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Effect of Electrodeposition Time on the Growth Rate of Carbon Nanotubes (CNT)

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ABSTRACT

Carbon Nanotubes (CNTs) are nano-sized carbon that resembles tubes and has the potential to be used in various aspects of applications. Electrodeposition is the precipitation of substances by using a direct electric current, with CO_2 as the reactant. One of the factors that influences the growth rate of CNTs is the electrodeposition time with variations used of 60, 90, 120, 150 and 180 minutes. The data collection process begins by shaping and measuring the weight of the electrode (Ni) with a diameter of 2 cm CNT deposition area. Measuring the weight and melting Li_2CO_3 at a temperature of 750^{o}C, then the CO_2 flow rate setting, voltage setting 5V and time setting were then characterized by SEM-EDX and XRD. The results of the study showed that the optimal time obtained with a time of 120 minutes, the resulting CNT deposition rate was 1,618 g.cm^{-2}.h^{-1}. Then based on the characterization of XRD and SEM, it shows that the longer the electrodeposition time, the less impurities are contained in the results obtained because the nature of impurities inhibits the deposition rate of CNTs and to increase CNT growth a greater electrodeposition time is needed above 150^0*C.*

Keywords: *Electrodeposition, carbon nanotube, time, growth Rate*

1. Introduction

Solar cells function to convert light (photons) which are converted into electrical energy. Sunlight is a large and unlimited source of energy [1]. *Solar cells* are one of the alternatives in meeting energy needs in Indonesia, but the high production cost of the silicon used and the complicated fabrication process limit its wide use [2], [3]. *Solar cells* use two types of semiconductors, namely type*n* and type *p*. The semiconductor is further researched to get better efficiency, one of the developments is to change semiconductor materials that often use silicon into *carbon nanotubes*.

Carbon nanotubes (CNTs) are nano-sized carbon materials that have the potential in various aspects of application, CNTs are materials that have advantages in electronic, thermal and mechanical properties [4], [5]. Some of the methods used in CNT production include *arc discharge*, the advantages of this method can produce SWCNT and MWCNT, for MWCNT production does not require catalysts, synthesis can be done in open rooms, arc discharge disadvantages require a lot of purification and in SWCNT production often obtain structural defects. There are 3 types of CNT production methods: Arc Discharge, Laser Ablation and Chemical Vapor Deposition (CVD). The Arch Discharge and Laser Ablation methods use graphite as raw material while the CVD method uses fossil hydrocarbons. All three methods can produce more than 70% CNT. CNT production costs using the CVD method are cheaper than the two methods above. In the CVD method, the raw material used is fossil hydrocarbons which are heated to a temperature of 1000^0 C.

The advantage of *laser ablation* is that the results obtained have good quality and high purity [6], while the disadvantage *of the laser ablation* method requires high power because it uses a laser. *The* advantage of this method is that it can be used for large-scale production, the process is simple, the diameter of the SWCNT can be controlled while the disadvantage of this method is that the results are often obtained defective (Saifuddin et al., 2013). Another method used is electrodeposition. This method was chosen because based on previous research revealed, the electrodeposition method has advantages including cheap production costs and easy to do [7]. This method also has other advantages, namely easy preparation, energy saving and cost-effective because the reactant used is CO2. Electrodeposition is the process of settling substances that use direct electric current (DC) so that a redox reaction occurs that will precipitate *carbon nanotubes* [5]. The electrodes used in the electrodeposition are the anode and cathode where inthe cathode there is a reduction where the CNT is deposited and the anode has an oxidation reaction.

Basically, the working principle of the electrodeposition process adheres to the working principle of electrolysis which utilizes redox reactions to precipitate a substance and components used, namely two electrodes, electrolyte and *power supply* to supply electric current to the electrodes in the electrodeposition process. There are several factors that affect the growth rate of *carbon nanotubes* in the electrodeposition process. Thereare several factors that affect the growth rate of *carbon nanotubes*: An increase in temperature will increase the conductivity of the electrolyte, so that the growth rate will increase. becomes faster with an increase in the partial pressure of CO_2 [8]. Koya Otake *et.al.,* (2014) revealed that the higher the *carbon source* fed in *molten salt, the* higher the carbon nanotubes deposited, but the higher the *carbon source* provided by the impurity will be formed. The efficiency of electrodeposition is also influenced by the selection of electrode materials, different electrode materials, the resulting potential is also different, where in the voltage series the moreto the right the position of an element, the stronger the oxidizer properties and the higher the reduction reaction that occurs which makes it easy for the metal to release electrons, this makes the deposit rateincrease [9]. Arcaro, et.al., (2019) revealed a similar thing, namely that the current efficiency increases when the electrode potential is getting negative. The time factor determines the number of CNTs produced, the high or low time used will affect the results of the electrodeposition process as expressed by Fontana (1987) "the higher the time in the experiment, the more deposits are formed, but the higher the time in the experiment, the rate of deposition will decrease", this happens because the thicker the carbon layer which causes the conductivity of the electrode to be low so that the electron transfer from the anode to the cathode annoyed. A similar opinion was expressed An increase in settling time led to a decrease in thesettling rate.

2. Methodology of Research

Electrode preparation: The electrode used in nickel. Then the wire-shaped electrode is cut and wrapped into a circle with a diameter of 2 cm so that CO_2 capture is effective. The electrode functions asa cathode and anode in the electrodeposition, the material used is Nickel (Ni) with a circumference diameter of 2 cm. The Ni used in the study is *pure* nickel and nickel (Ni) wire thickness is 2.5 mm.

Electrolysis: electrolysis is carried out in a furnace where *lithium carbonate* weighs 40 grams and is placed into a *crucible* measuring 50 ml. *The lithium carbonate* that has been put in *the crucible* is put into the *furnace* after which *the furnace* is turned on. *Lithium* is heated for 15 minutes at a temperature of 400^0C, then the *furnace* temperatureis raised to 600^0C and *annealed* for 15 minutes. Afterthe annealing process at 600^0C, the *furnace* temperature is raised again to 800^0C and annealed again for 15 minutes. The goal is to ensure that lithium carbonate melts perfectly. The CNT formed is packed in the cathode, removed from the furnace and washed using HCL with a concentration of 32 % to remove impurities mixed in the CNT, after washing the CNT is dried in the oven for 1 hour with100 meters, then calculate the growth rate of CNT.to get the optimal time, as for calculating the growth rate of CNT using the formula as next:

$$\text{CNT Growth rate} = \frac{\text{Total mass of deposit x wt\% CNT}}{\text{Deposition area x time}}$$

Total mass of deposit: the total carbon powder obtained on the electrodeposition. Wt% carbon : 32 %. Wt% obtained from XRD test results using MAUD software *Deposition Area*: the area where carbon is deposited. *Time*: The time used is 60, 90, 120, 150, and 180 minutes.

Characterization: Characterization of *carbon nanotubes* using SEM-EDX test equipment was carried out to analyze the growth rate of CNTs based on morphology in various variations of electrodeposition times. MAUD software that functions to calculate the growth rate of CNT.

In this study, the electrolyte of *Lithiumcarbonate* (Li_2CO_3) was used. The temperature used is 750ºC where the function is to melt *Lithiumcarbonate*, the temperature is slightly higher than themelting point of *Lithium carbonate* avoiding failure in the electrodeposition process [8] and the ideal reaction temperature is 750ºC [10]. The voltage used is 5V because in the study [11] the use of voltage 5V shows the deposit rate of *carbon nanotubes* tall. Theelectrode used in the electrodeposition is Ni (Nickel) because the potential standard has a negative value which makes Ni easily reduced so that Ni easily releases electrons. *Carbon Source* uses 180 ml/m, this refers to the research of Arcaro et al, (2019) where in the study using CO_2 as large as 0.04%, which is equivalent to 5 ml/m, therefore by using CO_2 of 180 ml/m with a high deposit CNT.

3. Result and Discussion

Electrochemical reduction of CO_2 to CNT through liquid salt electrolysis depends on the separation of the liquid electrolyte Li_2CO_3 into C, which is collected in the cathode [12]. Oxygen is produced at the anode and Li_2O in the electrolyte (reaction (1)). Li_2O then reacts with CO_2 to regenerate the electrolyte Li_2CO_3 (reaction (2)) [10]. Electrolyte. Li_2O regenerates the electrolyte Li_2CO_3 through a chemical reaction with the surrounding CO_2 .

$$Li_2CO_3 \rightarrow C + Li_2O + O_2 \qquad (1)$$

$$CO_2 + Li_2O \rightleftharpoons Li_2CO_3 \qquad (2)$$

Net with reaction 1

$$CO_2 \rightarrow C + O_2 \qquad (3)$$

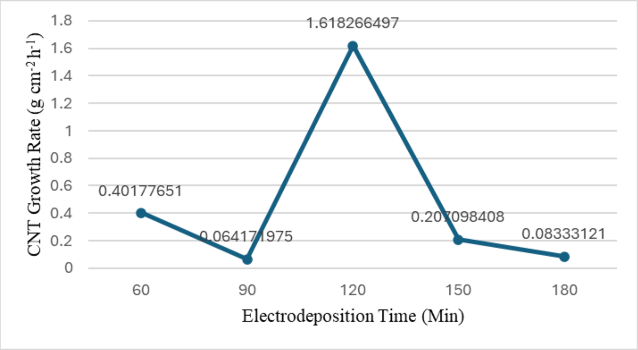

Figure 1. Results of CNT Growth Rate with different time

Figure 1 shows that the higher the time used in the electrodeposition process, the growth rate of *carbon nanotubes* decreases. This is because the higher the time used in the electrodeposition process, the lower the position of the ion distribution that willsettle decreases because the higher *the carbon nanotubes* that precipitate. Graph 4.1 shows the growth rate of *carbon nanotubes*, seen in the first experiment with an electrodeposition time of 60 minutes, the deposition rate *of carbon nanotubes* was 0.401 $g.cm^{-2}.h^{-1}$, then in the second experiment with an electrodeposition time of 90 decreased, the result obtained was 0.064 $g.cm^{-2}.h^{-1}$, this occurs when the electrodeposition process takes place, the current that flows is unstable or goes up and down, which causes the carbon ions that will settle to be disturbed so that the growth rate of CNT decreases. seen in Graph 4.1 shows the CNT obtained where the higher the time used the electrodeposition process isineffective where there is a maximum limit of the growth rate of *carbon nanotubes* increases, this limit occurs in the third experiment with an electrodeposition time of 120 minutes with a result of 1,618 $g.cm^{-2}.h^{-1}$, where the electrodeposition process with a time of 120 minutes is the optimal time. The fourth experiment with an electrodeposition time of 150 minutes the growthrate *of carbon nanotubes* decreased by 0.207 $g.cm^{-2}.h^{-1}$, in the last experiment with a time of 180 minutes also decreased, the result obtained was 0.083 $g.cm^{-2}.h^{-1}$. The decrease in deposit rate is caused by the thickening of *the deposited carbon nanotubes*, which inhibits the movement of ions that will settle on the cathode. The results obtained experimentally show that the tendency is greater the time used in theelectrodeposition process, the growth rate of *carbonnanotubes* decreases but the number of *carbon nanotubes* This is according to Faraday's law that theamount of precipitate that forms is proportional to the amount of time given, the longer the time is used, the thickness of *carbon nanotubes* deposited increases, but the deposit rate will decrease with the length of time used [13]. Research [14] revealed that the decrease in the rate of deposition is due to the conductance of the electrolyte starting to decrease and it determines the amount of the amount and movement ions in the electrolyte, where the thicker the conductivity layer, the smaller the deposit rate decreases. This is also revealed [15] where the deposit rate will decrease because the cathode efficiency is decreasing, the decrease in cathode efficiency is caused by the emergence of hydrogen gas bubbles (H_2) which inhibit the movement ofions that will settle on the cathode due to the polarization of the cathode. A decrease in the number of ions deposited in the cathode results in a decrease in the deposit rate.

Based on the results of the SEM test in Figure 2, it shows that at all variations in electrodeposition time, CNTs are produced. The morphology of CNTs is shown by the shape of an elongated tube in Figure 2 (a-e) It can be seen that the higher the electrodeposition process time, the more CNTs are formed and less impurities are formed. This is also supported by research [10] which reveals that a longerelectrodeposition time will result in CNTs of higher quality and quantity and do not require additional maintenance required.

X-Ray Difraction (XRD) test results to identify phases. CNTs with fewer impurities areindicated by a wider peak. CNTs with high peaks indicate the thickness of the CNT wall where higherthe peak indicates a thicker CNT wall. This is due to constructive interference on *Bragg*'s law that will behigher on thicker CNT walls [16]

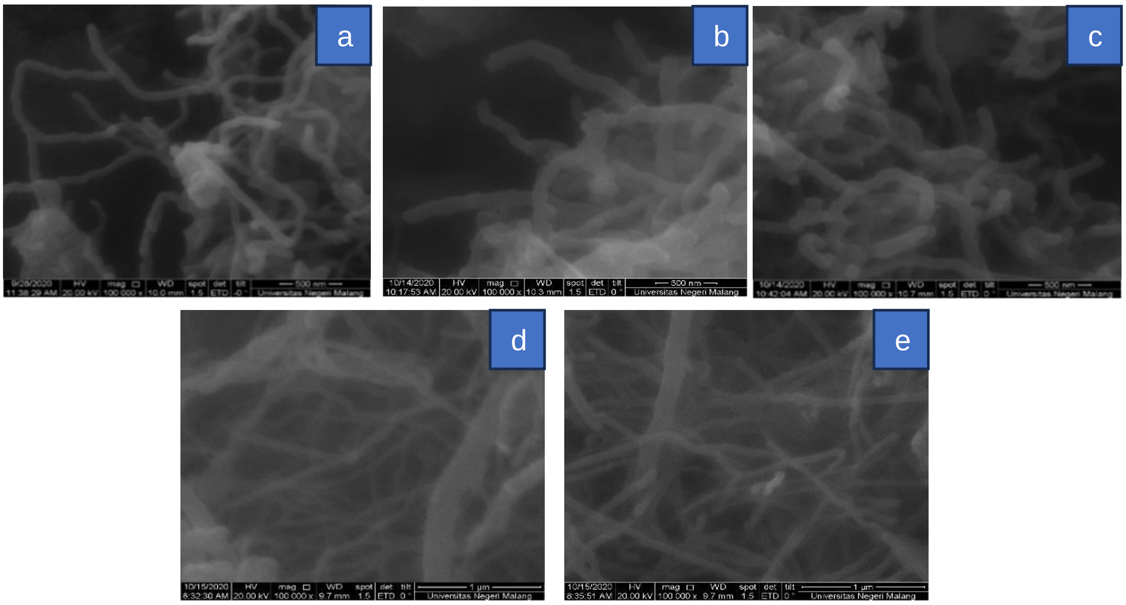

Figure 2. SEM images for CNT with time (a) 60 min (b)90 min (c) 120min (d) 150min (e) 180 min

The phases found in this study are *carbon nanotubes* and *lithium carbonate*. The crystalline phase in this study has not changed, indicated by the phase found to still be included in carbon. Based on the XRD results in figure 4.8, the presence of *carbonnanotubes* is shown at $2\Theta=26^{o}$. This is inaccordance with research [14] that *the peak* region shows peak *carbon nanotubes*. In another literature, namely in the study [17], his research also revealed asimilar thing where the position *of the CNT peaks* onthe difractogram graph is located at an angle of $2\Theta= 26^{o}$. While the *peak* of Li_2CO_3 is at $2\Theta =31.72^{o}$. the difractogram graph of the peak of Li_2CO_3 decreases with the increase of electrodeposition time, this is due to Li_2CO_3 evaporating or burning at longer electrodepositions

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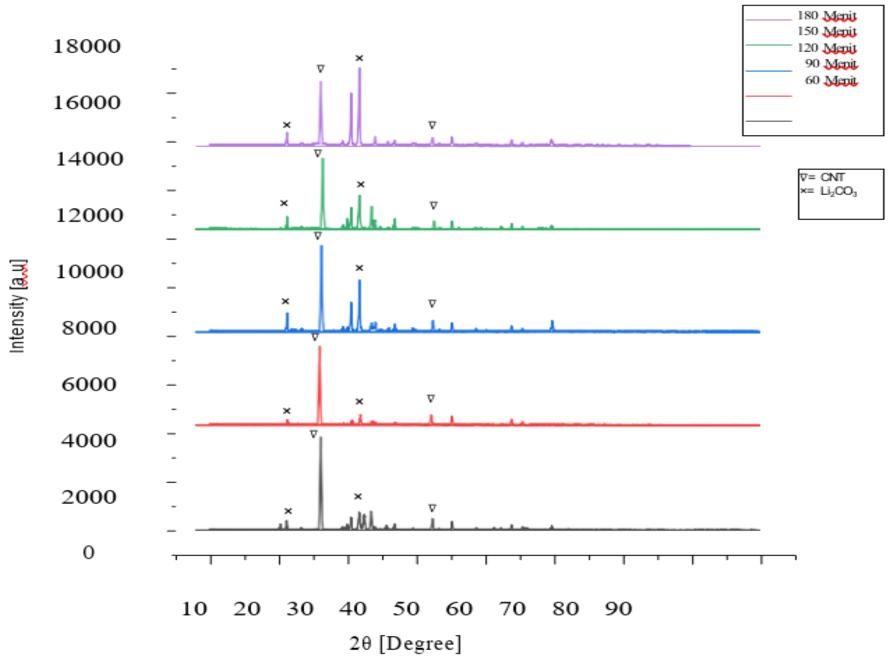

Figure 3. XRD Results

4. Conclusion

In this study, carbon nanotubes (CNTs) were successfully synthesized using the electrodeposition method with specific parameters: a voltage of 5V, a temperature of 750°C, a carbon source flow rate of 180 ml/min, and nickel electrodesCNT production with parameters voltage 5V, temperature 750^{o}C *carbon source* 180 ml/m, nickel electrode.

1. The increase in electrodeposition time, the growth rate of CNT will decrease effected of the conductance of the electrolyte begins to decrease and it determines the amount and movement of ions in the electrolyte
2. The thicker the conductivity layer the smaller it is, which makes the deposit rate decrease. The optimal time obtained in this study was 0.753 $g.cm^{-2}.h^{-1.}$ The growth rate value is the average time and the impact of impurities will influence CNT growth. CNT morphology
3. The characterization with SEM-EDX show that carbon nanotubes that formed is shown by the elongated tubular image.
4. The longer time of electrodeposition it will less impurity is formed.
5. The characterization with XRD showed that the peaks of CNT were at 2Ө = 26^{o} and from thecharacterization with XRD obtained quantitative data processed with MAUD software, the highest CNT was obtained with an electrodeposition time of 120 minutes where the results obtained were 8.9%.

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