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Analysis of KCl and H_2SO_4 Electrolyte Concentration Variations on Specific Capacitance of Electrodes (CNT/PVA) Through Cyclic Voltammetry (CV)

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Abstract
This research focuses on being a solution to the problem of increasing energy consumption, especially electrical energy. Supercapacitor components generally consist of electrodes, electrolytes, and separators. Electrolytes have an important role that can affect the specific capacitance of supercapacitors. This research resulted in analyzing the type and variation of electrolyte concentrations in the form of KCl and H_2SO_4 at concentrations of 0.4; 0.7 and 1 M, respectively. Cyclic voltammetry (CV) was conducted using carbon nanotube electrodes which were molded into sheets using Polyvinyl Alcohol (PVA) binder. CV analysis aims to determine the supercapacitor performance as measured by the specific capacitance value. Based on the observation of the results obtained, the best specific capacitance in each type of electrolyte KCl and H_2SO_4 at a concentration of 1 molar is 55.561 and 54.981 F/g, respectively.
Keywords: *electrolyte, electrode, specific capacitance, carbon nanotube, supercapacitor*

Abstrak
Penelitian ini berfokus untuk menjadi solusi terhadap permasalahan peningkatan penggunaan energi khususnya energi listrik. Superkapasitor salah satu piranti penyimpanan energi listrik yang memiliki performa lebih baik daripada kapasitor konvensional. Komponen superkapasitor pada umumnya terdiri dari elektroda, elektrolit dan separator. Elektrolit memiliki peran penting yang dapat mempengaruhi kapasitansi spesifik superkapasitor. Penelitian ini menghasilkan analisa jenis dan variasi konsentrasi elektrolit berupa KCl dan H_2SO_4 masing-masing pada konsentrasi 0.4 ; 0.7 dan 1 M. Pengujian cyclic voltammetry (CV) dilakukan menggunakan elektroda karbon nano silinder yang dibentuk menjadi lembaran menggunakan binder Polyvinyl Alcohol (PVA). Analisa CV bertujuan mengetahui performa superkapasitor yang dilihat dari nilai kapasitansi spesifik. Berdasarkan pengamatan hasil yang diperoleh, kapasitansi spesifik terbaik pada masing-masing jenis elektrolit KCl dan H_2SO_4 yakni pada konsentrasi 1 M sebesar 55.561 dan 54.981 F/g.
Kata Kunci: *elektrolit, elektroda, kapasitansi spesifik, karbon nano silinder, superkapasitor*

1. Introduction

The expanding human population has led to environmental degradation and a growing energy crisis. The limited availability of fossil fuels and environmental problems such as pollution, global warming, and so on cause the need for clean and renewable energy. The urgency of renewable energy sources is to perfect energy storage devices. One of the promising energy storage devices is supercapacitors [1]. Supercapacitors of various sizes and types are suitable for storing energy and their use as needed in various aspects such as electric vehicles [2,3] and households [4,5,6]. Supercapacitors, also known as ultracapacitors, are high performance capacitors. Supercapacitors are high-performance capacitors with capacitance values much higher than ordinary capacitors [7]. Supercapacitors have an almost unlimited fast charge-discharge range, low cost, and a modular design for easy installation [8].

The components that compile supercapacitors are important factors that affect energy storage. Supercapacitors are composed of electrode, electrolyte and separator components. Some types of electrode materials that have been analyzed by previous researchers are carbon, polymers, oxides and sulfides [9-14].

In the meantime, there are various types of electrolytes used in supercapacitors such as solution electrolytes, organic, ionic, and others. Electrolyte selection is based on the stable potential window in which the electrolyte can work. Solution electrolytes (such as acids, bases, or salts) have low specific resistance making them suitable for supercapacitor manufacturing. In addition, one of the main advantages of solution electrolytes is the very low price when compared to organic electrolytes [7]. The types of electrolytes that have been analyzed by Awitdrus and Farma include electrolyte solutions such as sulfuric acid (H_2SO_4), potassium hydroxide (KOH), sodium sulfate (Na_2SO_4), potassium chloride (KCl), and other electrolyte solutions. It was observed that the largest specific capacitance was obtained from the H_2SO_4 electrolyte [15,16]. This proves that the types of electrolyte solutions can affect the capacitance of supercapacitor cells because each electrolyte has different ionic size, electrical conductivity, and working voltage [16]. In the development of supercapacitors, the electrolyte plays an important role as the electron transfer balances between the two electrodes. The electrolyte in supercapacitors affects the capacitance value where the electrolyte ion size should be optimal. In addition, the electrolyte concentration also affects the performance of the electrolyte.

Electrolytes are solutes in which the ions theoretically have high ionic mobility, which makes it possible to take charge transport through migration due to the electric field generated by the potential difference [17]. The nature of the electrolyte determines the power density of the supercapacitor as the resistance of the electrolyte plays a major role in determining that power density.

The formation of supercapacitors involves the mobility of electrolyte ions into the electrode pores. This mobility will be reduced if the electrolyte concentration used is very high because under these conditions the ion activity is reduced due to less water hydration. On the other hand, if the electrolyte concentration is too low then the amount of ionic charge for the double layer will be insufficient. Therefore, many studies have been conducted to optimize the electrolyte concentration to improve ion transport into the electrode pores, which can lead to the formation of an effective supercapacitor double layer formation that can produce maximum specific capacitance [16].

In this study, the electrolyte concentration of KCl and H_2SO_4 solutions with carbon nanotube (CNT) electrodes was analyzed on the specific capacitance values obtained. Two electrolyte solutions were systematically observed for supercapacitor applications, using cyclic voltammetry (CV) testing [18]. The electrolytes used were sulfuric acid (H_2SO_4) and potassium chloride (KCl) with concentration variations of 0.4 M, 0.7 M, and 1 M, respectively.

2. Material and Methods

KCl and H_2SO_4 aqueous solution of 0.4; 0.7 and 1 M respectively were used in this study to be applied to supercapacitors. The electrodes used were carbon nanotube molded into sheets on the copper plate using PVA binder.

Preparation of KCl and H_2SO_4 Electolyte Solution

Preparation of KCl electrolyte solution began from the KCl solids and then placed into a glass beaker and the added aquadest to the mark. Make sure the KCl and distilled water are homogeneously mixed so that the desired concentration is achieved.

Fig. 1: Stages of electrolytes preparation a) KCl and b) H_2SO_4

While the stage of making H_2SO_4 electrolyte solution starts from 98% H_2SO_4 dropped using a measuring dropper and put into a volumetric flask. Added aquadest until it reaches the mark, the solution is homogenized to match the concentration. This process is carried out in a fume hood to avoid exposure to hazards from concentrated H_2SO_4. **Fig. 1** shows the stages of preparation of electrolytes a) KCl and b) H_2SO_4.

Cyclic Voltammetry (CV)

CV was conducted to review the performance of the electrolyte on the electrodes using an Autolab PGSTAT 101 potentiostat. CV analysis is in the form of supercapacitor specific capacitance data. **Fig. 2** shows the CV testing circuit uses 3 types of electrodes such as reference electrode (RE), counter electrode (CE) and working electrode (WE). RE used Ag/AgCl, CE in the form of Pt and WE in the form of electrode sheets on a copper plate with PVA binder. The process was \done by applying CNT/PVA solution to a 2x2.5 cm copper plate. The CNT/PVA sheet was subsequently dried at room temperature for ±24 hours. Measurements used a scan rate of 10mV/s with a potential range of -0.4 to 0.4 V as shown in **Table 1**. The scan rate and potential range parameters were set using NOVA 2.1.6 software connected to a potentiostat.

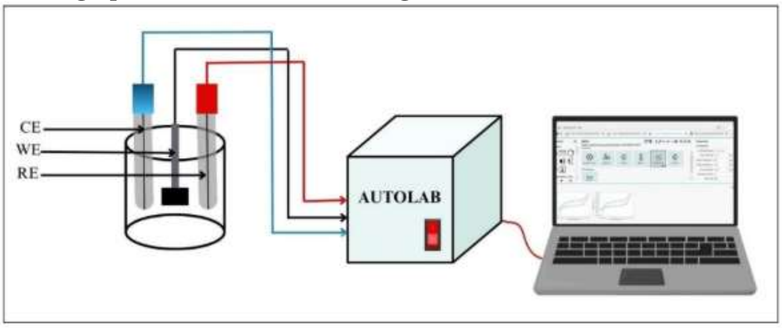

Fig. 2: Cyclic voltammetry (CV) test schematic

Table 1. Research Variables

Types of electrolytes	Molarity (M)	Scan rate (mV/s)	Analyze	Fixed variable
KCl and H_2SO_4	0.4 0.7 1	10	• Peak current value • Specific capacitance	• Potential range and *scan rate of* CV • CNT/PVA electrode • 17% PVA separator

3. Results and Discussion

Specific capacitance (Cs) on the different electrolyte concentration variations can be seen in **Fig.3**. Based on **Fig.3.** it can be seen that the curve forms a leaf-shaped plot with different areas in each electrolyte concentration. The upper curve shows the process of charging from left to right. The lower curve shows the reverse direction from right to left which indicates the occurrence of discharge. At a quick glance, the higher the electrolyte concentration, the wider the voltammogram curve formed. This indicates that the highest specific capacitance is obtained from the electrolyte that has the broadest curve. The specific capacitance value is calculated based on the voltammogram curve and using Equation 1.

$$C_s = \frac{1}{mk\,(V_2 - V_1)} \int_{t=0\,(V_1)}^{t(V_2)} i(V)dt \quad (1)$$

$$C_s = \frac{A}{2mk(\Delta V)} \quad (2)$$

m is the electrode mass (gram), k is the scan rate (V/s), V_1 he potential at charge (V), V_2 the potential at discharge, A is the area of the CV plot [19].

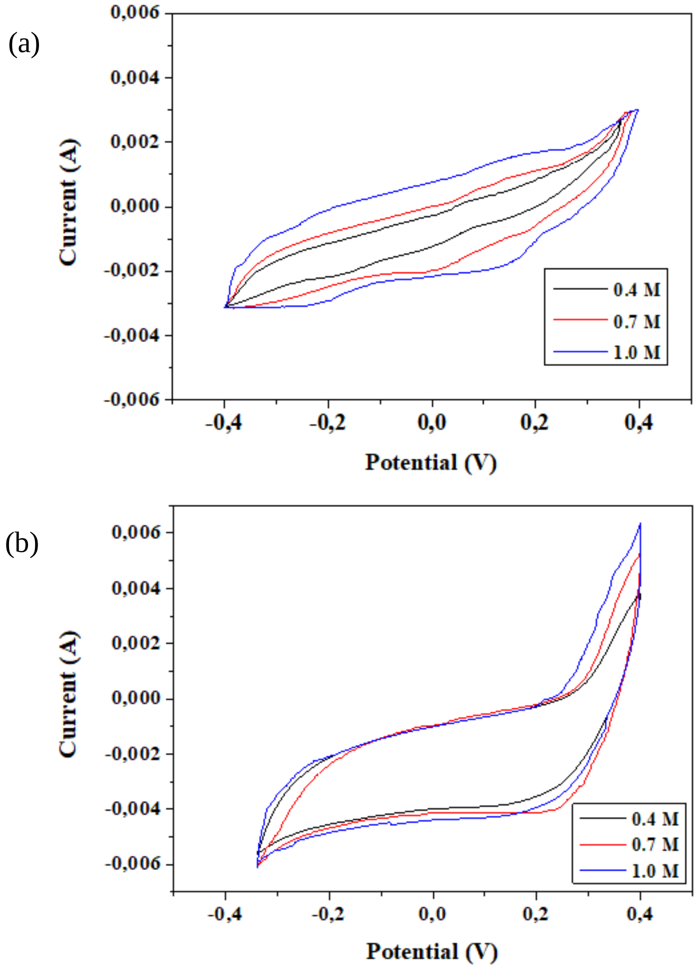

Fig. 3: Voltammogram curves E vs I of KCl (a) dan H_2SO_4 (b) Electrolytes

The area on the voltammogram curve was calculated using OriginPro software by applying the concept of integral math. **Table 2** shows the specific capacitance data from CV assays. Both KCl and H_2SO_4 electrolytes produce specific capacitance that increases with increasing concentration. This proves that high electrolyte concentrations provide a high amount of ionic charge. The appropriate electrolyte concentration will increase the transfer of ions into the CNT electrode.

Table 2. Results of Specific Capacitance Data of CV Analysis

Types of electrolytes	Molarity (M)	ΔV (V)	Specific Capacitance (F/g)
KCl	0.4	0.739	42.701
	0.7		48.059
	1		55.561
H_2SO_4	0.4	0.804	43.314
	0.7	0.784	50.403
	1	0.797	54.981

When comparing the two types of electrolytes used, the KCl electrolyte obtained a higher specific capacitance value than the H_2SO_4 electrolyte. Although the difference is not significant, KCl electrolyte is an electrolyte that has good ionic conductivity. KCl electrolyte is one type of salt electrolyte. Salt electrolytes are able to provide high energy density due to high electrochemical stability. H_2SO_4 electrolyte is an acidic electrolyte that causes corrosion thereby reducing system performance and reducing cycle life [7]. This is evidenced by the difficulty of the H_2SO_4 electrolyte dissolving the electrodes on the copper plate and corroding the copper plate during the CV test. Salt electrolytes that are less corrosive make good cyclic stability. However, the concentration of H^+ and OH^- in saline electrolytes is lower than that of acidic and basic electrolytes.

4. Conclusion

The enhancement of specific capacitance is followed by the molarity of the electrolyte used, in another word, the specific capacitance obtained is directly proportional to the molarity of the electrolyte used. The results obtained are in accordance with the theory, where the KCl electrolyte with a concentration of 1 M obtained the largest specific capacitance value of 55.561 F/g. On this basis, further analysis is needed at concentrations above 1 M. When comparing between KCl and H_2SO_4 electrolytes, each electrolyte has advantages and disadvantages. KCl electrolyte has few H^+ and OH^- ions so it needs the contribution of hydrogen and oxygen gas from the water solvent. Meanwhile, the H_2SO_4 electrolyte has abundant H^+ ions but is corrosive so that it triggers damage to the electrode. In addition, the H_2SO_4 electrolyte resulted in the rapid decay of the CNT/PVA electrode during testing.

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6. Abbreviations

CV	Cyclic voltammetry
PVA	Polyvinyl Alcohol
H_2SO_4	Sulfuric acid
KOH	Potassium hydroxide
Na_2SO_4	Sodium sulfate
KCl	Potassium chloride
CNT	Carbon nanotube
RE	Reference electrode
CE	Counter electrode
WE	Working electrode
M	Molarity
Cs	Specific capacitance

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