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Comparison of electrochemical performance of supercapacitor electrodes based on electrolyte solution variation

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ABSTRACT

The increasing global energy demand has accelerated the progress of renewable energy technologies and the creation of effective energy storage solutions such as supercapacitors. In this study, biomass obtained from the peel of the matoa fruit (Pometia pinnata) was employed as a raw material to produce activated carbon for supercapacitor electrodes. The preparation process consisted of an initial carbonization step, followed by chemical activation using a 0.7 M potassium hydroxide (KOH) solution, and then additional carbonization and physical activation stages. The synthesized material was characterized through density measurements and electrochemical testing, including cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) methods, conducted with KOH electrolytes at concentrations of 2, 4, and 6 M. Results demonstrated that combining chemical activation with pyrolysis yielded better outcomes than physical activation alone, as shown by a decrease in activated carbon density, indicating enhanced porosity and surface area. CV analysis revealed that increasing the KOH electrolyte concentration improved the supercapacitor's performance, reflected in higher specific capacitance during charge-discharge cycles. Moreover, GCD experiments showed that electrodes treated with 6 M KOH electrolyte achieved the greatest specific capacitance, energy density, and power density, recorded at 170.52 F/g, 23.68 Wh/kg, and 580.00 W/kg, respectively. These findings highlight that activated carbon derived from matoa fruit peel is a highly promising material for supercapacitor electrodes, combining excellent electrochemical characteristics, efficiency, and stable cycling behavior.

Keywords: Activated carbon; electrolyte; matoa fruit peel; supercapacitor

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INTRODUCTION

Global energy consumption is rapidly rising, primarily due to population expansion and fast-paced economic growth. Nevertheless, the heavy reliance on fossil fuels contributes to numerous environmental issues, including climate change, air quality deterioration, and the exhaustion of natural resources [1]. The extensive use of fossil fuels today has detrimental effects on the environment, particularly contributing to global warming and climate change. As a result, there is a rising demand for clean, renewable energy sources. These sustainable energy options are seen as the best alternatives to replace fossil fuels in the future.

Significant progress has been made in creating affordable renewable energy solutions, such as wind energy, solar energy, and biomass [2]. Shifting from conventional fossil fuels to renewable energy represents a crucial move toward achieving sustainable development. This shift depends largely on effective energy conversion and storage, with energy storage systems playing a vital role in facilitating the transition [3].

A major obstacle in harnessing renewable energy is its intermittent availability, which leads to fluctuations in power supply. This makes energy storage solutions like batteries and supercapacitors essential. Supercapacitors, in particular, offer advantages such as long-term energy retention and higher storage capacity [4].

Supercapacitors are storage devices developed from conventional capacitors. Supercapacitors have higher power density and better cycle endurance, making them highly effective in energy storage systems that are able

to respond to rapid power changes. There are two types of supercapacitors: electrochemical double layer capacitors (EDLC) that rely on adsorptive storage and pseudo-capacitors that use the Faradaic mechanism [5].

Biomass as an abundant renewable energy source on earth has an important role in supporting sustainability. Biomass is not only utilized for generating energy but also acts as the primary raw material for producing activated carbon. Research on carbonization techniques to convert waste into porous carbon is growing, especially because of its potential in various industrial applications [6].

KOH is a basic electrolyte because the energy density of supercapacitors using KOH is usually the same as the electrically conductive energy density [7]. The selection of electrolytes using appropriate ion size is essential to achieve optimal supercapacitor performance, Taer et al., (2020) emphasizes the significance of electrolyte ion size within the electrode.

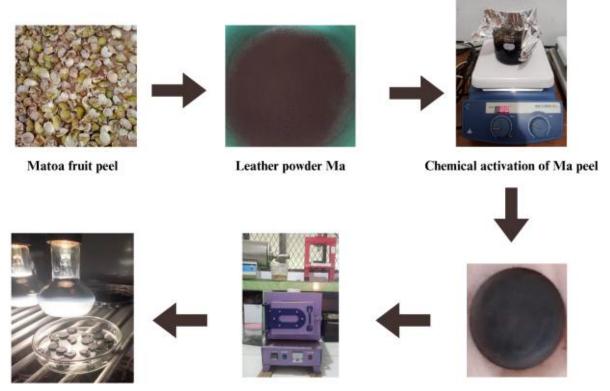
Biomass carbon is one of the materials often used for activated carbon. Several previous

studies have developed methods of making activated carbon for electrodes such as rice husk [9], bagasse [10], banana stem fiber [11] and matoa fruit peel [12]. This research uses biomass from matoa fruit peels using variations of KOH electrolyte solutions of 2 M, 4 M and 6 M using 0.7 M KOH activating agent as a supercapacitor electrode.

RESEARCH METHODS

Materials

This study used matoa (Pometia pinatta) fruit peel biomass material obtained from Tualang Village in Riau. Before the process of making supercapacitor electrodes, matoa fruit peels were dried and pre-carbonized. Carbon was activated using 0.7 M KOH activating agent. Electrochemical characterization with Cyclic Voltammetry and Galvanostatic Charge Discharge methods.



Ma neutral carbon electrode Carbonization and physical activation Ma activated carbon pellets Figure 1. Manufacturing process of Ma electrode.

Sample Preparation of Matoa Fruit Peel Biomass Activated Carbon

This preparation begins using collecting matoa fruit peels and then cut into small pieces up to 3-4 cm in size and dried under the sun for 4-5 days. A total of 30 grams of biomass was pre-carbonized in an oven at 200°C for 2 hours. The resulting carbon was crushed and sieved using a 53 μ m sieve to obtain a fine powder.

Chemical activation was carried out by mixing 20 grams of carbon powder into a 0.7 M KOH solution (100 ml of distilled water), stirred at 80°C and a rotation rate of 350 rpm for 15 minutes until homogeneous. Next, 20 grams of carbon powder was mixed using the KOH solution and stirred again under the same conditions for 2 hours. The mixture was kept at room temperature for 2 days, then dried in an oven at 110°C for 3 days.

The activated carbon produced was sieved again and formed into coin-shaped pellets measuring 8 mm in diameter and 2 mm in thickness by applying a pressure of 8 tons. Subsequent carbonization was performed in a furnace where the temperature was gradually increased from 30°C to 302°C at a rate of 1°C per minute and maintained for one hour, followed by a slow ramp-up to 600°C at 3°C per minute under a nitrogen atmosphere. Physical activation was continued by changing the N₂ gas to CO₂ and raising the temperature to 850°C (10°C/min), maintained for 2 hours and 30 minutes.

After controlled cooling using N2 to room temperature, the activated carbon was neutralized using distilled water to a pH close to 7 and dried again. The activated carbon was polished, washed and immersed in electrolyte before electrochemical testing.

Density is a quantity that shows the mass per unit volume of a material. In activated carbon material, density measurement is very important to determine the level of mass change and porosity in the material. Density is usually expressed in grams per cubic centimeter (gr/cm³). The density of each object is different

depending on the mass and volume of the object [13]. Density can be calculated using:

$$p = \frac{m}{v} \tag{1}$$

$$v = \pi r^2 t \tag{2}$$

Electrode material research, measurement of electrochemical properties can be done using methods such as Cyclic Voltammetry (CV), and Galvanostatic Charge-Discharge (GCD). These methods provide data such as: specific capacitance, current density, cycle stability and electron transfer kinetics. CV electrochemical testing aims to calculate the capacitance of supercapacitor cells [14].

Galvanostatic Charge-Discharge (GCD) testing is employed to evaluate the capacitive behavior, identify possible reversible faradaic processes, and determine key performance metrics of electrochemical capacitors, including capacitance, energy storage capacity, and power output [15]. This method is utilized to determine the electrochemically active surface area, double-layer capacitance, and hydrogen crossover current by employing a galvanostatic power source to acquire the necessary voltage readings [16]. The following formulas are applied to calculate the specific capacitance, energy density, and power density supercapacitor electrodes during galvanostatic charge-discharge (GCD) experiments [17]:

$$C_{sp} = \frac{2I.\Delta t}{m.\Delta V} \tag{3}$$

$$E_{sp} = \frac{C_{sp} \, \Delta V^2}{2} \times \frac{1000}{3600} \tag{4}$$

$$P_{sp} = 3600 \frac{E_{sp}}{\Delta t} \tag{5}$$

In this formula, I represents the current in amperes (A), t denotes the time in seconds (s), V stands for the voltage in volts (V), and m indicates the mass of the electrode in grams (g).

RESULTS AND DISCUSSION

Density Measurement

The low density of activated carbon generally indicates a porous structure, resulting from the chemical activation and pyrolysis process that opens and enlarges the pores, thus lowering the density. Measuring the density of activated carbon is crucial because it has a direct impact on the material's surface area and its ability to adsorb substances [18]. Figure 2 presents the changes in carbon's physical attributes such as mass, thickness, diameter, and density comparing values recorded prior to and following the pyrolysis treatment. Among these, thickness experiences the greatest shrinkage, followed by diameter, while changes in mass and density are comparatively minor. Post pyrolysis, the shrinkage of all parameters decreases, suggesting that the activated carbon's structure has become more stable and the mass to volume ratio remains consistent.

The almost stable density indicates the activated carbon produced has a porous and stable structure. The reduction in mass, diameter, thickness, volume, and density of the pellets following carbonization is due to the material breaking down during this process. During carbonization, elements such as oxygen, hydrogen, non-carbon components, as well as impurities are released from the material, leaving a carbon skeleton using a specific structure and the formation of pores in the carbon [19].

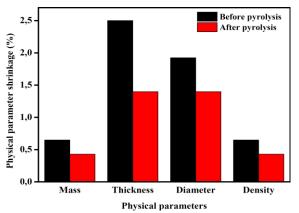


Figure 2. Mass shrinkage, thickness diameter and electrode density Ma.

Measurement of Electrochemical Properties

Electrochemical property measurement is an analytical process used to determine the characteristics of a material or system based on its response to electrical stimuli in an electrolyte environment. The primary goal of evaluating electrochemical characteristics is to assess the suitability of a material for use as an electrode in supercapacitor devices. The results of these measurements are very important to determine the performance, efficiency and lifetime of materials in electrochemical devices [20].

Cyclic Voltammetry (CV) is a widely utilized electrochemical method for analyzing the properties of electrode materials. This technique involves applying a linearly varying potential over time in repetitive cycles, while simultaneously recording the resulting current.

Figure 3 is the results of Cyclic Voltammetry (CV) measurements of matoa fruit peel biomass samples that have been activated using 0.7 M KOH, then tested in **KOH** electrolyte using variations concentrations of 2 M, 4 M and 6 M. The voltage (V) is shown on the x-axis, while the current density (A/cm²) is displayed on the yaxis. Each curve shows that the higher the scan rate, the larger the area under the curve which signifies an increase in charge storage capacitance. At elevated scan rates (10 mV/s), the curve's shape starts to deviate from the perfect rectangular form, suggesting presence of internal resistance and restricted ion movement within the electrode.

Visually, the CV curve for 4 M KOH has the highest peak current density, followed by 2 M KOH and 6 M KOH. This indicates that at a concentration of 4 M KOH, the speed of charge transfer at the electrode surface increases, as demonstrated by the elevated current produced. The figure indicates that a high electrolyte concentration increases the amount of K+ and OH- ions available in the solution. Cyclic Voltammetry (CV) is a widely utilized electrochemical method for analyzing the properties of electrode materials. This

technique involves applying a linearly varying potential over time in repetitive cycles, while simultaneously recording the resulting current. However, when viewed from the shape of the curve, all samples display a curve shape that tends to be symmetrical and resembles a rectangle, indicating good capacitive characteristics and high reversibility of the KOH electrode material.

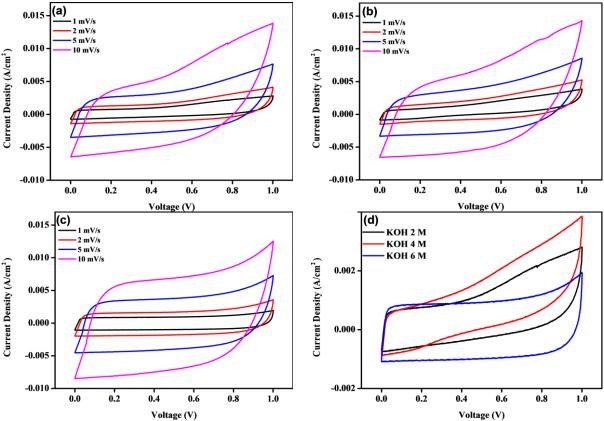


Figure 3. CV measurements of (a) 2 M KOH electrolyte, (b) 4 M KOH electrolyte, (c) 6 M KOH electrolyte, (d) comparison of (a), (b), (c) at a scan rate of 1 mV/s.

The electrode's specific capacitance in a 6 M KOH electrolyte generally exhibits a tendency to higher due to the lower current density value in CV generally associated using better charge transfer efficiency and less parasitic reaction. In addition, the symmetrical and stable curve shape at 6 M KOH indicates that the electrode is able to work optimally under high concentration electrolyte conditions, making it suitable for supercapacitor applications that require stability and high efficiency.

Galvanostatic Charge Discharge (GCD) is a technique in electrochemical testing where a steady current is used to both charge and discharge an electrode designed for energy storage. A constant current GCD process is applied so that the change in voltage versus electrode. A constant current GCD process is applied so that the change in voltage versus time during charging and discharging can be observed. These GCD curves provide important information about the specific capacitance, energy storage efficiency, internal resistance and cycle stability of the electrode material [21].

Figure 4 shows the Galvanostatic Charge Discharge (GCD) curve of the matoa fruit peel biomass-based electrode activated using 0.7 M KOH using three variations of KOH electrolyte concentration (2 M, 4 M, 6 M). This GCD curve illustrates the relationship between voltage (V) and time (s) during the charging and discharging process at constant current. Visually, the GCD curve for 6 M KOH shows the longest charge discharge time compared to

2 M KOH and 4 M KOH. This indicates that the electrode using 6 M KOH electrolyte is able to store and release charge in a longer time which is an indication of higher energy storage capacity. The shape of the curve which tends to be symmetrical and linear also indicates good capacitive characteristics and reversible charge discharge process.

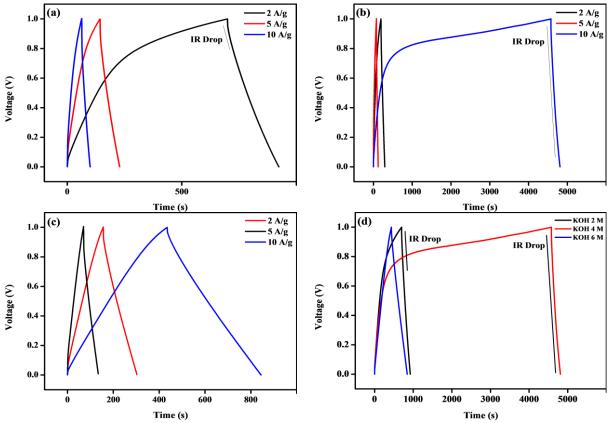


Figure 4. GCD measurements of (a) 2 M KOH electrolyte, (b) 4 M KOH electrolyte, (c) 6 M KOH electrolyte, (d) comparison of (a), (b), (c) at a scan rate of 2 A/g.

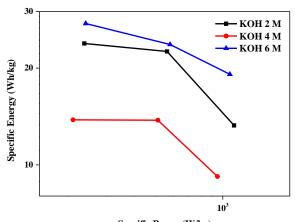
Table 1. GCD measurement results data.

| Sample code | C_{sp} | P_{sp} | E_{sp} |
|-------------|----------|----------|----------|
| | (F/g) | (W/kg) | (Wh/kg) |
| KOH 2 M | 95.51 | 561.87 | 22.53 |
| KOH 4 M | 99.15 | 511.11 | 13.77 |
| KOH 6 M | 170.52 | 580.00 | 23.68 |

Data Table 1 is the GCD data of specific capacitance (Csp), specific power (Psp) and specific energy (Esp) measurements for each electrolyte variation. The data indicate that the electrode utilizing a 6 M KOH electrolyte exhibits the greatest specific capacitance (Csp) at 170.52 F/g, along with the highest specific energy (Esp) of 23.68 Wh/kg. Additionally, the specific power (Psp) reaches its peak value of 580 W/kg with the 6 M KOH electrolyte.

The high specific capacitance value at 6 M KOH indicates that the electrode is able to store

more charge per unit mass which is also reflected in the longer discharge time on the GCD curve. This indicates that at higher KOH concentrations the number of ions available to interact using the electrode surface increases so that the charge storage process takes place more efficiently. Moreover, the material generates higher specific energy, demonstrating its efficient capability to store and discharge energy. In contrast, at 2 M and 4 M KOH although the final voltage achieved is almost the same the discharge time is shorter and the capacitance value and specific energy are lower. This can be caused by the limited number of ions available at lower electrolyte concentrations so that the charge storage process is not as efficient as at 6 M KOH. Figure 4 (d) comparison of the three electrolyte concentrations at a current density of 2 A/g clarifies the advantages of 6 M KOH, where the longest discharge time indicates low internal resistance and high ion transfer efficiency. The combination of KOH-activated porous activated carbon and high concentration KOH electrolyte provides the best supercapacitor performance, especially in terms of specific capacitance and cycle efficiency [22].



Specific Power (W/kg)

Figure 5. Plot Ragone.

Ragone plots illustrate the balance between specific energy and specific power in energy storage systems like supercapacitors. Typically, as specific power—which reflects the ability to deliver energy quickly—increases, the specific energy tends to decline [23]. Comparing the performance of the three electrolyte variations, the 6 M KOH sample shows efficient performance in storing and releasing energy at both low and high rates. This occurs because of the efficient interaction between ions and the electrode surface, allowing for greater charge storage and release during the charging and discharging cycles. The decrease in specific energy at high power is a common phenomenon in supercapacitors because at high currents the discharge time is shorter so that the total energy released is smaller. Overall, KOH 6 M is the recommended electrolyte for application of 0.7 M KOH-activated matoa fruit quit biomass-based supercapacitors because it is able to keep the specific energy high even at high specific power. The 6 M KOH electrolyte also showed good performance to improve the

supercapacitor efficiency for both long-term energy applications and instant power needs.

CONCLUSION

This study demonstrated that the type of separator material significantly influences the performance of activated electrochemical carbon electrodes derived from orange peel biomass supercapacitor applications. Among the three separators tested Whatman filter paper no. 40 (JR-800-W), eggshell membrane (JR-800-E), and orange fruit membrane (JR-800-O) the JR-800-W sample consistently exhibited the highest specific capacitance in both CV (191.82 F/g) and GCD (174.24)F/g) analyses. This superior performance is attributed to the uniform microporous structure and excellent electrolyte absorption of Whatman paper, which promotes faster ion diffusion and more efficient electric double-layer formation. The eggshell membrane separator (JR-800-E) showed moderate performance, with sufficient ionic mobility but slightly higher internal resistance. Meanwhile, the orange fruit membrane (JR-800-O) demonstrated the lowest performance due to its dense, non-uniform structure and limited electrolyte uptake, resulting in reduced ion transport and higher IR drop. These findings affirm that choosing a separator with high porosity, good wettability, and mechanical stability is critical to optimizing the energy storage efficiency and cycling stability of supercapacitor devices.

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