Investigation of H$_2$SO$_4$ and KOH aqueous electrolytes on the electrochemical performance of activated carbon derived from areca catechu husk

Erman Taer$^{1,*}$, Friska Febriyanti$^1$, Apriwandi$^1$, Rika Taslim$^2$, Agustino$^1$, Widya Sinta Mustika$^1$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences, University of Riau, 28293 Simpang Baru, Riau, Indonesia
$^2$Department of Industrial Engineering, State Islamic University of Sultan Syarif Kasim, 28293 Simpang Baru, Riau, Indonesia

*erman.taer@lecturer.unri.ac.id

Abstract. Aqueous electrolytes have shown great interest in developing high performance and environmentally friendly supercapacitors. This work focuses on systematic investigations of the symmetrical properties of activated carbon electrode for supercapacitors in different aqueous electrolytes. Here, we compare the performance of supercapacitors using 1M KOH and 1M H$_2$SO$_4$ different electrolytes based on carbon monolith electrodes derived from areca catechu husk waste. Carbon electrodes were synthesized using single-step pyrolysis both carbonization and physical activation without the addition of synthetic adhesive materials. The electrochemical properties were evaluated based on the cyclic voltammetry method at voltage windows of 0-0.5V and 0-1.0V with a scanning rate of 1 mV s$^{-1}$, 2 mV s$^{-1}$, 5 mV s$^{-1}$, and 10 mV s$^{-1}$. The electrode supercapacitor showed the highest specific capacitance of 150 F g$^{-1}$ and 112 F g$^{-1}$ at a scanning rate of 1 mV s$^{-1}$ for H$_2$SO$_4$ and KOH electrolytes respectively. The maximum specific energy was found as high as 20.97 Wh kg$^{-1}$ and the specific power of 75.57 kW kg$^{-1}$ at the voltage window of 0-1.0V were achieved for H$_2$SO$_4$ electrolytes. As addition, the physical properties of carbon electrode also characterized such as mass, volume, and density. This work provides consideration the selected of different aqueous electrolytes for high-performance supercapacitors.

1. Introduction
Energy storage technology currently being developed worldwide is a supercapacitor. In recent years, supercapacitors especially the type of electric double-layer capacitors have become one of the most prominent energy storage devices because of their high power density, long life circle, high charging rates, and low costs [1,2]. However, this device still has a lower energy density. To improve the supercapacitor energy density, many researchers reported various improvisations. The electrode material is the main key to enhance the supercapacitor's energy density [2,3]. Types of electrode material have been investigated such as porous carbon, transition oxide, and sulfide metals, polymer conductors, and various types of composite materials [4–7]. However, porous carbon from biomass waste shows high potential as the electrode material for supercapacitor [8]. Besides being able to improve supercapacitor performance, porous carbon material from biomass is superior to others...
because of its abundant availability, low cost, renewability, high surface area, and the provide suitable pores, high conductivity, and good chemical stability. These advantages could be to increase supercapacitor energy density [9–11]. However, this high energy density sacrifices its life cycle and its power density [12].

Electrolytes are the best solution to this problem. Electrolytes play a role in the transfer of internal charge to supercapacitor electrodes [13,14]. Electrolyte ions penetrate the pores between two opposite electrodes to achieve maximum charge transfer at the electrolyte interface. Several type of electrolytes that have been developed by researchers such as organic electrolytes, aqueous electrolytes, and ionic liquid electrolytes [13,15,16]. As far as electrolytes are considered, an aqueous electrolyte such as KOH, H2SO4, and Na2SO4 solutions have the advantage of high ionic conductivity, low cost, liquid nature, and low viscosity providing excellent interface contact, non-flammable, non-corrosive, safe and convenient assembly in the air, compared to organic electrolytes, which are believed to be less conductive, expensive, usually flammable, and toxic higher [17,18].

In this study, we optimized porous activated carbon from materials from areca catechu husk biomass on different aqueous electrolytes. Activated carbon is prepared by a simple and up-to-date method through chemical activation and an integrated one-step pyrolysis process. 0.6 M KOH was selected as a chemical activator agent and N2 and CO2 gases were used as carbonization and physical activation environments at high temperatures. H2SO4 and KOH in 1 M selected as aqueous electrolytes is the main discussion in improving the performance of biomass-based carbon electrodes. These results show that the performance of activated carbon has been increased from 112 F g⁻¹ to 150 F g⁻¹ through 1M H2SO4 electrolyte. Based on this comparative study and results, we recommend that 1 M H2SO4 is better used as an electrolyte on biomass-based carbon electrodes especially areca catechu husk compared to 1 M KOH.

2. Materials and Method

2.1. Synthesis of biomass-based carbon electrodes

Areca catechu husk is the raw material for synthesis activated carbon electrodes which collected from traditional market of Pekanbaru. Samples are sundried for 2 days and continued by dried in the oven for 48 hours at 110°C. Next, samples were pre-carbonized at 250°C for 2.5 hours and then demolished using mortars and ball milling for 24 hours to get pre-carbonized powder samples. Pre-carbonized powders were chemically activated by using 0.6 M KOH for 2 hours at a hot plate. The activated sample is converted into monolithic form by using hydraulic press at a diameter of 2 cm. Single-step pyrolysis process both carbonization and physical activation was performed which start with carbonization at N2 gas atmosphere from room temperature to 600°C and followed by physical activation using CO2 gas environment at a temperature of 900°C for 2.5 hours. Finally, the electrodes were neutralized using distilled water. After the neutral electrodes were polished using P600 and P1200 sandpaper until diameter and thickness are ± 7.00 mm and ± 0.20 mm thickness.

![Figure 1. Schematic of preparation of biomass-based carbon electrodes](image)

2.2. Dimensions measurement

Dimensions of carbon monolith were performed with measurements of diameters, thickness, volumes, mass, and density of the monolithic carbon electrodes. 20 monolith carbon samples were prepared to measure the mass, diameter and thickness. Density is obtained from standard equation.
2.3. Electrochemical measurement

The electrochemical properties were observed by using the cyclic voltammetry method with the Physics CV UR Rad-Er 5841 instrument with calibrated by using VersaStat II Princeton Applied Research, an error of ±6.05% in potential windows of 0-0.5V and 0-1.0V at scan rate of 1 mV/s, 2 mV/s, 5 mV/s, and 10 mV/s. The supercapacitor cell was rearranged by the coin type with an egg duck shell as a separator into the two-electrode system. The two aqueous electrolytes it the main focus in this study were H\textsubscript{2}SO\textsubscript{4} and KOH in 1 M solution. The values of specific capacitance (C\textsubscript{sp}, F g\textsuperscript{-1}), energy density (E, Wh kg\textsuperscript{-1}), and power density (P, W kg\textsuperscript{-1}) were obtained by using the standard equations. Were, I is the average current (charge and discharge, A), s is the scan rate (mV s\textsuperscript{-1}), m is the active mass of the electrode (g), V is voltage window (V), and Δt is time for discharge process (s).

\[
C_{sp} = \frac{2I}{s m} \tag{1}
\]
\[
E = \frac{1}{2} C_{sp} V^2 \cdot \frac{1000}{3600} \tag{2}
\]
\[
P = \frac{E}{\Delta t} \cdot 3600 \tag{3}
\]

3. Results and Discussion

3.1. Density analysis

Density is the initial review to evaluate the physical properties of carbon electrode in monolith form especially pore structure and porosity. Carbonization, chemical activation, and physical activation play an important role in developing the pore structure that exists on carbon electrodes. Chemically activation of KOH generated porous carbon by intercalating K+ into carbon. Initially, potassium hydroxide is decomposed to form potassium carbonate and resulting in the formation of micropore. At high temperature, potassium carbonate is converted into carbon dioxide and enlarge the micropores. Furthermore, CO\textsubscript{2} in physical activation reacts with carbon to form carbon monoxide and open previously inaccessible pore which is blocked by disordered carbon atom and heteroatom. The existing micropores continuously enlarged, and the mesopores developed by collapsing the wall between adjacent micropores. This contributed to decreasing the mass, volume and density of the sample. This is evidenced by the shrinkage of the mass, the volume of carbon monolith after carbonization and physical activation.

![Figure 2. Mass, volume, and density of the moonlit carbon electrode](image-url)
Fig. 2 shows the decrease in mass, volume, and density of monolith carbon derived from areca catechu husk. In pyrolysis (carbonization and activation) clearly influences the density of the sample where carbonization at 600 °C which releases volatiles such as oxygen, nitrogen, hydrogen [1]. The purpose of the carbonization is to reduce the volatile content of the starting material to convert the resulting char with a higher content of fixed carbon [3]. After the carbonization process is still needed an activation process that aims to produce porous activated carbon. Particle size is the main determinant of carbon monolith density values. Samples with larger particles will form larger pores between these particles, resulting in a smaller mass density, while smaller particle sizes will form smaller pores between these particles, resulting in greater density. The activation process also causes a decrease in sample density.

3.2. Electrochemical performances

The electrochemical behavior of the monolith biomass-based carbon electrode was evaluated in two-electrode system with two different aqueous electrolyte of acidic electrolyte H$_2$SO$_4$ and basic electrolyte KOH in 1 M solution. The potential window also varied of 0.5 V and 1.0 V. Fig. 3a shows a near-perfect rectangular CV curve at a voltage window of 0.5 V. This indicates the typical behavior of electrochemical double-layer capacitors [19,20]. Furthermore, H$_2$SO$_4$ electrolytes display a relatively large hysteresis area of CV curve compared to KOH. The large hysteresis area on the curve performed better electrode performance. Based on equation (1), the specific capacitance of H$_2$SO$_4$ electrolyte is higher as high as 112 F/g than KOH electrolyte of 89 F/g. An increasing voltage window to 1 V exhibits a malformed curvilinear curve that was mainly implied good conductivity of the samples, as shown in Fig. 3b. The specific capacitance could be enhanced higher, around 34% for H$_2$SO$_4$ electrolytes, and 29% for KOH electrolytes. This is due to the process of diffusion of ions into carbon pores better on the surface of the electrode at a higher voltage of 1 V compared to 0.5 V. Electrolyte ions have a relatively long time to diffuse at the electrode/electrolyte interface and exhibit more electric double-layer. However, H$_2$SO$_4$ electrolytes still showed better performance than KOH. This event is due to acidic electrolyte H$_2$SO$_4$ which is considered to have a diameter of ions that is more suitable for diffusion to the pores of biomass-based activated carbon compared to KOH which is a basic electrolyte. As has been widely reported, the differences observed in CV curves of monolith carbon electrode in different electrolytes come from different physical properties of the ions from these different electrolytes. Some of these properties include the ionic radius, radius of ionic hydration sphere, molar conductivity and ionic mobility.

**Figure 3.** CV curve of monolith carbon electrode with H$_2$SO$_4$ and KOH electrolyte in scan rate of 1 mV s$^{-1}$ at a potential window of (a) 0.5 V, and (b) 1.0 V

Therefore, the main factors in determining capacitive performance using different electrolytes have to be those of mobility and conductivity of the ions. Those of mobility and conductivity of the ions, H$^+$ cations have the highest ion conductivity of 350.1 cm$^2$Ω$^{-1}$mol$^{-1}$ which is almost five folds as compared
to that of K\textsuperscript{+} cations of 73.5 cm\textsuperscript{2} Ω\textsuperscript{-1}mol\textsuperscript{-1}, while radius of hydration sphere H\textsuperscript{+} smaller of 2.8 Å than K\textsuperscript{+} of 3.31 Å, thus H\textsuperscript{+} cation is the highest mobility and conductivity of the ions and smallest radius of hydration sphere. Consequently, H\textsuperscript{+} cations could be easily migrated into the electrode/electrolyte surface during charging and into the electrolyte bulk during discharging. However, the bigger SO\textsubscript{4}\textsuperscript{2-} anion of 3.74 Å than OH\textsuperscript{-} anion of 3.00 Å will reduce the mobility of H\textsuperscript{+} cation thus making the electrochemical behavior of the capacitor in the H\textsubscript{2}SO\textsubscript{4} electrolyte less favorable [15,17].

**Figure 4.** CV curve of monolith carbon electrode with H\textsubscript{2}SO\textsubscript{4} and KOH electrolyte in scan rate of 2 mV s\textsuperscript{-1} at a potential window of (a) 0.5 V, and (b) 1.0 V

The performance CV curves of monolith biomass-based carbon electrode at different scan rates are shown in Fig. 4. This CV curve maintains approximate quasi-rectangular shapes at 2 mV s\textsuperscript{-1} both of 0.5 V and 1.0 V voltage window. This is indicated by physical properties of monolith carbon such as morphology structure and pore structure which combination of micropores and mesopores which provide the relatively short diffusion distance of the ions diffusion in the electrolyte/electrode interface. However, 1.0 V window voltage still showed malformed curvilinear curve which shown in Fig 3b. Furthermore, this increasing scan rate from 1 to 10 mV s\textsuperscript{-1} caused smaller the specific capacitance as shown in Fig. 5. The specific capacitance is reduced from 150 F g\textsuperscript{-1} to 34 F g\textsuperscript{-1} for H\textsubscript{2}SO\textsubscript{4} electrolyte and from 115 to 34 F g\textsuperscript{-1} of KOH electrolyte at 10 mV s\textsuperscript{-1}. This might cause by enough time for electrolyte ions to move into the available pores and an increase in redox reaction in the outer surface of the electrode carbon monolith [21]. Interestingly, the specific capacitance produced from the KOH electrolyte is more stable than the H\textsubscript{2}SO\textsubscript{4} at high scanning rates which indicated with low in Figure 5. KOH only reduces specific capacitance around 70.4% compared to H\textsubscript{2}SO\textsubscript{4} around 77.4%. However, at a low scanning rate, H\textsubscript{2}SO\textsubscript{4} electrolytes showed better performance for carbon monolith electrodes.

**Figure 5.** The specific capacitance of monolith carbon electrode at different scan rates
Based on equations (2) and (3), the energy density of monolith carbon electrode in H$_2$SO$_4$ and KOH electrolytes were 20.83 and 15.97 Wh kg$^{-1}$ with a high power density of 75.06 and 57.54 W kg$^{-1}$, respectively. These results showed that the parameter values are within the range required for the porous activated carbon biomass electrodes because the porous carbon from coffee waste exhibits an energy and power density of 34 Wh kg$^{-1}$ and 215 W kg$^{-1}$, respectively [22].

4. Conclusion
Cyclic voltammetry method has been used to compare the electrochemical behaviors for the supercapacitors electrode based on the activated carbon material in form of monolith derived from areca catechu husk in 1 M H$_2$SO$_4$ and 1 M KOH electrolyte solutions. Monolith carbon electrode in 1 M H$_2$SO$_4$ performed excellent electrochemical storage properties including a highest specific capacitance of 150 F g$^{-1}$, energy density of 20.83 Wh kg$^{-1}$, and power density of 75.06 W kg$^{-1}$ at 1.0 V voltage window. However, the specific capacitance produced from the KOH electrolyte is more stable than the H$_2$SO$_4$ at high scanning rates of 10 mV s$^{-1}$ with reduced of 70.4%. These results suggest and confirm that 1 M H$_2$SO$_4$ is the ideal aqueous electrolyte for monolith biomass based-carbon electrode especially derived from areca catechu husk.

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