Production of activated carbon from palm empty fruit bunch as supercapacitor electrode material

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Abstract. Activated carbon is prepared by carbonization out by hydrothermal carbonization. Hydrother- mal carbonization is a process that carried out with aqueous media in a pressurized reactor at a lower temperature that the pyrolysis process. This research focused on production of activated carbon from empty fruit bunch by hydrothermal carbonization process using CaCl2 as activating agents. Ratio of raw material/activating agent/water was 1:2:3. Hydrothermal carbonization was carried out at 275℃ for an hour. Furthermore, hydrochar was activated at a temperatur of 800℃ in presence of CO2 for 2 hours. Activated carbon was modified with 1 M nitric acid (HNO3). A self-supporting and flexible activated carbon/graphene/carbon nanotube (AC/GP/CNT) electrode has been rationally designed for constructing high-performance supercapacitor. The CNT is beneficial for improving the electronic conductivity of the electrode, while AC particles could effecti- vely suppress the aggregation of GP and CNT due to their blocking effect. The synergistic effect among the AC-Ca, GP and CNT validate the AC-Ca/GP/CNT as a promising electrode for supercapacitor, exhibiting greatly enhanced electrochemical performances in comparison with the pure GP, pure CNT and AC-Ca electrode. The AC-Ca/GP/CNT electrode delivers a high specific capacitance of 53.51 F g⁻¹.

1. Introduction
Electrical energy is a major requirement that cannot be eliminated in this era. Technology which has a greater energy and power density as well as shorter charging times are needed to the future technology. The new energy storage device is a supercapacitor, with several advantages such as wide range of operating temperature, high power density and long cycling life. Supercapacitor devices are usually assembled in a traditional two electrode configuration using (Ni) foam or aluminum (Al) foil as current collectors [1]. Supercapacitors used a surface electrode and a thin dielectric electrolyte solution to achieve a larger capacitance than conventional capacitors.

Activated carbon has a hydrophobic surface that can decrease interaction between electrode and electrolyte ions. Therefore, surface modification is required to increase the accessible surface of activated carbon and can be improved through surface functionalization such as oxidation [2]. The surface oxidation of activated carbon produces a more hydrophilic surface with a large number of oxygenated surface groups. These functional groups increase the hydrophilicity of the activated carbon surface area, thus increasing the adsorption of electrolyte ions on the surface of the electrodes and increasing the effective surface area for the formation of an electric double-layer capacitance of electrode. Various reagents that have been used as oxidizers are concentrated nitric or sulfuric acid,
sodium hypochlorite, permanganate, bichromate, hydrogen peroxide, transition metals, and ozone-based gas mixtures [3-4].

Cheng and Teng (2003) observed surface modification of carbon using 2 N nitric acid in an ultrasonic mixer can increase the specific capacitance [5]. Another study confirmed that immersed the carbon with 4 M nitric acid can increase specific capacitance [6]. Shim et al (2001) confirmed that modification of carbon fiber with 1 M nitric acid using reflux can decrease the surface area and increase surface oxygen group [4]. Therefore, this study intends to investigate the effect of nitric acid concentration on surface modification using reflux on the physical characteristic and electrochemical behavior of activated carbon. scanning electron microscopy (SEM) can study the structural properties of activated carbon, N₂ adsorption-desorption isotherms, and FTIR (Fourier transform-infrared). The electrochemical analysis of activated carbon-based supercapacitor electrode was studied by cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS).

2. Materials and methods

2.1. Preparation
Electrode of supercapacitor required additional materials other than activated carbon, namely graphene and CNT (commercial). Activated carbon was produced from Empty fruit bunch (EFB) which was collected from PT Perkebunan Nusantara VII in Bogor. EFB was washed and dried. Figure 1, dried EFB was then crushed using a disc mill and sieved into coarse granules (35-80 mesh) [7]. The precursor was leached with 1 M hydrofluoric acid (reagent grade, 1:25) for two hours [8]. Furthermore, the sample was washed with demineralized water until a pH of 6 was obtained for the rinse. The sample was dried at 105°C for 24 hours. Activated carbon was prepared by physicochemical activation of the sample with CaCl₂ (SmartLab, analytical grade) and CO₂. Nitric acid (reagent grade) was used to surface modification of activated carbon. Hydrochloric acid (Merck, 37%) was used to wash the activated carbon, KOH (Merck, analytical grade) and ethanol (Merck, analytical grade) for the supercapacitor electrode preparation [9].

2.2. Activated carbon production
Hydrothermal reactor was charged with 10 g sample (EFB after leaching with HF) and CaCl₂ solution in mass ratio of EFB:CaCl₂:water=1:2:3. The samples were held at 275°C for an hour. The obtained hydrochar was filtered and dried at 105°C for 24 hours [7-9].

The hydrochar was loaded into a ceramic boat and positioned inside the tubular furnace for activated. The furnace temperature was ramped to 800°C at a rate of 10°C/min in the presence of N₂ flow. After the temperature was reached, N₂ was replaced with CO₂ flow for two hours. Afterward, the furnace was chilled to room temperature in the presence of N₂ flow. The products were stirred for 30 min in 150 mL hydrochloric acid (0.1 M) and washed with demineralized water until a pH of 6 was obtained for the rinse. Then, activated carbon was dried at 105°C for 24 hours [7-9].

2.3. Activated carbon production
Activated carbon was modified by oxidation treatments using nitric acid with varying concentrations. 1 g of activated carbon was suspended in 150 mL of 1 M nitric acid solution at 75°C under refluxing for 4 hours. The activated carbon was washed with demineralized water until a pH of 6 was obtained for the rinse and dried at 105°C for 24 hours [9].

2.4. Activated carbon production
Scanning electron microscopy (SEM) using SEM Hitachi SU3500 conducted in Pusat Penelitian Nanosains dan Nanoteknologi Institut Teknologi Bandung was carried out to see the physical characteristics of activated carbon. Surface area and pore diameter of activated carbon were analyzed by a gas sorption Quantochrome Instruments Nova 3200e in Laboratorium Instrumentasi Teknik Kimia ITB. The Crystal structure of CNT was obtained from a powder X-ray diffraction pattern by using a Bruker D8 advanced diffractometer with monochromatized Cu K radiation [9].
CV tests on potentiostat/ galvanostat (Gamry V3000) use to analyzed the electrochemical properties of the supercapacitors and electrochemical impedance spectroscopy (EIS) with a frequency response detector at room temperature. Symmetrical two-electrode configurations were used to evaluate the capacitive performance of produced activated carbon. Nanocarbon (AC-Ca:GP:CNT) was wetted by ethanol, then mixed with polynylidene fluoride (PVDF) in a mass ratio of 9:1. Some variations in the characterization of AC-Ca:GP:CNT was 90:10:0, 90:0:10, and 90:5:5. The materials were pressed and dried at 105°C. Sandwich-type supercapacitor was assembled with two activated carbon electrodes separated by Nafion 212 in a button cell. The electrochemical behavior of samples was characterizations using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS).

**Figure 1.** Process diagram of activated carbon electrode.

3. Results and discussion
Activated carbon was produced through hydrothermal carbonization and activation processes. In this study, two-stage activation processes consisting of a chemical activation step (CaCl$_2$ as an activating agent during hydrothermal carbonization at 275°C) followed by physical activation (CO$_2$ activation at 800°C) [9]. Physicochemical activation has also been used to enhance porosity development and uniformity the pore size distribution of activated carbon [10]. The mass yield of activated carbon is 3.54 g from 10 g of EFB. CaCl$_2$ supports the polymerization reactions which occur among the aromatic hydrocarbons and tar-forming compounds. These reactions result in the formation of larger molecules in the structure of activated carbon products and an increase in the carbon yield [11].

**Figure 2.** SEM images of (a) AC-Ca, (b) Graphene commercial and (c) CNT commercial.

Morphologies of raw materials of activated carbon with CaCl$_2$ as an activating agent (AC-Ca), GP and CNT presented in Figure 2, can be observed that each material electrodes present the self-supporting, mechanically and physical characteristics. Figure 2a indicates that AC-Ca has more pore on the surface. A large surface area is more advantageous for applied as a supercapacitor electrode. Figure 2b, the GP exhibits highly structured properties on the surface and layer structure on the inside of the
electrode, this phenomenon is called the typical restacking of the graphene sheets, usually driven by the layer-to-layer van der Waals force. However, the stacked surface and oriented layer structure are unfavorable for the fast charge/discharge processes of the suitable supercapacitor, resulting in a small enough specific capacitance due to the little utilization of the specific surface of GP sheet [12]. Randomly tangled and intertwined structure as displayed at Figure 2c is pure CNT. In addition with the CNT, the value of conductivity of electrode could also be increased.

![Figure 3. XRD curve of (a) AC-Ca, GP and CNT (b) AC-Ca, AC-Ca Hidro and AC commercial](image)

The XRD curve of AC-Ca, GP, CNT, AC commercial and AC-Ca hidrofilization shown in Figure 3. Shows that only the GP, CNT and AC commercial shows a diffraction peak at 26.0°, which the meaning its high graphic characteristic and good conductivity. This fixed value of 5% is the best percentage weight for CNT and GP in the mix electrode of Ac-Ca/GP/CNT, which is good for efficient electron transportation during charge/discharge processes without sacrificing much of the total specific capacitance [13]. Figure 3. shows the AC-Ca shows a weak long range ordering characteristic. The pattern of AC-Ca Hydrofilization from XRD is not too prominent because the activated carbon has been oxidized.

Figure 4a show the CV curves of the electrode supercapacitors using the pure AC-Ca electrode at different scan rate of 2, 4, 6, 8 and 10 mV s⁻¹. The shape of the CV curve resembles a rectangle according to the electrostatic adsorption capacitance [14]. All the electrodes show the CV curves of the defect rectangles, which indicate the presence of electrochemical adsorption capacitance and electrostatic adsorption as shown in Figure 4. The electrostatic capacitance from the AC, GP or CNT, while the electrochemical adsorption capacitance is adsorption and desorption occurring on the OFG (oxygen containing functional group) (Figure 4c). It is found that the AC-Ca/GP/CNT electrode shows the maximum CV curve area, which showed the largest specific capacitance achieved by AC-Ca/GP/CNT at 90:5:5. Compared to the AC-Ca/GP/CNT 90:10:0 electrode indicates the smallest curve area (Figure 4b). Figure 4c, AC/GP/CNT 90:5:5 electrode CV curve is shown at different scan rate at 2, 4, 6, 8, and 10 mV s⁻¹. The CV curves shows a curve shape similar to a deformed rectangle although at high scan rate it can be seen, which are a good enough power capability of the AC-Ca/GP/CNT 90:5:5 electrode. Comparison on Figure 4d of AC-Ca before and after hydrophilization modify.

Table 1. shows the modification of activated carbon has the smallest surface area and average pore size. This is caused by a decrease in micropore volume due to pore blocking by surface oxide groups obtained from nitric acid oxidation [4]. The reason could be an activated carbon absorbs the molecule or ions of nitric acid, which occupies some pore volume. Furthermore, the produced functional groups on the carbon surface reduce pore size, even blocking partial micropores. Besides, increasing the nitric acid concentration leads to a decrease in surface area and average pore size. These results indicate that high concentrations of nitric acid cause the collapse of partial pores and oxygen-containing groups can block some micropores [3]. Surface area and pore size are very influential on activated carbon performance when applied as a supercapacitor electrode material. High surface area coupled with the presence of mesopores of appropriate sizes in activated carbon can improve the charge storage performance of supercapacitors [15].
Figure 4. CV curves of (a) pure AC-Ca electrode at different scan rate; (b) variation of AC-Ca/GP/CNT electrode at scan rate 2 mV s\(^{-1}\); (c) electrode of AC-Ca/GP/CNT 90:5:5 at different scan rate; and (d) AC-Ca hydrophilization.

Table 1. Specific capacitance of activated carbon electrodes

| Sample                  | Specific capacitance (F/g) |
|-------------------------|-----------------------------|
| AC-Ca                   | 29.46                       |
| AC-Ca-hydro             | 24.85                       |
| AC-Ca/GP/CNT (90:5:5)   | 53.51                       |
| AC-Ca/GP/CNT (90:10:0)  | 5.36                        |
| AC-Ca/GP/CNT (90:0:10)  | 24.19                       |

The EIS measurement has been carried out to investigate the electrochemical properties. The EIS curve of the assembled electrode double-layer supercapacitors as shown in Figure 5. The impedance spectrum shows the semicircle located at high to medium frequency region that is associated with the charge transfer impedance (R\(_{ct}\)), and an oblique line located at low frequency region representing the Warburg impedance (W) [4]. The intercept at high frequency with real axis is the electrolyte resistance (R\(_e\)). The EIS results are shown in Figure 5 it can be observed that the AC-Ca hydro (Figure 5b) electrode smallest resistance (0.10 ohm) while the AC-Ca before hydrophilization (Figure 5a) shows the largest resistance (22 ohm). In comparison of the AC-Ca/GP/CNT 90:10:0 (Figure 5d) electrode smallest resistance (-20 ohm) while the AC-Ca/GP/CNT 90:0:10 (Figure 5c) shows the largest resistance (17 ohm).
Figure 5. EIS of (a) AC-Ca electrode; (b) AC-Ca hydrophilization with 1 M HNO₃; (c) AC-Ca/GP/CNT 90:0:10 electrode; and (d) AC-Ca/GP/CNT 90:10:0 electrode.

The galvanostatic charge-discharge curve of all activated carbon supercapacitor cells have a triangle and symmetric shape which indicates the supercapacitor cells have the same charging and discharging time [17]. GCD analysis for each supercapacitor cell was performed at a constant current density of 1 mA/cm². The GCD curve of AC-Ca has the lowest cell voltage. The GCD curve of AC-Ca hydro (Figure 6c) have higher cell voltages that cause a decrease in specific capacitance. The specific capacitance of GCD results in accordance with the results of cyclic voltammetry (CV) analysis.

The charging and discharging curve (GCD) of the electrodes for different materials can be seen in Figure 6. This analysis carried out at a constant current and measures the magnitude of the voltage as a function of charging and discharging times. It can be seen in the GCD analysis image of each sample in the form of a linear and symmetrical curve. This indicates that the supercapacitor made has good capacitive performance. Because the results of the electrode GCD curve with carbon material will generally be isosceles triangle. It can be observed in Figure 4a, similar to the CV curve, it also shows that electrostatic adsorption/desorption mainly occurs at the low potential stage. The pure AC-Ca electrode in Figure 6a has almost no adsorption capacitance, which is only around -0.069 V this results loss of the specific area. In Figure 6c, it can be compared that shows a higher specific capacitance of charge/discharge than the AC-Ca electrode during the longer cycle (Figure 6ca). Occurs that the AC-Ca/GP/CNT electrodes show higher capacitance retention than the AC-Ca electrodes, which is considered a synergistic effect of the AC, GP and CNT compound.
Figure 6. long-term cycling performances of the (a) AC-Ca; (b) GP; (c) AC-Ca hydro; and (d) AC-Ca/GP/CNT 90:10:0

4. Conclusions
Activated carbon material as an electrode material of supercapacitor can be produced from oil palm empty fruit bunch through the hydrothermal carbonization process and physicochemical activation. The specific capacitance value of supercapacitor from unmodified activated carbon (AC-Ca) is 29.46 F g⁻¹. Increasing the nitric acid concentration on surface modification leads to an increase in hydrophilicity of activated carbon, a decrease surface area, a decrease pore diameter and a decrease in the specific capacitance. Modified activated carbon with 1 M nitric acid has a specific capacitance value of 24.85 F g⁻¹. The self-supporting AC-Ca/GP/CNT electrode has been successfully synthesized for supercapacitor and work very well. The surrounding CNT could be enhanced the electronic conductivity value of the AC-Ca and GP. With the AC-Ca/GP/CNT 90:5:5 electrode is able to deliver a high specific capacitance of 53.51 F g⁻¹.

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References
[1] Xing Li, Yao Tang, Junhua Song, Wei Yang, Mingshan Wang, Cheng Zhu, Wengao Zhao, Jianming Zheng, Yuehe Lin. Self-supporting activated carbon/carbon nanotube/reduce graphene oxide flexible electrode for high performance supercapacitor. 2018 Carbon
[2] Davies A and Yu A 2011 Can. J. Chem. Eng.
[3] Liu Y, Hu Z, Xu K, Zheng X and Gao Q 2008 Acta Phys-Chim Sin.
[4] Wang H, Yuan X, Zeng G, Wu Y, Liu Y, Jiang Q, Gu S Three dimensional graphene based materials: synthesis and applications from energy storage and conversion to electrochemical sensor and environmental remediation.
[5] Cheng P and Teng H 2003 Carbon
[6] Jin H, Wang X, Gu Z and Polin J 2013 J. Power Sources
[7] Hendriansyah R, Prakoso T, Widiatmoko P, Nuridin I and Devianto H. manufacturing carbon material by carbonization of cellulosic palm oil waste for supercapacitor material. 2018 MATEC Web Conf.
[8] Larasati T D, Prakoso T, Rizkiana J, Devianto H, Widiatmoko P and Nuridin I. Nano carbon produced by advanced mild hydrothermal process of oil palm biomass for supercapacitor material. 2019 IOP Conf. Ser. Mater. Sci. Eng.
[9] Gumulya C, Prakoso T. Rizkiana J, Devianto H, Widiatmoko P and Nuridin I 2019 IOP Conf. Ser. Mater Sci. Eng
[10] Sevilla M and Mokaya R 2014 Energy Environ. Sci.
[11] Ahmadpour A and Do D D 1997 Carbon
[12] Chen H, Muller M B, Gilmore K J, Wallace G G, Li D Mechanically strong, electrically conductive, and biocompatible graphene paper Adv. Mater.
[13] Huang H, Zhang W, Fu Y, Wang X. Controlled growth of nanostructured MnO2 on carbon nanotubes for high-performance electrochemical capacitors Electrochim.
[14] Xiong C, Li T, Zhao T, Dang A, Li H, Ji X, Jin W, Jiao S, Shang Y, Zhang Y, and conversion to electrochemical sensor and environmental remediation, Adv.
[15] Jain A, Xu C, Jayaraman S and Balasubramanian R 2015 Microporous Mesoporous Mater.
[16] Yu A, Chabot V and Zhang J 2013 Electrochemical Supercapacitors for Energy Storage and Delivery (Boca Raton: CRC Press)
[17] Abioye A M, Noorden Z A and Ani F N 2017 Electrochim. Acta
[18] Farma R, Deraman M, Awitdrus A, Talib I A, Omar R, Manjunatha J G, Ishak M M, Basri N H and Dolah B N M 2013 Int. J. Electrochem. Sci.