Synthesis of Carbon Nano Materials Originated from Waste Cooking Oil Using a Nebulized Spray Pyrolysis

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Abstract. Synthesis of nanocarbon on snake fruit-peel’s activated carbon from waste cooking oil palm was conducted by a nebulized spray pyrolysis process (NSP) by varying the processing temperature from 650 to 750 °C. Ferrocene was used as a catalyst with constant concentration of 0.015 g/ml of carbon source. The structure of nanocarbon was studied by using scanning electron microscope (SEM), x-ray diffraction (XRD), surface area analyzer and Raman spectroscopy. SEM results showed that the structures of carbon products was in the form of carbon nanopsheres (CNS). XRD and Raman analysis confirmed the CNS structure. The carbon products were then tested as electrode’s materials for lithium ion capacitors (LIC) by cyclic voltammetry (CV) instruments. From the CV results the specific capacitance was estimated as 79.57 F/g at a scan rate of 0.1 mV/s and voltage range from 2.5 - 4 V. This study shows that the nano carbons synthesized from the waste cooking oil can be used as prospective electrode materials for LIC.

1. Introduction
Carbon is one of the most abundant elements in the world and it has many forms of allotropes. One type of carbon allotropes is the nano-carbon family. Nano-carbon is a carbon based material possessing a specified structure with nanometer-scaled particle size [1]. The application of nano carbons is very broad in various fields, such as construction, mechanical, electrical, renewable resources, etc. Because of the structure of nanocarbon is strong, high temperature resistance and have a good electrical properties, it has a good potential to applied in the electrochemical field, especially at energy storage such as supercapacitors [3-5]. Supercapacitor or also called ultracapacitor emerged after the innovation in enlarging the surface area and minimize the distance between the plates so the power and the capacity becomes much greater than conventional capacitors. Supercapacitor is expected to replace the battery as a media of electrical energy storage. This is due to the advantages of supercapacitors that power densities is much greater, the charging time is very short and longer life cycles [6].

Nanocarbon can be produced through various methods, such as chemical vapor deposition, laser ablation and many others. Simple method which can be used to synthesize nano-carbons from liquid or gas precursors is the nebulized spray pyrolysis (NSP) method. This method has several advantages compared with other methods, one of which is that it can produce large scale nanocarbon with good homogeneity carbon nanotubes (CNT) quality [7]. NSP technique requires a carbon source which can come from the organic solvent or various kinds of oil. The renewable resorces that can be used for the production of nano carbons is the palm oil. The use of palm oil in Indonesia is very high, up to 5 L/month from every household, producing a waste cooking oil. Hence, it is required to use the
abundant waste cooking as raw materials for functional products such as nano carbons.

In this work, nano-carbons were synthesized by a nebulized spray pyrolysis using waste cooking oil as carbon precursors, salacca peel based activated carbons as substrate and ferrocene as metal catalyst. The specific objectives of this work were to investigate the effects of pyrolysis temperatures on the structural characteristics of produced nano carbons. The utilization of cooking oil as carbon precursors for the production of nano carbons has been explored by some researchers [8-9]. Furthermore, the nano-carbons were then tested as cathode materials in lithium ion capacitors.

2. Experimental

The nebulised spray pyrolysis equipment is shown in Fig 1. One gram of salacca peel based activated carbon, which was used as substrate, was filled in the small quartz tube. Ferrocene with a concentration of 0.015 g/ml was dissolved in the waste cooking oil and then placed in the nebulisation container. The nebulisation container was then loaded in the nebulisation unit (D). The small tube was then loaded in the middle of the outside quartz tube (D). The outside quartz tube was then loaded in the furnace (C) and was connected with hose to water bubbler and with the container (C). The container (D) was also connected with flowmeter (F) which has a function to read the flowrate of nitrogen as carrier gas in the flow of 1.21 sccm. The furnace was then switched on and heated to various temperatures (650, 700 and 750 °C). After the furnace reached the operation temperature, the nebulisation unit was turned on in the frequency of 1.7 MHz for 20 minutes. After the reaction, furnace and nebulisation unit were allowed to cool down to room temperature.

![Fig 1. Process and Instrumentation of Nebulized Spray Pyrolysis, A (Water bubbler), B (quartz cylinder), C (Horizontal Furnace), D (Nebulizer), E (quartz reaction cylinder), F (Flowmeter), G (Nitrogen Gas)](image)

The structural characteristics of carbon products were investigated by scanning electron microscope (FEICompany, Nova 200), Raman spectroscopy (Renishaw, in Via Raman Microscope), BET analyzer and x-ray diffraction (Rigaku, Ultima IV). The surface texture and porosity of the carbon products were examined by N\textsubscript{2} adsorption at 77 K. The specific surface area was calculated from the N\textsubscript{2} adsorption isotherm using the BET equation.

The electrochemical performance of the nano-carbons was evaluated in a two-electrode cell. Electrodes were prepared by mixing 90 wt% active material, 5 wt% carbon black (Mitsubishi), and 5 wt% polyvinylidene-fluoride in N-methyl pyrrolidone to form slurry. The slurry was painted in a 1 cm\textsuperscript{2} area on Cu foil, with typically 2 mg carbon applied to each electrode. A sandwich type cell was constructed from two electrodes, with similar weights, facing each other and separated by glassy fiber paper. The 1 M LiPF\textsubscript{6} electrolyte was added to the cell under vacuum to reduce air contamination and improve wettability of the electrodes. Cyclic voltammetry (CV) was conducted using Maccor automated battery tester (series 4000). CV test was done at scan rate 0.1, 0.5 and 1 mV s\textsuperscript{-1}, with
voltage window 2.5 - 4 V. Cell capacitance from CV test \( [F \cdot g^{-1}] \) was calculated by Eq. 1:

\[
C_{CV} = \frac{\sum |I| \Delta t}{2 \cdot m \Delta V}
\]

where \( \sum |I| \Delta t \) is the area of the current \([A]\) against time \([s]\) curve, \( m \) the mass of active material in the electrode \([g]\), and \( \Delta V \) the voltage window \([V]\).

3. Results and Discussion

Fig 2 shows the SEM images of nano carbons produced at different reaction temperatures. It can be seen that the agglomeration of carbon nanospheres (CNS) occur at each of the temperature variations. The agglomerates with the size of ~200 nm were observed. It seems that the amount of agglomerated CNS increases as the temperature raises from 550 to 750 °C due to the high activity of ferrocene catalyst at higher temperature [10].

Table 1. Textural Properties of Carbon Products

| Sample                                      | Surface Area (m²/g) | Average Pores Size (Å) |
|---------------------------------------------|---------------------|------------------------|
| Salacca Peel Based Activated Carbon (Substrate) | 2500                | 22.65                  |
| Nano Carbons at 650 °C                      | 983.35              | 21.46                  |
| Nano Carbons at 700 °C                      | 1053.385            | 21.67                  |
| Nano Carbons at 750 °C                      | 957.88              | 19.91                  |

Fig 2. SEM images of nano carbons produced by a nebulized spray pyrolysis at reaction temperature of (a) 650, (b) 700 and (c) 750 °C.

Table 1 shows the textural properties of carbon products synthesized at different reaction temperatures compared to the activated carbon substrate. It can be observed that the surface area was reduced after the growth of nano carbons on the surface of activated carbon substrate. However the average pore size remains in the range of 19 to 22 Å.

The XRD profiles of CNSs synthesized with different reaction temperatures are presented in Fig 3. Two distinct peaks normally observed in CNSs, those are (002) peak at ~23° and (100) peak at ~44°, can be clearly seen in all samples. It can be seen that those profiles are very different with the
activated carbon supports. Peak C(002) indicates the graphitic structure formation in the sample. This also shown that the crystallinity of the material from NSP process is much higher than that of the activated carbon substrates.

![XRD profiles of nano carbons produced by a nebulized spray pyrolysis at reaction temperature](image)

**Fig 3.** XRD profiles of nano carbons produced by a nebulized spray pyrolysis at reaction temperature

**Table 2.** $I_D/I_G$ Value of Carbon Products

| Reaction Temperature | Wave Length $I_D$ | Wave Length $I_G$ | $I_D/I_G$ |
|----------------------|------------------|------------------|----------|
| 650 ºC               | 1333.7           | 1593.73          | 0.89901  |
| 700 ºC               | 1341.63          | 1587.19          | 0.88703  |
| 750 ºC               | 1342.87          | 1592.74          | 0.87242  |
| Salacca peel         | 1341.63          | 1586.1           | 0.94494  |
| Activated Carbon     | 2238.79          | 2369.24          |          |

The results of the analysis of the carbon structures using raman spectroscopy are shown in Table 2. It can be seen that the value of $I_D/I_G$ ratio is reduced after the deposition of nano carbons on the surface of activated carbon substrates. It indicated that the NSP can increase the amount of graphitic carbons. The higher process temperatures will reduce the value of $I_D/I_G$ ratio. At higher temperatures, the amount of carbon that binds with a graphitic process will increase along with the growth rate of nanocarbon.

**Fig 4** shows the cyclic voltammetry profiles of nano carbons synthesized at temperature of 750 ºC, measured at various scan rate. Voltammogram profiles shows a shape like a rectangle with a kind of horn/peak formed on cut-voltage above 3.5 V. This phenomenon appears on every scan rate. This indicates that the charge process will slower at the higher voltage value.
Fig 4. Cyclic Voltametry Profiles of Nano Carbons Derived from Waste Cooking Oil

Table 3 Specific capacitance of nano carbon samples

| Cycle / Scan Rate | 0.1 mV/s | 0.5 mV/s | 1 mV/s |
|-------------------|----------|----------|--------|
| 1\textsuperscript{st} Cycle | 79.57 F/g | 65.10 F/g | 56.65 F/g |
| 2\textsuperscript{nd} Cycle | 63.06 F/g | 55.13 F/g | 50.72 F/g |

Table 3 present capacitancy data on every scan rate. It can be seen that the capacitance decreases with the increase in scan rate. This phenomenon occur because the decreasing of the rate of ion diffusion in pores at higher scan rate. Capacitance would be decreased in the second cycle. The capacitance reduction value will be smaller on the greater scan rate. This indicates that the stability of the electrode will be better on the greater scan rate. The capacitance value reached 79.57 F/g in the first cycle on scan rate 0.1 mV/s.

4. Conclusion

In summary, the nano carbon electrodes for lithium ion capacitors were prepared by a nebulized spray pyrolysis using waste cooking oil as carbon precursors by varying reaction temperatures from 650 to 750 °C. The structure of nano carbons were confirmed as carbon nano spheres (CNS) from the SEM observations. Raman and XRD analysis determined that the formation of graphitic carbon structures in samples. The specific capacitance of carbon products was obtained by cyclic voltammetry analysis conducted at various scan rate. The specific capacitance of carbon products was estimated as 79.75 at the first cycle at scan rate of 0.1 mV/s. This study shows the prospect of waste cooking oil based carbon products as electrode materials for electrochemical applications.
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