Matoa Fruit peel-based Activated Carbon and its Application as an Electrode Materials in Supercapacitor Devices

Erman Taer1*, Agustino1, and Rika Taslim2
1Department of Physics, University of Riau, SimpangBaru, Pekanbaru 28293
2Deparment of Industrial Engineering, State Islamic University of Sultan Syarif Kasim, Simpang Baru, Pekanbaru 28293
*erma.taer@lecturer.unri.ac.id

Abstract. The use of matoa fruit peel waste-based activated carbon as electrode materials for supercapacitor devices is described in this paper. The chemical and CO2 activation were used to prepared the activated carbon. In the chemical activation process, zinc chloride 0.1 M was used as a chemical reagent. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements are used to assess the electrochemical performance of as-prepared electrode materials. After CO2 activation process, the density of the MFP samples have been decreased. From the CV and GCD data, the MFP-0.1 sample has optimum specific capacitance are 158 F g⁻¹ and 187 F g⁻¹, respectively. The electrochemical results demonstrated that the MFP sample is a potential choice for supercapacitor electrode materials.

1. Introduction
Recently, with the growth of portable electronic devices getting faster, a require continuous demand to produce electrical energy or rechargeable energy storage systems. Supercapacitors are one of the most attractive and efficient electrochemical power sources due to their high energy and power densities, fast charge-discharge rates, and long life cycle [1–5]. The high energy density is due to the high surface area and specific capacitance of electrodes, and the high power density is related to fast ion motion in the electrolytes and electrodes [6,7].

Biomass waste conversion and reuse as raw material to produce activated carbonaceous is considered a promising low-cost production strategy due to its abundant availability, eco-friendly, and relatively simple processing [8]. Generally, chemical and physical activation have been used to activate raw materials. The chemical activation by using chemical reagents (KOH, H₃PO₄, ZnCl₂, NaOH, etc) and while the physical activation used CO₂, air, steam, etc. Chemical reagents are used as dehydrating agents in chemical activation, which affect pyrolytic decomposition, resulting in the materialization of tar and increased carbon yield, whereas physical activation are used to remove a large amount of internal carbon mass, which is necessary to impart well-built carbon structures. [9,10]. Taer E and coworkers successfully converted biomass-based activated carbon made from Tectona grandis leaf as supercapacitor electrode material and obtained the optimum specific capacitance is 168 F g⁻¹ used applying the chemical activation and CO₂ activation with different temperature [11]. In another work, obtained the specific capacitance is 306 F g⁻¹ for activated carbon from orange peel [4].
Elaiyappillai and coworkers were prepared carbon electrode with specific capacitance 404 F g\(^{-1}\) by KOH activation using *Cucumis melo* fruit peel as raw materials [12].

Matoa fruit (*Pometia pinnata*) is commonly used for its fruits, but the peel is neglected and discarded without utility, resulting in the majority of them being discarded as natural waste. The use of matoa fruit peel-based activated carbon as an electrode material for supercapacitor devices was examined in this study. Furthermore, using a combination of chemical and CO\(_2\) activation, researchers investigated the potentiality and usability of matoa fruit peel waste as supercapacitor electrode materials. 0.1 M and 0.7 M ZnCl\(_2\) were used to the chemical activation process. The CO\(_2\) activation was carried out in a furnace box at 850°C for 2.5 hours. The electrochemical properties were discussed in this work. Furthermore, the MFP sample was compared with the previously reported electrode materials for supercapacitors made from other biomass materials. As far as our knowledge, there are no study has been reported on the production of supercapacitor electrode materials from the matoa fruit peel by the combination of ZnCl\(_2\) and CO\(_2\) activation.

2. Experimental method

2.1 Materials

The raw materials were used in this work is Matoa fruit peel waste. Matoa fruit peel waste were collected from the Riau university area, Pekanbaru, Indonesia. The supporting materials includes (i) zinc chloride as chemical reagent (Merck KGaA), distilled water, sodium sulfate (Merck KGaA), eggs shell membrane, Teflon, acrylic, and stainless steel 316L.

2.2 Preparations

In this work, matoa fruit peels (MFP) waste was used as the precursor to prepare activated carbon electrode. Matoa fruit peel waste was pre-carbonize in electric oven at 250 °C for 2.5 hours. Then, the pre-carbonize sample was ballmilled to produce small powder size (<60 μm). 20 g small powder was activated using chemical reagent ZnCl\(_2\) 0.1 M and 0.7 M at temperature of 80 °C. After naturally cooled in to room temperature, the activated sample were molded into pellet form by hydraulic press at 8 metrics tons. Then, the activated sample was pyrolysis in a nitrogen atmosphere at temperature 600 °C and followed by activation under carbon dioxide (CO\(_2\)) atmosphere at temperature of 850 °C for 2.5 hours. Finally, the activated sample was washing until pH neutral and dried at 110 °C for 48 hours. The sample was denoted as MFP-x where x is ZnCl\(_2\) concentration (0.1 M and 0.7 M). The activated carbon preparation process is shown in Figure 1.

![Figure 1. The activated carbon preparation process](image-url)
2.3 Characterization
The characterization of the MFP samples include physical parameter and electrochemical performance. The shrinkage of the mass, diameter, thickness, and density of the MFP samples before and after CO₂ activation were used to characterize physical parameters. The electrochemical performance of the MFP samples were investigated by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). From the CV and GCD curve, the specific capacitance \( C_{sp}, \text{ F g}^{-1} \) was calculated by the formulas:

\[
C_{sp} = \frac{2I}{sxm} \tag{1}
\]

\[
C_{sp} = \frac{Ix\Delta t}{mx\Delta V} \tag{2}
\]

The energy density \( E, \text{ Wh kg}^{-1} \), and power density \( P, \text{ W kg}^{-1} \) were calculated by the equations [13–15]:

\[
E = \frac{CV^2}{7.2} \tag{3}
\]

\[
P = \frac{Ex3600}{\Delta t} \tag{4}
\]

Where \( I, \Delta t, \Delta V, s, m \) are current (A), discharge time (s), voltage window (V), scan rate (mV s⁻¹), and mass of the sample, respectively.

3. Result and Discussion
The density of the MFP samples before and after CO₂ activation is shown in Figure 1. The density of MFP samples increased prior to CO₂ activation due to an increase in ZnCl₂ concentration. Furthermore, the density of MFP samples after CO₂ activation decreased, it was due to the release of several elements other than carbon, such as water molecules and volatile contents, during the activation process [16]. Meanwhile, after CO₂ activation, the density of the MFP-0.1 and MFP-0.7 samples decreased by 15.95% and 15.63%, respectively.

![Figure 2. The density of the MFP samples](image-url)
Figure 3. The CV curve of (a) MFP-0.1 at scan rates 1 and 2 mV s\(^{-1}\), (b) MFP-0.7 at scan rates 1 and 2 mV s\(^{-1}\), (c) MFP-0.1 and MFP-0.7 at scan rates 1 mV s\(^{-1}\), and (d) specific capacitances vs. scan rate.

With 1 M H\(_2\)SO\(_4\) solution as electrolyte, a two-electrode configuration was used to evaluate the electrochemical performance of MFP samples and displays in Figure 3. The CV curve of the MFP-0.1 and MFP-0.7 samples at a scan rates of 1 and 2 mV s\(^{-1}\) (Figure 3a and 3b) shows quasi-rectangular shape, indicating dominant double layer capacitance in the samples. Figure 3c display the CV curve of the MFP-0.1 and MFP-0.7 sample at scan rate of 1 mV s\(^{-1}\). Based on this curve, the MFP-0.1 sample outperforms the MFP-0.7 sample in terms of electrochemical performance, as evidenced by the wider \(I_c\) (charge current) and \(I_d\) (discharge current) curves, indicating that the MFP-0.1 sample has a higher specific capacitance [16]. The MFP-0.1 and MFP-0.7 samples have specific capacitances of 158 F g\(^{-1}\) and 87 F g\(^{-1}\), respectively. Figure 3d represent the specific capacitance of the MFP samples vs. scan rate. It can be seen that the specific capacitance of the MFP decreased with an increase in scan rate. This decrease occurred due to the time required for the ions to completely diffused into the electrode pores is very short at higher scan rates [17]. The details of specific capacitances based on CV curve at different scan rates are shown in Table 1.

| Scan rates (mV s\(^{-1}\)) | Specific capacitances (F g\(^{-1}\)) | MFP-0.1 | MFP-0.7 |
|---------------------------|-------------------------------------|--------|--------|
| 1                         | 158                                 | 87     |        |
| 2                         | 138                                 | 81     |        |
| 5                         | 85                                  | 61     |        |
| 10                        | 43                                  | 28     |        |
Figure 4 shows the GCD curve of the MFP samples at constant current 1 A at potential windows 0 up to 1 V. The GCD curve show the quasi-isosceles triangular shape, suggesting of dominant contributions by double layer capacitance. In addition, there is an internal resistances (IR) drops in both samples at voltages of 0.984 V (15 mΩ) for the MFP-0.1 sample and 0.945 V (54 mΩ) for the MFP-0.7 sample. The higher the IR drop, indicating the lower the specific capacitance, it was due to the presence of impurities which can be inhibit electrolyte ion diffusion on the electrode surface. Meanwhile, a small iR drop can be indicative of the electrode has high electrical conductivity [18,19].

The specific capacitance of the MFP-0.1 and MFP-0.7 sample based on GCD curves are 187 F g⁻¹ and 126 F g⁻¹, respectively. The MFP-0.1 sample has the optimum energy and power densities of 25.97 Wh kg⁻¹ and 57.75 W kg⁻¹, respectively. Table 2 shows the electrochemical performance of the MFP samples compared to other biomass waste-based activated carbon electrode. The electrode materials made from matoa fruit peel waste-based activated carbon show the suitable for used in supercapacitor devices.

Table 2. The electrochemical performance of the MFP sample compared to other biomass-based activated carbon electrode

| Biomass          | Electrolyte      | Specific capacitance (F g⁻¹) | Energy density (Wh kg⁻¹) | Power density (W kg⁻¹) | References |
|------------------|------------------|-------------------------------|--------------------------|------------------------|------------|
| Orange peel      | 6M KOH           | 306                           | 31.4                     | 4000                   | [4]        |
| *Cucumisemelo*   | 1M KOH           | 404                           | 29.3                     | 279.78                 | [12]       |
| Fruit peel       |                  |                               |                          |                        |            |
| Banana peel      | 1M H₂SO₄         | 68                            | 0.75                     | 31                     | [20]       |
| Shaddock         | 1M               | 550                           | 46.88                    | 300                    | [21]       |
| Endotheliums     | BMIMBF₄/AN       |                               |                          |                        |            |
| *Tectona grandis* | 1M H₂SO₄       | 168                           | 23.19                    | 83.56                  | [11]       |
| Leaf             |                  |                               |                          |                        |            |
| Corn husk        | 6M KOH           | 127                           | 4.4                      | 0.24                   | [22]       |
| Cotton stalks    | 1 M Et₄NBF₄      | 114                           | -                        | -                      | [23]       |
| Fallen teak leaves | 1M H₂SO₄      | 280                           | 9.72                     | 70.12                  | [24]       |
Lumpy bracket 6M KOH 223 9.4 - [25]
Tobacco waste 6M KOH 148 2.66 51 [26]
Willow leaf 6M KOH 216 - - [27]
Cassava green stem 1M H$_2$SO$_4$ 165 22.86 - [28]
Matoa fruit peel 1M H$_2$SO$_4$ 187 25.97 39.99 This work

4. Conclusion
In summary, electrode materials-based activated carbon for supercapacitor devices were synthesized using matoa fruit peel waste via combination of chemical and CO$_2$ activation. After CO$_2$ activation process, the density of the MFP-0.1 and MFP-0.7 samples have been decreased of 15.95% and 15.63%, respectively. In two-electrode configuration, the optimum specific capacitance of the MFP samples based on CV and GCD data are 158 F g$^{-1}$ and 187 F g$^{-1}$, respectively. In addition, the performance of electrochemical properties showed that the MFP sample is a promising suitable for used as electrode materials for supercapacitor devices.

Acknowledgements
The authors are grateful for financial support from Kementerian Pendidikan, Kebudayaan, Riset, dan Teknologi Republik Indonesia through the third year basic research grant (hibah penelitian dasar) 2021 (contract no. 1418/UN.19.5.1.3/PT.01.03/2021).

References
[1] Yadav N, Ritu, Promila and Hashmi S A 2020 Hierarchical porous carbon derived from eucalyptus-bark as a sustainable electrode for high-performance solid-state supercapacitors Sustain. Energy Fuels 4 1730–46
[2] Xu C, Li Z, Yang C, Zou P, Xie B, Lin Z and Zhang Z 2016 An Ultralong, Highly Oriented Nickel-Nanowire-Array Electrode Scaffold for High-Performance Compressible Pseudocapacitors Adv. Mater. 28 4105–10
[3] Niu Z, Zhou W, Chen X, Chen J and Xie S 2015 Highly Compressible and All-Solid-State Supercapacitors Based on Nanostructured Composite Sponge Adv. Mater. 27 6002–8
[4] Shen H, Xia X, Ouyang Y, Jiao X, Mutahir S, Mandler D and Hao Q 2019 Preparation of Biomass-Based Porous Carbons with High Specific Capacitance for Applications in Supercapacitors ChemElectroChem 6 3599–605
[5] Valente Nabais J M, Teixeira J G and Almeida I 2011 Development of easy made low cost bindless monolithic electrodes from biomass with controlled properties to be used as electrochemical capacitors Bioresour. Technol. 102 2781–7
[6] Chmiola J, Yushin G, Gogotsi Y, Portet C and Taberna P L 2006 Anomalous Increase in Carbon Capacitance at Pore Sizes Less Than 1 Nanometer Science (80-. ). 313 1760–4
[7] An-hui L U 2017 Two-Dimensional Carbon-Based Porous Materials: Synthesis and Applications Acta Physico-Chimica Sin. 33 709–28
[8] Raymundo-Pin’ero E, Cadek M and Be’guin F 2009 Tuning Carbon Materials for Supercapacitors by Direct Pyrolysis of Seaweeds Adv. Funct. Mater. 19 1032–9
[9] Zhang J, Gong L and Sun K 2012 Preparation of activated carbon from waste Camellia oleifera shell for supercapacitor application J. Solid State Electrochem. Vol. 16 2179–86
[10] Zequine C, Ranaweera C K, Wang Z, Singh S, Tripathi P, Srivastava O N, Gupta B K, Ramasamy K, Kahol P K and Dvornic P R 2016 High Per formance and Flexible Supercapacitors based on Carbonized Bamboo Fibers for Wide Temperature Applications Nature 31704
[11] Taer E, Melisa M, Agustino A, Taslim R, Sinta W and Apriwandi A 2021 Biomass-based activated carbon monolith from Tectona grandis leaf as supercapacitor electrode materials Energy Sources, Part A Recover. Util. Environ. Eff. 00 1–12
[12] Elaiyappillai E, Srinivasan R, Johnbosco Y, Devakumar P, Murugesan K, Kesavan K and
Johnson P M 2019 Low cost activated carbon derived from Cucumis melo fruit peel for electrochemical supercapacitor application Appl. Surf. Sci. 486 527–38

[13] Hao E, Liu W, Liu S, Zhang Y, Wang H, Chen S, Cheng F, Zhao S and Yang H 2017 Rich sulfur doped porous carbon materials derived from ginkgo leaves for multiple electrochemical energy storage devices J. Mater. Chem. A 5 2204–14

[14] Zhu X, Yu S, Xu K, Zhang Y, Zhang L, Lou G, Wu Y, Zhu E, Chen H, Shen Z, Bao B and Fu S 2018 Sustainable activated carbons from dead ginkgo leaves for supercapacitor electrode active materials Chem. Eng. Sci. 181 36–45

[15] Zhao J, Lai H, Lyu Z, Jiang Y, Xie K, Wang X, Wu Q, Yang L, Jin Z, Ma Y, Liu J and Hu Z 2015 Hydrophilic hierarchical nitrogen-doped carbon nanocages for ultrahigh supercapacitive performance Adv. Mater. 27 3541–5

[16] Taer E, Agustino A, Awitdrus A, Farma R and Taslim R 2021 The synthesis of carbon nanofiber derived from pineapple leaf fibers as a carbon electrode for supercapacitor application J. Electrochem. Energy Convers. Storage 18 031004-1-031004–8

[17] Awitdrus, A., Deraman, M., Talib, I.A., Farma, R., Nor, N.S.M., Ishak, M.M. and Dolah B N . 2016 Cyclic Voltammometry of Binderless Activated Carbon Monoliths based supercapacitor from Mixtures of Pre-carbonized of Fibers of Empty Fruit Bunches and Green Petroleum Coke KnE Eng. 1 1–8

[18] Wang D W, Li F, Liu M, Lu G Q and Cheng H M 2008 3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage Angew. Chemie - Int. Ed. 47 373–6

[19] Sodtipinta J, Ieosakulrat C, Poonyayant N, Kidkhunthod P, Chanlek N, Amornsakchai T and Pakawatpanurut P 2017 Interconnected open-channel carbon nanosheets derived from pineapple leaf fiber as a sustainable active material for supercapacitors Ind. Crops Prod. 104 13–20

[20] Taer E, Taslim R, Aini Z, Hartati S D and Mustika W S 2017 Activated carbon electrode from banana-peel waste for supercapacitor applications AIP Conf. Proc. 1801 040004-1-040004–4

[21] Yang S, Wang S, Liu X and Li L 2019 Biomass derived interconnected hierarchical micro-meso-macro-porous carbon with ultrahigh capacitance for supercapacitor Carbon N. Y. 147 540–9

[22] Usha Rani M, Nanaji K, Rao T N and Deshpande A S 2020 Corn husk derived activated carbon with enhanced electrochemical performance for high-voltage supercapacitors J. Power Sources 471 228387

[23] Chen M, Kang X, Wumaier T, Dou J, Gao B, Han Y, Xu G, Liu Z and Zhang L 2013 Preparation of activated carbon from cotton stalk and its application in supercapacitor J. Solid State Electrochem. 17 1005–12

[24] Taer E, Mardiah M A, Agustino A, Mustika W S, Apriwandi A and Taslim R 2021 A green and low-cost of mesoporous carbon electrode based activated carbon monolith derived from fallen teak leaves for high electrochemical performance J. Appl. Eng. Sci. 19 162–71

[25] Serafin J, Baca M, Biegun M, Mijowska E, Kaleńczuk R J, Sreńsczek-Nazzal J and Michalkiewicz B 2019 Direct conversion of biomass to nanoporous activated biochars for high CO2 adsorption and supercapacitor applications Appl. Surf. Sci. 497 143722

[26] 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

[27] Liu Y, Wang Y, Zhang G, Liu W, Wang D and Dong Y 2016 Preparation of activated carbon from willow leaves and evaluation in electric double-layer capacitors Mater. Lett. 176 60–3

[28] Taer E, Yanti N, Mustika W S, Apriwandi A, Taslim R and Agustino A 2021 Porous activated carbon monolith with nanosheet/nanofiber structure derived from the green stem of cassava for supercapacitor application Int. J. Energy Res. 44 10192–205