Less Expensive and Eco-Friendly Preparation of Activated Carbon Derived from Coffee Leaf as an Supercapacitors Electrode

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Abstract. In this paper, less expensive and eco-friendly biomass-based activated carbon from coffee leaf (CL) was prepared as electrode materials for supercapacitor applications using KOH activation, carbonization, and physical activation in a CO2 atmosphere. Using cyclic voltammetry and galvanostatic charge/discharge techniques, the CL sample was tested in a two-electrode configuration operating in 1 M H2SO4. After physical activation, the percentage reduction of the mass, diameter, thickness, and diameter are 76.47%, 29.38%, 28.57%, and 38.04%, respectively. The CL sample exhibits specific capacitance, energy and power densities of 210 F/g, 29.17 Wh/kg, and 39.99 W/kg at constant current 1 A, respectively. Therefore, the CL sample obtained through KOH activation, carbonization, and physical activation using CO2 atmosphere has a promising future applied as an electrode material for supercapacitor applications.

1. Introduction
In human civilisation, there has been a race for decades to develop an effective energy storage device to meet the demand of existing technology. In terms of charge storage capacity and cycle life, electrochemical capacitors or supercapacitors are much superior to regular capacitors and existing batteries [1,2]. The supercapacitor’s excellent energy storage performance reserves its wide application for electronics, automobiles, medical devices and other industrial applications [3–5]. The electrode material and electrolyte are the two main components of a supercapacitor. High specific surface area, distributed pores, and high electrical conductivity are typical characteristics of electrode materials [6].

Carbon materials are used as both positive and negative electrodes for symmetrical supercapacitors. Due to their high specific surface area and electrical conductivity, carbonaceous materials such as activated carbon [7–9], graphene [10,11], carbon nanotubes [12,13], and others are commonly used in conventional. Activated carbon (AC) has been extensively developed and mainly used in commercial devices to date. Compared to other forms of carbon, the production of AC is significantly less expensive. The biomass materials or petroleum by-product is usually used to produce it. AC is primarily prepared by pyrolyzing and activating biomass precursors including fallen teak leaf [14], Tectona grandis leaf [15], pineapple leaf [16], and Ginkgo biloba leaves [17,18], acacia leaf [19], etc.
have been investigated as electrodes for supercapacitor, demonstrating that high-performance supercapacitors can be achieved using such natural sources.

Coffee plants are woody evergreens that can be grow up to 10 m in the wild. The majority of the world’s coffee is grown arround the equator. The region covers parts of Central and South America, Asia, Africa and the Middle East. It is one of the most valuable commodity crops in the world and is a major export product from several countries including Central and South America, the Caribbean and Africa. 

*Coffea arabica*, also known as "Arabica" accounts for 60% to 80% of global production of coffee and *Coffea canephora*, known as the "robusta" represent approximately 20% to 40%, are the two most popular in the world [20].

Here, we report less expensive and eco-friendly preparation of activated carbon derived from coffee leaf in the development of electrode materials for supercapacitors. The preparation of activated carbon from coffee leaf by chemical activation, carbonization, and physical activation using CO$_2$ was investigated in this study. Coffee leaves are chemically activated with KOH, then carbonized at 600 °C in N$_2$ atmosphere and activated at a higher temperature with CO$_2$ atmosphere. The prepared activated carbon improved the electrochemical performance in a two-electrode configuration, displaying high specific capacitances with high energy and power densities.

2. Experimental method

In this study, coffee leaf (CL) was used as a raw material. The coffee leaf was sun-dried for two days before being oven-dried at 110 °C for 48 hours. The leaves were pre-carbonized for 2.5 hours at 250 °C after drying. The carbonized samples were mixed with KOH (concentration 0.5 M) in 150 ml destilled water before being heated in a hot plate stirrer for 2 hours at 80 °C. The activated sample was molded into a monolith using hydraulic press at 8 metric ton pressure, then carbonized at 600 °C under N$_2$ atmosphere and activated under CO$_2$ at 850 °C for 2.5 hours with a heating rate of 10 °C/min. The preparation process of the CL sample is shown in Figure 1.

![Pre-carbonized](image1)
![KOH activation](image2)
![Furnace](image3)

**Figure 1.** The CL sample preparation process.

This study examined the physical parameter and electrochemical properties of CL sample. Before and after activation, physical parameters such as mass, diameter, thickness, and density were calculated. The electrochemical measurements of CL has been assessed by cyclic voltammetry (CV) and galvanostatic charge/discharge (CV). Two-electrode configuration in 1 M H$_2$SO$_4$ solution has been used for these measures.
3. Result and discussion

Figure 2 display the shrinkage of physical parameters of CL samples before and after physical activation. After the physical activation process, the physical parameters include mass, diameter, thickness, and density of the CL samples have been shrinkage. The shrinkage percentage of the mass, diameter, thickness, and density are 76.47%, 29.38%, 28.57%, and 38.04%, respectively. The release of non-carbon materials when the physical activation take a place, causing the shrinkage of the physical parameters [21,22].

![Figure 2. CV curve of CL sample at different scan rates](image)

The electrochemical performance of the CL sample were tested using CV and GCD measurements in a two-electrode system. The CV curves of a CL sample measured at scan rates of 1 and 2 mV/s are shown in Figure 2. Obviously, the CV curves retain their quasi-rectangular shape across all scan rates. Based on CV curve, the specific capacitance of CL was calculated with the Equations (1):

\[
C_{sp} = \frac{I_c - I_d}{s \times m} \quad (1)
\]

where \(C_{sp}\) is specific capacitance (F/g), \(I\) is current (A), \(s\) is scan rate, and \(m\) is average mass of electrode (g). The specific capacitances of CL sample are 119 F/g and 108 F/g, respectively. It outperforms carbon-based electrodes reported in our previous study, such as Terminalia cattapa leaf (54 F/g) [23], pandanus tectoricus leaf (56 F/g) [24], and banana peel (68 F/g) [25].
Figure 3. The specific capacitance versus scan rates.

Figure 3 depicts the specific capacitance of the CL sample at various scanning rates. The CL sample’s specific capacitance has decreased at higher scan rates, it can be attributed to the CL sample has pore structure and larger micropore, as well as the relatively short diffusion time ions from the mesopores to the micropores [26].

Figure 4. GCD curve of the CL sample at constant current

Figure 4 shows the GCD curve of the CL sample. Noticeably, the lower relative IR drop (0.943 V) suggests a low equivalent series resistance (ESR). The specific capacitance of CL from the GCD curve was calculated by the Equations (2):
where $C_{sp}$ is specific capacitance (F/g), $I$ is current (A), $s$ is scan rate, $m$ is average mass of electrode (g), $\Delta t$ is discharge time (s), and $\Delta V$ is voltage (V). The calculated specific capacitance based on GCD curve was estimated to be 210 F/g at constant current 1 A. The energy and power densities of CL sample were calculated by the Equations (3) [27,28]:

\[ E = \frac{1}{2} CV^2 \times \frac{1}{\Delta t} \quad (3) \]

\[ P = \frac{E}{\Delta t} \times 3600 \quad (4) \]

where $E$ is energy density (Wh/kg), $P$ is power density (W/kg), $C$ is specific capacitance (F/g), $V$ is voltage (V), and $\Delta t$ is discharge time (s). The energy and power densities of the CL sample were calculated by equations 3 and 4 are 29.17 Wh/kg and 39.99 W/kg. It is worth noting that the assembled CL sample exhibits a higher energy density of 29.17 Wh/kg, higher than previously reported biomass-based carbon electrode for supercapacitors, such as *Syzygium cumini* fruit shells and *Chrysopogon zizanioides* roots (27.22 Wh/kg and 16.72 Wh/kg) [5], *Tectona grandis* leaf (23.19 Wh/kg) [15], pineapple leaf waste (4.41 Wh/kg) [16], banana peel (0.75 Wh/kg) [25], pineapple leaf fibers (26.53 Wh/kg) [29], aloe vera (8.6 Wh/kg) [30], cassava green stem (22.86 Wh/kg) [31], argy wormwood (17.51 Wh/kg) [32] and lumpy backet (9.4 Wh/kg) [33].

4. Conclusion

KOH activation, carbonization, and physical activation in a CO$_2$ atmosphere were used to preparation of activated carbon with less expensive and eco-friendly made from coffee leaf. In two-electrode configuration operating in 1 M H$_2$SO$_4$ solution, cyclic voltammetry and galvanostatic charge/discharge techniques were used to measured the electrochemical performance of the CL sample. The physical parameters of the CL sample i.e mass, diameter, thickness, and density have been shrinkage after physical activation process. The CL sample has a promising future for applied as an electrode material for supercapacitor applications based on their electrochemical performance. Specific capacitance, energy, and power densities for the CL sample are 210 F/g, 29.17 Wh/kg, and 39.99 W/kg, respectively.

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