicals activated agent such as KOH, ZnCl$_2$, H$_3$PO$_4$, NaOH, while physical activation is carry out using certain temperature in the CO$_2$ gas atmosphere. In this study we will examine the relationship of surface area of carbon electrode from rubber wood sawdust biomass (RWSD), mission grass flower (MGF) and banana peel (BP) to the cell capacitance of the its electrode.

2. Experimental method

The main materials used in this study consist of several biomass materials such as RWSD, MGF and BP. These materials were used as the starting material for the produced of carbon electrodes. Supporting materials used include KOH, ZnCl$_2$, NaOH, distilled water, acrylic sheet, teflon, duck egg shell membrane and stainless steel. The raw material was pre-carbonized at a temperature of 250 °C and followed by a grinding process using a ballmiling to produce a pre-carbon powder. Samples were chemically activated using several activator materials such as KOH, ZnCl$_2$, and NaOH. The monolithic green carbon electrode was formed by pressing at a pressure of 8 tons using a Hydraulic press [9,10], subsequently production of the carbon electrode is carried out through the carbonization and activation process using a furnace at a temperature of 600-900 °C. Before the supercapacitor cell assembling and measuring the electrodes are polished to a certain thickness and washed using distilled water until the pH washing water becomes neutral. The method of preparing carbon electrode monolith and the activation material for various sample completely shown in Table 1, while the production process is shown in Figure 1.
Table 1. Type of materials, activator agent, carbonization temperature and physical activation temperature

| Sample Code | Materials | Chemical activation | Carbonization Temperature | Physical activation temperature |
|-------------|-----------|---------------------|---------------------------|--------------------------------|
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
|             |           | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |
| ACM1        | ACM 2     | ACM 3              | ACM 4                     | ACM 5                          | ACM 6                          | ACM 7                          | ACM 8                          | ACM 9                          | ACM 10                         | ACM 11                         | ACM 12                         | ACM 13                         | ACM 14                         | ACM 15                         | ACM 16                         | ACM 17                         | ACM 18                         | ACM 19                         |

Characterization of carbon electrode include physical properties test using N₂ gas adsorption-desorption method to know the specific surface area of electrode and electrochemical properties test using Cyclic Voltammetry (CV) method to find out the value of specific capacitance of supercapacitor cell. The N₂ gas adsorption-desorption test was performed by Brunauer Emmet Teller (BET) method using Quantachrome Instruments version 11.0. The CV measurement were performed using Physics CV UR Rad-Er 5841 and it was calibrated with standard VersaStat II Princeton Applied Research calibrator tool. The CV test was performed at 0 – 0.5 V potential window and 1 mVs⁻¹ scan rate [11,12,13]. The specific capacitance value (Csp) of the supercapacitor cell can be calculated using the following equation 1.

\[
C_{sp} = \frac{Ic - Id}{sxm}
\]

Where Csp, I, s and m are specific capacitance (Fg⁻¹), current density (Am⁻²), scan rate (mVs⁻¹) and mass of electrode (g), respectively. The relationship of supercapacitor capacitance to the surface area is theoretically expressed by using the following equation 2.

\[
C = \frac{\varepsilon}{4\pi\delta}
\]

Where C is the capacitance, A is the surface area of the electrode, ε is the electrolyte dielectric constant, δ is the distance from the surface of the electrode to the center of the ionic layer [7].

3. Results and Discussion

Based on the results of N₂ gas adsorption-desorption test and electrochemical properties using cyclic voltammetry, obtained a relationship between the specific surface area and the specific capacitance for difference carbon electrode made from various raw material and its shown in Fig. 2. The carbon electrodes made from RWSD were produce by using three type categories such as: (i) variation of
KOH concentration, (ii) the variation of activator agent such as NaOH, KOH, ZnCl₂ and (iii) the addition of Sodium Dodecyl Sulfate (SDS) surfactant on the KOH activated agent show the different value on specific surface area and specific capacitances, shown by red color. An increasing in both specific surface area and specific capacitance of carbon electrode is indicated by each type variation in the RWSD sample.

The carbon electrodes from MGF were shown by green color with various by three type of sample preparation process: (i) physical activation temperature using CO₂ gas, (ii) KOH concentration and (iii) particle size assisted by chemical activation using NaOH shows increased specific surface area and specific capacitance. While the carbon electrodes from BP were produce by using variation in the temperature of: (i) physical activation using CO₂ gas and (ii) carbonization using N₂ gas, It's also shows an increase in specific surface area and specific capacitance for each variation and mark by the blue color. The highest specific capacitance of the carbon electrodes was found on the ACM15 sample made from MGF indicated by green triangle, while the highest specific surface area was found on the ACM8 sample made from RWSD indicated by red triangle.

The carbon electrodes from RWSD and MGF showed higher specific surface area and specific capacitance compared to the carbon electrode from BP, the difference was due to the dissimilar preparation process of carbon electrodes, in which the carbon electrodes from RWSD and MGF are made by compression pressure into shapes a pellet form while the BP electrodes was prepare by made casting technique into a form of carbon electrodes [14]. In general, for all raw material it is seen that the increase in the specific surface area of the carbon electrode followed by an increasing in the specific capacitance of the supercapacitor cell. The other studies showed a similar results, in which the higher specific surface area of electrode was produced a higher specific capacitance also [15,16].

![Figure 2](image)

**Figure 2.** Relation of specific surface area to the specific capacitance of supercapacitor cell carbon electrodes

The relation of surface area and cell capacitance was shown in Figure 3. The cell capacitance data and surface area in Figure 3 were obtained by multiplying the specific capacitance and specific surface area with the average mass for each sample. These data shows little difference with data of specific surface area and specific capacitance in Figure 2. The surface area and the cell capacitance were influenced by the electrode mass for each sample. The higher of electrode mass, the higher surface area and cell capacitance. The highest cell capacitance was found on the ACM3 sample made from RWSD and it shown by the red circle in Figure 3. The highest surface area of the electrode was found
on the ACM8 sample made from RWSD and shown by the red triangle. The lowest surface area and cell capacitance was found on the ACM16 sample made from BP shown by the blue circle.

Generally, Figure 2 and 3 show a similar trend in which an increase in the specific surface area corresponds to an increase in the surface area of the electrode, whereas the increase in the specific capacitance related to the cell capacitance. The relation of the specific surface area and the specific capacitance in Fig. 2 and the relation of the surface area and the cell capacitance in Fig. 3 were fitted by SigmaPlot12.5 software using linear equations giving a different in slope (a) values. The results of this fitting show different values in a slope (a) where Figure 2 has a slope of 0.113 while Figure 3 has a slope of 0.122, the detail linear equations were insert in Figure 2 and 3, respectively. These experimental data agree with the theoretical study as shown by equation 2, where the capacitance of the supercapacitor cell (C) is directly proportional to the surface area (A) and inversely proportional to the distance from the surface of the electrode to the center of the ionic layer (\( \delta \)), so that the higher of surface area of the electrode resulting the higher cell capacitance.

![Figure 3](image)

**Figure 3.** The relationship of the surface area to the cell capacitance of the supercapacitor cell carbon electrodes

4. Conclusions

Based on all data analysis it can be concluded that the difference in raw material and production process of the carbon electrodes monolith shows the same data trend, where the specific capacitance increased with the increasing specific surface area. The same result is shown by the cell capacitance and the surface area of the electrode. This result proves theoretical study, in which the surface area of the electrode affects the cell capacitance.

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