Carbon Nanotube (CNTs) Production From Waste Cooking Oil As Anode Material For Li-Ion Batteries

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Abstract. Carbon nanotube (CNTs) have received growing interest as anode material on Li-ion batteries due to high electrical conductivity, large surface area and strong structure. In this study, CNTs were synthesized from waste cooking oil (WCO) by chemical decomposition process with various reaction temperatures (800, 900 and 1000 °C) and using ferrocene as catalysts. The characteristics of CNTs were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and gas adsorption analysis. Results show that the trend of pore size decreased, whereas the specific surface area of CNT increased with increasing reaction temperature. The electrochemical performance of CNTs samples as anode material for lithium-ion batteries were investigated at C/4 rate. The results found that the highest specific discharge capacity was CNTs at reaction temperature 900 °C (474.34 mAh/g for first cycle and 213.75 mAh/g for 30 cycles) due to pore size and the specific surface area were suitable for Li-ion storage properties.

Keywords: Carbon nanotube, Li-ion battery, Waste cooking oil, Chemical vapor deposition.

1. Introduction
Since the 20th century, most economic activities need energy from fossil fuel, e.g., coal, crude oil, and natural gas. Earth's fossil fuel resources are limited with continue higher price. Meanwhile, Energy demand increases continuously following economic growth and population growth. Over-consumption of fossil fuels can lead to serious environmental issues such as air pollution, climate change and global warming from release carbon dioxide, nitrogen dioxide, sulfur dioxide, dust, carbon monoxide if incomplete combustion etc. From these problem, alternative energy e.g., solar cell, hydro, wind and nuclear energy, are way of supplementing increasing energy needs and sustainable future. That why trend of technology in each industry is developed to support electrical energy and new electricity consuming gadgets. They were invented and commercialized on a massive scale – starting with light bulbs, radios, refrigerators, motors, fans, washers and dryers, dishwashers, TVs, air conditioning, electronic devices, personal computers, printers and so on – the demand kept rising. However, there is an important problem, the electrical energy cannot generate power all the time, so battery is the key to
solve this problem [1]. One of the greatest challenges to today’s electrical energy is to provide highly efficient and low-cost energy storage for electronic devices. As the performance of energy storage is affected by the properties of the material used to synthesize them. Among diverse energy storage, Lithium Ion Batteries (LIBs) are the most popular. According to there are many advantages such as High- energy density, lower self-discharge, and low maintenance. However, the major disadvantage of LIBs are high cost and low lifecycle. To overcome this problem, it is important to develop new electrode materials with a large surface area, a short diffusion path for ionic transport and high electronic/thermal conductions [2]. Carbon nanotubes (CNTs), One of the most extensively investigated nanomaterials, have displayed great potential to be used in anode material of LIBs owing to their novel structural, electrical and mechanical properties, wherewith simple way to synthesis from carbon sources those like methane, parafilm, kerosene and cooking oil. Hence, in this study, the development of value-added waste cooking oil especially in food industry was studied by converting WCO into CNTs using CVD process in order to use as Anode in Li-ion batteries.

2. Experiment
In this research, there are two main parts of the experiment. The first part describes the synthetic process of CNTs, and the second part is testing the efficacy of synthetic CNTs used as an anode in Li-ion batteries.

2.1. Materials
The CNTs were synthesized from WCO by horizontal CVD system (Fig.1) and using ferrocene (Fe(C5H5)2; purity 98%) as catalysts with different reaction temperatures (800, 900 and 1000 °C).

![Horizontal CVD system](image)

**Figure 1** Horizontal CVD system

The substrate was used WCO (1 g) as a carbon source and ferrocene (1 g) as a catalyst. First, the substrate was placed in a ceramic boat which was situated in a quartz tube reactor with an inner diameter of 40 mm and removed oxygen gas under a nitrogen gas (inert gas) flow rate of 1000 ml/min for 20 min. After that, the flow rate was reduced and fixed at 100ml/min. Then, the system was heated by setting the temperature of the inlet zone at 550°C to change the state of the substrate to vapor and move to the reaction zone with nitrogen gas. In the reaction zone, the substrate was maintained at the studied temperatures (800, 900, and 1000 °C) to ensure complete reaction.
2.2 Material characterization
2.2.1 SEM analysis
HITACHI-SU8010 was employed for SEM observation of the prepared CNTs and porous carbons. Each powder sample was mounted onto a double-side sticky tape over aluminum stubs and coated with gold under vacuum before the study.

2.2.2 XRD analysis
Structural properties of the CNTs were determined by XRD (LYNXEYE-XE-T) and analyzed between 20° and 80° (2θ). The accelerating voltage and the applied current were 40kV and 30mA respectively.

2.2.3 N₂ adsorption isotherm analysis
The N₂ adsorption of the porous carbons was measured at -196 °C on an ASAP 2020N instrument. The sample was degassed at 300 °C for 12h to obtain a residual pressure of less than 1x10⁻⁶ mmHg.

2.3 Electrochemical measurement
All electrodes were prepared through a slurry-coating method. Firstly, the slurry was made by mixing the prepared CNTs and polyvinylidene difluoride (PVDF) with the weight ratio of 90:10 in N-Methyl-2-pyrrolidone (NMP) solvent and coated on copper foil using the doctor blade. Then, dry in a vacuum oven at 100 °C for 12 hr. The coil cells (2032-CR), using 1 M LiPF6 in ethylene carbonate/diethyl carbonate (EC/DEC) (1:1, volume ratio) and Li foil which used as the counter electrodes, were assembled in a glovebox under Ar atmosphere with lower than 0.1 ppm of oxygen and water content.

Electrochemical tests were conducted on BTS electrochemical workstation with current density 25 mAh/g and range of voltage 0.01-3.0 V.

3. Results and Discussion
From the synthesis of CNTs at different reaction temperature (See in Table 1), the WCO behaved as a carbon source because their molecules decompose into a rich concoction of hydrocarbon containing C, H and O molecules. The yield of CNTs increases from 37.16 wt.% (800 °C) to 54.33 wt.% (900 °C) due to enhanced diffusion and reaction rate of carbon. A further increase in the synthesis temperature above 1000 °C oppositely resulted in a decrease in the yield to 47.27 wt.% because at higher temperatures, a significant side effect of disproportionate hydrocarbon decomposition is the deposition of an as produced graphitic shell around the catalyst particles, preventing further reaction from the carbon source needed for growth and thus reducing catalyst lifetime [3].

| Reaction Temperature (°C) | Yield (wt.%) | Surface area (m²/g) | Diameter (~nm) |
|--------------------------|-------------|---------------------|---------------|
|                          |             |                     | Average      | S.D.     |
| 800                      | 37.16       | 146.71              | 60.29        | 15.82    |
| 900                      | 54.33       | 177.53              | 51.60        | 10.13    |
| 1000                     | 47.27       | 182.22              | 36.21        | 16.59    |

The XRD patterns of the synthesized CNTs are shown in Fig.2. All of them have a similar trend and the prominent peak at 2θ = 26.58° and 44.87°. The diffraction peak at 2θ = 26.58° is attributed to the amorphous carbon and graphitic carbon. The broad peaks at 2θ = 44.84° is assigned to iron carbide (Fe3C) which correlated to the morphological in the SEM images of the synthesized CNTs at various reaction temperature (800, 900 and 1000 °C). The result suggests that the product consisted of CNTs and some
amorphous carbon. Besides, as demonstrated in Fig. 3, the increase in reaction temperature resulted in the decrease of diameter of CNTs due to the unstable of Fe3C at higher temperature [2]. At high temperature, the Fe3C will dissociate into the small particles and resulted in the formation of CNTs on the catalyst surface [4].

![Figure 2 XRD patterns of synthetic CNTs](image)

**Figure 2** XRD patterns of synthetic CNTs (a) 800 °C, (b) 900 °C, and (c) 1000°C

![Figure 3 SEM image of CNTs](image)

**Figure 3** SEM image of CNTs at 800, 900 and 1000 oC reaction temperature respectively.

### 3.1 Electrochemical characterization

The condition was set up at 0.01 - 3 voltage, 25 mAh/g, and LiPF6 in EC/DEC. For active material, the synthetic CNTs (800, 900, 1000 °C) were compared to the commercial CNTs. According to the result in Fig 4, all of the samples have the same trend. In 1st cycle, commercial CNTs have the highest capacity (424.94 mAh/g). While CNTs 800, CNTs 900, CNTs 1000 have a capacity of 85.83, 474.34, and 229.80 mAh/g, respectively. The commercial CNTs contain a small amount of amorphous carbon as an impurity. This makes it able to get a lot of electrons. It differs from synthetic CNTs which has a mixture of amorphous carbon, as shown in Figure 4. For the 2nd cycle, the capacity of CNTs is rapidly decreasing from less acceptance of an electron due to some residual electrons within the complex structure of the CNTs [5].
Figure 4 Galvanostatic discharge/charge at 25 mA/g

Figure 5 shows the result after test CNTs for 30 cycles. It was indicated that CNTs has the ability to store electrons due to the CNTs structure compose mainly of carbon which is strong and maintains the structure well [5]. Considering, the capacity of CNTs at 30 cycles, it was found that CNTs 900 exhibit the highest capacity at 213.75 mAh/g due to pore size, and the specific area were suitable for Li-ion storage properties. Furthermore, the suitable proportion of the CNTs and amorphous carbon will solve the problem of the reduced capacity of the residual electrons in the structure [6].

Figure 5 Retention time of various active material
4. Conclusions
The waste cooking oil could be potentially converted to carbon nanotubes (CNTs) via chemical vapor decomposition using ferrocene as catalyst. In this work, the reaction temperature in range of 800-1000 °C were studied. The results revealed that the synthesized CNTs with the diameter in range of 30-80 nm exhibited 37 – 54 wt.% yield. The properties and characteristics of the CNTs changed according to the reaction temperature. So, the excellent performance for using as Anode in battery of the synthesized CNTs 900 is the capacity 213.75 mAh/g at cycle 30.

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References
[1] S.H. Mohr, J. Wang, G. Ellem, J. Ward, D. Giurco, Projection of world fossil fuels by country, Fuel. 141 (2015) 120-135.
[2] S. Goriparti, E. Miele, F.D. Angelis, E.D. Fabrizio, R.P. Zaccaria, C.Capiglia, Review on recent progress of nanostructured anode materials for Li-ion batteries, J. P. Sour. 257 (2014) 421-443.
[3] N. Quang, S. PhamLeighAnn, C. LarkinCarina, B. LisboaChristopher, Effect of growth temperature on the synthesis of carbon nanotube arrays and amorphous carbon for thermal applications, Phys. Stat. solid. 214 (2017).
[4] R. Kumar, R. Rajendiran, H.K. Choudhary, N. Kumar, B. Balaiah, A.V. Anupama, Role of pyrolysis reaction temperature and heating-rate in the growth and morphology of carbon nanostructures, Nano. Stru. Nano. Obj. 12 (2017) 229-238.
[5] M.R. Al Hassan, A. Sen, T. Zaman, M.S. Mostari, Emergence of graphene as a promising anode material for rechargeable batteries: a review, Mat. T. Chem. 11 (2019) 225-243
[6] S.M. Mahocha, Porous carbons, Sadh. 28 (2003) 335-348