Material characteristics and electrochemical performance of lithium-ion capacitor with activated carbon cathode derived from sugarcane bagasse

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Abstract. Lithium-Ion Capacitor (LIC), a hybrid energy storage device, is believed to be an ideal option for energy storage device applications due to its properties with high specific energy and high specific power. In this study, LIC’s cathode material is made of activated carbon derived from sugarcane bagasse prepared by the carbonization process at 500°C for 60 minutes and activation process utilizing KOH as an activating agent at varying temperatures and varying ratios of carbon to KOH mass. This paper also compares the material characteristic and electrochemical performance. In this paper, full cells of LIC are fabricated using activated carbon as the cathode material and LTO as the anode material. Sugarcane bagasse activated carbons are characterized by Scanning Electron Microscopy (SEM) and Brunauer Emmett Teller (BET). The electrochemical performance of LIC is obtained from cyclic voltammetry (CV) and charge-discharge (CD). Sugarcane bagasse activated carbon (SBAC) produces a high specific surface area with values from 1095 m²/g to 3554 m²/g. The assembled LIC can produce a maximum specific capacitance of 31.94 F/g, the highest specific energy of 35.49 Wh/kg, and high specific power of 2954.36 W/kg.

1. Introduction
The increasing consumption of primary energy in the world is also followed by the increasing use of fossil fuels, which results in the production of greenhouse gas emissions [1]. This consequently escalates the development of solar and wind power [2]. However, renewable energy cannot work properly and effectively without energy storage devices to adjust the input and output energy [3]. Lithium-ion batteries are the most commonly used device due to their high energy density (150-200 Wh/kg), but the slow process of Li⁺ diffusion on the electrodes creates small power density (<1000 W/kg) and low cycling life (<1000 cycles) [4]. Supercapacitors have the ability to go through the adsorption/desorption process of ions quickly [5], so they have high power density (>10 kW/kg) and great cycling stability (>10,000 cycles) [6] but their the energy density is limited (<10 Wh/kg) [7]. For this reason, a lithium-
ion capacitor is made from a combination of a lithium-ion battery and supercapacitor to have superior power and good energy density capabilities.

Activated carbon is a porous material that has a specific surface area value more than 2000m$^2$/g. There are three types of pores based on its size, namely micropores (<2nm), mesopores (2-50 nm), and macropores (>50 nm) [8]. Recently, activated carbon material made from biomass waste has attracted the attention of researchers because it is cheap, and abundant. It also encourages recycling habits for certain types such as rice husks [9], Chinese chives [10], and pitaya peel [11]. Sugarcane bagasse derived from the process of grinding sugarcane is one of them. Generally, sugarcane bagasse is used for a material mixture of paper pulp [12], animal food, and fertilizer [13]. New utilization is needed to increase its economic value. One of its ways is to use it as an activated carbon material. Sugarcane bagasse has a carbon content that reaches 24.7% [14]. Therefore, the potential use of sugarcane bagasse is quite promising.

In this study, sugarcane was used as the main material for cathode, and a commercial LTO was used as the anode material. The process of making activated carbon carried out by carbonization at a temperature of 500°C for 60 minutes continued by the activation process with a holding time of 90 minutes. The activated carbon produced was characterized by SEM and BET. The activated carbon produced then was made into a cathode and put together with the LTO anode on coin cell 2032. Coin cell of LIC was tested by Cyclic Voltammetry (CV) and Charge-discharge (CD).

2. Experimental Methods
2.1. Activated Carbon Production Process

The activated carbon production process is represented in Figure 1. The sugarcane bagasse was collected from a sugar industry located in Blora, East Java, Indonesia.

![Figure 1. Activated carbon production process](image)

In the first step, the sugarcane bagasse is meshed by 100 mesh to equate the sample size. Then it is dried up using an oven at 80°C for 12 hours to remove the water content. Then the bagasse is ground into a powder to equate the size of the bagasse. The next step is carbonization in which the bagasse is burned in a horizontal tube furnace at 500°C for 60 minutes with an argon flow rate of 500 cc/min. Then the carbonized bagasse is washed three times using distilled water to remove any impurities and then dried up overnight at 80°C.

| No | Sample Name | Carbon:KOH | Temperature |
|----|-------------|------------|-------------|
| 1  | SBAC600     | 1:3        | 600°C       |
| 2  | SBAC700     | 1:3        | 700°C       |
| 3  | SBAC840     | 1:3        | 840°C       |
| 4  | SBAC12      | 1:2        | 800°C       |
| 5  | SBAC13      | 1:3        | 800°C       |
| 6  | SBAC14      | 1:4        | 800°C       |
| 7  | SBAC15      | 1:5        | 800°C       |
From Table 1, the activation process was divided into two sections. In the first section, carbon was mixed by KOH as a chemical activator agent with a fixed ratio KOH to the carbon of 1:3. Then the mixed was pyrolyzed at four different holding temperatures of 600°C, 700°C, 800°C, and 840°C for 90 minutes with a rate of 10°C/minute under flowing argon at 200cc/min so the sample names SBAC600, SBAC700, SBAC840 are given. In the second section, carbon was mixed by KOH with variations in the ratio of KOH to the carbon of 1:2, 1:3, 1:4, and 1:5 at a fixed holding temperature of 800°C for 90 minutes, so the sample names SBAC12, SBAC13, SBAC14, and SBAC15 are given. All activated carbon produced were neutralized using HCL solution until the pH is equal to 7, and they were rinsed with distilled water. Finally, the sugarcane bagasse activated carbon (SBAC) were put into the oven at 80°C for 24 hours.

2.2. Material Characterization
Scanning Electron Microscopy (SEM) images were obtained using Zeiss EVO MA10. The specific surface area values were obtained from test carried out with Nova Instruments 200e calculated by BET method based on nitrogen (N₂) adsorption.

2.3. Electrode Synthesis
The cathode consists of SBAC, super-P (acetylene black), and polyvinylidene fluoride in the ratio of 85:5:10. The synthesis process begins with mixing the polyvinylidene fluoride and N-Methyl-2-pyrrolidone (NMP) as a solvent at a temperature of 80°C for 15 minutes until PVDF is dissolved evenly. The SBAC and super-P which have been mixed were inserted and stirred at 0°C for 2 hours until it reached the right thickness. The slurry was cast onto the aluminium foil as a current collector using a doctor blade so that the electrode sheet was created. The electrode sheet was dried up using vacuum oven at 80°C overnight to make it moisture free, and then it was cut into a circle shape with the size of 2032-coin cell.

The anode was made by mixing the Li₄Ti₅O₁₂ power (LTO), super-P (acetylene black), and polyvinylidene fluoride in the ratio of 80:10:10 then proceeded with the same procedure as the cathode synthesis process but different in the current collector material, copper foil.

2.4. Electrochemical Performance Testing
Cyclic Voltammetry (CV) was measured by WBCS3000. CV test was performed within a voltage range of 1-3 V at variations in scan rate values of 5,10,15, and 20 mV/s. The capacitance of LIC can be obtained from the CV curve and calculated using the following equation (1).
\[ C = \frac{\int_{v_1}^{v_2} i(v) \, dv}{v \times m \times \Delta V} \]  

where \( C \) is the specific capacitance (F/g), \( \int_{v_1}^{v_2} i(v) \, dv \) is the closed-loop area of CV curve, \( v \) is the scan rate (mV/s), \( m \) is the mass of activated carbon in the electrode, and \( \Delta V \) is the potential window.

\[ E = \frac{1}{2} C (V_1^2 - V_2^2) \]  

where \( E \) is the specific energy (Wh/kg), \( C \) is the specific capacitance, \( V_1 \) is the upper voltage limit (V), and \( V_2 \) is the lower voltage limit (V).

Charge-discharge (CD) test produces a discharge time values for all samples so the specific power can be obtained using the following equation (3).

\[ P = \frac{E}{t_{\text{discharge}}} \]  

where \( P \) is the specific power (W/kg), and \( t_{\text{discharge}} \) is the discharge time.

3. Material Characteristics

3.1. Scanning Electron Microscopy

In this study, the microstructure of the sugarcane bagasse activated carbon (SBAC) was enlarged with 5000× magnification. In Figure 3 (a), it can be seen that SBAC12 have many pores with a diameter size smaller than the diameter size of other samples. In Figure 3 (c) SBAC14 has small pores in a large pore. It indicates that SBAC14 has a large specific surface area. SBAC13, SBAC600, SBAC700, and SBAC840 have a morphology with a honeycomb shape and there are several pores on their surface as we can see in Figure 3 (b), (e), (f), and (g) whereas in Figure 3 (d) SBAC15 produces several pores, but there are cracks which indicate damage to the pore structure. In general, all samples of sugarcane activated carbon (SBAC) has a microporous and scattered structure.

3.2. Brunauer-Emmet-Teller

The KOH activator could corrode the carbon structures so it will form a porous structure which leads to an increase of specific surface area value \[15\]. The calculated specific surface area is given in Table 2 after trying four different temperatures. We got the optimum temperature for this substance which is 800°C with a specific surface area of 2236.926 m²/g obtained from the SBAC13 sample. Then, we applied four different ratios of KOH and found out the highest specific surface area obtained from the sample with carbon to KOH ratio of 1:4 (SBAC14). The specific surface area value of SBAC12,
SBAC13, SBAC14, and SBAC15 of 2136 m²/g, 2236 m²/g, 3554 m²/g, and 2747 m²/g were obtained from previous studies which were presented in [16].

Table 2. Specific surface area values

| Sample  | Specific Surface Area (m²/g) |
|---------|-----------------------------|
| SBAC600 | 1219.948                    |
| SBAC700 | 1095.622                    |
| SBAC840 | 2050.875                    |

4. Electrochemical Performance

4.1. Cyclic Voltammetry

The electrochemical performance of LIC cell was evaluated by cyclic voltammetry (CV) and charge-discharge (CD) test. The cyclic voltammetry (CV) curves of LIC SBAC12, SBAC14, and SBAC15 were shown in Figure 4 (a), (b), and (c) respectively. As we can see in these figures, the resulting CV curves have a similar shape to the shape of a leaf. It happens because LIC has a combination CV curve of activated carbon which has a quasi-rectangular shape with no redox peaks and LTO which has two peaks which correspond to the Li⁺ insertion and extraction [17].

From each CV curve which can be seen in Figure 4 (a), (b), and (c), the higher the value of the scan rate given to the sample, the higher the current density value generated. It happens because the higher the applied voltage to the sample, the faster the electron movement will occur. It will affect the specific capacitance value. When the currents and ions flow faster, ions have a shorter time to penetrate and reside in all the available electrode pores so the activated carbon cannot fully absorb PF₆ ions, and the specific capacitance value produced will be smaller [18].

The specific capacitance values of SBAC12, SBAC14, and SBAC15 were calculated using equation (2) at a scan rate ranging from 5 to 20 mV/s. As we can see in Figure 4 (b), the higher the value of the scan rate given to the sample, the lower the specific capacitance value produced. At a low scan rate of 5 mV/s, SBAC15 presents the highest specific capacitance of 31.94 F/g, indicating SBAC15 possesses the larger accessible electrode/electrolyte interface area for LiPF₆ electrolyte at this low scan rate [19].

The energy stored in the lithium-ion capacitor is proportional to its specific capacitance value. The specific energy value of each sample can be calculated using equation (3).
Figure 4. Cyclic voltammetry curves of LIC cell SBAC12 (a), SBAC14 (b), SBAC15 (c) in various scan rates of 5 mV/s, 10 mV/s, 15 mV/s, 20 mV/s, and specific capacitance for all samples.

4.2. Charge Discharge

Charge-Discharge curves for SBAC12, SBAC14, and SBAC15 cells, measured at different current rates of 250 µA/g, 375 µA/g, 500 µA/g, 1mA/g and voltage range of 1V – 3V, are shown in Figure 5 (a), (b), (c) respectively. From these figures, all these curves have a triangular shape with a voltage value that varies with the time during the charging and discharging process. This type of curve has a more dominant form to the charging and discharging curve of a carbon-based supercapacitor [20].

From Figure 5 (a), (b), (c), it can be seen that the higher the rated current given to the sample, the shorter the charging and discharging time produced for each sample as can be seen in Figure 5 (d). At a current of 250 µA/g, SBAC14 produces the longest discharging time of 1894 seconds. Meanwhile, at a current value of 500 µA/g, SBAC12 produces the fastest discharging time of 8 seconds.

From the discharging time data obtained, the specific power value of SBAC12, SBAC14, and SBAC15 can be calculated using equation (4), and these values are presented in Figure 5. From equation (4), it can be seen that the relationship of discharging time with specific power is inversely proportional so that the shorter discharging time, the higher specific power produced. At a current value of 500 µA/g, the SBAC12 produces the highest specific power value of 2954.36 W/kg.
Figure 5. Charge-discharge curves of LIC cell SBAC12 (a), SBAC14 (b) in current of 250 µA/g, 375 µA/g, 500 µA/g, SBAC15 (c) for current of 500 µA/g, 750µA/g, and 1mA/g. (d) discharge time for all samples.

LIC SBAC12, SBAC14, and SBAC15 have a specific capacitance value of 5.54 F/g, 6.12 F/g, 31.94 F/g, a specific energy value of 6.15 Wh/kg, 6.80 Wh/kg, 35.49 Wh/kg, and a specific power value of 2954.36 W/kg, 73.31 W/kg, 67.78 W/kg respectively. From the obtained data, SBAC15 produces the highest specific capacitance value of 31.94 F/g. Also, SBAC15 produces the highest specific energy of 35.49Wh/kg. This result indicates that the higher the specific surface area value held by the sample, the higher the value of the capacitance and energy values [16]. The SBAC12 owned the highest specific power value of 2954.36 W/kg, and this value is higher than the research using water hyacinth as the electrode material which can only produce a specific power value of 160.53 W/kg [21].

Table 3. Specific capacitance, specific energy, and specific power values

| Sample   | Specific Capacitance (F/g) | Specific Energy (Wh/kg) | Specific Power (W/kg) |
|----------|----------------------------|-------------------------|-----------------------|
| SBAC12   | 5.54                       | 6.15                    | 2954.36               |
| SBAC14   | 6.12                       | 6.80                    | 73.31                 |
| SBAC15   | 31.94                      | 35.49                   | 67.78                 |

5. Conclusions
In summary, the activated carbon derived from sugarcane bagasse has been successfully synthesized and applied as the primary material of the lithium-ion capacitor electrode. The SEM images prove that SBAC has many pores which indicates that activation process has succeeded in enlarging the pore surface area. The BET data shows that SBAC has a large specific surface area. SBAC LIC cell produces the largest specific capacitance of 31.94 F/g at low scan rate (5mV/s), a specific energy of 35.49 Wh/kg, and a specific power of 2954.36W/kg at a current density of 500 µA/g and also the voltage window is fixed at the value of 1.0-3.0 V. Moreover, the result of this study can help the utilization of sugarcane bagasse waste in the application of energy storage device, especially on the lithium-ion capacitor field.
6. References

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