Wettability improvement of carbon nanotube for supercapacitor electrode

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Abstract. Carbon Nanotube (CNT) has outstanding properties such as electrical conductivity, specific surface area, charge transport capability, mesoporosity, and very high electrolyte accessibility. Based on these properties, CNTs are very suitable to be used as high-performance supercapacitor electrodes which can be seen from the capacitance. One of the factors that can lead to increase capacitance is the high interface interaction between CNT and the electrolyte. The interface interaction of CNT and electrolyte can be improved by increasing the CNT wettability using hydrophilization. CNT is synthesized by pyrolysis with Palm Oil Mill Effluent (POME) as the main raw material. In this study, hydrophilization was carried out using chemical activation HNO₃ with various concentrations and activation times (1M for 1, 3, 6 hours, and 13M for 1 hour). The results of CNT structure were characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscope (TEM), and X-Ray Diffraction (XRD), as well as electrochemically characterized using cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) dan galvanostatic charge-discharge (GCD), as supported data to evaluate which concentration and activation time with the highest efficiency to improve CNT performance as a supercapacitor. Based on CV characterization, the capacitance of CNT before hydrophilization, and after hydrophilization using HNO₃ (1M for 1 hour, 3 hours, 6 hours, and 13M for 1 hour) were 10 F/g, 13.30 F/g, 14.28 F/g, 26.95 F/g and 24.5 F/g respectively. When CNT hydrophilized at 13M for 1 hour, capacitance decreased. Due to surface damage of CNT, therefore the performance of the supercapacitor decreased. This was supported by the results of the GCD characterization, where some charges could not completely release.

1. Introduction
Indonesia is one of the largest country that produces palm oil in the world. Palm oil then processed to make crude palm oil (CPO) with a large amount for each year, in 2020 CPO had been produced about 40 million tons [1]. From the CPO process then produce biomass waste such as solid waste and liquid waste. POME (Palm Oil Mill Effluent) is one of the liquid wastes that had a 70% bigger amount than solid waste [2]. Utilization of POME such as biogas, compost, and carbon nanotube are the attempts to make use of it that are not wasted. Production of biogas and compost needs a large field and longer time to decompose, while the production of carbon nanotube did not need a large field, and POME can be used directly without decomposition. On the other side, POME had carbon content that made it possible to produce carbon nanotube which has higher sales value than others. CNT is a carbon allotrope with a nanometer size of the cylindrical model. CNT has outstanding properties such as the biggest electrical conductivity than copper with 3000 W/K, tensile strength 11-63 GPa, modulus young 270-950 GPa, and small resistance with 0.34-10⁻⁴ ohm.cm [3]. From that characteristic, CNT can be used for the
supercapacitor electrode because of the carbon characteristic which had corrosion resistance, stable at high temperature, high surface area, and low operating cost. KPEE-ITB Laboratory succeeded to produce CNT from POME by pyrolysis. However, the capacitance of supercapacitor with the CNT electrode still low because of the hydrophobicity of CNT. This study investigated the effect concentration and activation time of nitric acid on CNT morphology and capacitance of supercapacitor by performing hydrophilization on CNT.

2. Methods
One of the synthesized processes of CNT by using the pyrolysis method. Pyrolysis is one of the thermodynamical processes which material degraded become smaller component at high temperature without the presence of oxygen. Pyrolysis is the easiest process that had many advantages such as storage, transportation, and flexibility for example turbines, boiler combustion equipment, engine, etc [4]. Here are the materials and methods that needed to synthesize CNT and hydrophilization.

2.1. Materials
The main material used for synthesized of CNTs is POME that was collected from the palm oil mill of PT. Perkebunan Nusantara VIII, in Cikasungka Bogor. The POME is wastewater with rich organic carbon with a colloidal suspension of 95 – 96% water, 0.6 – 0.7% oil, and 4 – 5% total solids, including 2 – 4% suspended solids (Kumar, 2016). Formaldehyde (Merck, purity 37%) used to polymerize POME and ammonium hydroxide (Merck, purity 28%) as a catalyst. The resin that produces by polymerization method used for synthesized CNT by pyrolysis method. Ferrocene (purity 98%) used as a catalyst in nitrogen flow. Ferrocene is frequently used as a precursor to prepare carbon nanostructures because it cannot only act as a carbon source but also give rise to small metal clusters as catalysts. For CNT hydrophilization by using HNO₃ (Merck, purity 63%).

2.2. CNT Production
The resin that has been ready to mix with 30% ferrocene (w/w) and ethanol mixed in order to homogeneous between resin and ferrocene. Once it was homogeneous, the ethanol evaporated and after that, the mixture put into the furnace to be pyrolyzed. The pyrolysis process is carried out by adjusting the increase rate of the temperature of 10 °C/minute under the nitrogen atmosphere. During the process, the temperature held at 200 °C for 1 hour for the carbonization process. Then the temperature was raised until 900 °C and held for 1.5 hours for the formation of the CNT.

2.3. CNT Hydrophilization
The CNT that has been formed then hydrophilized to improve the wettability of CNT. The chemically activation process was using HNO₃ with several variations of concentration and duration of activation. CNT used for hydrophilization was 0.25 gr for each variation and the temperature was set close to the boiling point of the solution with HNO₃ concentration 1M for 1 hour, 3 hours, and 6 hours and 13M for 1 hour.

2.4. Supercapacitor Cell
Electrode preparation of 0.06 gr of CNT that had been measured contact angle wettability, mixed with polyvinylidene fluoride (PVDF), and dissolved with ethanol until it shaped like a slurry. SS mesh used as a current collector. The upper surface of the ss mesh is coated by 1 cm² slurry CNT then dried in the oven for 24 hours at temperature 80 °C. After slurry CNT dried then weighed and stored as electrodes. The electrodes dripped with 5 drops of KOH solution as electrolyte with 6M concentration for each electrode by using microsyringe and bounded by nafion 212.

2.5. Characterization
The morphology of CNT was characterized by using scanning electron microscopy (SEM) (Hitachi SU3500, Japan) and transmission electron microscope (TEM) (Hitachi H9500, Japan). The crystal
structure of CNT was obtained from a powder X-ray diffraction pattern by using a Bruker D8 advanced
diffractometer with monochromated Cu K radiation.

The electrochemical characterization of supercapacitor were studied by cyclic voltammetry (CV),
galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) methods. The
electrochemical measurements were carried out using Gamry V3000 potentiostat-galvanostat. The
data obtained were needed to evaluate the highest efficiency of the hydrophilization method with the
optimum concentration and activation time to improve CNT performance as a supercapacitor. The
specific capacitances of supercapacitors were computed from CV curves by using the following equation

\[ C_{sp} = \frac{I \Delta t}{m \Delta V} \]  

Where ‘\(C_{sp}\)’ is the specific capacitance (F.g\(^{-1}\)), ‘I’ is the current (A), ‘\(\Delta t\)’ is the discharge time (s), m is
the mass for one electrode material (g) and ‘\(\Delta V\)’ is the change in voltage during the discharge process
(V).

3. Result and Discussion
Here is the result of the research based on structure characterization and electrochemical characterization
of CNT as a supercapacitor electrode.

3.1. CNT Structure Characterization
The samples analysed consisted of commercial CNTs, CNT before hydrophilization, and CNT after
hydrophilization (CNTH). Before that, the contact angle of CNT was measured first to review the effects
before and after chemical activation performed on CNT wettability.

![Contact angle measurement images](image)

**Figure 1.** Contact angle measurement (a) commercial CNT (b) lab synthesized CNT (c) CNTH 1M 1 hour (d)
CNTH 1M 3 hours (e) CNTH 1M 6 hours (f) CNTH 13M 1 hour.

Based on the results of contact angle measurements shown in Figures 1 (a) and (b) indicates that the
contact angle on commercial CNT was lower (hydrophilic) than lab synthesized CNT. Lab synthesized
CNTs are still hydrophobic, so to make CNTs become hydrophilic the surface of CNTs need
functionalization by hydrophilization using nitric acid. In figures 1 (c) to (f) it can be seen that the
contact angle decreases, indicating that the CNT is hydrophilic. The lower the contact angle, the greater
the wettability. That way, the ions contained in the electrolyte easily enter the CNT pore and stick to the
inner surface so that it can increase the capacitance [6].
Based on the SEM results above in Figure 2 (b), it shows the formation of a CNT that almost resembles a commercial CNT. Then comparing Figures 2 (c) to (f), it shows that there is a change in the structure on the CNT surface. The nitric acid that used for the hydrophilization process can reduce impurities on the CNT, but also can change the structure of the CNT. In this figure, it can be seen that at the end of the CNT found a white spot that looks like it was broken into several parts. This is due to the side effect of nitric acid which made the CNT structure truncated and shorter. On the other hand, the concentration of nitric acid that been used and the duration of activation also greatly influence the changes in the CNT structure [7].

 TEM characterization was carried out to see the innermost part of the CNT where the nanocarbon has tubular space so the internal and external diameters can be measured. In Figure 3 (a) the CNT has a diameter of 5-10 nm, while Figure 3 (b) has a diameter of 14 nm. Compared to commercial CNT, the CNT diameter between lab synthesized by the previous researchers and commercial CNT had little difference. While in the current lab synthesized CNT had a bigger diameter, approximately 35.7 nm that shows in Figure 3 (c). This was caused when synthesizing CNT by pyrolysis, the reaction temperature increases and there was agglomeration between metal particles which causes the size of the metal particles to increase, resulting in a larger CNT diameter [8].
Figure 4. XRD characterization of commercial CNT, lab synthesized CNT and CNTH.

Based on the XRD characterization above, the graphite C (002) structure was at the vertex of 2θ with a value of about 26.97°. The peak of the graphite structure on the CNT before and after hydrophilization tends to be low compared with commercial CNT. The vertex of the 2θ angle at a value of 44.14° (100) was a reflection of the CNT multi-walled graphite structure [9].

3.2. CNT Electrochemical Characterization
Characterization of CV aims to determine the specific capacitance of supercapacitor cells before and after hydrophilization with various concentrations and activation time. The result of CV characterization is shown below.

Figure 5. CV characterization with scan rate 2 mV/s on (a) lab synthesized CNT (b) duration of chemical activation (c) concentration of nitric acid.
From the curve above it can be seen that the longer activation, the greater the capacitance that obtained. Hydrophilized CNT based on the difference concentration in Figure 5 (c) shows that the higher the concentration, the capacitance also increase. The capacitance of hydrophilized CNT with a concentration of 13M was 24.5 F/g that higher compared to hydrophilized CNT with concentration 1M which only had a capacitance of 13.4 F/g. The specific capacitance for each CNTH can be seen in the table below.

| Sample          | Capacitance (F/g) |
|-----------------|-------------------|
| CNTH 1M 1 hour  | 13.4              |
| CNTH 1M 3 hours | 14.28             |
| CNTH 1M 6 hours | 26.95             |
| CNTH 13M 1 hour | 24.5              |

Figure 5 (a) is a combination of CNT that had been hydrophilized. To see how the effect of activation time on fixed nitric acid concentration is shown in Figure 5 (b) and the effect of different concentrations on fixed activation time is shown in Figure 5 (c). For the effect of activation time, the CNT that has the largest capacitance was when 6 hours of activation time with 26.95 F/g.

GCD characterization aims to see how much voltage of the supercapacitor cell when it was tested at a constant current. The curve formed on GCD characterization was isosceles triangle which shows the time required for the charging process was the same as the time for discharge of the charge. The supercapacitor cells that had been tested were CNT electrode commercial CNT, lab synthesized CNT, and hydrophilized CNT.

In Figure 6 (a) above, the lab synthesized CNT was not discharged completely. In the 200th second the curve should touch axis 0, but the curve stops at point 0.01 second. GCD curve shows the Faradaic process which in the supercapacitor cell there was a reaction of oxygen adsorbed on the electrode surface with water to form OH\(^-\) or HO\(^2-\). Because of this reaction, the charge that should had been released during the discharge process was trapped until the discharge time had been completed [10].

Furthermore, EIS characterization was carried out which aims to provide information on the interaction between electrodes and electrolytes from the supercapacitor cells. The setup for EIS measurement was made at a frequency of 100,000 Hz to 0.001 Hz. The result was a Nyquist curve that could be seen as the amount of resistance in the supercapacitor cells. The following are the results of EIS characterization on commercial CNT, lab synthesized CNT, and CNTH.
The Nyquist plot for supercapacitor cells generally consists of 3 parts, such as semicircles at high frequencies (>100,000 Hz), straight lines with a slope of 45°, and vertical lines with an angle of 90° at medium to low frequencies [11]. The starting point of the curve shows the resistance from the electrolyte ($R_s$), while the semicircles show the resistance of charge transfer at the electrical double layer interface of the electrode with the electrolyte. The value of $R_s$ did not affect the capacitance of the supercapacitor electrode ($Z_{\text{imag}}$) and was real resistance ($Z_{\text{real}}$).

The frequency that used for this EIS measurement was 100,000 Hz-10 Hz, which the semicircles results shown in Figure 7 (a). When the semicircles were compared between lab synthesized CNT with commercial CNT, the semicircle in lab synthesized CNT was smaller than those of commercial CNT. This semicircle represents a voltage as shown in Figure 7 (a) requiring a high voltage to store the charge. The higher the voltage, the smaller the capacitance. One of the factors of low semicircles size in the research was due to the increased wettability of the electrode surface that reducing the repulsive force between the electrode and the electrolyte [12].

4. Conclusions
From the results that had been researched, it can be concluded that the nitric acid that used for hydrophilization of the CNT greatly affects the CNT structure. When the CNT was hydrophilized, the tip of the CNT had a white spot which indicates that the CNT had broken into several pieces and became shorter. On the other hand, CNTH had the lowest contact angle 22.73° with a concentration of nitric acid 1M and an activation time of 6 hours obtained the specific capacitance 26.95 F/g.

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