Supercapacitor Electrodes Based on Corn Stalk Binderless Activated Carbon

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Abstract. Activated carbon electrodes from cornstalk core waste have been produced using combination of chemical and physical activation for supercapacitor application. Cornstalk was processed into self-adhesive carbon grains. The chemical activation of self-adhesive carbon grains was conducted using 0.4 M KOH at room temperature, and simultaneously followed by carbonized at 600°C in N2 environment, and physical activation in the CO2 environment with difference temperature of 600, 700 and 800°C using a multi-step heating profile. The physical properties of the cornstalk based activated carbon electrode which involve microstructure, functional groups and porosity parameter were evaluated using X-ray diffraction, Fourier transform infrared analysis, and N2 adsorption/desorption isotherm at 77K, respectively. The electrochemical measurement of supercapacitor cells was conducted using cyclic voltammetry technique. The activation temperature of 700°C resulted cornstalk based activated carbon electrode with a higher BET surface area of 826 m2/g and stack diameter of 1.0461 nm, corresponding to higher of specific capacitance of 109 F/g.

1. Introduction

Economic growth and development as well as an increase in population result in depletion of energy resources [1]. So that there is a need for sustainability in the development of renewable energy sources that are focused on increasing energy density and environmental problems. This renewable energy source prioritized in the development of electric vehicles, hybrid electric vehicles, and energy-saving devices [2].

Supercapacitor is one of the energy storage systems that can be recharged and is considered as one of the most attractive in terms of high power density, relative short charge and discharge time (CDC), long life cycle, and simple cell repair [3-5]. Supercapacitor, based on the storage mechanism, are classified into two types, i.e. (1) electric double-layer electrochemical capacitors (EDLC), which is charge discharge accumulation in the double layer produce by electrostatic forces on the electrode and electrolyte interface [6,7], and (2) pseudocapacitors which come from a redox reaction on the electrode [8]. Compared to EDLC, the commercial application of pseudocapacitor material are limited because it produces weak electrical conductance, poor compatibility, and narrow potential window. These disadvantages are due to organic electrolytes use and short life cycle.

The most important components of the supercapacitor are electrode and electrolyte, where the storage of charge takes place on the electrode and electrolyte interface, therefore surface area of the electrode and electrolyte greatly affect the performance of the device. Electrode properties such as
material types, electrode thickness, surface area, and pore size distribution greatly determine supercapacitor performance [9]. One of the electrode materials that is often used is activated carbon which good physical and electrochemical properties, high availability, low price and easy preparation methods.

Stalk or wood biomass based activated carbon has the potential to develop pore structures. This material has been widely used as an absorber in various applications. There are two main processes to make activated carbon from biomass materials, namely carbonization and activation. The carbonization process based on the stalk produces low porosity and their structure consists of slit-like pores filled by pyrolysis products [10]. In the activation process, the pores covered by tar will open and form porous structure.

Activated carbon with micro, meso and macro structures has electrochemical performance better compared to single-sized pore material [11]. However, activated carbon has a wide distribution and randomly arranged micro, meso and macropores. The irregular intrinsic pores of the activated carbon limit the access of electrolyte ions during the charge and discharge process. Experiments and control over the surface area and pore size of the electrode material are needed [12].

In the present study, the activated carbon was synthesized from cornstalk core using combination of chemical-potassium hydroxide and physical activation. Carbonization and activation were conducted simultaneously. Chemical activation is a method that is widely used in carbon synthesis. The most important advantage of chemical activation is the possibility to synthesize high specific pore carbon material, close to the theoretical limit for carbon material [13]. Physical activation was carried out by combustion in the atmosphere of CO$_2$ gas and by varying the temperature of activation of 600 °C, 700 °C, and 800 °C. The supercapacitor cells made of cornstalk based activated electrode were measured using cyclic voltammetry method.

2. Materials and Methods

2.1. Preparation of activated carbon
Cornstalk core was used as a precursor to produce activated carbon using combination of chemical and physical activation. The cornstalk was collected from smallholder corn farm in vicinity of University of Riau campus. Pre-carbonization of cornstalk core with size of 5 mm was conducted in electric oven at temperature of 250 °C and followed by milling and sieving to obtain grain with particles size less than 100 μm. Chemical activation of pre-carbonized carbon grains was carried out using potassium hydroxide (KOH) as an activating agent. The pre-carbonized carbon grains were mixed into 0.4 M KOH for 3 hours at the temperature of 80 °C and then neutralized using distilled water until pH reach ~7. The carbon grains were converted into coin type of pellet without binder using a mold with 2 mm in diameter and 8 metric ton of compressive pressure.

Carbonization and physical activation were conducted simultaneously. The carbonization of coin type of pellets was conducted up to 600 °C in N$_2$ atmosphere using our multi step heating profile [14] and then physical activation using CO$_2$ with flow rate of 1.5L/min for 3 hours. The temperatures of activation were varied i.e. 600, 700 and 800 °C. The coin type of pellets was polished to thickness of 0.3 mm and then washed using distilled water and DI water until the pH of solution achieve 7 and they used as electrode. The cornstalk based activated carbon electrodes were labeled as AC600, AC 700 and AC800 correspond to activation temperature of 600, 700 and 800 °C, respectively. The symmetrical supercapacitor cells were constructed by sandwich model. Layers of the supercapacitor cell are constructing by current collector (stainless steel 316L), activated carbon electrode, separator (duct egg shell), activated carbon electrode, and current collector.

2.2. Physical and electrochemical properties
The cornstalk based activated carbon electrodes were characterized to find the physical properties, i.e. microstructural using X-ray diffraction, element composition using energy dispersive X-ray, porosity parameters such as BET surface area, total pore volume and diameter pore using N$_2$
adsorption/desorption isotherm, and concentration of hydroxyl group using Fourier transform infrared. Electrochemical property of supercapacitor cell was analyzed using cyclic voltammetry (CV) method. Specific capacitance \( C_{sp} \) of supercapacitor cells were calculated using equation (1):

\[
C_{sp} = \frac{I_c - I_d}{s \times m}
\]

(1)

where \( C_{sp} \) is specific capacitance (F/g), \( I_c \) is current at charge (A), \( I_d \) is current at discharge (A), \( s \) is scan rate (mV/s), and \( m \) is mass of electrode (g).

3. Results and Discussion

3.1. Physical properties of activated carbon

Microstructure of cornstalk based activated carbon was conducted using X-ray diffraction. X-ray diffractogram of AC700 and AC800 were shown in Figure 1. There are two types of peak, broadening peaks and sharp peaks. The positions of two broadening peaks are at 2\( \theta \) around 24.7\(^o\) and 43.9\(^o\) which associated with diffraction plane of (002) and (100), respectively. The two broadening peaks indicated typical cornstalk based activated carbon pattern. The three sharp peaks are located at 29.5\(^o\), 35.1\(^o\) and 57.4\(^o\) which indicate CaCO\(_3\). CaCO\(_3\) is natural compound in the cornstalk. The presence of CaCO\(_3\) in the activated carbon is due to the temperature of 700 \(^o\)C and 800 \(^o\)C which is not sufficient to eliminate the CaCO\(_3\). According to Tampieri et al. [15], the CaCO\(_3\) will evaporate at the temperature of 1484 \(^o\)C.

![Figure 1. XRD pattern of activated carbon](image)

| Sample | Interlayer spacing (nm) | Microcrystalline dimension (nm) | \( L_c \)/\( L_a \) |
|--------|--------------------------|--------------------------------|-------------------|
| AC700  | 3.6011                   | 13.3736                        | 0.5560            |
| AC800  | 3.5858                   | 11.5305                        | 0.4158            |

The microstructure of cornstalk based activated carbon i.e. interlayer spacing \( d_{hkl} \) and microcrystalline dimension (stack height \( L_c \) and stack diameter \( L_a \)) relating to diffraction peaks (002) and (100) respectively were calculated using Bragg equation, \( n\lambda = 2d \sin \theta \) and Scherer equation, \( L_{c,a} = \frac{K\lambda}{\beta_{c,a}\cos \theta} \) respectively, where \( K \) is shape factor (0.89 for \( L_c \) and 1.84 for \( L_a \)), \( \beta \) is full width at half maximum and \( \theta \) is diffraction angle. The microstructure data was listed in Table 1. All
data as shown in Table 1 are obtained from fitted X-ray diffraction data using microcal origin software before calculated.

The interlayer spacing of cornstalk based activated carbon both of AC700 and AC800 are not significantly different. The interlayer spacing $d_{002}$ and $d_{100}$ were decrease with increasing temperature of physical activation. The decrement of interlayer spacing indicated effect of temperature of physical activation. Increasing in temperature of physical activation caused decrease of $L_c$ and increase of $L_a$. The decreasing of $L_c$ at the temperature of 800 °C was caused by excessive oxidation during activation vice versa the $L_a$ increase with increasing temperature of physical temperature [17]. The variation of $L_c$ and $L_a$ as shown in Table 1 with the higher temperature of physical activation resulted the number of graphitic layers in microcrystalline reduce. The number of graphitic layers were calculated using ratio of $L_c$ and $d_{002}$ [18,19]. Ratio of $L_c$ and $L_a$ represents the relative density of the edge and basal planes in microcrystalline [19]. The $L_c/L_a$ ratio can be used as referral to surface area analyze. The ratio of $L_c/L_a$ is proportional to surface area of cornstalk based activated carbon [20].

Elemental composition of cornstalk based activated carbon was carried out using energy dispersive X-ray. Figure 2 shows the elemental atomic percentage composition consists of C, O and Ca. The temperature of activation influence the percentage of C, O and Ca content. The C contents increase with increasing the temperature of activation on the contrary O and Ca decreased. The atomic percentage of C, O and Ca were found to be 96.29%, 3.39% and 0.32% respectively for AC700 and 97.28%, 2.42% and 0.30 respectively for AC800.

![Elemental composition of cornstalk based activated carbon for (a) AC700 and (b) AC800](image)

**Figure 2.** Elemental composition of cornstalk based activated carbon for (a) AC700 and (b) AC800

The FT-IR spectra of cornstalk based activated carbon was shown in Figure 3. The presence of diverse surface functional groups on the activated carbon contributes to privileged uptake for different molecule species [21]. The C-H function groups were detected by stretching vibrations at wave numbers 2877 cm$^{-1}$ and 860 cm$^{-1}$. The carbonization and activation processes have also produced stretching vibrations C = C at the peak of 1522 cm$^{-1}$. This C = C aromatic ring is a constituent of the structure of activated carbon. Peak at wave number of 1311 cm$^{-1}$ is due to C-N vibration [22]. This C-N occurs because of a reaction between the N$_2$ and carbon produced during carbonization process. The FT-IR resulted as shown in Figure 3 indications a very complex activated carbon surface. The carbon chain plays an important role in the forming of double layers in supercapacitor electrodes.
Figure 3. FT-IR spectra of cornstalk based activated carbon for AC700 and AC800

Figure 4 shows the N$_2$ adsorption/desorption isotherm of cornstalk based activated carbon for AC700 and AC800 recorded at 77 K (AC600 is not shown here). The isotherm of AC700 and AC800 have similar pattern showing a combination of types I and IV shape according to IUPAC standard [23] which indicated the activated carbon prepared from cornstalk core is porous carbon containing a combination of micro and mesopore. At the beginning of relative pressure (< 0.2), the volume adsorption is increase rapidly which indicated the micropores presence, which is followed by volume adsorption increase with increasing the relative pressure up to 0.95. From Figure 4, the adsorption and desorption curve shows the hysteresis loop clearly, which shows the presence of mesopores.

Figure 4. N$_2$ adsorption/desorption isotherm of AC700

The porosity parameter data were calculated from the N$_2$ adsorption/desorption isotherm data as listed in Table 2. The temperatures of physical activation significantly influence on the BET surface area with the highest of BET surface area of 826 m$^2$/g for AC700. The BET surface area of AC700 was predicted previously by the highest stack height $L_c$. The BET surface area increased with
increasing temperature of physical activation as high as 700 °C and the BET surface area slightly decreased at the temperature of physical activation of 800 °C. All of cornstalk based activated has an average pore diameter less than 2 nm which means the pores have micropores dimension.

### Table 2. Porosity parameter of AC700

| Sample  | $S_{\text{BET}}$ (m$^2$/g) | $V_{\text{Tot}}$ (cm$^3$/g) | Average diameter (nm) |
|---------|-----------------|-----------------|-----------------|
| AC600   | 320             | 0.1807          | 1.1280          |
| AC700   | 826             | 0.4318          | 1.0461          |
| AC800   | 294             | 0.1638          | 1.0684          |

#### 3.2. Physical properties of activated carbon

Cyclic voltammogram of supercapacitor cells using 1 M H$_2$SO$_4$ as electrolyte solution are shown in Figure 5 over the potential measured range of 0 – 0.5 V at the scan rate of 1 mV/s. All supercapacitor cells exhibit a typical shape of cyclic voltammogram and have a nearly symmetrical at the zero current axes. The curves show a rectangular like shape indicating the good electrochemical properties of cornstalk based activated carbon electrode. There is no evident peak at the middle of potential region designating the absence of pseudocapacitive properties. The charge discharge reaction of the supercapacitor cells is nearly electrostatic. The area of rectangular of AC700 is broader than AC600 and AC800 that indicating the temperature of activation of 700 °C has the specific capacitance higher. It can be seen that the negative branch of cyclic voltammogram is flatter than the positive branch. The negative and positive branch difference suggests that the electrodes charging with anions of electrolyte solution produces a steady state that is the electrical potential more influent than charging with cations of electrolyte solution [19]. The $C_{\text{sp}}$ were calculated from cyclic voltammogram data using equation (1). The $C_{\text{sp}}$ of supercapacitor cells are 77, 109 and 70 F/g for AC600, AC700 and AC800 respectively. The $C_{\text{sp}}$ valued of cornstalk based activated carbon electrodes corresponds to the higher BET surface area and stack height $L_c$ as predicted above.

![Figure 5. Cyclic voltammogram of AC600, AC700 and AC800 at the scan rate of 1 mV/s](image)

#### 4. Conclusion

The preparation of cornstalk core based activated carbon electrodes for supercapacitor application has been done using combination of chemical-KOH activation and physical-CO$_2$ activation. Activated carbon electrodes were processed simultaneously by carbonization and activation. The resulting
activated carbon electrodes have a semicrystalline structure which indicated by two broader peaks. The temperatures of activation have affected the physical properties and performance of supercapacitor with the optimum temperature of 700 °C. The L_{ac} atomic carbon content, BET surface area and specific capacitance of AC700 are 13.3736 nm, 96.29%, 826 m²/g, and 109 F/g, respectively. The processes of activated carbon electrodes are low cost with high electrochemical performance.

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