Bamboo-Based Activated Carbon as Binder-Free Electrode of Supercapacitor Application

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Abstract. Activated carbon has been an ideal material for supercapacitor electrodes. Its extensive use due to abundant, renewable, and cost-effective production. In this work, we developed activated carbon monolith materials through carbonizing bamboo stems wastes and treating them with ZnCl\textsubscript{2} in high-temperature pyrolysis as binder-free electrode of supercapacitor application. ZnCl\textsubscript{2} impregnation carried out in one-step, two-step, and three-step. Different steps of ZnCl\textsubscript{2} impregnation were employed to evaluate the activated carbon preparation variables including one-step, two-step, and three-step. The reduction of monolith dimensions has been reviewed as physical properties. Furthermore, the symmetric supercapacitor was performed with cyclic voltammetry in sandwich-type at 1 M H\textsubscript{2}SO\textsubscript{4}. In addition, the thicknesses of electrode carbon monoliths were varied such as 0.1 mm, 0.2 mm, and 0.3 mm. The one-step ZnCl\textsubscript{2} impregnation in 0.1 mm thickness of carbon monolith were exhibit best electrochemical performance with highest specific capacitance of 145 F g\textsuperscript{-1} and followed by two-step and three-step impregnation as high as 132 F g\textsuperscript{-1} and 131 F g\textsuperscript{-1} in low scan rate of 1 mV s\textsuperscript{-1}, respectively. These results demonstrate that the bamboo stem-based activated carbon monolith materials are promising as binder-free electrode for supercapacitor energy storage.

1. Introduction
Bamboo is the plant which family of the Phocaea and subfamily of the Bambuseae. Today, more than 1642 species in 75 genera of bamboo have been shown to be distributed worldwide [1]. Bamboo is the plant that family of the Phocaea and subfamily of the Bambuseae. Its fast growth and fast ripening, as well as high co-product as wastes, make bamboo as fast forest development, environmentally manufacturing, and ecological production. However, the high usability of bamboo is certainly accompanied by a large amount of waste.

Waste bamboo stems have a high utilization value, especially in providing a porous activated carbon-based material. Activated carbon is a porous carbon material that is most widely used as a base material for an electrode in energy storage devices, especially supercapacitor including EDLC and pseudocapacitor[2,3]. Activated carbon has a well-developed porous structure and surface chemistry functionality to enhance interactions with both polar and non-polar [4]. Bamboo stem waste could be converted to activated carbon through several methods including carbonization, heat treatment, hydrothermal, chemical activation using KOH [5], ZnCl\textsubscript{2}[6], NaOH[7] and etc., and physical activation in CO\textsubscript{2} and steam atmosphere [8,9]. Lee et al. has focused on the preparation and electrochemical properties of bamboo-based activated carbons in powder form through carbonization and subsequent steam activation at 900 °C. This method could enhance the specific surface areas from 445 to 1025 m\textsuperscript{2} g\textsuperscript{-1} with the highest specific capacitance of 60 F g\textsuperscript{-1}[10]. In other reports, the bamboo
stem has converted into activated carbon with heat treatment followed KOH activation in 900 °C and they reported that a high specific surface area increase of 3061 m$^2$ g$^{-1}$ which could enhance the specific capacitance of 258 F g$^{-1}$[11]. A similar method has been found in the higher performance of activated carbon bamboo-based with a specific capacitance of 293 F g$^{-1}$ which reported by Zhang et al., 2018 [12]. However, all of these reports provided activated carbon electrodes in powder form which require adhesives material to test capacitive properties such as PVDF and PTFE. These adhesive materials could inhibit the conductivity of the material from which the activated carbon is based. Recently, activated carbon from the bamboo stem has been prepared in a monolith form and without the addition of adhesive materials. However, chemical activation is limited to KOH activating agent.

This study converted the bamboo stem to activated carbon through ZnCl$_2$ activation and subsequent one-stage integrated pyrolysis both carbonization and physical activation. The ZnCl$_2$ activation carried out in multi-step including one-step, two-step, and three-step with constant 5 M concentration. The activated carbon was prepared in monolith form as a binder-free electrode. In addition, the thicknesses of electrodes testing were varied. Moreover, the specific capacitance was exhibit by using cyclic voltammetry (CV) in symmetrical supercapacitor electrode at low scan rate of 1 mV s$^{-1}$.

2. Methods

Bamboo stems wastes were collected from handicraft production houses in the Pekanbaru area. Bamboo stems were cleaned and cut crosswise/cross sectional in the form of coins/monoliths, in diameter and thickness of 8 cm and 2 cm, respectively.

![Figure 1. Schematic preparation of activated carbon monolith bamboo-based.](image)
The samples were prepared in 20 monoliths and subsequently carbonized in an N₂ gas environment from room temperature to 600 °C. The ZnCl₂ was selected as the chemical activation agent. The samples chemically activated with different steps include one-step, two-step, and three-step activation. Furthermore, the sample is put in a furnace tube and pyrolysis at a high temperature of 700 °C in a CO₂ gas environment. Based on the differences in chemical activation treatments, the samples were labelled ACB1, ACB2, and ACB3, respectively. Details of bamboo activated carbon preparation are shown in Figure 1.

The dimensions of activated carbon monolith were measured including diameter, thickness, volume and mass for each ZnCl₂ activation treatment. Based on dimensional data, density can be calculated using standard formulas. Furthermore, the electrochemical properties were carried out using the cyclic voltammetry (CV, CV UR Rad-Er 5841 instrument, calibrated with VersaStat II Princeton Applied Research, an error of ±6.05%) at a low scan rate of 1 mV s⁻¹. The symmetric supercapacitor cells were rearranged in sandwich-type including ACB-X electrodes, electrolyte, and separator. 1 M H₂SO₄ was selected as electrolyte and separator was from egg duck shell membrane. In addition, the thicknesses of ACB-X electrodes were three differences such as 0.1 mm, 0.2 mm, and 0.3 mm, respectively. The specific capacitance (Cₛₚ, F g⁻¹), energy density (E, Wh kg⁻¹), and power density (P, W kg⁻¹) were evaluated by using the standard equations based on CV curve data’s.

3. Results and Discussion
The carbonization and ZnCl₂ impregnation in high-temperature activation of 700 °C have successfully converted bamboo stem waste into activated carbon as a binder-free electrode. This method directly affects the monolith dimensions of the sample including mass, thickness, diameter, and density as shown in Figures 2a and 2b.

![Graph showing changes in mass, thickness, and diameter of activated carbon monoliths](image)

**Figure 2.** (a) Reduction of mass, thickness, and mass, and (b) Density of carbon monolith before and after physical activation.

The mass, thickness, and diameter of the monolith decreased after the pyrolysis process included carbonization and physical activation from room temperature to high temperature. Carbonization is a initial process of pyrolysis in biomass waste with nitrogen gas at a temperature of 600 °C which could reduce the volatile content, organic acids, and light tar in the monolith carbon samples[14,15]. The evaporation of these contents all causes a decrease in mass, thickness and the diameter of bamboo monoliths and produce charcoal by expanding the surface area and initial pores. The ZnCl₂ impregnation treatment in one-step, two-step, and three-step showed irregular dimensions reduction as shown in Figure 2a. The physical activation process is carried out with reacted the biochar with carbon dioxide atmospheres. This process could enhance the initial pores, removes non-carbon content in the pores, develops new pores and optimizes the texture morphology of the samples[15]. This process results in a reduction in mass, thickness, and diameter. However, these dimensions reductions exhibited an irregular value. The density of carbon monolith is calculated based on the mass and volume during the pyrolysis process. The formation of pores in the final CO₂ also affects the density.
After the pyrolysis process, the carbon monolith is reduced about 45% from the initial value with a standard deviation of about 0.10, as shown in Figure 2b.

The capacitive properties of ACB-X were performed by the cyclic voltammetry (CV) method. The supercapacitor cell was assembled in coin layers, consist of electrode carbon, current collector, egg shell membrane as separator, and aqueous electrolytes[16,17]. The samples were prepared in a two-electrode system with three different thicknesses including 0.1 mm, 0.2 mm, and 0.3 mm. Figure 3a showed the cyclic voltammogram of ACB1, ACB2, and ACB3 in a thickness of 0.2 mm. The curves showed the quasi-rectangular shape which typical of the electrical double-layer[18,19].

![Figure 3. CV curve of ACB1, ACB2 and ACB3 in (a) 0.2 thickness of electrode, (b) 0.1 thickness of electrode, and (c) in 0.3 thickness of electrode.](image)

Samples ACB1 and ACB2 show a more ideal rectangular curve compared to ACB3. This indicates that the ACB1 and ACB2 samples have a pore combination between micropores and mesopores that is suitable for diffusion of electrolyte ions on the electrode surface, it could contribute to forming an ideal electric layer. This analysis is relevant with several scientific reports which stated that the micropores enhanced a high surface area to increase the many active sites in the ion diffusions and mesopores provide relatively smooth ion transport pathways without obstacles to the electrode/electrolyte interface, it could allow more double-layer[20,21]. In contrast to ACB1 and ACB2, the ACB3 sample showed a disturbed rectangular curve. At higher voltages, the specific capacitance increases significantly which due to the fact that the pores that develop in the three-step ZnCl$_2$ impregnation tend to be larger and lead to the formation of macropores. Furthermore, the area of the rectangular shape indicates the specific capacitance of the carbon monolith electrode. ACB1 shows the largest area with the highest specific capacitance of 154 F g$^{-1}$ and followed by ACB2 and ACB3 samples of 132 F g$^{-1}$ and 131 F g$^{-1}$, respectively. The one-step ZnCl$_2$ impregnation turned out to be more suitable for producing a combination of micro- and mesopores on activated carbon monolith which contributed to the high capacitive properties. The addition of the ZnCl$_2$ impregnation step including two-step and three-step tends to expand the existing pores towards mesopores and macropores. Similar trend CV curves were also shown with 0.1 mm and 0.3 mm electrode thicknesses,
as shown in Figures 3b and 3c. ACB1 has the highest specific capacitance at 143 F g\(^{-1}\) and 103 F g\(^{-1}\) for 0.1 mm and 0.3 mm thickness.

![Figure 4. CV curve in 0.1 mm, 0.2 mm, and 0.3 mm for (a) ACB1, (b) ACB2, and (c) ACB3.](image)

Moreover, Figure 4 showed CV curve with three different thickness of electrode of 0.1 mm, 0.2 mm, and 0.3 mm for ACB1, ACB2, and ACB3. CV curves from Figure 4 were rectangular-like at different thicknesses. This caused enhanced the pore structures of the samples. Furthermore, an increase in thickness to 3 mm reduced the specific capacitance for ACB2 and ACB3 at 70 F g\(^{-1}\) and 70 F g\(^{-1}\). However, ACB1 exhibits different trend data, the highest specific capacitance was found in 0.2 mm of 154 F g\(^{-1}\), and followed by 0.1 mm and 0.3 mm of 143 F g\(^{-1}\) and 102 F g\(^{-1}\) respectively. Table 1 showed the specific capacitance of bamboo-based activated carbon as binder-free electrode. These specific capacitance were similar with other study with different source such as banana stem [22], rotten carrot [23], and tobacco waste [24].

| Thickness | Specific capacitance (F g\(^{-1}\)) |
|-----------|-----------------------------------|
|           | ACB1 | ACB2 | ACB3 |
| 0.1 mm    | 143  | 0.1 mm | 143 |
| 0.2 mm    | 154  | 0.2 mm | 154 |
| 0.3 mm    | 102  | 0.3 mm | 102 |
4. Conclusion
In this study, we developed activated carbon monolith derived from bamboo stems wastes via carbonization process and different steps of ZnCl$_2$ impregnation in high-temperatures. The thicknesses of electrode carbon monoliths also varied including 0.1 mm, 0.2 mm, and 0.3 mm. As a result, one-step ZnCl$_2$ impregnation was shown highest specific capacitance of 154 F g$^{-1}$ in 0.2 mm thickness at low scanning rate of 1 mV s$^{-1}$. Furthermore, two-step and three-step ZnCl$_2$ impregnation in ACB2 and ACB3 samples were reduced the specific capacitance as well as an increase in thickness to 0.3 mm. Based on these results, the bamboo stem-based activated carbon monolith materials are promising as a binder-free electrode through carbonization and one-step ZnCl$_2$ impregnation for supercapacitor energy storage.

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References
[1] Goyal, Arvind Kumar B K B 2014 Antioxidant and nutraceutical potential of bamboo: an overview Int. J. Fundam. Applied Sci 3 2–10
[2] Gao Z, Zhang Y, Song N and Li X 2017 Biomass-derived renewable carbon materials for electrochemical energy storage Mater. Res. Lett 5 69–88
[3] Iro Z S, Subramani C and Dash S S 2016 A brief review on electrode materials for supercapacitor Int. J. Electrochem. Sci 11 10628–43
[4] Abbas Q, Raza R, Shabbir I and Olabi A G 2019 Heteroatom doped high porosity carbon nanomaterials as electrodes for energy storage in electrochemical capacitors: A review J. Sci. Adv. Mater. Devices 4 341–52
[5] Cheng P, Li T, Yu H, Zhi L, Liu Z and Lei Z 2016 Biomass-Derived Carbon Fiber Aerogel as a Binder-Free Electrode for High-Rate Supercapacitors J. Phys. Chem. C 120 2079–86
[6] Erabee I K, Ahsan A, Zularisam A W, Idrus S, Daud N N N, Arunkumar T, Sathyamurthy R and Al-Rawajfeh A E 2017 A new activated carbon prepared from sago palm bark through physiochemical activated process with zinc chloride Eng. J 21 1–14
[7] Dobele G, Dizhbite T, Gil M V., Volperts A and Centeno T A 2012 Production of nanoporous carbons from wood processing wastes and their use in supercapacitors and CO2capture Biomass and Bioenergy 46 145–54
[8] Farma R, Deraman M, Awidrus A, Talib I A, Taer E, Basri N H, Manjunatha J G, Ishak M M, Dollah B N M and Hashmi S A 2013 Preparation of highly porous binderless activated carbon electrodes from fibres of oil palm empty fruit bunches for application in supercapacitors Bioresour. Technol 132 254–61
[9] Taer E, Apriwandi A, Taslim R, Malik U and Usman Z 2019 Single Step Carbonization Activation of Durian Shells for Producing Activated Carbon Monolith Electrodes 14 1318–30
[10] Kim C, Lee J, Kim J and Yang K 2006 Feasibility of bamboo-based activated carbons for an electrochemical supercapacitor electrode 23 592–3
[11] Yang C S, Jang Y S and Jeong H K 2014 Bamboo-based activated carbon for supercapacitor applications Curr. Appl. Phys 14 1616–20
[12] Zhang G, Chen Y, Chen Y and Guo H 2018 Activated biomass carbon made from bamboo as electrode material for supercapacitors Mater. Res. Bull 102 391–8
[13] Faraji S and Nasir F 2015 The development supercapacitor from activated carbon by electroleless plating — A review Renew. Sustain. Energy Rev 42 823–34
[14] Zhang Y, Yu S, Lou G, Shen Y, Chen H, Shen Z, Zhao S, Zhang J, Chai S and Zou Q 2017 Review of macroporous materials as electrochemical supercapacitor electrodes J. Mater. Sci 52 11201–28
[15] Poonam, Sharma K, Arora A and Tripathi S K 2019 Review of supercapacitors: Materials and
devices *J. Energy Storage* **21** 801–25

[16] Taer E, Apriwandi A, Ningsih Y S, Taslim R and Agustino 2019 Preparation of activated carbon electrode from pineapple crown waste for supercapacitor application *Int. J. Electrochem. Sci* **14** 2462–75

[17] Taer E, Natalia K, Apriwandi A, Taslim R, Agustino A and Farma R 2020 The synthesis of activated carbon nano fiber electrode made from acacia leaves (Acacia mangium wild) as supercapacitors *Adv. Nat. Sci. Nanosci. Nanotechnol.* **11** 25007

[18] Pandolfo A G and Hollenkamp A F 2006 Carbon properties and their role in supercapacitors *J. Power Sources* **157** 11–27

[19] Taer E, Dewi P, Sugianto S, Syech R, Taslim R, Salomo S, Susanti Y, Purnama A, Apriwandi A, Agustino A and Setiadi R N 2018 The synthesis of carbon electrode supercapacitor from durian shell based on variations in the activation time *AIP Conf. Proc* **1927**

[20] Gou G, Huang F, Jiang M, Li J and Zhou Z 2020 Hierarchical porous carbon electrode materials for supercapacitor developed from wheat straw cellulosic foam *Renew. Energy* **149** 208–16

[21] Li Y, Wang X and Cao M 2018 Three-dimensional porous carbon frameworks derived from mangosteen peel waste as promising materials for CO2 capture and supercapacitors *J. CO2 Util* **27** 204–16

[22] Subramanian V, Luo C, Stephan A M, Nahm K S, Thomas S and Wei B 2007 Supercapacitors from activated carbon derived from banana fibers *J. Phys. Chem C* **111** 7527–31

[23] Ahmed S, Ahmed A and Rafat M 2018 Supercapacitor performance of activated carbon derived from rotten carrot in aqueous, organic and ionic liquid based electrolytes *J. Saudi Chem. Soc* **22** 993–1002

[24] Chen H, Guo Y C, Wang F, Wang G, Qi P R, Guo X H, Dai B and Yu F 2017 An activated carbon derived from tobacco waste for use as a supercapacitor electrode material *New Carbon Mater* **32** 592–9