Variation sweep rate cyclic voltammetry on the capacitance electrode activated carbon/PVDF with polymer electrolyte

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Variation sweep rate cyclic voltammetry on the capacitance electrode activated carbon/PVDF with polymer electrolyte

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Abstract. Sweep rate of the process voltammetry cyclic characterization is very influential towards the electrode capacitance value, especially on activated carbon electrodes/PVDF. A simple method of this research by use a mixing for electrode activated carbon /10 wt. % PVDF and the separator is made of a polymer electrolyte (PVA/H_3PO_4) by a sol gel method. The prototype supercapacitor is made in the form of a sandwich with a separator placed between two electrodes. Electrodes and separators are arranged in layers at a pressure of 1500 psi, then heated at 50°C for 10 minutes. Next done cyclic voltammetry in a potential range of -1 V to 1 V with a sweep rate of 5 mV/s, 10 mV/s, 20 mV/s, 25 mV/s and 50 mV/s. This results of curves voltammogram is reversible, the most wide curve on the sweep rate of 5 mV/s and most narrow curve on a sweep rate of 50 mV/s. Supercapacitor capacitance values obtained by 86 F/g, 43 F/g, 21 F/g, 16 F/g, and 8 F/g.

1. Introduction

Supercapacitor is one of the best energy storage devices, besides being economical and environmentally friendly. Supercapacitor is also large storage electric energy devices by large density, huge loading capacity, fast and durable charging and discharging processes when compared to other energy storage devices such as generally capacitors [1]. Supercapacitor constructions are similar to generally capacitors consisting of pair electrodes filled by electrolyte and separated of dielectric material serves as a separator [1]. In his research [2], supercapacitor devices consist of electrodes, separators, electrolytes and current collector. The supercapacitor devices consists of two electrodes, wherein one electrode is connected to a positive electric current source so as to be called a positive electrode, while the other electrode is connected to a negative pole and an electrolyte solution. The electrolyte solution used in this supercapacitors are H_3PO_4 and Na_2SO_4 [3], [4]. Usually the materials used in the supercapacitor electrode are graphene, carbon nanotube, carbon aerogel, porous carbon (carbon-active), and mineral-carbon composites. Conditions for electrodes, such as low electronic resistance, good electrolyte accessibility, good chemical and mechanical stability, and high capacitance values [5].

Electrodes wich made from active carbon nanopore have advantages, including relatively cheap, easy to obtain, polarized, stable to acidic and alkaline compounds, regularly arranged natural pores and large of surface area about 400-2200 m^2/g [6]. Nanopore activated carbon can be made from natural materials, one of them from coconut shells, with carbon content of coconut shell fixture that is 66.79% [7]. In the study [8] about the manufacture of active carbon electrodes from coconut shells, obtained carbon surface area 414 m^2/g and belongs to the mesopore category which has a capacitance of 10 F/g. When compared with *Kluwak* shells (*Pangium edule*), which has higher carbon content than

coconut shell that is 77.1% but has a much smaller capacitance value ie 0.192 F/g [9]. However, the shortage of electrodes made from activated carbon is the value of relatively small capacitance and poor mechanical stability. To meet the drawback the active carbon electrode needs to be added with the polymer binder. One of the polymers used is PVDF (polyvinylidenedifluoride).

PVDF is a pure thermoplastic fluropolymer and is not very reactive. PVDF has advantages such as lightness, flexibility, high resistance to strong impact, has an easier melting process because of its relatively low melting point and low density compared to other fluropolymers. PVDF is known as a binder polymer which requires volatile organic solvents, for example N-Methyl-2-Pyrrolidone (NMP). Based on [10] in his research on the manufacture of electrodes made of 90 wt. % activated carbon/ 10 wt. % PVDF obtained the value of capacitance of 325 F/g. According to [11], preparation of electrodes 30 mg activated carbon / 1 wt. % PVDF which tested voltammetry cyclic with variations sweep rate (5 mV/s, 10 mV/s, 20 mV/s, 25 mV/s dan 50 mV/s) obtained the highest capacitances value at sweep rate 5 mV/s amount 47 F/g. At low sweep rate, electrons will diffuse evenly into the electrode surface until mesopore, resulting in an increase in the width of the current curve which indicates a large capacitance value, and vice versa at high sweep rate, the electrons can diffuse rapidly but only up to the surface of the electrode, the electron just enter the macropore [12]. The electrode pores of unelectable electrons produce narrow curves that indicate low capacitance values.

In the supercapacitor, the main components to consider in addition to the electrode are the electrolyte and the separator. Separators are placed between two electrodes to prevent the direct transfer of electrons between two electrodes. Separators should be thin enough and have a porous layer. This is to ensure the smooth flow of ions in the electrolyte to diffuse into the pores of both electrodes [13]. One of the polymers that can be used as an electrolyte polymer is a polymer PVA (polyvinyl alcohol) with phosphoric acid electrolytes (H_3PO_4). PVA is a polymer that has advantages that are cheap, non-toxic, and chemically stable. In terms of electrical properties, PVA is an insulator material with high resistivity of 3.1–3.8 x 107 Ωcm [14]. PVA dissolved in polar solvents such as water, dimethyl sulfoxide, acetamide and dimethylformamide.

Bases on the reference [4] about the supercapasitor electrode of coconut shell activated carbon with the electrolyte polymer separator (PVA/H_3PO_4), ratio of carbon and activator solution (1:1, 1:2, and 1:3) capacitance obtained of 15 F/g, 18 F/g and 26 F/g. Research on supercapacitor with commercial activated carbon electrodes/PVDF and electrolyte polymer separators (PVA/H_3PO_4) obtained capacitance value of charging and discharging value of capacitance respectively 34.7 F/g and 38.39 F/g [3]. According to these studies, it is necessary to conduct research on the manufacture of active carbon electrodes/PVDF with electrolyte polymer whose results were tested with cyclic voltammetry of sweep rate variations between 5 mV/s to 50 mV/s. The results of this study expected that the electrode have an optimal capacitance value.

2. Materials and Methods

The materials used in this study: gading coconut shells, natrium oxide (NaOH 0,5M), aquades, aquades, hydrochloric acid (HCl 1M), polyvinylidene flouride (PVDF), N-Methyl-2-pyrrolidone (NMP), polyvinyl alcohol (PVA), and ortho-phosphorid acid (H_3PO_4). There are several processes for making activated carbon and composites.

2.1. Preparation of Activated Carbon

Preparation of activated carbon from coconut shells consists of 3 processes, they are dehydration, carbonation and activation. Preparation of activated carbon in the carbonation process by simple heating methods and activation process with chemical activation. In the dehydration process, the coconut shell is dried under sunlight for ± 7 days. The carbonization process uses simple heating method by burning a coconut shell in a furnace at a temperature 400°C in 2 hours. Then crushed carbon powder, after that sieved until the carbon powder get away from the filter (200 mesh). Activation process used the activator NaOH 0.5 M, carbon powder soaked in NaOH 0.5 M for 24 hours, ratio of carbon:NaOH = 1:3, then heated at temperature 800°C in 5 hours. After that the carbon

is washed by HCl 1M and aquades repeatedly up to pH 7 remove the alkaline salt compound, dried at temperature 110°C in 5 hours to remove water vapor that is trapped inside the pores [8].

2.2. Preparation of Activated Carbon Electrodes/PVDF

Preparation of activated carbon electrodes supercapacitor/PVDF used 90 wt. % activated carbon of coconut shells and 10 wt. % polyvinylidene flouride (PVDF). PVDF dissolved by N-Methyl-2-pyrrolidone (NMP) at temperature 40°C for 30 minutes, after that mix 90 wt. % activated carbon on PVDF solution by mixing methods [10], stirring by magnetic stirrer in 30 minutes to homogeneous composite. Activated carbon electrodes/PVDF characterized by SEM to know the morphological of composite.

2.3. Preparation of Electrolytic Polymer Separator

Preparation of electrolyte separator used sol-gel methods, the first dissolves 2 grams PVA to aquades and stirring by magnetic stirrer at temperature 70˚C. After homogeneous solution, added H_3PO_4 by 50% concentration which is then printed on the petri plate. The next dried at room temperature for 14 days [3]. The electrolytic polymer membrane is characterized by Brunauer Emmet Teller (BET) to determine the porosity of the membrane.

2.4. Preparation of Prototype Supercapacitor

Prototype supercapacitor made in sandwich shape. Between the two activated carbon electrodes/PVDF (in pellets shape) added electrolyte membrane of PVA (Figure 1). Further, two electrodes and the electrolyte membrane are simultaneously compressed at the pressure1500 psi, after that heating at temperature 50°C in 30 minutes. The function of this process to produces good contact between activated carbon electrodes/PVDF and membrane. Furthermore, supercapacitor with weight of 0.6 gram is tested with cyclic voltammetry in the potential range -1,0 V to 1,0 V by sweep rate 5 mV/s, 10 mV/s, 20 mV/s, 25 mV/s and 50 mV/s. The electrolyte solution used in this study is ortho-phosphorid acid *(*H_3PO_4) 85% solution.

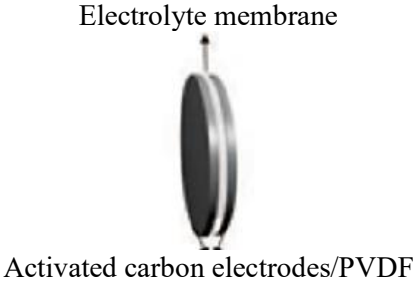

Figure 1. Illustrations of supercapacitor devices [1].

2.5. Calculating The Electrode Capacitance Value

Data of cyclic voltammetry test for all samples on sweep rate variation are 5 mV/s, 10 mV/s, 20 mV/s, 25 mV/s and 50 mV/s can be processed by Matlab software. Furthermore, to calculate of specific capacitance value supercapasitor using equations (1) and (2) [1], ie:

$$C_{sel}(F) = \frac{\int i dV}{\Delta V \times V_s} \quad (1)$$

$$C_s(F/g) = \frac{2C_{sel}}{m} \quad (2)$$

Information:

Csel = cell capacitance (F)
i = discharge current (A)

Vs = sweep rate (V/s)
ΔV = range of potensial (V)
Cs = specific capacitance (F/g)
m = mass (g)

3. Result and Discussion

3.1. The Result of BET

In this research the sample tested is electrolyte polymer separator sample (PVA/H_3PO_4) by using characterization tools BET Quantrachrome NovaWin.

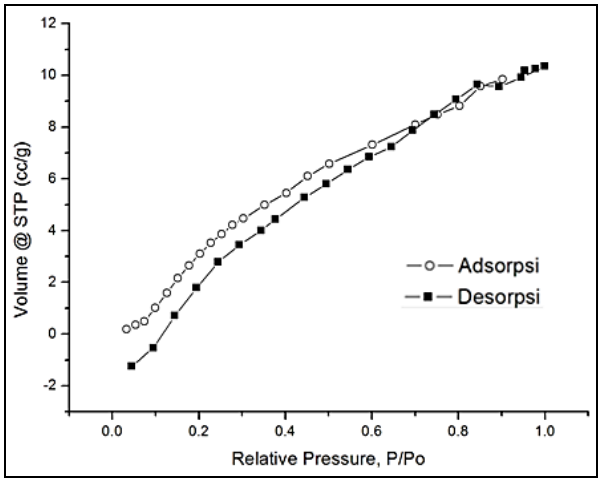

Figure 2. Isothermal graphics of electrolyte polymer separator.

Figure 2 showed isothermal graphics of electrolyte polymer separator (PVA/H_3PO_4) which shows the relationship graph between relative pressure at temperature 77.35 K and volume of gas adsorbate ie nitrogen gas (N_2). The isotherm graph shows that the electrolytic separator adsorption-desorption is a type IV of adsorption-desorption which forms a hysteresis loop over a relative pressure range is 0.75–0.85 P/P_o or Langmuir isotherm for the IUPAC classification which is a type IV of adsorption-desorption occurring in mesopore materials [15]. The open shape of the end curve shows that the volume of gas absorbed and released when the adsorption-desorption not the same. This indicates that not all nitrogen gas is removed during the adsorption process, which means that nitrogen gas is retained within the pore. When analogous to charge storage, the charge stored in the supercapacitor is proportional to the amount of gas volume difference absorbed and released during the adsorption-desorption process.

To find the size pore of the electrolyte polymer separator by looking at the largest pore size distribution in the data BJH (Barret-Joyner-Hallenda) adsorption and desorption. Pore distribution (Figure 3) as mathematic written $\frac{dV_p}{dr_p}$ or $\frac{dA_p}{dr_p}$ as the function r_p, where V_p = volume of pore, r_p = radius of pore, A_p = surface area or wall of pore.

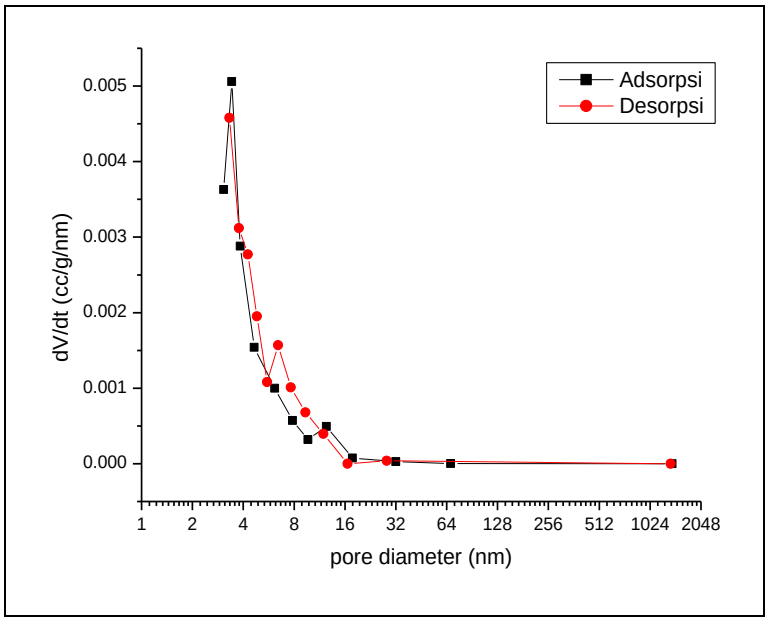

Figure 3. Pore Size Distribution of Electrolytic Polymer Separator.

Figure 3 The largest adsorption pore distribution is 0.005059 cc/g/nm at the pore diameter ie 3.423 nm, while the largest desorption pore distribution is 0.004579 cc/g/nm at the pore diameter is 3.308 nm. So obtained pore size in the range 3.3–3.4 nm, so included in the category mesopore (2 nm – 50 nm) [16]. Separators with mesopore structures can perform rapid charge transfers of electrolyte ions to diffuse into the pores of the electrodes in the process of charging and discharging the supercapacitor [15].

3.2. The Result of Voltammetry Test

Voltammetry cyclic is a voltammetric technique in which the current is measured during sweeping potential from initial potential to final potential and back to initial potential. The material tested by voltammetry cyclic in this study is supercapacitor composed of activated carbon electrodes/PVDF with electrolyte polymer separator (PVA/H_3PO_4).

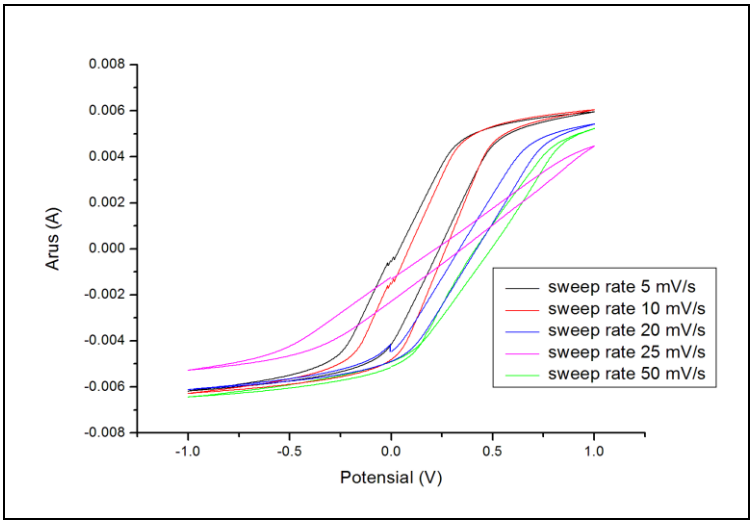

Figure 4. The voltammogram curve of supercapacitors electrode by sweep rate variation.

Figure 4 showed voltammogram curve of supercapacitors electrode by electrolyte polimer. The figure show that the resulting voltammogram curve is reversible. The curve at the sweep rate of 5 mV/s and 10 mV/s closer to the ideal curve of the capacitor means that the current density is almost constant (at the currents ± 5mA) along by the given of difference potential, thus allowing large stored loads.

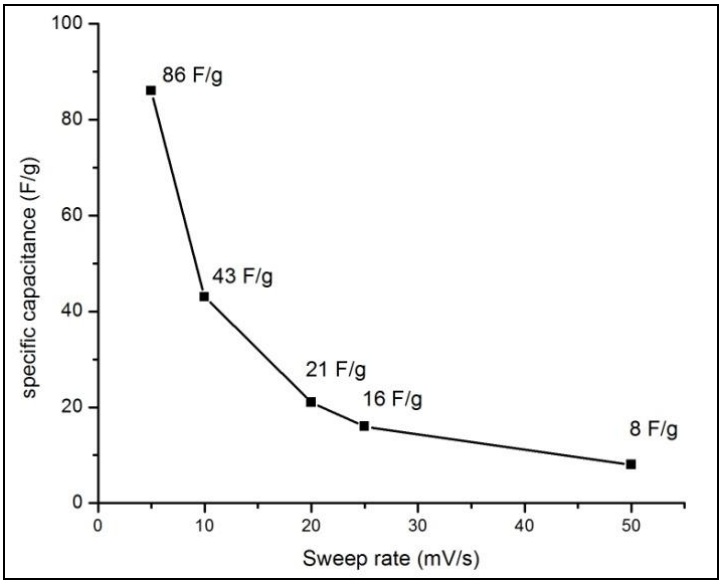

Figure 5. Supercapacitor Capacitance Value.

Figure 5 shown the capacitance value of supercapacitor on sweep rate 5 mV/s, 10 mV/s, 20 mV/s, 25mV/s, and 50 mV/s each is 86 F/g, 43 F/g, 21 F/g, 16 F/g and 8 F/g. The largest capacitance value is obtained at sweep rate 50 mV/s is 8 F/g. Capacitances value in this study better than the results of research [3] and [11]. However, the resulting capacitance value is smaller than [10] which uses one electrode. In the voltammetry cyclic test of one electrode, the ions from the electrolyte will go directly into the pores of the electrode leading to rapid charging and discharging process while in the voltammetry cyclic test of two electrodes, there is separator which acts as an insulator to prevent the direct transfer of electrons between the two electrodes, which leads to fast charging process and long evacuation process. Separators should be sufficiently thin and have high porosity so as to increase the drainage of ions in the electrolyte to diffuse into the pores of the electrode [13]. Sweep rate of voltammetry cyclic affect the shape of the voltammogram curve and the capacitance value of the supercapacitor. At low sweep rates, electrons have long time to diffuse evenly into the electrode surface and the charge transfer (stored and given charge) gets larger so that the voltammogram curve forms wider and higher capacitance values, while the higher the sweep rate curve shape the voltammogram is narrower and the capacitance value is smaller. This happens because at a high sweep rate, the electrons can diffuse rapidly but the charge transfer on the electrode surface is limited.

3.3. The Result of SEM

Based on SEM- micrographs (Figure 6) by magnification 7500 × can be seen that activated carbon electrodes/PVDF porous, but there is still lump indicating that the sample has not been mixed evenly. Some PVDF particles are well distributed into the pores of activated carbon, but others just stick to the surface. This can affect the diffusion process of ions or electrons. It affects the diffusion process of ions or electrons.

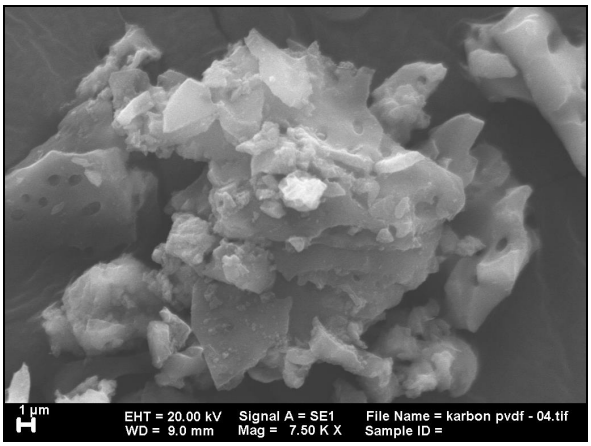

Figure 6. SEM- micrographs of activated carbon/PVDF.

4. Conclusion

The capacitance value of the supercapacitor by the voltammetry cyclic characterization sweep rate 5 mV/s, 10 mV/s, 20 mV/s, 25 mV/s and 50 mV/s obtained the largest capacitances value in sweep rate 5 mV/s ie 86 F/g, while the smallest capacitance value on sweep rate 50 mV/s is 8 F/g. The smaller of sweep rate used, the capacitance value of electrodes supercapacitor activated carbon/PVDF is greater.

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