Electrochemical Properties of Activated Carbon Electrodes for Supercapacitor Application: The Effect of Various Electrolyte Concentrations of Na$_2$SO$_4$

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ABSTRACT

To achieve the high accomplishment of the supercapacitor, various electrolyte concentrations of Na$_2$SO$_4$ (0.5 M, 1 M, and 2 M) were added to the activated carbon (AC) electrode. The AC has a moderate surface area of 1,500 m$^2$/g and a pore size of 1 nm (micropore scale). The AC electrode was deposited from the mixture of AC, carbon black, and polytetrafluoroethylene (PTFE) with a weight ratio of 8:1:1 using the doctor blade method. Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD), and Electrical Impedance Spectroscopy (EIS) were used to characterize the electrodes electrochemically. Based on CV, GCD, and EIS characterizations, the measured specific capacitance of 17.2 F/g and ESR of 4.4 $\Omega$ exhibit the best performance due to their high ionic conductivity. We can conclude that 2 M Na$_2$SO$_4$ is a viable option for the ionic electrolyte of the microporous AC for the high performance of a supercapacitor.

INTRODUCTION

Supercapacitors have been regarded as potential storage devices because of their high specific capacitance, lengthy lifespan, and quick charging/discharging (Mohanadas & Sulaiman, 2022; Poonam et al., 2019; Yadlapalli et al., 2022). Supercapacitor research is expanding rapidly, coupled with nanotechnology and material advancements. Researchers have designed many nanoarchitectures, such as nanotubes, nanowires, nanosheets, and nanopores, as electrode materials to develop high storage capacity. Also, these nanoarchitectures have been integrated with a metal oxide or conducting polymer to compete with the battery in terms of energy density (Najib & Erdem, 2019; Wang et al., 2021). There are numerous applications of the supercapacitor, notably in portable electronics and hybrid electric vehicles (Huang et al., 2019; Sharma & Kumar, 2020).

Supercapacitor electrodes can be made from carbon-based material (activated carbon (AC), carbon nanotube (CNT) and graphene), metal oxide (ruthenium oxide, nickel oxide, manganese oxide) and conducting polymers (polyaniline) (González et al., 2016). Activated carbon (AC) is one of the legendary electrodes for supercapacitors owing to superior surface area, good electrical properties, and moderate cost. (González et al., 2016; Iro et al., 2016; Poonam et al., 2019). A large surface area will provide more ions to be adsorbed in the electrode. As a result, the capacitance will be increased. Electrical property is also needed to deliver electric charges along the system.
Numerous advancements in AC have been made gradually, including investigating various electrodes and incorporating many types of electrolytes. An electrolyte solution is used in supercapacitors to enable ion settling on the AC (Pal et al., 2019). Aqueous electrolytes remain popular among researchers because of their strong ionic conductivity, safety, and convenience of handling despite the development of many different forms of electrolytes. The other electrolytes are organic, gel, and redox (Cao et al., 2021; Qin et al., 2020; Xu et al., 2021; Chen et al., 2019). The aqueous electrolytes H2SO4, H3PO4, Na2SO4, KOH, and KCl are frequently employed (Awitdrus et al., 2022; Li et al., 2019; Su et al., 2020).

Many researchers have created various types of electrolytes to provide good ionic mobility into the pores of AC. Ionic concentration affects ionic mobility. The charge that fills the electrode pores decreases if the ionic concentration is too low. On the other hand, if the electrolyte concentration is excessively high, diminished water hydration will reduce ionic mobility. Recent progress in supercapacitors employs extremely high concentrations of 6 M KOH to gain excellent specific capacitance compared to the low concentrations of 1 M or 2 M KOH (Guo et al., 2019). However, the high concentration of KOH would induce the corrosion problem.

To overcome this problem, neutral electrolytes such as Na2SO4 can be good alternatives for electrolyte leading of the high voltage window of 1.6 V (voltage window of KOH is 1.0 V), excellent cycle stability and good candidate for flexible supercapacitor (Du et al., 2021; Haider et al., 2022; Al Jahdaly et al., 2022; Lobato-Peralta et al., 2021; Krishnan & Biju, 2021; Mishra et al., 2020). The high voltage can induce high energy density. Due to its neutral electrolyte, Na2SO4 has ideal double-layer capacitive behavior. On the contrary, KOH can exhibit pseudocapacitive characteristics from its oxygen-containing functional groups of the AC that reduce the lifetime of the supercapacitor (Li et al., 2022). Based on the advantages of the environmentally safe and good prospect of Na2SO4, we preferred to utilize Na2SO4 for supercapacitor electrolyte. As far as we know, few studies compare electrolyte concentration to capacitance performance. Previous research has reported the best capacitance using only 0.5 M Na2SO4 (Tsay et al., 2012). As far as we know, no literature reports the effect of various concentrations of 0.5-2M Na2SO4 on the electrochemical properties of the AC electrodes. We hypothesize that the high electrolyte concentration can increase the capacitance due to its high ion content. Therefore, in this study, we explored the effect of various concentrations on the electrochemical performance of the electrodes. We restricted the maximal Na2SO4 concentration of 2M due to its low solubility above 2M. In the laboratory, if we increase molarity above 2M, it cannot dissolve well. The salt content is very low if we use a concentration under 0.5M.

METHODS
1. Preparation of electrodes
AC with a surface area of 1500 m²/g and average pore size of 1 nm was purchased from Chemical Bonding, U.S.A. carbon black from Graphene Supermarket (U.S.A.), and polytetrafluoroethylene (PTFE) from China were combined to create the supercapacitor electrode. Here, we use the micropore AC (pore size < 2 nm) with its moderate surface area to represent the typical commercial supercapacitor. The chemicals were purchased from different countries due to material availability. The flow chart of this

(Kurniawan et al., 2019; Poonam et al., 2019; Wang et al., 2021; Glogic et al., 2022). For sustainable and large mass production, cost also must be considered. AC can be derived from many kinds of biomass, such as coconut shells, rice husks, corn cob, banana stems and starch (Arief et al., 2023; Hajar et al., 2022; Novita et al., 2022; Ghosh et al., 2019; Sundriyal et al., 2021; Keppetipola et al., 2021; Saikia et al., 2020).
procedure is given in Figure 1. The mixture of AC, carbon black, and PTFE with a mass ratio of 8:1:1 was selected based on our experience in the laboratory. To prepare the electrode, PTFE (1 wt%) was dissolved in N-methyl pyrrolidone (NMP, Sigma Aldrich) at a temperature of 40°C. PTFE has good mechanical properties and is stable at various temperatures and pH levels. PTFE was stirred for 2 hours to ensure the solution was homogeneous. Then, while continuously stirring, the AC and carbon black were added. The slurry was complete after the mixture was homogeneous. The electrode was created by coating the slurry on a 1 × 1 cm² piece of stainless steel plate with a thickness of 0.05 mm. Previously, conductive carbon glue was applied to stainless steel to improve the adhesion of all carbon particles to the stainless steel. The finished electrodes were dried at 110°C in a vacuum oven for two hours.

2. Electrochemical Characterization

An integrated Corrtest CS310H, which consists of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge (GCD), was used to evaluate the performance of the supercapacitor electrode. Three set-up electrode modes were used in all of the measurement. The AC electrodes served as the working electrode, Pt as the counter electrode, and Ag/AgCl was the reference electrode. All three electrodes were immersed in various electrolyte concentrations of 0.5 M, 1 M, and 2 M alternately. The procedure of immersion was intended to condition stable charging and discharging. The scan rate of 10 mV/s was used for the CV. GCD was operated at a current density of 1 mA/g. The frequency range was applied between 0.1 Hz to 1 kHz for the EIS method. EIS spectra can identify the internal resistance by the intercept of the x-axis due to the electrode and electrolyte resistance. Also, it represents the capacitance behavior of the straight line in low frequency. EIS spectrum analyzer software was utilized to fit the EIS data using an equivalent circuit model. Repeated measurements were taken for all the data and the average result was calculated.

RESULTS AND DISCUSSION

Figure 1. Experimental Procedure Flow Chart

Figure 2 shows the produced supercapacitor electrodes. The square box's extremely dark portion is made of AC, and the stainless steel plate is visible on the glossy rod.

Figure 2. Digital Images of the Three Electrodes

Figure 2 displays the CV curve for AC with various electrolyte concentrations. All the AC samples with various electrolyte concentrations exhibit the typical double-layer curve that resembles a rectangle-like curve. This characteristic is like the previous studies (Xu et al., 2019; Cheng et al., 2020; Wang et al., 2020). Comparing the three CV
curves, the 0.5 M Na₂SO₄ has the least area under the curve. The value of the area under the curve is linear concerning capacitance. The higher the area under the curve is, the higher the capacitance. The calculated specific capacitance (table 1) is calculated using the equation as reported by Wei (Wei et al., 2022).

Figure 2. CV of Electrodes Supercapacitor with Different Electrolyte Concentration

Figure 3 shows the GCDs curve of the supercapacitor electrodes with different electrolyte concentrations. All the samples show a triangular shape. The electrolyte concentration of 0.5 M Na₂SO₄ generally has a rapid charging/discharging time compared to the others. This is probably due to the fact that only a small number of ions could travel into the electrode's pores and fill them quickly. GCD curve of the concentration of 1 M and 2 M has an overlapping curve and quite similar charging/discharging time. The longer charge/discharge time represents the better capacitance (Nguyen et al., 2023).

Figure 3. GCD of Electrodes Supercapacitor with Different Electrolyte Concentration

Figure 4 provides EIS curves of the AC at various electrolyte concentrations. The fitted EIS curve matches the analogous electrical component as depicted in the inset image of Figure 4. In various electrolyte concentrations, the Nyquist spectra have similar shapes of a small semicircle with a straight line. The semicircle shape offers resistance data of $R_{ESR}$ and $R_{CT}$. The $R_{ESR}$ (Equivalent Series Resistance), which is shown as a semicircle intersection with the Z-axis, represents the solution electrolyte resistance. $R_{CT}$ originated from the charge transfer at the electrode/electrolyte interface. The Warburg impedance relates to the diffusion ions in the electrode as a transition between the semicircle and the straight line (Sivachidambaran et al., 2019). In Figure 4, the 2 M of Na₂SO₄ has the lowest semicircle intersection, which indicates the lowest ESR of 4.4 Ω. Other ESR values are given in Table 1. Also, the straight line of 2 M of Na₂SO₄ represents the angle closest to 45°, which implies good ionic diffusion.

Figure 4. EIS of Electrodes Supercapacitor with Different Electrolyte Concentration

Table 1 lists the supercapacitor's specific capacitance and the ESR. Compared to the AC in the 0.5 M and 1 M of Na₂SO₄ (1.3 F/g and 15.6 F/g, respectively), the AC in the 2 M of Na₂SO₄ had the highest capacitance at 17.2 F/g. Specific capacitance increases linearly with the Na₂SO₄ concentration. On the other hand, the ESR decreases with the
increase of Na$_2$SO$_4$ concentration. The lowest ESR, 4.4 $\Omega$, is found in the electrolyte of 2 M of Na$_2$SO$_4$. ESR values for other electrolytes of 0.5 M and 1 M Na$_2$SO$_4$ are 7.2 $\Omega$ and 5.8 $\Omega$, respectively. These results indicate that 2 M of Na$_2$SO$_4$ is the best electrolyte for the highest specific capacitance due to the low diffusion resistance of the ESR value. It is shown that a high electrolyte concentration can induce low resistance of electrolytes due to their high mobility along the electrode. On the other hand, the high electrolyte concentration contributes to the high amount of ions to be stored in the supercapacitor.

Table 1. Electrochemical Characteristics of Electrodes Supercapacitor

<table>
<thead>
<tr>
<th>Na$_2$SO$_4$ (M)</th>
<th>Results</th>
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<tr>
<td></td>
<td>C (F/g)</td>
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<tr>
<td>0.5</td>
<td>1.30</td>
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<tr>
<td>1</td>
<td>15.6</td>
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<tr>
<td>2</td>
<td>17.2</td>
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CONCLUSION AND SUGGESTION

The supercapacitor electrodes based on AC have been made and characterized with various electrolyte concentrations of 0.5-2 M. The electrode performs best in 2 M of Na$_2$SO$_4$ according to the CV, GCD, and EIS curves. This study showed that AC with an average size of 1 nm performs optimally for electrolyte concentration of 2 M Na$_2$SO$_4$. For further study, different concentrations of Na$_2$SO$_4$ electrolyte can be assessed for mesopore carbon or other nanocomposite electrodes.

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REFERENCES


