The Physical and Electrochemical Properties of Activated Carbon Electrode Derived from Pineapple Leaf Waste for Supercapacitor Applications

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Abstract. This study aims to the physical and electrochemical properties of the supercapacitor carbon electrodes derived from pineapple leaf waste. The production of carbon electrodes was conducted using combinations of chemical activation, carbonization, and physical activation. The chemical activation was carried out using a 0.9 M KOH activator. The carbonization and physical activation were conducted using a one-step process. The PAL-AC electrode was obtained showed porosity in the mesoporous range, large pore volume, and high specific surface area. The surface morphology of the PAL-AC electrode is dominated by carbon and nanofibers particles. The nanofibers diameter based on the SEM micrograph is in the range of 44-137 nm. Elemental contents of the PAL-AC electrode are dominated by carbon and oxygen with an atomic percentage of 86.03% and 9.49%, respectively. The XRD pattern of the PAL-AC electrode shows the presence of two wide peaks at scattering angle of 23° and 45°. The specific capacitance of the PAL-AC electrode as high as 127 F g⁻¹ in 6 M KOH electrolyte solution using two-electrode configuration. The pineapple leaf waste based-carbon electrodes show promising potential for use as supercapacitor electrodes.

1. Introduction
The increasing environmental problems and the reduction in resources at this time are caused by the dependence of energy consumption on fossil fuels so that it is estimated to cause problems in the world economic and ecological. With increasing dependence on fuel cells energy, the search for clean, sustainable, and renewable resources is urgently needed for the development of green, high-performance electrochemical energy storage systems. Supercapacitors or electrochemical capacitors have a higher power density, better cyclic efficiency, acceptable energy efficiency, cost-effectiveness, and highly reliable operational features are considered to be the best choice among existing energy storage devices [1,2]. The electrode materials are one of the most important components for charge storage in the supercapacitor, which influences the capacitive performance of the electrochemical capacitors in terms of energy and power density.

Carbon materials with their high surface area (SSA), well-developed pore size distribution, relatively low cost, physical and chemical stability, and a wide range of operating temperatures more preferred to used as supercapacitor electrodes [3,4]. In recent years, biomass waste-based carbon materials are preferred for use as electrodes in supercapacitor devices. Biomass-waste materials such as ginkgo biloba leaves [5,6], willow leaves [7,8], pineapple leaves [9,10], acacia leaves [11],
terminalia cattapa leaves [12], eucalyptus leaves [2], etc. have been widely used as raw materials for supercapacitor carbon electrodes.

Besides the electrodes, the electrolyte is one of the most essential and significant constituents in supercapacitors and plays a very crucial role in transferring and balancing charges between the two electrodes [13]. The electrolytes for supercapacitors are classified into various categories such as liquid electrolytes, solid-state or quasi-solid-state electrolytes, and redox-active electrolytes. The key to safe and high performance supercapacitive devices is on the choice of electrolyte [13].

In this study, we used pineapple leaf waste as a raw material for the production of supercapacitor carbon electrodes. The production of carbon electrodes was carried out using combination of chemical activation, carbonization, and physical activation. The chemical activation was carried out using a 0.9 M KOH activating agent. The carbon electrodes obtained showed porosity in the mesoporous range, large pore volume, and high specific surface area. The pineapple leaf waste-based carbon electrodes showed good capacitive properties performance with specific capacitance as high as 127 F g$^{-1}$ in 6 M KOH electrolyte solution using two-electrode configuration. Based on the electrochemical properties measurements results, the pineapple leaf waste based-carbon electrodes show promising potential for use as supercapacitor carbon electrodes.

2. Experimental method

2.1. Preparation of activated carbon

The initial treatment of the pineapple leaf (PAL) includes (i) washing, (ii) cutting with a size of $\pm 5$ cm, (iii) sun-dried for 24 hours, (iv) drying at a temperature of 110 °C using an oven for 48 hours, and (v) pre-carbonization process. The process of pre-carbonization of pineapple leaf waste refers to we have reported previously study [14–17]. The pre-carbonized powder was then milled for 20 hours and continued sieving with a size of 53 µm. Furthermore, the chemical activation process of pre-carbonization of the PAL using KOH with a concentration of 0.9 M. After these process, the sample converted into pellet form using a hydraulic press with a pressure of 8 tons [18,19], followed by the process of carbonization and physical activation. The carbonization was carried out at 600 °C in the N$_2$ gas atmospher and followed by physical activation using CO$_2$ gas for 2.5 hours at temperature of 850 °C with heating rate 10 °C min$^{-1}$. The next process is washing the pellets using distilled water until neutral pH (pH~7). The sample was labelled PAL-AC electrode.

2.2 Characterization of activated carbon

2.2.1. Physical characterization of activated carbon.

The physical properties characterization of the activated carbon from pineapple leaf includes N$_2$ gas adsorption-desorption isotherm, surface morphology, elemental content, and crystallinity structure. The measurement of N$_2$ gas adsorption-desorption isotherm was carried out using a Quantachrome Touch Win v1.2 instrument at a temperature of 77 K. Scanning electron microscopy and energy dispersive X-ray (JEOL-JSM 6510LA) are used to characterize surface morphology and elemental content. The crystallinity structure was characterized using X-ray diffraction (Simadzu 7000) with CuK$_\alpha$ source and 0.154 nm of wavelength ($\lambda$).

2.2.2 Electrochemical properties characterization

The electrochemical properties of electrode was performed by using cycling voltammetry method in the 6 M KOH electrolyte solution with two-electrode configuration. The CV measurement was carried out using potential windows range of 0-1 V with scan rate 1 mV s$^{-1}$. The specific capacitance of the electrode was calculated the following equation.

$$C_p = \frac{2I}{Sm}$$

Where $C_p$ is specific capacitance (F g$^{-1}$), I is the current (A), S is the scan rate (mV s$^{-1}$) and m is the electrode mass (g). The energy density (E) and power density (P) is given by equation [5,6,20].
\[ E = \frac{1}{2} C_{sp} V^2 / 3.6 \]  
\[ P = \frac{E}{\Delta t} 3600 \]

Where \( E \) is energy density (Wh kg\(^{-1}\)), \( C_{sp} \) is specific capacitance (F g\(^{-1}\)), \( V \) is the cell voltage (V), \( P \) is the power density (W kg\(^{-1}\)), and \( \Delta t \) is discharge time (s).

3. Result and Discussion

3.1 The physical characterization of PAL-AC electrode

The specific surface area and pore structure of the PAL-AC electrode was investigated using N\(_2\) gas adsorption-desorption isotherm at temperature of 77 K (Figure 1). The specific surface area was calculated using the BET method (Figure 1a) and the pore size distribution was evaluated using the BJH method (Figure 1b). The isotherm curve exhibits type IV according to the IUPAC classification with the presence of hysteresis loops that appear at the relative pressure \( P/P_0 = 0.43-0.99 \), which can be attributed to capillary condensation in mesoporous size for carbon materials [21–23]. The highest specific surface area (\( S_{BET} \)) of PAL-AC electrodes is 992 m\(^2\) g\(^{-1}\) with a total pore volume of 0.529 cm\(^3\) g\(^{-1}\). The pore size distribution based on the BJH method of the PAL-AC electrode in a range of >2 nm.

![Figure 1](image_url)

**Figure 1.** (a) The N\(_2\) gas adsorption-desorption isotherm at 77 K and (b) Pore size distribution of the PAL-AC electrode

The surface morphology of the PAL-AC electrode is shown in Figure 2a, it appears that the electrode is dominated by carbon and nanofibers particles. Carbon particles formed have an irregular structure. The nanofibers formed on the PAL-AC electrode are derived from pineapple leaves which naturally contain nanocellulose. The nanofibers diameter of the PAL-AC electrode based on the SEM micrograph in the range of 44-137 nm.

Figure 2b shows the elemental content based on the energy X-ray dispersive spectroscopy (EDS) characterization in the PAL-AC electrode. The elemental contents in the PAL-AC electrode consist of carbon (C), oxygen (O), magnesium (Mg), potassium (K), and calcium (Ca). The PAL-AC electrode is dominated by carbon and oxygen with an atomic percentage of 86.03% and 9.49%, respectively.
Figure 2. (a) The surface morphology of the PAL-AC electrode at 40,000 times of magnification and (b) elemental contents of the PAL-AC electrode

Figure 3 shows the X-ray diffraction pattern of the PAL-AC electrode with scattering angle in the range of 10°-60°. The XRD pattern of the PAL-AC electrode shows the presence of two wide peaks at scattering angle (2θ) of 23° which reflected the graphite structure of the electrodes [10] and 45° which indicate that the electrode has an amorphous structure [24–26]. Furthermore, sharp peaks also are seen on the PAL-AC electrode, it was predicted to show the presence of calcium carbonate (CaCO₃) and cellulose (C₆H₁₀O₅) on the electrodes [14,27].

Figure 3. XRD pattern for PAL-AC electrode

3.2 The electrochemical properties of PAL-AC electrode
Figure 4 show the electrochemical properties of the PAL-AC electrode based on cyclic voltammetry method. Figure 4 (a) show the cyclic voltammogram of the PAL-AC electrode in the 6 M KOH electrolyte solution using two-electrode configuration. The CV curve has almost like-rectangular shape which indicates a presence contribution of double-layer capacitance on the electrodes. This shape is an ideal for supercapacitor electrodes based-carbon materials [28]. The specific capacitance, energy density, and power density of the PAL-AC electrode are 127 F g⁻¹, 4.41 Wh kg⁻¹, and 10.59 W kg⁻¹, respectively.
Figure 4. (a) The CV curve of the PAL-AC electrode at a scan rate 1 mV s\(^{-1}\) and (b) The relationship between specific capacitance to the scan rate variation.

Figure 4 (b) show the relationship between specific capacitance to the scan rate variation. Based on these curves, the specific capacitance of the PAL-AC electrode at scan rates of 1, 2, 5 and 10 mV s\(^{-1}\) are 127, 122, 66, and 33 F g\(^{-1}\), respectively. The comparison capacitive properties performance of the PAL-AC electrode with various biomass materials completely are shown in Table 1.

Table 1. The comparison capacitive properties performance of the PAL-AC electrode with various biomass materials

| Materials             | Electrolyte | Specific capacitance (F g\(^{-1}\)) | Energy density (Wh kg\(^{-1}\)) | Power density (W kg\(^{-1}\)) | References |
|-----------------------|-------------|-------------------------------------|--------------------------------|-------------------------------|------------|
| Ginkgo Biloba leaves  | 6 M KOH     | 364                                 | -                              | -                             | [5]        |
| Willow leaves         | 6 M KOH     | 216                                 | -                              | -                             | [7]        |
| Hierarchically porous carbons | 6 M KOH | 61.5                                 | 8.42                           | 17.22                         | [29]       |
| Carbide               | 6 M KOH     | 120                                 | 5.7                            | 43.1                          | [30]       |
| Tree leaves           | 6 M KOH     | 367                                 | -                              | -                             | [31]       |
| Stiff silkworm        | 6 M KOH     | 235                                 | 7.9                            | 234                           | [32]       |
| Pineapple leaf        | 6 M KOH     | 127                                 | 4.41                           | 10.59                         | This work  |

4. Conclusion

The physical and electrochemical properties of pineapple leaf waste based-activated carbon electrode with combination of chemical activation, carbonization, and physical activation have been successfully investigated. The specific surface area (\(S_{BET}\)) of PAL-AC electrode which calculated by using BET method as high as 992 m\(^2\) g\(^{-1}\). The surface morphology of the PAL-AC electrode is dominated by nanofibers with diameter in the range of 44 nm - 137 nm. The elemental contents of the PAL-AC electrode is dominated by carbon and oxygen with an atomic percentage range of 86.03% and 9.49%, respectively. The PAL-AC electrode shows the presence of two wide peaks at 23° scattering angle and 45°. The specific capacitance, energy density and power density of the PAL-AC electrode based on the CV method as high as 127 F g\(^{-1}\), 4.41 Wh kg\(^{-1}\), and 10.59 W kg\(^{-1}\), respectively.

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