Cycle stability of activated carbon/PANi composite as supercapacitor electrode based on natural material

N Anggraini1, L Rohmawati 1,a, and W Setyarsih1

1Departement of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya, Kampus Unesa Ketintang, Surabaya 60231, Indonesia

aE-mail : lydiarohmawati@unesa.ac.id

Abstract. Fabrication activated carbon/PANi electrode from coconut shell was successfully made using the simple heating method. Polymerization of PANi using chemical polymerization method showed the oxidation form was emeraldine salt. The highest specific capacitance was 289 F/g at the 1 mV/s for the 18 wt% of PANi. The stability of the electrode cycle of activated carbon/PANi lasted up to 20 cycles with a decrease of the capacitance value of 21.9%. The stability of this cycle indicates that the electrolyte accessibility is good. Alloys of activated carbon and PANi have been shown to strengthen the stability of PANi. Activated carbon has good cycle stability and PANi has good conductivity so that these two materials contribute to each other.

1. Introduction
In recent years, the development of charge storage device is growing rapidly. One of the charge storage devices is supercapacitor. Supercapacitors commonly referred to as electrochemical or ultracapacitor capacitors with many advantages including having a long life cycle, and simple working principles [1]. The construction of a supercapacitor similar to that of a conventional capacitor consists of a pair of electrodes filled with electrolyte and separated by a dielectric [2,3]. In the supercapacitor storage process occurs on the electrode, therefore the electrode material is a very important part. The ion transfer mechanism occurs in electrodes that play a role in charging and discharging the supercapacitor. The voltage applied to the opposite electrode causes the ion to be attracted to the surface of the two electrodes (charging). Instead, the ion will move away when the supercapacitor is used (discharging). The requirements of the supercapacitor electrode are as follows: Good electrolyte accessibility [4]. A large capacitance value with a range of 0.043-2700 F, life cycle 25-30 years [5]. Therefore, electrode material selection is very important to support supercapacitor load storage performance. Based on its function, the supercapacitor electrode material can be divided into three types, namely: active carbon electrode, the metal oxide electrode, and conductive polymer electrode. An electrode based on carbon material has been widely developed by many scientists. Some studies suggest that activated carbon can be obtained from organic plant waste such as Durian skin (Durio) [6], date palm (Phoenix dactylifera) [7], oil palm shell (Elaeis) and coconut shell (Cocos nucifera) [8]. Activated carbon can be obtained by the activation process of carbon by chemical activator or physical activator. The process of storing the charge on the electrode is affected by the pore size distribution of the electrode material. Activated carbon electrodes have several advantages, but there are some disadvantages, that is low conductivity and small capacitance. Rohmawati et al conducted a study of supercapacitor electrodes from coconut shell activated carbon obtained capacitance value of 2.26 F / g [9]. To increase the value of the capacitance, an innovation is required by combining with other
materials, such as conductive polymers like polyaniline (PANi). The conductive polymers are widely used in supercapacitor electrodes due to their high conductivity [10] and excellent capacitive properties [11]. Polyaniline (PANi) is one of the promising organic conducting polymers [12]. PANi can be obtained from polymerization of aniline monomer in an oxidation solution. Polimerization of PANi can be made by several methide, one of them is chemical polymerization. Many studies have examined the preparation of a supercapacitor electrode made from activated carbon/PANi by several methods. Tian and Mao making a supercapacitor electrode from the activated carbon/PANi composite using in situ polymerization method obtained a capacitance value of 409 F/g [13]. In another study successfully made activated carbon/PANI composite with scan rate variation of 2-100 mV/s and obtained the highest specific capacitance value at 2 mV/s scan rate of 337.5 F/g and 55.8 F/g at 100 scan rate mV/s with the addition of champor-10-sulfonic acid doping to activated carbon/PANi electrode [14]. Activated carbon/PANI composites have a fairly good cycle stability. Qin et al reported that electrode from activated carbon/PANi composites have the specific capacitances value at the first cycle are ~415 F/g and ~383 F/g at the fiftieth cycle. This value just decreases about 7% that indicates this composite has a good stability more than PANi electrode. The specific capacitances of the PANi electrode at the first cycle are ~520F/g and ~334 F/g at the fiftieth cycle, respectively this capacitance decrease 36% after the fiftieth cycle [12].

Based on the in the researches above, this paper will be reported about the cycle stability from activated carbon/PANi supercapacitor electrode from natural material. Activated carbon is made from coconut shell using simple heating method. Then PANi is made using polymerization of aniline monomer. Activated carbon/PANI composites is made using a simple methode that is dry mixing methode. Dry mixing is a process of mixing dry powder with dry powder to produce a homogenous powder mixture. This mixing methode often called dry powder mixing methode. Dry mixing is an efficient technique for making polymer/activated carbon composites. Dry mixing methode can be used by tool or manually. The electrode will be characterized using cyclic voltammetry at the scan rate 1 mV/s on the Na2SO4 electrolyte solution. Then the electrode will be characterized using cyclic voltammetry with scan rate 1 mV/s for the 20th cycles to know the specific capacitance stability of the electrode.

2. Materials and Method

2.1 Materials

Materials that used in this research such as : Coconut shell (Cocos nucifera), Sodium Hydroxide (NaOH) 0.5M, Hydrochloric Acid (HCl), aniline monomer, Ammonium persulphate (APS), deionized water, Na2SO4, and Polyethylene Glycol (PEG) 4000 as a binder. This chemical materials are a pure analyst and used without purification.

2.2. Synthesis of Activated Carbon

Preparation of activated carbon from coconut shell using the simple heating method. Starting with the dehydration method of the coconut shell under the sunlight during 7 days. Then carbonated at temperature 400°C and pounded until smooth. This charcoal sifted with sieve 200 mesh then activated with chemical activator NaOH 0.5 M with a ratio of carbon mass : NaOH = 1:3 and left overnight. After that the immersion calcined at temperature 800°C during 5 hours, then rinsed with deionizing water until reach pH 7 [15]. The activated carbon dried at temperature 110°C during an hour to removed water content. The final form is black activated carbon powder.

2.3. Polymerization of Polyaniline (PANi)

Polymerization of PANi using the chemical polymerization. Firstly aniline monomer dissolved into the hydrochloric acid solution, at the same time APS dissolved into the deionized water, then both of the solution stirred together until homogen and the solution changes color become emerald green. After that this solution rinsed using HCl 0.2 M and the deposition dried at temperature 60°C for 24 hours.
2.4. Fabrication of Supercapacitor Electrode
Fabrication of activated carbon/PANi for electrode supercapacitor using dry mixing method. The composition of 82 wt% activated carbon and 18 wt% PANi. Activated carbon powder and PANi powder pounded together with PEG 4000 until homogenous with ratio 1:1 [15]. This mixing powder then compacted using pressure 1.5x10^6 Pa until shaped like a pellet. Compaction is a compression method of powder to receive a sample with a certain shape that follows the mold shape.

2.5. Instrumentation
Activated Carbon/PANi electrode characterized using cyclic voltammetry to know the electrochemical activity of the electrode. Cyclic voltammetry is the best method to measure electrochemical activity from electrode material [14]. Cyclic voltammetry using Ag/AgCl as a reference electrode, and Pt as a counter electrode. In this research used scan rate 1 mV/s and the potential range 0-1 V in the Na_2SO_4 1 M as an electrolyte solution. Cyclic voltammetry characterization use to know the specific capacitance of the electrode. This characterization generates the voltammogram curve as the relation between the current (A) and potential (V). Cycle stability of the electrode measure with the cyclic voltammetry at the same scan rate and potential range for the 20th cycles.

3. Result and Discussions
Activated carbon/PANi electrode characterized using the cyclic voltammetry to know the electrochemical activity and to calculate the specific capacitance of the electrode. The result of this characterization is a voltammogram curve that indicated in Figure 1.

![Voltammogram curve of activated carbon/PANi electrode at scan rate 1 mV/s](image)

Based on the voltammogram curve above indicated that the shape of the curve is like a rectangle curve. This due to the double layer capacitance behavior from activated carbon and pseudocapacitive capacitance from conducting polymer [14]. Moreover, this indicated that at the low scan rate the resulting current is stable as potential increases and when discharging process the charge that comes out also tends to be stable [16]. To calculate the specific capacitance is using the Matlab program [17]. Specific capacitance can be calculated with the equations:

\[ C_{sel}(F) = \int \frac{i \, dV}{\Delta V \times V_s} \]  

\[ C_s(Fg^{-1}) = \frac{2 \, C_{sel}}{m} \]
From the calculation obtained the specific capacitance value of 289 F/g. This result indicated that at the low scan rate the electron will have a long time to diffuse into the electrode pores [11]. Furthermore this is possible at a low scan rate during the reduction process of the electron cathodic pole that can be completely bonded by the electrode material, so that the reduction process also takes longer showing that the electrode have good capacitive and the electrons can be stored perfectly by the electrode poles [18]. Then, to know the cycle stability of the electrode re-characterization using the cyclic voltametry at scan rate 1 mV/s and at potential range 0-1 V. A graph of the relationship between the specific capacitance and cycle shown on Figure 2 below:

Figure 2. Graphic specific capacitance vs cycles of the electrode

Figure 2 shows that in the first cycle to the fourth cycle the specific capacitance value is unstable. At the first cycle specific capacitance value is 289 F/g then at the second cycle become 290 F/g. Then at the third cycle specific capacitance value become 287.667 F/g and at the fourth cycle become 288.467 F/g. This instability is due to cycle 1 to cycle 4 that the ion transfer process is not evenly distributed across the surface of the electrode which is possible because of polymer agglomeration at one point. Besides that it also causes electrolyte accessibility to the electrode surface poorly [12]. In the 5th and 6th cycles, there was a significant decrease from 279.333 F/g to 231.333 F/g. In the 7th cycle it can be seen that the specific capacitance value is stable until the 20th cycle. In the 20th cycle the specific capacitance value becomes 225.667 F/g from the initial 289 F/g in the first cycle. The decrease in the specific capacitance value is 21.9% in the 20th cycle. This decreases is due to swelling and deswelling from PANi which is known as the causes of degradation of PANi [12,19]. Thus, the cycle stability of the activated carbon/PANi electrode is considered to be quite good from the 7th cycle to the 20th cycle. The stability in this cycle indicates that the electrolyte accessibility is good. Alloys of activated carbon and PANi have been shown to strengthen the stability of PANi. Activated carbon has good cycle stability and PANi has good conductivity so that these two materials contribute to each other. This result proves that the activated carbon/PANi electrode has sufficient cyclical stability, and has good electrolyte accessibility so that it meets the criteria as a super capacitor electrode material.

Conclusion
Activated carbon has been successfully made using the simple heating method. PANi has been successfully polymerized using the chemical polymerization. Activated carbon/PANi composite was made using dry mixing method. The specific capacitance value with the composition of 82 wt% activated carbon and 18 wt% PANi is 289 F/g at the scan rate 1 mV/s. At the low scan rate the reduction process of the electron cathodic pole that can be completely bonded by the electrode material, so that the reduction process also takes longer showing that the electrons can be stored
perfectly by the electrode poles. Cycle stability of the activated carbon/PANI electrode can last up to 20th cycle with a decrease of specific capacitance value is 21.9%. This result shows that the activated carbon/PANI electrode has a good stability and qualifies as a supercapacitor electrode material.

Acknowledgement
Thanks to the Direktorat Riset Pengabdian Masyarakat Direktorat Jendral Penguatan Riset dan Pengembangan Kementrian Riset, Teknologi, dan Pendidikan Tinggi in the fiscal year 2017 trough UNESA Rector’s decision number 522/UN38/HK/LT/2017 and fiscal year 2018 number 252/UN38/HK/LT/2018. This research has been supported by The Department of Physics Universitas Negeri Surabaya, Laboratory of Materials Physics Laboratory of Universitas Negeri Surabaya, Laboratory of Materials and Metallurgy and Chemical Engineering Laboratory of Institut Teknologi Sepuluh Nopember.

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