Effect of ZnCl\textsubscript{2} on properties of graphene produced from palm empty fruit bunch

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Abstract. The production of palm oil in Indonesia is increasing every year. Along with the increase in production, the waste generated by the palm oil mill is also increasing. Waste from the production of palm oil can be used as raw material for high value-added products such as graphene. Graphene is the two dimensional hexagonal lattice of sp\textsubscript{2} carbon atoms. Due to its excellent electrical conductivity and high theoretical surface area, graphene has very promising applications in nanoelectronics components including transistors, lithium ion batteries and supercapacitor. This study aims to characterize the effect of activating agent ZnCl\textsubscript{2}: biomass ratio on the structure and properties of graphene production from palm oil waste with catalyst FeCl\textsubscript{3} via two-stage pyrolysis. Experiment results showed that surface properties of graphene sheets depend on the ZnCl\textsubscript{2}: biomass ratio. The effective surface area increased with increasing ZnCl\textsubscript{2}: biomass ratio. Graphene sheets shows favourable features such as nanosheet frameworks (2-4 atomic layers), graphite-like interlayer spacing (0.3380 nm) and also high crystalline degree ($I_G/I_D = 9.35$).

1. Introduction

Palm oil industry is one of industrial sector that contributes most significantly to Indonesia’s economy. The production of palm oil (CPO) in Indonesia in 2015 reached 33.5 million tons [1]. The palm oil industry generates large quantity of wastes including empty fruit bunch (EFB), mesocarp fiber (MF), palm kernel shell (PKS), palm kernel meal (PKM), and palm oil mills effluent (POME). The production of these wastes is abundant and can be found in 65% of provinces in Indonesia as oil palm plantation area [2].

Solid wastes from palm oil industry are occasionally left scattered at the field sites, and consequently, jeopardizing the quality of the surrounding environment. Therefore, instead of viewing them as a burden, some efforts must be done to increase the economic value of the waste. In this study, empty fruit bunch (EFB) is utilized as precursors of graphene synthesize.

Graphene is prominent for its large surface area and pore size distribution as well as good surface exposure to electrolytes, has been recognized as an excellent component for supercapacitors. Other incredible properties of graphene include high thermal conductivity of up to 5000 W m\textsuperscript{-1}k\textsuperscript{-1}, great strength with a Young’s modulus of around 1 TPa and extensive surface area with a theoretical value of 2630 m\textsuperscript{2} g\textsuperscript{-1}. It is one atom thick and can be easily obtained from graphite [3]. Graphene can be applied in nanoelectronics and nanocomposite components including solar cells, transistors, lithium
ion batteries, and molecular sensors. In addition, graphene can also be utilized as a sturdy electrode material for supercapacitors [4].

Supercapacitor is a new technology developed from conventional capacitors as modern energy storage. This capacitor used a large electrode surface and an electrical double layer to achieve much larger capacitance value than a conventional capacitor. This allows the supercapacitor to have much greater energy density than the conventional capacitors and much greater power density than the batteries [5].

Preparation of graphene with biomass precursors can be done using pyrolysis process comprising carbonization and activation. Carbonization is a slow pyrolysis process that aims to produce the main product in the form of charcoal [6]. The activation process aims to open and add pores to graphene. This process can be done with two methods, there are physical activation techniques and chemical activation techniques. In the process of physical activation, the carbon is heated at a temperature of 800-1100°C and is contacted with oxidizing gases such as water vapor, CO₂, and N₂ [7].

Chemical activation is a direct process that includes an impregnation step prior to heat treatment in an inert atmosphere at temperature of 400°C to 600°C. Compared to physical activation, this activation is economically viable because it has lower activation temperature, shorter processing time, and higher carbon yield. The chemicals applied as potential activators include alkaline group such as potassium hydroxide (KOH) and potassium carbonate (K₂CO₃); acidic group such as phosphoric acid (H₃PO₄) and sulphuric acid (H₂SO₄); and transition metal salt like zinc chloride (ZnCl₂). The different types of chemical react differently with the precursors, and thus, influence the adsorption behaviour [8].

In recent years, ZnCl₂ has increasingly been used in the production of graphene by chemical activation method. Graphene have been prepared from biomass precursors such as coconut shells by ZnCl₂ chemical activation method [9]. Herein, we report investigations of the effect of ZnCl₂ ratio, on the surface properties of graphene.

2. Experimental

2.1 Graphene production

Empty fruit bunch (EFB) as carbon source was obtained from PT Perkebunan Nusantara VIII Bogor, Indonesia. Zinc chloride (ZnCl₂) as activating agent, Ferric trichloride (FeCl₃) as graphitic catalyst precursor, ethanol, hydrochloric acid (HCl, 37%), and potassium hydroxide (KOH) were purchased from Merck Chemicals, PT. Brataco Chemika, Indonesia. The EFB was washed with demineralized water. Dried EFB was ground and sieved into granules (170-200 mesh). In a typical synthesis, 3 g of EFB was mixed with 3 g of ZnCl₂ in 50 mL of 3 M ferric trichloride (FeCl₃) solution. Furthermore, the mixed materials was stirred and evaporated at 80°C on a hot plate for 2 h and then dried at 100°C in a conventional oven, the carbon precursor was obtained. Afterwards, the activation and graphitization process of the carbon precursor was carried out in a tubular furnace under a N₂ atmosphere by heating the sample at a rate of 5°C min⁻¹ up to 250°C and held for 60 minutes, then the temperature increased up to 900°C and held for 90 minutes as described in Figure 2. The sample was denoted as FLG1, where 1 denotes the mass ratio of ZnCl₂/empty fruit bunch. As prepared FLG1 was immersed in 2 M hydrochloric acid to remove iron species and dried at 80°C for 12 h. Experiments were repeated with mass ratio of ZnCl₂/empty fruit bunch varied 2:1 and 3:1, denoted as FLG2 and FLG3 respectively. A series of experiments were performed to investigate the effect of ZnCl₂: empty fruit bunch mass ratio on the microstructure of FLG materials.

2.2 Characterization

The morphology of FLG were examined by Scanning Electron Microscopy (SEM) using SEM Hitachi SU3500 and Transmission Electron Microscope (TEM) using HR TEM Hitachi H9500, conducted in Pusat Penelitian Nanosains dan Nanoteknologi Institut Teknologi Bandung. The crystalline structure of graphene was analyzed by X-ray diffraction (XRD) technique using Bruker D8 Advance with Cu-K radiation (λ = 1.54Å) conducted in Laboratorium Instrumentasi Teknik Kimia ITB. Raman spectra were recorded on HORIBA Raman Spectrometer in Pusat Sumber Daya Mineral Batu Bara dan Panas.
Bumi Bandung. Surface area and pore diameter of graphene were analyzed by a gas sorption Quantochrome Instruments Nova 3200e in Laboratorium Instrumentasi Teknik Kimia ITB.

2.3 Electrochemical measurement
Assymetrical two-electrode configurations were used to evaluate the capacitive performance of FLG as supercapacitor electrode materials. The negative electrodes were prepared by mixing the FLG materials with polyvinylidene fluoride (PVDF) at a weight ratio of 90:10. The above materials were coated onto a 1 cm$^2$ stainless steel mesh current collector and dried at 80°C for 8 h. The positive electrodes were prepared by mixing nickel oxide with polyvinylidene fluoride (PVDF) at a weight ratio of 90:10. The above materials were coated onto a 1 cm$^2$ stainless steel mesh current collector and dried at 80°C for 8 h. Nafion 212 was sandwiched between two electrodes as separator. The test was performed in 6 M KOH aqueous electrolyte solution under ambient conditions using Gamry V3000. Capacitive performance of samples was studied by using cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) techniques. EIS was performed with a computer-controlled Impedance Analyzer in a frequency range from 100 kHz to 0.01 Hz.

![Figure 1. Schematic representation for the synthesis of FLG active material and its subsequent integration into a supercapacitor](image1)

![Figure 2. Pyrolysis temperature step](image2)

3. Result and discussion
Few layers graphene can easily obtain by pyrolysis process from palm oil waste such as empty fruit bunch with simple method and high yield. The pyrolysis process in this experiment is carried out in
two stages, these method is done in order to obtain higher yield of graphene. Expected pyrolysis products from this experiment are char. To obtain greater amount of char, pyrolysis process should be carried out in low temperature [6]. Furthermore, graphene formation occurs at higher temperature (>700°C) [7]. Therefore, we proposed two stages pyrolysis to produce graphene.

The characteristics of prepared FLG would be favourable for their application in supercapacitors. The structure of FLG was studied by SEM, TEM, XRD, Raman spectroscopy, and nitrogen adsorption–desorption tests.

![SEM images](image)

Figure 3. SEM images of (a) FLG1, (b) FLG2, (c) FLG3 and (d) TEM images of typical FLG from EFB.

Figure 3(a-c) shows the results of the SEM and (d) TEM analysis of FLG with variation of ratio ZnCl$_2$: biomass. From the analysis it can be seen that FLG presents few-layer and multilayer graphene-like structure. Beside that, ZnCl$_2$ impregnation ratio plays an important role to achieve and/or optimize surface area of graphene, higher ZnCl$_2$ causes the formation of more pores during carbonization process.

Water molecules from the lignocellulosic structures were extracted during impregnation with ZnCl$_2$. ZnCl$_2$ triggers the hydrolysis reactions when reaches the inner parts of the raw material. This reaction causes volatiles removal, weight loss, increase the elasticity and also weakening of the carbonaceous structure. The impregnation of ZnCl$_2$ also causes particle swelling. During carbonization, tar formation decreases, so yield of the product increases. Apparently ZnCl$_2$ tends to remove hydrogen and oxygen atoms in the form of water instead of the hydrocarbons and oxygenated organic compounds. And after the removal of non-carbon elements from the structure, carbon skeleton is remained largely untouched with a well-developed porosity [10].
The X-ray diffractogram of FLG is presented in Figure 4a, it can be seen that there is a peak at an angle of $2\theta \sim 26^\circ$ which indicates the graphite structure in the sample [9]. The peak on the widened XRD spectrum shows the amorphous carbon structure generated by the destruction process of the initial graphite structure during the pyrolysis process. The resulting carbon structure is an intermediate structure between graphite and amorphous structures called turbo static structures or lattice structures of random layers.

The distance between the pseudo graphitic layers ($d_{002}$) was calculated using Match software. From the calculation, we obtained that the value of $d_{002}$ ranges (0.3380 nm) represents graphitic like structure. Furthermore, the degree of product graphitization is calculated using the following equation:

$$G = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \times 100\%$$

In the equation, the value 0.3440 refers to the interlamellar distance of the turbo static graphite (in nm) and 0.3354 refers to the interlamellar distance of a single graphite crystal (in nm). From the calculation, the degree of product graphitization reached 70%. The high graphitization degree of multiple layers of graphene indicates good electrical conductivity [4].

A Raman spectroscopy analysis was performed to determine the carbon structure of the graphene. Figure 4b shows the Raman spectra of FLG. The G peak is at a wave number of about 1573 cm$^{-1}$ and the D peak is at a wave number of about 1346 cm$^{-1}$. The peak intensity of G and D depends on the percentage of the graphite domain containing the sp2-carbon layer of hybridization in graphene formed. Integral intensity ratio of $I_G / I_D$ is proportional to the crystalline degree of carbon material [11].

Raman spectra of graphene shows a typical graphitic character, due to the intensity of G peak that is much higher than the peak intensity D. The $I_G / I_D$ value is 9.35, suggesting the quite high graphitization degree of FLG. The peaks at 2690 and 2697 cm$^{-1}$ represent the 2D band. The position and height profile at the peak indicate layering on graphene. The 2D band on graphene monolayer, is at 2679 cm$^{-1}$. The 11 cm$^{-1}$ shifts to the higher wave numbers indicate 2-4 layers of graphene [11].

Advanced supercapacitor electrode materials also need a large BET surface area. The nitrogen adsorption–desorption isotherm of the FLG sample (Figure 5.) shows a typical type IV curve with a clear H1-type hysteresis loop in the relative pressure region of 0.5–0.8 P/P0, indicating the existence of mesopores [9]. The pore size distribution (Table 1) was calculated from the adsorption branch of the isotherm by the Nonlocal Density Functional Theory (NLDFT) method. The result reveals that the formation of the pores with an average pore size of about 3-6 nm.

Surface area analysis using BET calculations was performed to determine the surface area and pore distribution of graphene. These parameters are very important to know because they affect the
performance of graphene when applied as an electrode to the supercapacitor. As shown in Table 1. The BET surface area of FLG samples increase as the increase of ZnCl$_2$:empty fruit bunch ratio, which may be due to higher ZnCl$_2$ causes the formation of more pores during carbonization process [12].

![Figure 5. Typical nitrogen adsorption–desorption isotherm and pore distribution (inset) of FLG.](image)

The high specific surface area and plentiful pores of FLG provide lots of ion adsorption sites and a high density of interconnected ion diffusion pathways that favour electrolyte ion transport in the FLG electrode material [9]. Electrochemical analysis was performed to test the electrochemical performance of the resulting graphene, when applied as a supercapacitor electrode.

| Sample | Surface area (m$^2$/g) | Average volume (cc/g) | Average pore size (nm) |
|--------|------------------------|-----------------------|------------------------|
| FLG1   | 222                    | 0.349                 | 6.307                  |
| FLG2   | 290                    | 0.334                 | 4.612                  |
| FLG3   | 470                    | 0.202                 | 3.08                   |

The electrochemical performance of FLG as an active material for supercapacitor was studied using assymetrical two-electrode cell configuration in 6M KOH electrolyte under ambient temperature as described in section 2.2.

Cyclic voltammetry is used to observe cell characteristics and to calculate the capacitance. In CV measurements with a scan rate of 5 mV/s, the CV results show less ideal curves (not quasi-rectangular). The increasing cycle of slope cycle indicates the existence of leak current. Leak current may occur due to side reactions between the electrolyte and the functional group in the sample. This can be minimized by electrolyte optimization [13]. Figure 6a shows the CV measurement results at higher scan rates at 10 mV/s up to 500 mV/s. It is seen that with the increase in scan rate, there is more elongated shape of the curve and resulting higher current. This indicates a barrier when ion transfer from the electrolyte to the electrode surface [14].
Figure 6. (a) Cyclic voltammogram of FLG3 (ratio of \(\text{ZnCl}_2\) : empty fruit bunch is 3:1), (b) Nyquist curve of FLG3, and (c) Equivalent circuit of FLG3.

The specific capacitance of FLG can be calculated from voltammogram according to the following equation:

\[
C = \frac{\sum |I| \Delta t}{m \Delta V}
\]

(2)

with \(I \Delta t\) is the area of the curve \(I\) (A) to \(t\) (sec), \(m\) (gram) is the mass of the active ingredient in the cell, \(\Delta V\) (V) is the operating range of the cell voltage. The calculation results shows in Table 2.

| Sample   | Capacitance (F/g) |
|----------|-------------------|
| FLG1     | 1.345             |
| FLG2     | 1.474             |
| FLG3     | 1.885             |

The low capacitance caused by the cell resistance. The cell resistance then analyzed using electrochemical impedance spectroscopy.

Electrochemical impedance spectroscopy (EIS) was further done to investigate the electron transfer and the facilitated ion behavior of the supercapacitor cell, and also to estimate resistance of the supercapacitor cell. As shown in Figure 6b, in the low frequency, the nyquist plot results are described with a straight line 45° which shows the characteristics of typical capacitors, unlike the ideal supercapacitor, which drawn with a straight line approaching 90°, the more vertical the line is closer to the ideal supercapacitor [15]. This indicates a considerable resistance value at the time of electrolyte diffusion to the electrode.

In medium frequency, there are electrolyte interphase resistance into the pores of electrodes with domino effect. In high frequency, the semicircle of the real axis represents the electrode-electrolyte interface resistance. This equivalent electrical circuit is modeled by the Schrodinger coupled nonlinear equation (CNLS) shown in Figure 6c. The capacitor circuit is constituted by \(R_1, R_4, \text{CPE}, a_3, R_6\) and \(W_7\). \(R_1\) is the sum of the contact resistance and material resistance (electrode, electrolyte and separator). \(W_5\) is the Warburg resistance which is related to the ion diffusion/transport in the
electrolyte. R4 and R9 are interface resistances for mass transfer of electrolytes into the electrode pores [9]. C5 is related to capacitors formed during charge-discharge process and CPE is not ideal capacitor. The cell resistance values of the equivalent electrical circuit model are presented in Table 3.

Active materials can have large electronic resistance. The internal resistance in the paste electrode is caused by low conductivity and the availability of a sufficient conduction path to traverse the thickness of the electrode layer. These internal barriers are a feature of certain active materials. Graphene is hydrophobic, thus the graphene surface will experience a repulsion force with an aqueous electrolyte which is a polar compound, thus affecting the performance of graphene as a supercapacitor electrode. Graphene surface modifications can be made to make the graphene surface more hydrophilic, using the hydrophilization method [16].

The internal resistance in the electrode paste matrix can be reduced by increasing percolation by the addition of 10 to 20% conductive carbon filler. Current collectors and conductive pastes contribute to the weight that could not be ignored in the device. Any non-capacitive weights in cells reduce device performance. As a result, the additive paste used should be as minimal as possible and optimal, as well as the current collector used should be thin and light [17].

Optimum proportion of the component materials for graphene-based supercapacitor electrodes has been studied. By using the extreme vertices design, the optimized proportion is determined to be (FLG : PVDF = 0.95 : 0.05) [18]. One of the key component of cell assembly is proper cell sealing. If the cell is not sealed properly, the oxidation of electrode, the evolution of gases from electrolyte degradation, and corrosion could be a problem [19]. When the cell is sealed tightly the water and gas molecules would not enter the cell. Moreover, proper sealing can prevent shunt resistance between adjacent cells and electrodes. The shunt current significantly increases self-discharge and reduces the efficiency of the device. Bad seals will be damaged over time which causes degradation and short circuit [20]. Heat can be applied to make the plastic shrink and tightly seal the envelope that isolates the cell.

Table 3. Cell impedance of FLG3.

| Parameter | Value  | Units   |
|-----------|--------|---------|
| R1        | 48.66  | ohm     |
| Yo2       | 43.06e-6 | S*s^a |
| a3        | 559.7e-3 |       |
| R4        | 168.0  | zohm    |
| C5        | 51.89e-3 | F      |
| R6        | 11.55  | ohm     |
| W7        | 6.81   | S*s^(1/2)|

4. Conclusions
We have successfully prepared FLG from a novel lignocellulose precursor material empty fruit bunch by zinc chloride (ZnCl₂) activation. We have carried out the systematic studies on the effects of ZnCl₂ impregnation ratio on the surface properties of few layer graphene. We found that surface properties (surface area, pore size distribution, and pore volume) of the FLG derived from EFB can be controlled by ZnCl₂ impregnation ratio. Surface area increase as the increase of ZnCl₂:empty fruit bunch ratio. However, when FLG applied as a supercapacitor electrode, the specific capacitance is still low due to the large cell resistance.

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