Effect of Polyaniline Mass Composition on Electrochemical of Active Carbon/Polyaniline as Supercapacitor Electrode

Lydia Rohmawati 1,2, Nuricha Anggraini1, Siti Holisa SP1, Sahara Hamas Intifadhah1, and Woro Setyarsih1

1Departement of Physics, Universitas Negeri Surabaya, Surabaya
2email: lydiarohmawati@unesa.ac.id

Abstract. Supercapacitor electrodes have been developed using natural materials from coconut shells (Cocos Nucifera) and polyaniline conductive polymers. This electrode fabrication uses the dry mixing method, with the addition of 10-20 wt% polyaniline to activated carbon. Electrochemical characterization of supercapacitor electrodes is examined using cyclic voltammetry at a scan rate of 100 mV/s. This result of characterization showed that the addition of mass of polyaniline affects the specific capacitance value of the supercapacitor electrode. Active carbon electrode/18 wt% polyaniline has a maximum specific capacitance value of 4.1 F/g. Furthermore, the activated carbon electrode/18 wt% polyaniline was tested for electrochemical impedance spectroscopy (EIS). The addition of wt% polyaniline has an impact on the value of the electrical conductivity of the supercapacitor electrode when compared to the activated carbon electrode alone. The electrical conductivity of activated carbon electrodes/18 wt% polyaniline is 4.25 x 10^{-2} S/cm, while the electrical conductivity of activated carbon electrodes is 1.04 x 10^{-2} S/cm.

1. Introduction
Supercapacitor is a charge storage device that has several advantages, that is greater power from batteries and higher energy compared to conventional capacitors, and has a high specific capacitance value [1]. The process of storing a charge on a supercapacitor depends on its electrodes material, that is activated carbon, metal oxides, and conductive polymers [2]. Carbon-based electrodes such as activated carbon, graphene, and carbon nanotubes have excellent cycle stability and high power density as supercapacitor electrodes [3]. Among these supercapacitor electrode materials, activated carbon is a material that has been widely studied because it has a large surface area, high life cycle and high specific capacitance, abundant presence and cost effectiveness and is environmentally friendly [4]. Electrodes from coconut shell activated carbon have a capacitance value of 3.38 F/g[5]. The specific capacitance of the electrode is greater than that of activated carbon from the Kluwak shell of 0.037 F/g [6], and the candlenut shell of 0.0117 F/g [7]. Based on the effect on the capacitance value, the activated carbon from the coconut shell is best used as a supercapacitor electrode. Activated carbon from coconut shell is easily obtained in the surrounding environment, often even used as briquette media. However, electrodes from activated carbon have weaknesses, one of which has relatively low conductivity so that it is not advantageous in the process of fast charge/discharge and good cycle stability [8]. For this reason, another material is needed to be made as a composite with activated carbon, that is polyaniline conductive polymer (PANi). Polyaniline (PANi) is one of the promising organic conductive polymers [9]. Polyaniline is widely used in supercapacitor electrodes...
because it has high electrical conductivity [10] and excellent capacitive properties [3]. The electrical conductivity of Polyaniline ranges from 10-10 S/cm to 100 S/cm [11] and has three oxidation states (leucomeraldine, emeraldine, and pernigraniline) [12]. The conductive form of Emeraldine Base is called Emeraldine Salt (ES) [13]. Commercial activated carbon electrodes/polyaniline with in situ polymerization method, with a weight percent ratio of PANi: activated carbon = 1.1: 1 a capacitance value of 409 F/g was obtained at a scan rate of 2 mV/s [14]. Qin et al, (2008) reported that PANi electrodes/activated carbon with electrochemical polymerization methods obtained capacitance values of 587 F/g at a scan rate of 5 mV/s [9]. Electrodes of activated carbon/PANI with doping champor-10-sulfonic acid, have a specific capacitance value of 55.8 F/g at a scan rate of 100 mV/s [14]. Anggraini, et al in their research on the fabrication of activated carbon electrodes from coconut shell /18wt% PANi has a specific capacitance of 289 F/g at a scan rate of 1 mV/s [15]. Based on the results of these researchers, fabrication of activated carbon/polyaniline composite, initial identification was done by analyzing the absorption peak using the FTIR (Fourier Transform Infrared) test. After that the electrochemical characterization was done using cyclic voltammetry and EIS, to determine the effect of adding percent weight of polyaniline to the activated carbon electrode. The results of this study are expected that the addition of weight percent polyaniline to activated carbon electrodes can increase specific capacitance and be more conductive.

2. Materials and Methode

2.1. Materials

Materials used in this study include coconut shell (Cocos Nucifera), natrium oxide (NaOH) 0.5M, hydrochloric acid (HCl), aquades, aniline monomers, ammonium persulphate (APS), Poly Ethylene Glycol (PEG) 4000 as a binder and deionize water.

2.2. Synthesis of Activated Carbon

In this research, the carbon charcoal produced by coconut shell carbonization was carried out by the activation process using 0.5 M NaOH solvent for 24 hours. Furthermore, the results of the immersion were heated at a temperature of 800°C for 5 hours then cooled to room temperature, and formed a black powder. After that, the powder is washed with HCl and distilled water until it reaches pH 7 and dried at 110°C for 1 hour [17].

2.3. Synthesis of Polyaniline (PANI)

Polyaniline synthesis uses chemical polymerization methods. In this synthesis two solutions are made as follows: first solution (1) aniline monomer dissolved in 50 ml HCl 2M, second solution (2) APS mixed with 50 ml deionize water. Then the two solutions are stirred until homogeneous and allowed to stand for 1 hour. After 1 hour, the two solutions are mixed into a beaker and stirred until the color turns purple and feels warm. The purple solution is washed with 100 ml 0.2 M HCl then filtered and the result is washed with acetone to form a solution with a bluish green precipitate. Then the filtering process is carried out using filter paper and the results are heated at 60°C for 24 hours and cooled at room temperature.

2.4. Fabrication of Supercapacitor Electrode

Fabrication of activated carbon/PANi electrodes using the dry mixing method with the addition of 10 wt%, 12 wt%, 14 wt%, 16 wt%, 18 wt% and 20 wt% PANi. Active Carbon Composite / PANi added Poly Ethylene Glycol (PEG) as the adhesive. All materials are crushed into one for approximately 1 hour using mortal and pestle until homogeneous. Next, the electrode powder was compacted at a pressure of 1.5x10⁶ Pa and formed pellets.
3. Instrumentation

Activated carbon/PANi electrodes in the form of pellets were tested with the Shimadzu 8400 FTIR brand to determine the peak absorption of the active carbon and polyaniline functional groups at certain wave numbers. FTIR characterization was carried out at wave numbers 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). The results of this characterization are in the form of graphs of the relationship of wave numbers to the percentage of transmittance. Electrochemical characterization used cyclic voltammetry and EIS. Cyclic voltammetry (CV) has 3 electrodes, that is a working electrode, a comparison electrode and a counter electrode. The activated carbon electrode/PANi in this study is a working electrode, while for the comparative electrode Ag/AgCl material is used, and as a counter electrode is Pt. The solution used during the characterization of cyclic voltammetry is a 1M Na\(_2\)SO\(_4\) solution. The potential range during the characterization process is 0 V to 1 V with a scan rate of 100 mV/s, the result of which will be in the form of a voltamogram curve of the relationship between potential and current. EIS characterization using 1M Na\(_2\)SO\(_4\) solution with a frequency of 100 kHz - 100 mHz. The data obtained in the form of a Nyquist diagram showing the relationship between real and imaginary impedance.

4. Result and Discussions

The result of fabrication of activated carbon / PANi electrodes in the form of pellets was carried out FTIR characterization. The results of this characterization are in the form of a graph showing the peak absorption of functional groups (Figure 1).

![Figure 1. FTIR characterization results (a) polyaniline, (b) activated carbon/polyaniline](image)

The peak of polyaniline uptake is in the wave number, i.e 586 cm\(^{-1}\), 621 cm\(^{-1}\), 700 cm\(^{-1}\), 802 cm\(^{-1}\), 879 cm\(^{-1}\), 1122 cm\(^{-1}\), 1242 cm\(^{-1}\), 1298 cm\(^{-1}\), 1472 cm\(^{-1}\), 1568 cm\(^{-1}\), 2918 cm\(^{-1}\), 3200 cm\(^{-1}\), and 3425 cm\(^{-1}\). Similarly, the activated carbon / polyaniline electrode has an absorption peak at the wave number 592 cm\(^{-1}\), 804 cm\(^{-1}\), 1109 cm\(^{-1}\), 1242 cm\(^{-1}\), 1298 cm\(^{-1}\), 1483 cm\(^{-1}\), 1570 cm\(^{-1}\), and 3435 cm\(^{-1}\). Wave numbers 586 cm\(^{-1}\) in Figure 1(a) and 592 cm\(^{-1}\) in Figure 1(b) indicated 1,4 disubstitution in benzene ring [18]. The absorption peaks at 700 cm\(^{-1}\) and 802 cm\(^{-1}\) in Figure 1(a) and 804 cm\(^{-1}\) in Figure 1(b) formed 1,2 and 1,3 substitutions on benzene ring bonds. The results of the absorption peak at the wave number are in accordance with previous researchers, i.e 740 cm\(^{-1}\) dan 805 cm\(^{-1}\) [19]. The absorption peak at wave number 621 cm\(^{-1}\) is indicated by IR vibrations in the aryl nitro compounds [20]. Polyaniline Figure 1(a) 1,3 bond disstitution in benzene ring formed at wave number 879 cm\(^{-1}\) [21] and formed 1,4 substitution bonds on the benzene ring at wave number 1122 cm\(^{-1}\) [19]. The decrease absorption peaks in wave numbers between 800 cm\(^{-1}\) to 880 cm\(^{-1}\) (Figure 1b) is an indication of the polyaniline functional group due to the milling process when mixing with activated carbon, where the composition
of the mass of carbon is more than that of polyaniline. The activated carbon function group in Figure 1(b) formed C-C groups (valence) ionic bonds at wave number 1109 cm\(^{-1}\), according to the results of previous researchers that is 1091.6 cm\(^{-1}\) [22]. Carboxyl group vibrations on benzene ring formed at the wave numbers 1242 cm\(^{-1}\) and 1298 cm\(^{-1}\) observed in Figures 1(a) and 1(b), where the peak absorption results are in accordance with the results of several researchers, that is 1240 cm\(^{-1}\) and 1270 cm\(^{-1}\) [19], [23]. The quinoid ring C=C bonding on polyaniline was observed at wave number 1472 cm\(^{-1}\) (Figure 1a) according to the investigation results of 1473 cm\(^{-1}\) [24]. Quinoid stretching on aniline and nitro aniline ring can be observed in Figure 1(a) with a wave number of 1568 cm\(^{-1}\). Likewise, the C-H stretching vibration in CH\(_3\) bond can be observed at wave number 2918 cm\(^{-1}\) and the N-H stretching vibrations bond occurs at 3200 cm\(^{-1}\) and 3425 cm\(^{-1}\) [25]. Wave numbers 1483 cm\(^{-1}\) and 1570 cm\(^{-1}\) in Figure 1(b) are corresponding to the C = C of activated carbon. Likewise, the wave number 3435 cm\(^{-1}\) (Figure 1b) is an O-H ion bonding stretching mode of the hydroxyl group and adsorbed water. The existence of O-H bonds, activated carbon as a supercapacitor electrode has a tendency to be more polar, thus affecting the process of ion diffusion between the electrolyte solution and the electrode surface. Moreover, these activated carbon electrodes are combined with polyaniline which has conductive properties, causing capacitance values to increase. Furthermore, to determine the electrochemical properties of the activated carbon/polyaniline electrode, cyclic voltammetry and EIS can be characterized, the results of which can be observed in Figures 2 and 3.

![Figure 2. Voltamogram Curve of Activated Carbon Electrode with Variations wt% Polyaniline](image)

The voltamogram curve of the activated carbon electrode with a variation of wt% polyaniline (Figure 2) produces different shapes and curves. At 18 wt% PANi, the resulting current response increases with increasing potential given when compared to only activated carbon electrodes or other wt% PANi additions, with the result that affecting the specific capacitance value. In general, the voltamogram curve in Figure 2 is a resistive curve that shows that at a high scan rate the current produced is unstable or it can be said that the current continues to increase with increasing potential given [26]. However, at the addition of 12 wt% polyaniline, it has a smaller area compared to 10, 14, 16, 18 and 20 wt% polianilin, where the cathodic current or anodic current produced is very small. Thus causing the least charge stored on the surface of the electrode due to the process of ion diffusion with an electrolyte solution. The specific capacitance can be determined using equations (1) and (2), as follows:

\[
C_{set}(F) = \frac{\int idV}{\Delta V \times V_s} \tag{1}
\]

\[
C_s(Fg^{-1}) = \frac{2 C_{set}}{m} \tag{2}
\]
Information; C_sel= cell capacitance (F), i= emptying flow (A), Vs= scan speed (mV/s), ∆V= potential range (V), Cs= specific capacitance (F.g⁻¹), m= mass of electrodes (g).

Table 1. Specific Capacitance Value of Supercapacitor Electrodes with wt% Polyaniline

| Polyaniline compositions (wt.%) | \(\int iv\) | Cs (F/g) |
|-------------------------------|-----------|---------|
| 0                            | 0.1014    | 3.37    |
| 10                           | 0.1079    | 3.60    |
| 12                           | 0.0985    | 3.28    |
| 14                           | 0.1125    | 3.75    |
| 16                           | 0.1161    | 3.87    |
| 18                           | 0.123     | 4.10    |
| 20                           | 0.1054    | 3.51    |

The specific capacitance value depends on the mass variation of polyaniline on the activated carbon electrode (Table 1). The highest specific capacitance in this study was found in the addition of 18wt% polyaniline, which was 4.1 F/g. In this composition, the maximum cathodic current produced when compared to the current generated by other polyaniline wt% can be observed in Figure 2. However, the resulting current is not stable as the potential increases, this results in an oxidation process which is also faster, meaning that when charging takes place quickly as well as the process of discharging the charge so that it affects the specific capacitance value of the electrode. EIS characterization produces a nyquist plot that shows the relationship between \(Z\) (real impedance) and \(-Z^\prime\) (imaginary impedance) whose results can be observed in Figure 3.

![Figure 3. Nyquist Plot (a) Activated Carbon Electrode, (b) Activated Carbon/Polyaniline Electrode](image)

Figure 3 is the result of a nyquist diagram of the activated carbon electrode and activated carbon/polyaniline electrode. Based on the nyquist diagram above, there is a part that describes the shape of a semicircle at high frequencies and straight lines at low frequencies. Based on the nyquist plot can also be seen the value of electronic resistance (R_e) and load transfer resistance (R_CT). Electronic resistance is obtained from the lowest point of the semicircle and the magnitude of the charge transfer resistance (R_CT) is obtained from the highest point on the semicircle. The R_e for activated carbon and activated carbon/polyaniline were 17.827 \(\Omega\) and 3.673 \(\Omega\) respectively. The R_CT values for activated carbon and activated carbon/polyaniline are 18.96 \(\Omega\) and 6,246 \(\Omega\). The conductivity value of the activated carbon electrode is 1.04 x 10⁻² S/cm while the activated carbon/polyaniline electrode is 4.25 x 10⁻² S/cm. The addition of polyaniline in the activated carbon...
5. Conclusion
In this study the addition of wt% polyaniline to supercapacitor electrodes greatly influenced the electrochemical properties, in terms of cyclic voltammetry and EIS characterization. The highest specific capacitance value was found in the activated carbon electrode/18 wt% polyaniline at 4.1 F/g, when compared with the activated carbon electrode alone which was 3.37 F/g. Likewise with the value of electrical conductivity where the activated carbon/polyaniline electrode has an electrical conductivity of 4.25 x 10^-2 S/cm, while the activated carbon electrode alone is only 1.04 x 10^-2 S/cm.

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electrode shows that the role of polyaniline greatly influences the electrical conductivity of the electrode, whereas polyaniline itself is more conductive than activated carbon alone.