Biocellulose (BC) Impregnated with Carbon Nanotubes (CNTs) for Zinc Air Fuel Cell application

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Abstract. Bacterial cellulose (BC) and bacterial cellulose impregnated with carbon nanotubes (BC/CNTs Bio-composite) was synthesized in this project. An investigation on the characteristic of BC and BC/CNTs bio-composite and its performance as electrochemical separator in zinc air fuel cell was done. BC/CNTs bio-composite was synthesized using new CNTs impregnation method, namely spraying method. Bacterium, Acetobacter xylinum was used for fermentation. Three manipulating parameters were used. First, BC-CNTs bio-composite was synthesized in 5 days, 7 days and 10 days of fermentation. Then, amount of CNTs impregnated into BC/CNTs bio-composite was varied. 0.02% CNTs, 0.05% CNTs and 0.08% CNTs were used. Third, two types of CNTs were used, namely CNTs synthesized via floating catalyst chemical vapour deposition (FC-CVD) and CNTs synthesized via fixed bed chemical vapour deposition (FB-CVD). From the results, BC-CNTs bio-composite shows better conductivities (42.7 S/m at 2.00E+10 Hz), and higher thermal stability. BC/CNTs bio-composite impregnated with CNTs FB-CVD and CNTs FC-CVD did not shows any significant different in their electrical conductivities and thermal stability in analytical test. BC and BC/CNTs bio-composite were used as electrochemical separator in zinc air fuel cell. About six cells were able to move a toy car that required 1.5V. The shelf life of cell was estimated to be 12 minutes 24 second. In conclusion, BC and BC/CNTs bio-composite are conductive materials. BC/CNTs bio-composite can be alternative used as electrochemical separator in zinc air fuel cell.

Keywords: *Acetobacter xylinum*, Fermentation, Biocomposite, Carbon Nanotube (CNTs), Zinc Air Fuel Cell

1.0 INTRODUCTION

High awareness on the environmental issues have become a forcing factor to implement a new sustainable energies which can replace fossil fuels and nuclear energy. Various alternative energies such as hydropower, solar, geothermal, winds already being practiced and some are in the phase of commercialization [3] Latest, the introduction of fuel cell as one of feasible power generating system which is known to efficiently converts fuels to electricity with production of environmental friendly byproducts has received much attention among researchers. Fuel cells are electrochemical devices which can directly convert chemical energy into electrical energy by means of chemical reaction. Differ from battery, fuel cell is an energy converting device while battery is an energy storage device although the stack arrangement between both are quite similar. A structure of a fuel cell consists of an electrolyte layer sandwiched between a metal anode (negative) and an oxygen cathode (positive). The energy production from the fuel cells will be continuously produced as long as the main element to operate the cell is there which is hydrogen. Among all fuel cells, metal-air fuel cells also known as air-depolarized batteries can be the most suitable environmentally alternative energy generator [3,5].

Various metals in the periodic table such as Ca, Li, Al, Mg, Fe and Zn are applicable for metal-air fuel cells. In terms of energy per unit mass and energy density, Al has the advantages over the other metals. However, the corrosion rate of Al is faster in alkaline electrolyte compared to Zn where the corrosion rate is much more slower whether in aqueous or alkaline electrolyte. Besides, Zn is highly electro-positive with a relatively abundant at low cost making it the most feasible metal anode in a metal air fuel cell [5]. The stack arrangement of zinc air fuel cell consists of cathode and anode separated by an electrochemical separator. The function of the separator is to provide a free ionic transportation medium and at the same time preventing physical contact between the positive and negative electrolytes. An electrochemical separator needs to be ionically conductive but electrically non-conductive. Nafion, a sulfonated perfluoropolymer has been widely used as ion exchange membrane separator due to its high ion exchange capability and chemical stability. However, Nafions are expensive compared to other hydrocarbon separator [3]. In this research, bacterial cellulose or biocellulose (BC) impregnated with carbon nanotubes are used as an electrochemical separator in zinc air fuel cell.

BC is a natural and low cost biopolymer synthesized from gram negative bacteria called Acetobacter xylinum. It demonstrates unique properties including high crystallinity, high water holding capacity and high porosity [7]. BC exists as a basic structure of fibril that consists of β-1$\rightarrow$4 glucan chain with molecular formula (C6H10O5)n where the glucan chains are held together by inter and intra hydrogen bonding [2]. The presence of hydroxyl group on its backbone caused the BC to exhibits hydrophilic properties which is crucial for the operation of polymer electrolyte membrane fuel cell. The objective of this research is to evaluate and compare the performances of different BC/CNTs biocomposite in zinc air fuel cell system.

2.0 MATERIALS AND METHOD

2.0.1 Extraction of Dates using Water Extraction

50 g of dates without seed were added into 500ml conical flask which contains 500ml of distilled water. The ratio of dates and distilled water was 1:10 (w/v). The mixture was then sonicated in an ultrasonic water bath for 30 minutes. After sonication, the solution was stirred for 15 minutes using magnetic stirrer to complete the extraction procedures. Next, the solution was filtered to remove the debris

2.0.2 Preparation of Hestrin-Schramm Culture Medium using Dates Extract

Hestrin-Schramm (HS) culture medium was prepared by adding 0.5g peptone, 0.27g disodium hydrogen phosphate (Na_2HPO_4), 0.115g citric acid, 0.5g yeast extract and 34ml dates extract into 66ml distilled water to make up approximately 100ml of HS medium. Glucose content was replaced with dates extract in the amount of 34 ml for 100 ml culture medium. The pH was adjusted to 6.0 by adding acetic acid or sodium hydroxide (NaOH).

2.0.3 Preparation of Inoculums

The *A. xylinum* strain provided by MARDI was cultured in HS medium. Culture medium with bacteria was incubated at 30°C for 3 days (optimum growth incubation period). After 3 days of fermentation, a gelatinous layer was formed at air liquid interface. The flask was shaken vigorously to release the cells into the medium remain. Then, the remaining medium was used as inoculums. For every preparation of new inoculums, the volume of previous inoculums added into culture medium was 10% of the total volume of the culture medium.

2.0.4 Preparations of Carbon Nanotubes (CNTs) Medium

10ml HS medium was mixed with 0.02 w/v% (0.02g) of CNTs and sonicated using ultrasonic water bath for 30 minutes and sterilized. Two types of Carbon Nanotubes (CNTs) were used; CNTs synthesized via fluidized-bed chemical vapour deposition (FB-CVD) and CNTs synthesized via floating-catalyst chemical vapour deposition (FC-CVD).

2.0.5 Impregnation of CNTs Culture Medium onto BC Surface

10 ml of CNTs culture medium was sprayed onto BC surface for 15 to 20 times. Frequencies of the spraying depend on the distribution of CNTs culture medium onto BC surface and it was ensured that the BC surface was fully covered with CNTs.

2.0.6 Harvesting Method for BC and BC/CNTs Bio-composite

BC and BC-CNTs bio-composite was filtered out from culture medium remaining and rinsed with distilled water. It was then boiled in 0.5M NaOH for 20 minutes to remove live bacteria on the surface of BC and BC/CNT biocomposite. The BC and BC/CNT biocomposite were soaked overnight in distilled water before used [4].

2.1 ANALYTICAL METHOD FOR BC AND BC/CNTs BIOCOMPOSITE

2.1.1 Dielectric Properties

Dielectric test was conducted using dielectric analyzer. Dielectric analyzer was used to measure dielectric properties and ion conductivity which calculated from the dielectric loss factor. Dielectric properties of BC oand BC/CNTs biocomposite were tested in wet form and initial frequency used was 200 Mega Hz. The range of frequencies is between 200 Mega Hz to 20100 Mega Hz.

2.1.2 Morphology and Microstructure

SEM was used to identify morphology and microstructure of BC and BC/CNTs bio-composite. BC and BC/CNTs bio-composite were then coated with gold before scanning. The magnification in SEM was controlled and the images were capture at 5k, 10k and 20k.

2.1.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was carried out for BC and BC/CNTs bio-composite to analyze their thermal stability and degradation profiles. The analysis was done on a dried sample with an operating temperature from 25°C to 900°C at 10°C/minute in Nitrogen atmosphere with a purge rate of 20mL/min.

2.2 BC AND BC/CNTs BIO-COMPOSITE FOR ZINC AIR FUEL CELL APPLICATION

2.2.1 Preparation of BC and BC/CNTs Bio-composite for Performance Test

BC and BC/CNTs bio-composite were soaked in 1.0M sodium hydroxide for 24 hour. BC and BC/CNTs bio-composite was filtered out from sodium hydroxide and the weight of BC or BC/CNTs bio-composite was measured.

2.2.2 Performance Test for BC or BC-CNTs Bio-composite

BC and BC/CNTs bio-composite was sandwiched between Zinc plate and an activated carbon, covered with nickel plate at the end of the stack arrangement. Design of zinc air fuel cell was shows in **Figure 1**. The voltage, current and resistance of zinc air fuel cell were measured using multi-meter in every 15 minutes for 3 hours before applied to a toy car which requires 1.5V.

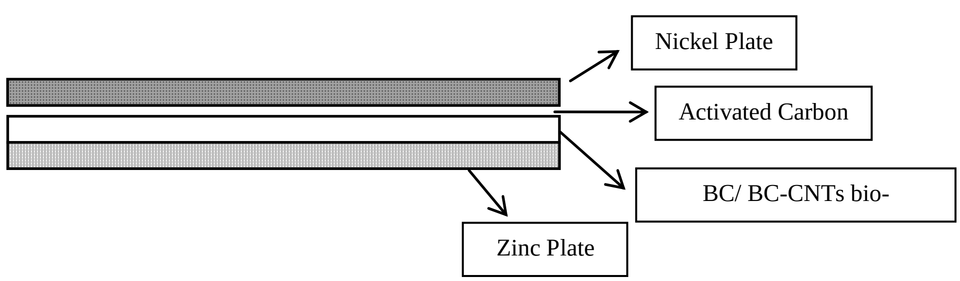

FIGURE 1: Design of Zinc Air Fuel Cell

3.0 RESULTS AND DISCUSSION

3.1 Physical Characteristic of BCs and BC/CNTs Bio-composites

Physical characteristic of BC and BC/CNTs bio-composite were measured. The results are shown in **Table 1**. Fom the result, the weight and thickness of BCs and BC/CNTs bio-composites increased paralleled with days of fermentation. This is due to the ability of the bacteria in the culture medium to form a new layer of fiber as the fermentation days increased.

TABLE 1. Diameter, Thickness and Weight of BC and BC-CNTs Biocomposite

Samples	Weight, g	Thickness, mm	Diameter, mm
BC5-CNTs2FB-CVD	10.597	2.680	71.600
BC5-CNTs5FB-CVD	12.013	2.730	72.480
BC5-CNTs8FB-CVD	9.340	2.900	71.130
BC7-CNTs2 FB-CVD	18.334	4.590	73.300
BC7-CNTs5 FB-CVD	21.239	5.210	72.430
BC7-CNTs8 FB-CVD	20.384	4.770	72.380
BC10-CNTs2 FB-CVD	31.055	7.510	71.380
BC10-CNTs5 FB-CVD	29.065	7.110	70.760
BC10-CNTs8 FB-CVD	29.484	7.210	71.120
BC7-CNTs2 FC-CVD	18.387	3.800	72.750
BC7-CNTs5 FC-CVD	18.904	4.250	71.190
BC5	12.954	3.070	71.630
BC7	20.054	4.640	72.290
BC10	8.650	2.310	72.480

3.2 Dielectric Properties Analysis for BCs and BC/CNTs Bio-composites

Figure 2 shows graph of conductivity vs frequencies which used to illustrate the electrical properties of BC and BC/CNTs biocomposite. Dielectric loosed and dielectric constant is measured. CNTs act as a conductor in bacterial cellulose since it has high electrical conductivity and suitable as electron field emitters [6]. The impregnation of CNTs enhances the conductivity of bio-composite. The comparison can be made with pure BC where it has low conductivity.

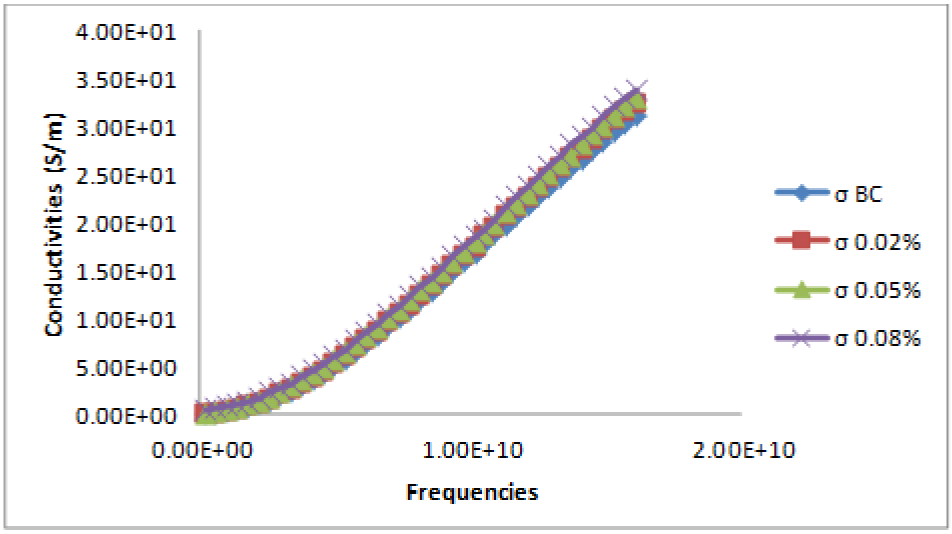

FIGURE 2: Conductivities of BC5, BC5-CNTs2 FB-CVD, BC5-CNTs5 FB-CVD, BC5-CNTs8 FB-CVD at Different Frequencies

3.3 Dielectric Properties Analysis for BC/CNTs Bio-composites for Different CNTs Synthesis Techniques

Two types of CNTs were used to synthesis 0.05% BC/CNTs bio-composite. CNTs used are synthesis via fluidized-bed chemical vapor deposition (FB-CVD) technique and floating-catalyst chemical vapor deposition (FC-CVD) technique. From **Figure 3**, it shows there is no significant difference in conductivity values for different type of CNTs. This means that synthesized method for CNTs is less dominant compared to the effect of different weight percent of CNTs impregnated in BC.

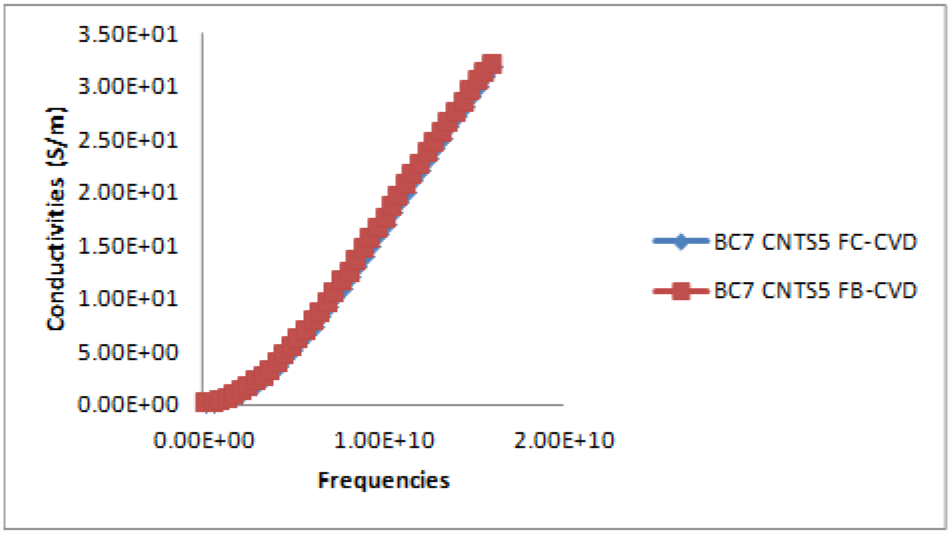

FIGURE 3: Conductivities of BC7-CNTs5 using CNTs synthesized via FB-CVD and BC7-CNTs5 CNTs synthesized via FC-CVD

3.4 Morphology and Microstructure of BC and BC-CNTs Bio-Composites

Figure 4 shows morphology of BC and BC-CNTs bio-composite produced from static culture with CNTs sprayed method. In **Figure 4 (a), (b)** and **(c)**, the microstructure of BC/CNTs bio-composite has a complex line formation. An extra line network is formed on the BC/CNTs bio-composite. The thick line on the figures indicate CNTs were successfully impregnated. From the morphology of BC-CNTs bio-composite, it can be concluded CNTs can well impregnated on the BC surface using spray method. **Figure 4 (d)** shows the microstructure of pure BC. Microstructure of BC is hardly to analyze since there is sodium hydroxide remained on the BC surface where it should be removed during the harvesting process.

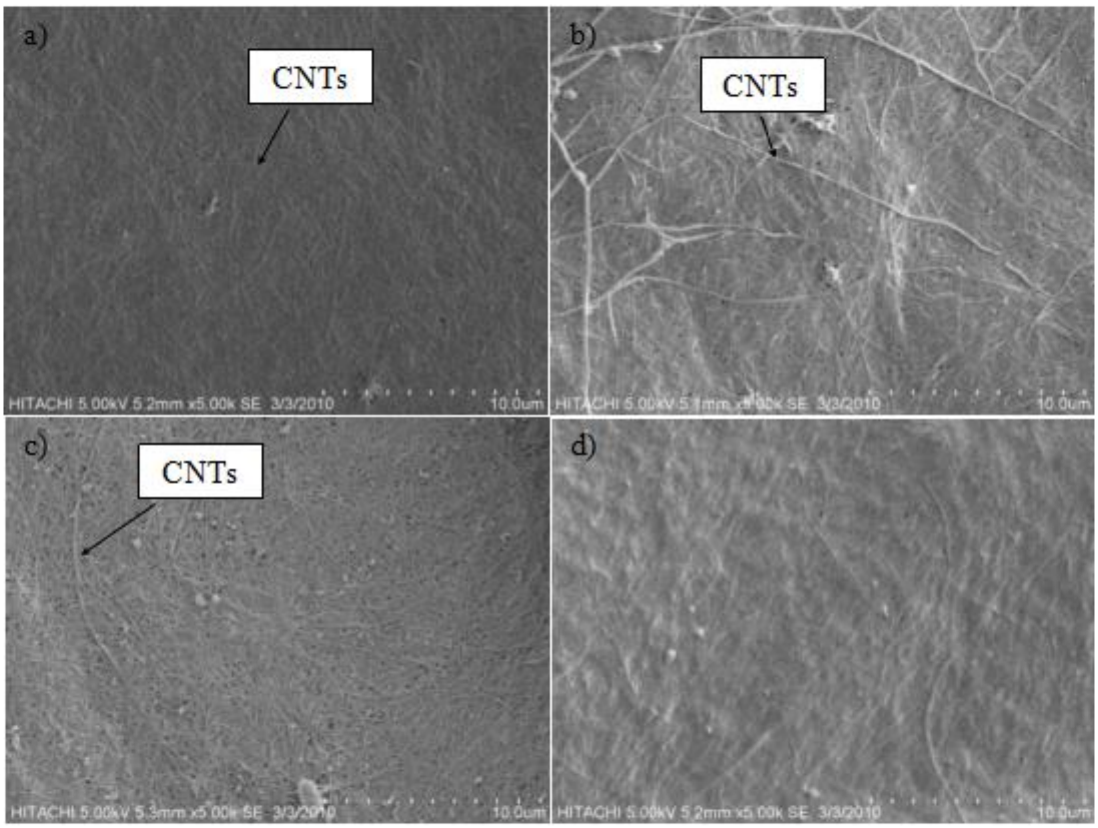

FIGURE 4:: Morphology of (a) BC7/CNTs2, (b) BC7/CNTs5, (c) BC7/CNTs8, and (d) BC7

3.5 TGA for BC and BC/CNTs Bio-Composites

In this section, three results are compared; namely BC7/CNTs5 FB-CVD, BC7/CNTs FC-CVD and BC7. From the TGA result, maximum temperature degradation (T_d), temperature degradation and percentage weight loss in several stages of the material tested can be identified. **Figure 5, Figure 6** and **Figure 7** show TGA results for BC7, BC7/CNTs5 FB-CVD and BC7/CNTs5 FC-CVD respectively.

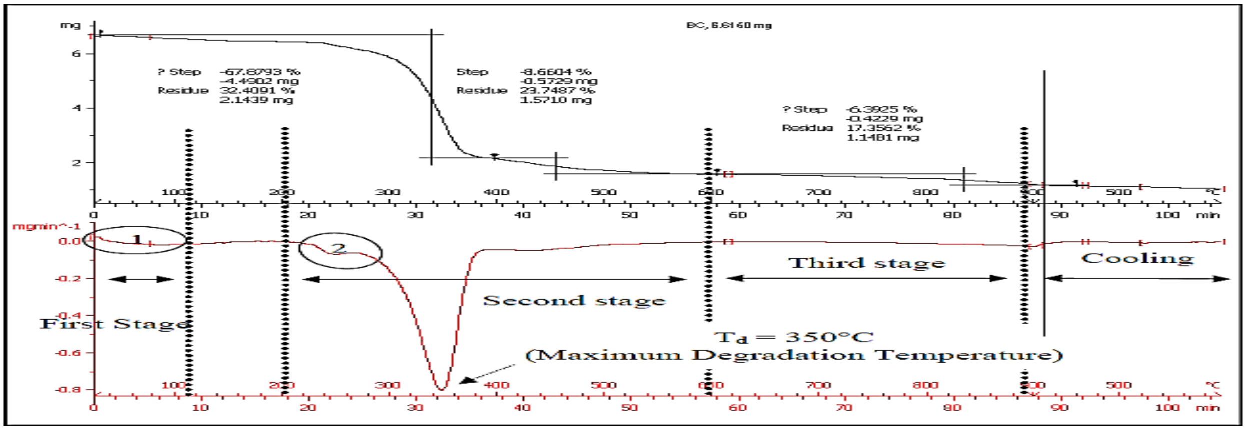

FIGURE 5: Sample TGA result for BC7

Figure 5 shows a thermal profile of pure BC which ranges from 25°C to 900°C. There are three stages for BC and BC/CNTs biocomposite. First stage represents the weight loss of liquid content in the material. The peak temperature for first stage is 70°C shows the vaporization of liquid content in the BC resulted in weight loss of the sample. Second stage in TGA graph indicates cellulose degradation. The degradation started from 200°C and end at 600°C. In between degradation temperature, there are two peaks appeared during BC degradation. The first peak is associated with thermal degradation of proteinaceous matter present in BC [1], whilst the second peak is associated with the degradation of cellulose ring and cellulose bond [1] Maximum degradation temperature is occur at 350°C for BC.

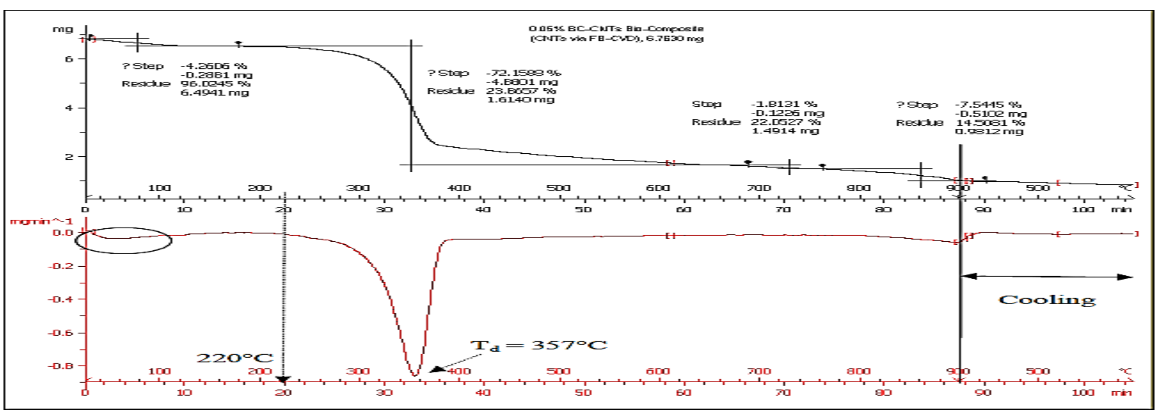

FIGURE 6: Sample TGA result for BC7/CNTs5 FB-CVD

Similar trend of thermal profile is observed for BC7CNTs5-FB-CVD from **Figure 6**. First stage indicated weight loss of water content adsorbed in BC-CNTs Bio-composite. Temperature range in first stage is 25°C to 100°C and percentage weight loss is 4.3%. Thermal degradation for second stage has one peak only and degradation is started at 220°C while maximum temperature degradation is 357°C. Impregnation of 0.05% CNTs resulting increased in maximum temperature degradation and initial degradation temperature of cellulose. The peak observed in second stage can be explained by CNTs impregnated in BC/CNTs bio-composite mixed together with proteinaceous matter present at outer cellulose ring resulting in thermal stability of cellulose. Thus degradation of cellulose ring, bond and proteinaceous matter started simultaneous. Percentage weight loss of BC7/CNTs5 FB-CVD in second stage is 72.2%.

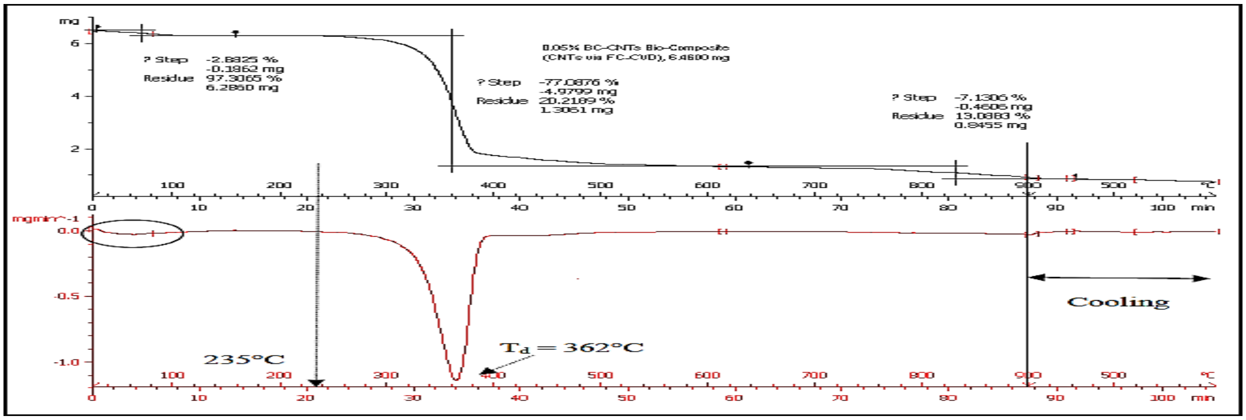

FIGURE 7: Sample TGA result for BC7/CNTs5 FC-CVD

Figure 7 illustrates thermal profile of BC7/CNTs5 FC-CVD. In this section, comparison between two types of CNTs (CNTs synthesized via FC-CVD technique and CNTs synthesized via FB-CVD technique) is done to investigate the effect of different method of CNTs synthesis towards thermal profile of bacterial cellulose. Therefore, **Figure 7** is compared with **Figure 6**. From the findings, the similarities between two figures are both have two stages, weight loss of water appear in first stage and degradation (one peak only) of cellulose in second stage. The percentage of weight loss in first stage is 2.9% while the weight loss in second stage is 77.1%. Maximum degradation temperature and initial degradation temperature for second stage in BC7/CNTs5 FC-CVD is slightly higher than the value in BC7/CNTs5 FB-CVD, which is 235°C and 362°C respectively. Degradation of cellulose in BC7/CNTs5 FC-CVD has increased by 1.4% (which can be considered significant small). Therefore, types of CNTs used do not have any different in their thermal profile.

3.6 Application of Fuel Cell in a Toy Car

Combinations of different number of fuel cells arranged in series were experimented. Different electrochemical separator was used and tested as shown in **Table 2** while the results of different number of cell stacks used is shown in **Table 3**. When installed and tested in the car, the six cells arrangement provided the highest power and thus moved the car. The power supply was sustained up to 12 minutes and 24 second; the toy car was moved by a 7.20V and 15.1A supply. The actual voltage for a toy car to move is 1.5V. Large voltage and current in zinc air fuel cell was needed because electrical resistance also increased as more fuel is used

After oxidation reaction for zinc air fuel cell, it is found that white layer of zinc oxide was formed on the electrochemical separator and also on zinc plate as byproduct in the reaction. Corrosion of zinc plate and formation of zinc oxide is a common problem in zinc air fuel cell. Performance of zinc air fuel cell will degrade as time goes. Zinc oxide layers that formed between the interfaces will affect the flow of electron in electrolytes. Thus, this will directly reduce the voltage and increase electrical resistance value.

TABLE 2. Electrochemical Separator used in Single Fuel Cell

No	Sample
1	BC7-CNTs2 FB-CVD
2	BC7-CNTs5 FB-CVD
3	BC7-CNTs8 FB-CVD
4	BC7
5	BC5-CNTs5 FB-CVD
6	BC10-CNTs5 FB-CVD

TABLE 3. Voltage and Current of Cell Stack in Series Arrangement

Cell Stack	Voltage, V	Current, I
1+2	3.23	6.3
1+2+3	3.63	7.3
1+2+3+4	5.05	10.4
1+2+3+4+5	6.00	12.4
1+2+3+4+5+6	7.20	15.1

4.0 CONCLUSION

Based on the results obtained in this experiment, it can be concluded that BC and BC/CNTs biocomposite can be used as electrochemical separator in zinc air fuel cell. From the analytical test, BC/CNTs biocomposite shows higher conductivity (42.7 S/m at 2.00E+10 Hz) and higher thermal stability compared to BC. BC/CNTs biocomposite which impregnated with CNTs synthesized via FC-CVD has lower electrical resistance in performance test compared to CNTs synthesized via FB-CVD. From the findings, BC-CNTs biocomposite synthesis in 5 days fermentation and impregnated with 0.08% shows a good conductivity with low electrical resistance and high voltage since it has compact CNTs structure thin layer of BC compared to BC synthesis from longer fermentation day. Although spraying method (manually sprayed) was proven to be successful in impregnating CNTs on BC surface, it should be noted that the intensity of spraying is important to ensure the CNTs is uniformly distributed on BC surface. Thus, instead of manually sprayed the CNTs, automatic spraying or spin coater can be used. Besides, self-cleaning for the BC/CNTs biocomposite used as an electrochemical separator can be develop to increase the efficiency of the fuel cell.

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