Analysis of Charging/Discharging Supercapacitor Active Carbon/rGO Based on Natural Materials

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Abstract. Active carbon/rGO based on natural materials as coconut shell has been assembled with a coin cell in shape of prototype supercapacitor. The physical feature of active carbon/rGO electrode were characterized by FTIR, and FESEM. The Electrochemical performance of supercapacitor in 1 M LiPF6 electrolyte solution with density current of 12 mA/g until 163 mA/g were analyzed by galvanostatic charge-discharge test. The result showed that active carbon/rGO had absorption peaks at wave numbers 1592.27 cm$^{-1}$ and 1288.45 cm$^{-1}$ which were functional groups as C = C and C-O. The morphology of activated carbon has been covered by the presence of rGO that determines the agglomeration of rGO around the pore of activated carbon so that it affects the performance of supercapacitors. Supercapacitor has a specific capacitance charging of 20.5 F/g, and discharging of 19 F/g in density current 12 mA/g.

1. Introduction

Supercapacitors are an innovation in the world as an energy storage device that has higher capacitance than conventional capacitors [1], excellent cycle stability [2], fast and long-lasting charging-discharging cycle rates. Generally, supercapacitors consist of electrodes, separators, and current collectors. One of them affected the effectiveness of supercapacitors is electrodes. Most activated carbon is used as a supercapacitor electrode. Nevertheless, this electrode has low the conductivity of electricity so that not benefit the process of charging-discharging fast as well as excellent cycle requirements [2]. rGO material is used to improve the properties of these electrodes in the form of composites. Activated carbon/rGO from the coconut shell has been used as a supercapacitor electrode [3]. Electrodes and separators greatly influence the performance of supercapacitors. Factors affecting the performance of separators are thin size, compact, durable and free from leakage. This separator has a feature of semi-permeable so it allows the movement of electrolyte ions between the two electrodes. Separators can be electrolyte polymers namely PVA/H$_3$PO$_4$ [4]. But along with the experiment, it failed because the separator was made too thick and bubbly so that another alternative material is needed, namely Celgard separator. This separator is made from polyethylene (PE) and polypropylene (PP) raw materials which have both polarity properties and liquid electrolyte low absorption with high dielectric constant. Material is said to be a supercapacitor if it has a specific capacitance value of 0.0043-2700 F/g [5].

The results of research from several researchers among other supercapacitors with activated carbon electrodes/rGO with mass ratio of 2:1 having a maximum specific capacitance value of 486 mF/g at a current density of 0.2 mA/cm$^2$ [6], activated carbon electrodes/rGO hybrid aerogels have a specific capacitance value of 294 F/g at a current density of 0.05 A/g using an electrolyte solution 6 M KOH [7].
Yu et al (2014) reported that activated carbon/graphene nanosheet electrodes had a specific capacitance value of 205 F/g at a current density of 2 A/g \[8\]. Activated carbon electrode/10 wt% rGO from coconut shell with a dry mixing method has a specific capacitance value of 336 F/g at a scan rate of 1 mV/s [3]. The potential for activated carbon/10 wt% rGO as a supercapacitor electrode, then in this study a prototype supercapacitor was made in the form of assembling coin cells in a glove box. Furthermore, the supercapacitor is characterized by charging-discharging at a current density of 12 mA/g to 163 mA/g in the hope that the supercapacitor that has been made has supercapacitor characteristics that have high specific capacitance values.

2. Materials and Method
2.1. Materials
Materials used are coconut shell, activated carbon, rGO, Celgrad separator, 1 M LiPF6 solution, PVDF (polyvinylidene fluoride), Super P carbon black, DMAC

2.2. Preparation of Supercapacitor Activated Carbon/10wt% rGO
The first stage is the preparation of ingredients with a comparison of active materials (Activated Carbon: rGO: PVDF: Super P = 90: 10: 10: 10). Furthermore, activated carbon and RGO are put into a beaker glass covered with aluminum foil and then oven 2 hours. DMAC of 3 ml was put into the beaker glass with a magnetic bar placed on a hotplate with a temperature of 70 °C and a rotation of 150 rpm for 15 minutes. Furthermore, PVDF was mixed in the beaker glass that had previously been inserted DMAC until dissolved about 15 minutes. After that, super P is put into the mixture of DAMC and PVDF until homogenously. Then, add the active material (activated carbon/rGO) slowly and let it stir over the hotplate until the desired slurry.

The second stage is coating, where this step is the making of slurry sheets. The tool used is Automatic Thick Film Coater. The manufacturing process is aluminum foil placed on a doctor blade and vacuumed, then aluminum foil is cleaned with acetone. Furthermore, measure the thickness of the doctor blade with a thickness gauge of 0.2 mm. After that, Slurry is poured over the aluminum foil little by little and running using an Automatic Thick Film Coater with a coating speed of ± 6-7 rpm until the aluminum foil is completely coated. Then the activated carbon/rGO electrode sheet is dried with a dry box at 80 °C until it dries for 1 hour.

The third stage is the dry carbon electrode sheet/10 wt% rGO that has dried and the Belgard separator is cut into small pieces with a size of 1.9 cm with the stipulation that the size of the separator is greater than the electrode to avoid direct contact between the cathode and the anode while in a coin cell. After that arrange in order starting from the top (can), spaser, electrode, and separator into the glove box to produce good contact between the two electrodes and the separator. Next, LiPF6 electrolyte solution is dripped on the entire surface until it is spread evenly. Then put spaser, then wave spring. Then closed with a cap (stamp) as in Figure 1. Next, press it using the Hydraulic Crimping Machine at a pressure of 1000 psi so that it becomes the prototype of the supercapacitor. The finished supercapacitor prototype was tested for charging-discharging.
3. Instrumentation

The Activated Carbon/10 wt % rGO electrode was characterized using FTIR (Fourier Transform Infrared Spectroscopy) of a Shimadzu brand tool with a wavelength of 400-4000 cm\(^{-1}\). FTIR characterization techniques provide information in the form of infrared spectra and wavenumber values. Samples are tested in the form of pellets, where activated carbon and rGO are compacted under certain pressures. The sample is tested by reflecting infrared through the sample place and contact occurred with the surface of the material occurs so that the functional groups contained in the sample can be known. The results of this analyst in the form of wavenumbers that will be matched with the database so that the type of functional groups formed is can be known. The morphological form of the sample can be characterized using FESEM with the brand Hitachi SU-3500 at the voltage of 15 kV and magnification of 2000 x. The supercapacitor electrochemical performance is carried out of the galvanostatic charge-discharge test, namely Automatic Battery cycler WonATech WBCS3000. The potential used in the test is 0 - 1.2 V with a constant current.

4. Results and Discussion

Result of The FTIR characterization shows the activated carbon, rGO, and activated carbon/rGO The FTIR spectra of activated carbon (figure 2a) shows the absorption of active groups C = C and C = O respectively at numbers 1539 cm\(^{-1}\) and 1845 cm\(^{-1}\). Figure 2 (b) rGO shows the absorption of the functional group C = C at the wave number 1589 cm\(^{-1}\) and the absorption of the O-H functional group at the wave number 3468 cm\(^{-1}\). Meanwhile of figure 2 (c) wavenumbers 1591 cm\(^{-1}\) and 1288 cm\(^{-1}\) show absorption of functional groups C = C and C - O as indicated by activated carbon/10wt% rGO. The peak of the wavenumber of the three particles has similarities with the results of previous studies, namely in activated carbon there is a C = C functional group in the wavenumber between 1400 cm\(^{-1}\) until 1600 cm\(^{-1}\) and the C = O functional group in the wavenumber 1751 cm\(^{-1}\) [10] [11]. Whereas in rGO there are functional groups with wave numbers 2560 cm\(^{-1}\) [6] and 3500 cm\(^{-1}\) [12]. For activated carbon/10wt% rGO supercapacitor synthesized there are absorption groups of the functional groups C = C and C-O, each wave number 1589 cm\(^{-1}\) and 1288 cm\(^{-1}\) [13]. In this case, the result getting from the formation of the basic structure from rGO that binds to each other and forms a hexagonal where the double bond is a covalent bond formed from sp\(^3\) hybridization into sp\(^2\) and difficult to break because it has large bond energy.
Figure 2. FTIR spectra of (a) activated carbon (b) rGO (c) Activated Carbon/rGO composite electrode

Field Emission Scanning Electron Microscopy (FESEM) is an instrument used to visualize very small topographic details on a surface or all objects of an object. This instrument has the same working principle as SEM (Scanning Electron Microscopy), but with magnification and clearer picture with different Field Emission Sources. The results of the characterization FESEM on activated carbon/10 wt % rGO supercapacitor electrodes are shown in Figure 3.

Figure 3 shows the results of FESEM of activated carbon/10 wt % rGO electrodes with a magnification of 5000 x, it can be seen that RGO is a thin sheet that fills and covers the pore surface in activated carbon. Some rGO particles accumulate in some regions even though they have been deposited into carbon. This can affect the mobility of ions during the diffusion process [14] and this can increase the capacitance value.
The charging-discharging curve for activated carbon/10 wt % rGO supercapacitor (figure 4) is symmetrical and reversible. The symmetrical triangle shows the charging time which is faster than the discharging time, where the discharging time needed is longer. Based on the charging-discharging curve (Figure 4), it appears that along with the increasing current density, to reach a voltage of 1.2 V requires a relatively short charge-discharge time. Such as at a current density of 12 mA which is during the charging process, the time needed to reach a voltage of 1.2 V is relatively long as well as when the voltage drops from 1.2 Volts to 0 volts require a long time anyway. Giving large current can cause an increase in ion charge in the electrolyte solution. As a result, the charge adsorbed by the surface of the electrode is not optimal during the ion diffusion process.

The amount of charge stored on the surface of the electrode influences the specific capacitance value of the supercapacitor. The greater the current density, the smaller the specific capacitance value [15]. The highest specific capacitance value in this study is at the current density of 12 mA/g which is 20.5
F/g during the charging process and 19 F/g during the discharging process (Table 1). Therefore, the results of charging-discharging above the material in this study can be said to be a supercapacitor, which has a specific capacitance in units of order farad which has a capacitance of 10^6 greater than conventional capacitors [16].

Table 1. Specific capacitance supercapacitor activated carbon/10wt% rGO

| Current density (mA/g) | Time (s) | specific capacitance (F/g) | Time (s) | specific capacitance (F/g) |
|------------------------|----------|-----------------------------|----------|-----------------------------|
|                        | charge   | discharge                   | charge   | discharge                   |
| 12                     | 2624     | 20.5                        | 2444     | 19                          |
| 21                     | 1168     | 17.4                        | 1076     | 16.8                        |
| 36                     | 500      | 14.9                        | 470      | 14.6                        |
| 58                     | 228      | 12.8                        | 216      | 12.6                        |
| 100                    | 94       | 10.7                        | 91       | 10.9                        |
| 163                    | 40       | 8.9                         | 39       | 8.9                         |

5. Conclusion

Based on the results of research that the electrochemical performance of activated carbon/10wt% rGO supercapacitors in a 1 M LiPF₆ solution has the optimum specific capacitance value at a current density of 12 mA/g that is equal to 20.5 F/g when charging and 19.0 F/g when discharging. The capacitance value decreases with increasing current density. The greater the current density, the time required during the charging process is getting shorter, neither when during the discharging process.

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