Porous Activated Carbon Binder-free *Scleria sumatrensis* Stem-Based for Supercapacitor Application

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**Abstract.** Green, sustainable and effective development technique to obtain high porous activated carbon biomass based is important to boosting supercapacitor performance with environmentally friendly effect as conversion system and energy storage devices. We reported porous activated carbon binder-free *Scleria sumatrensis* stem-based as electrode material high performance of symmetric supercapacitor. Precursor biomass of *Scleria sumatrensis* stem was converted into porous carbon through simple ZnCl\(_2\) impregnated with different concentration of 0.4M, 0.5M, 0.6M, and 0.7M at high-temperature phyrolysis. All samples confirmed good amorphous carbon with small amounts of oxidative compounds. In two-electrode system, the optimum sample of ACSS0.6 significantly boosting the specific capacitance as high as 142.62 F g\(^{-1}\) at scan rate of 1 mV s\(^{-1}\). Furthermore, the optimum energy density was found to be 19.80 Wh kg\(^{-1}\) at a maximum power density of 71.35 W kg\(^{-1}\) in 1 M H\(_2\)SO\(_4\) aqueous electrolyte. These results confirm that the porous activated carbon binder-free *Scleria sumatrensis* stem-based through simple ZnCl\(_2\) impregnated as an electrode material to boosting the electrochemical behavior of supercapacitors.

1. Introduction

The provision of environmentally friendly energy with high performance is a future needed for every country, especially pollution-free electrical energy. For developing countries such as Indonesia, the supply of energy is a very influential factor in encouraging development and the feasibility of living standards of the people. Indonesia's electrical energy consumption in the range years of 2000 to 2025 is estimated to increase by an average of 7.1% per year, triggering an increase in the use of energy sources which in fact can affect the global climate [1]. In order to create an energy source that is environmentally friendly and pollution-free and renewable, researchers report potential renewable energy sources including sunlight, water, wind, and biomass. However, its effectiveness requires high-performance electrical energy storage. Developments in electrical energy systems are very important for generalizing the effectiveness of natural...
cycles of renewable energy sources [2]. Thus, there is a need for in-depth studies on the development of effective, efficient, and high-performance energy storage.

Supercapacitor is an electrochemical energy storage technology that is considered leading compared to other energy storage devices such as batteries and capacitors [3,4]. Besides higher power density, infinite cycle life, and longer lifetime than batteries their electrode-based material which provides high surface area, controllable pores, nanoscale structure, relatively good thermal and electrical stability, and high conductivity makes it promising for applications such as a wider range of electronic devices [5–7]. Biomass-based porous carbon is considered as the based material for the electrodes which gives them all their advantages in it. Recently, Selvaraj et al., 2021 demonstrated excellent results of biomass from Prosopis Juliflora wood-based supercapacitor with capacitive properties reaching 426 F g⁻¹ [8]. They also reported an ultrahigh-specific surface area of 2943 m² g⁻¹. Furthermore, the wild jujube pit biomass displayed almost the same potential with a specific surface area of 2438 m² g⁻¹. Interestingly they confirmed the presence of oxygen heteroatoms as doping elicited a pseudocapacitive effect with a specific capacitance of 345 F g⁻¹ [9]. In addition, through easy chemical impregnation, nori confirmed a porous carbon with a capacitive property of 220 F g⁻¹ [10]. These results confirm the potential of biomass that can improve the high performance of energy storage devices with their respective advantages such as high surface area, a combination of hierarchically connected 3D pore structures, and confirmed heteroatoms. However, most of them still use complicated, complex, toxic manufacturing methods, using excessive chemical components such as polymers, adhesives, and metal oxides. Although these can maintain the high performance of the electrodes, however, they do not take into account the effects of environmental pollution and side effects.

Here, we report a binder-free monolithic porous activated carbon based on Scleria sumatrensis stem as an electrode material for supercapacitor applications. Porous carbon is obtained by simple ZnCl₂ impregnation at high-temperature pyrolysis. The difference in concentration became the focus of data analysis covering 0.4M, 0.5M, 0.6M, and 0.7M. Furthermore, the porous carbon is prepared in the form of a binder-free monolith. In a two-electrode system, the optimum sample of ACSS0.6 significantly boosting the specific capacitance as high as 142.62 F g⁻¹ at a scan rate of 1 mV s⁻¹. Furthermore, the optimum energy density was found to be 19.80 Wh kg⁻¹ at a maximum power density of 71.35 W kg⁻¹ in a 1 M H₂SO₄ aqueous electrolyte. These results confirm that the porous activated carbon binder-free Scleria sumatrensis stem-based through simple ZnCl₂ impregnated as an electrode material to boosting the electrochemical behavior of supercapacitors.

2. Materials and Methods

2.1. Preparation of activated carbon free-binder monolith Scleria sumatrensis stem-based

Scleria sumatrensis stems were obtained from the swamp area of Rokan Hulu District, Riau province. Samples were collected and cut into small pieces with sizes ranging from 2x5cm. Next, the sample is cleaned and washed to remove impurities such as soil and sand. Furthermore, the samples were sun-dried for 36 hours followed by oven-dried for 36 hours. A total of 30 g samples were pre-carbonized using a vacuum oven at a maximum temperature of 250°C for 2 hours 30 minutes. After that, the sample was crushed through a grinding machine to obtain a pre-carbonized powder. Chemical activation was performed by mixing ZnCl₂ solution at different concentrations (0.4, 0.5, 0.6, and 0.7M) with carbon powder in a ratio of 150ml: 30g. Furthermore, the chemically activated sample was converted into a free-binder monolith by means of a hydraulic press instrument. A total of 20 monolith samples were put in a furnace tube for high-temperature pyrolysis. Pyrolysis consists of a one-step carbonization and physical activation process up to a maximum temperature of 900 °C in the N₂ and CO₂ gas environment. Finally,
the activated carbon *Scleria sumatrensis* stem-based (ACSSs) was neutralized by immersing the monolith sample with distilled water. The result of the water immersion has measured the pH to neutral.

### 2.2. Material Characterizations

The properties of monolithic activated carbon material based on *Scleria sumatrensis* stems were characterized including density shrinkage, microcrystal phase, and surface functional group. Density was evaluated by measuring the dimensions of the monolith (mass, thickness, and diameter) before and after the high-temperature pyrolysis process [17]. Next, the microcrystal phase was examined using X-ray diffraction technique (XRD, Philip Expert 2.1 instrument) with Cu-Kα source in the angle range of 15°-55°. The d₀₀₂ and d₁₀₀ interlayer spacing and L_c and L_a microcrystalline dimensions were also evaluated based on XRD data [18–20]. Furthermore, the surface functional group was performed using the Fourier-Transform Infrared Spectroscopy (FTIR, IR Prestige-21 instrument) technique at a wavelength range of 450-4500 cm⁻¹.

### 2.3. Electrochemical performance measurement

Electrochemical properties consisting of specific capacitance, energy density, and power density were evaluated through the general technique of cyclic voltammetry. The supercapacitor cell is based on a two-electrode system consisted of a carbon monolith binder-free *Scleria sumatrensis* stem-based, separator, and electrolyte. Duck eggshell membrane was selected as organic separator [21] and 1 M H₂SO₄ as aqueous electrolyte. Cyclic voltammetry was performed at a constant voltage window of 0-1.0V at different scan rates including 1, 2, 5, and 10 mV s⁻¹. Specific capacitance, energy density, and power density are evaluated through equations 1, 2, and 3 [22,23].

\[
C_{sp} = \frac{t_c - t_d}{s \cdot m} \tag{1}
\]

\[
E_{sp} = \frac{c \cdot V^2}{\tau^2} \tag{2}
\]

\[
P_{sp} = \frac{E_{sp}}{\tau} \cdot 3600 \tag{3}
\]

### 3. Result and Discussion

The mass, thickness, and diameter of the carbon monolith *Scleria sumatrensis* stem-based were measured to determine the density shrinkage before and after the high temperature pyrolysis process. Density data is displayed in the form of a bar graph based on different concentrations of ZnCl₂, as shown in Figure 1. Figure 1 showed that each sample has decreased density. The decrease in density is influenced by several factors such as chemical activation, carbonization, and physical activation [6]. The chemical activation process causes the activating agent to react directly with the carbon powder, while physical activation through the CO₂ gas environment reacts on the electrode surface which results in density shrinkage in all samples [4]. The process of carbonization and physical activation can decompose volatile elements and water content in activated carbon samples [24]. The carbonization process from room temperature to 600 °C can decompose complex compounds including cellulose, hemicellulose, and lignin [25], indicating an increase in the number of pores. The physical activation process from 600 °C to 900 °C can remove impurities that are still not completely decomposed [6]. The following is the percentage value of density shrinkage for each variation of ZnCl₂ concentration.
As summarized in Table 1, the largest decrease in density was found in sample ACSS0.6 which indicated an increase in ZnCl$_2$ concentration from 0.4 to 0.6 M. Density reduction was due to ZnCl$_2$ acting effectively as a dehydration reagent. The addition of concentration up to 0.6 M resulted in a decrease in the optimum density indicated by the levels of elements other than decomposed carbon. The decomposed elements produce a pore structure that affects the surface area of the electrode [26].

Fourier Transform Infra-Red (FTIR) analysis is used to study changes in physicochemical properties, determined functional groups and carbon chain structure contained in the activated carbon *Scleria sumatrensis* stem-based sample material. The FTIR spectrum of ACSSs after the pyrolysis process showed the presence of broad and intense absorption peaks located in the band of the wavenumber range of 450-4500 cm$^{-1}$. The wavenumber value of 2950 cm$^{-1}$ shows the stretching vibration of the C-H group. In addition, the C-O functional group was detected in the wavenumber band around 1300-1500 cm$^{-1}$, and in wavenumber 890-900 cm$^{-1}$, it showed vibrations and C-C strain in the phenol functional group [27]. The spectrum of the resulting image from the FTIR characterization can be seen in Figure 2.

As shown in Figure 2, the results of FTIR characterization for *Scleria sumatrensis* stem-based carbon monolith with ZnCl$_2$ concentration of 0.4 M, 0.5 M, 0.6 M, and 0.7 M, it can be seen that there is a higher absorption in the transmittance range of around 17% to 30%. In the range of wavenumbers of 3900-4100 cm$^{-1}$ is a stretching vibration in the O-H functional group [28]. The high O-H strain absorbance on the activated carbon could perform pseudo-capacitive properties in energy storage devices [29,30]. In the wavenumber band of 2950 cm$^{-1}$, it shows stretching vibrations of the C-H group.
1300-1400 cm\(^{-1}\) is a functional group of C-O, for the wavenumber band 860-900 cm\(^{-1}\) shows the stretching vibration of C-C for the functional group of phenol [31].

X-ray diffraction characterization was shown to determine the microcrystalline phase of the monolith free-binder activated carbon *Scleria sumatrensis* stem-based of ACSS0.4 and ACSS0.6 samples. The XRD pattern displays two gently broad peaks and several sharp peaks at 20 angles around 23-25° and 42-44° (JCPDS No. 41-1487), as confirmed in Figure 3. This clearly indicates the amorphous carbon properties were confirmed significantly for all ACSSs samples. These results are considered normal for porous carbon-based biomass [32,33]. Furthermore, the XRD pattern also displays several sharp peaks indicating a small proportion of crystalline compounds. As shown in Figure 3, two gentle peaks are found at an angle of 20 which are located at 23.602° to 25.736° and 42.018° to 44.948°. In addition, sharp peaks were also found at different angles indicating crystalline compounds such as SiO\(_2\), CaO and CaCO\(_3\). CaO compounds are found at angles 32°, 33° and 42° (JCPDS No. 79-2205) and CaCO\(_3\) is found at angles 37° and 39° (JCPDS No. 82-1690). Meanwhile, SiO\(_2\) compounds are found at angles 27° and 29° (JCPDS No. 89-1668). Table 2 summarizes in detail the lattice parameters including \(d_{002}\), \(d_{100}\), \(L_c\), and \(L_a\).
Figure 3. XRD pattern of ACSS0.4 and ACSS0.6 samples

Table 2. Lattice parameters of $d_{002}$, $d_{100}$, $L_c$, and $L_a$ for ACSS0.4 dan ACSS0.6 samples

| Activated carbon | $\theta_{002}$ (°) | $2\theta_{100}$ (°) | $d_{002}$ (Å) | $d_{100}$ (Å) | $L_c$ (Å) | $L_a$ (Å) |
|------------------|--------------------|--------------------|---------------|---------------|-----------|-----------|
| ACSS0.4          | 23.602             | 44.948             | 3.766         | 2.015         | 10.454    | 12.743    |
| ACSS0.6          | 25.736             | 42.018             | 3.458         | 2.148         | 5.076     | 8.752     |

The value of $d_{002}$ obtained is 9.89% higher than that of normal graphite, indicating that the carbon monolith binder-free sample produced is carbon with a good amorphous structure. Furthermore, the $L_c$ value is closely related to the specific surface area of the material. Based on the empirical formula [20,34], a small $L_c$ value will produce a large surface area. This confirms that the ACSS0.6 sample has the smallest $L_c$ which indicates the largest specific surface area.

The electrochemical properties of the supercapacitor were evaluated by means of the cyclic voltammetry (CV) technique at a scanning rate of 1 mV s$^{-1}$ in a voltage window of 0-1.0V. The supercapacitor cell is arranged like a sandwich layer in a two-electrode system consisting of two carbon monolith binder-free, an organic separator, and an aqueous electrolyte. The curve of the cyclic voltammetry test results is a distorted rectangle formed from current density (A cm$^{-2}$) and voltage (V), as shown in Figure 4. The current density value consists of two, including charge current ($I_c$) and discharge current ($I_d$). The $I_c$ is current when charging the charge coming from the electrolyte which decomposes into positive ions and when the voltage is increased, and $I_d$ is current when the charge is discharged when the voltage is lowered. As shown in Figure 4, the CV curve confirms the distorted rectangular shape for all samples indicating the double-layer electrochemical properties are relatively ideal [35,36]. Furthermore, the effect of pseudocapacitance was also observed in the sample, which was characterized by a spike in current density in the voltage range of 0.4-0.7V. This is due to the doping of heteroatoms, particularly oxygen elements. The presence of oxidizing compounds in the sample allows oxygen to act as self-doping in the samples [37,38]. This was confirmed clearly on the XRD curve and FTIR spectra which were discussed earlier. In addition, this effect can increase the high performance of the supercapacitor.
Furthermore, the ACSS0.6 sample significantly displayed the largest CV curve indicating the highest specific capacitance of 142.2 F g⁻¹, followed by ACSS0.7, ACSS0.5, and ACSS0.4 of 132.84, 117.23, 72.87 F g⁻¹, respectively. Chemical activation using ZnCl₂ activating agent with a concentration variation of 0.4 M to 0.6 M can significantly increase the specific capacitance value from 72.87 to 142.62 F g⁻¹. This is because increasing the concentration of ZnCl₂ can increase the specific surface area and increase the pores as the contact area of the electrolyte ion diffuses on the electrode surface [8,39], as confirmed by XRD analysis. Furthermore, the increase in the value of this specific capacitance also affects the energy density and power density values of the carbon electrodes from which they increase approximately twofold, as shown in Table 3.

![Figure 4. The CV curve of ACSS0.4, ACSS0.5, ACSS0.6, and ACSS0.7 samples](image-url)

**Table 3.** The electrochemical behaviors of activated carbon monolith binder-free *Scleria sumatrensis* stem-based

| Electrodes  | Mass loading (g) | \( C_{sp} \) (F g⁻¹) | \( E_{sp} \) (Wh kg⁻¹) | \( P_{sp} \) (W kg⁻¹) |
|-------------|------------------|-----------------------|------------------------|------------------------|
| ACSS0.4     | 0.0108           | 72.87                 | 10.12                  | 36.47                  |
| ACSS0.5     | 0.0119           | 117.23                | 16.28                  | 58.67                  |
| ACSS0.6     | 0.0126           | 142.62                | 19.80                  | 71.35                  |
| ACSS0.7     | 0.0148           | 132.84                | 18.45                  | 66.48                  |

As summarized in Table 3, it can be seen that the concentration of the activating agent ZnCl₂ 0.6 M displays the highest specific capacitance value possible because at a concentration of 0.6 M ZnCl₂ can produce an optimal combination of micropore and mesoporous structures [40,41] which are supported by the density characterization data. This optimal combination of micro and mesopores affects the surface area value of the resulting carbon electrode [42,43]. The specific capacitance value of the *Scleria sumatrensis* stem-based carbon electrode with 0.6 M ZnCl₂ can be compared with the results of previous studies, as shown in Table 4.
Based on Table 4, it can be seen that the specific capacitance value generated from the carbon electrode \textit{Scleria sumatrensis} stem-based can compete with the specific capacitance value derived from different biomass and activators. The relationship between the scan rate variation and the specific capacitance value can be seen in Figure 5. Based on Figure 5 it can be seen that the relationship between the scanning rate and the specific capacitance is inversely proportional, where the lower the scanning rate the higher the specific capacitance value will be. This is influenced by the time it takes for the ions from the electrolyte to diffuse relatively short which causes the ions to not be absorbed optimally [44,45].

![Figure 5. The specific capacitance vs. scan rate of ACSS0.4, ACSS0.5, ACSS0.6, and ACSS0.7 samples](image)

| Biomass sources       | Activating agents | $C_{sp}$ (F/g) | Referensi |
|-----------------------|-------------------|---------------|-----------|
| Coconut husk          | KOH               | 184           | [16]      |
| Coffee ground         | ZnCl$_2$          | 100           | [14]      |
| Coffee husk           | H$_3$PO$_4$       | 51            | [46]      |
| Bamboo stem           | KOH               | 293           | [47]      |
| \textit{Scleria sumatrensis} stem | ZnCl$_2$      | 142.62        | This study |

### 4. Conclusion

In conclusion, porous activated carbon monolith binder-free \textit{Scleria sumatrensis} stem-based has been successfully prepared for electrical energy storage applications, especially EDLC supercapacitor. The precursor biomass was converted into porous activated carbon with the dependent variable being ZnCl$_2$ activating agent and the independent variable being the concentration of the activating agent (0.4M, 0.5M, 0.6M and 0.7M). In general, different concentrations could affect the material behaviors and enhanced the electrochemical properties of supercapacitor cells. All samples clearly displayed good amorphous carbon with decorated oxidative compounds in relatively small amounts. Furthermore, with higher concentration from 0.4 to 0.6M ZnCl$_2$ could boost the specific capacitance from 72.87 F g$^{-1}$ to 142.62 F g$^{-1}$, as shown in ACSS0.6 samples. Moreover, in the two-electrode system, the supercapacitor cell based on ACSSs confirmed a high energy density of 19.80 Wh kg$^{-1}$ at a maximum power density of 71.35 W kg$^{-1}$ in 1 M H$_2$SO$_4$ aqueous electrolyte. Based on these results, the activated carbon monolith binder-free \textit{Scleria sumatrensis} stem-based can be an attractive alternative material for EDLC supercapacitors.
**sumatrensis** stem-based is promising as an electrode material through ZnCl$_2$ impregnation at one-step integrated pyrolysis for electrochemical energy storage application.

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