Study of Ramie Fiber (*Boehmeria nivea L.*) into Electric Double Layer Capacitor Material by Using Ammonia (NH_3) Gas in Pyrolysis Process

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***Abstract*—A novel green electric double-layer capacitor (EDLC) has been successfully made from carbonized ramie fiber using a single step method with ammonia gas (NH_3). Ramie (*Boehmeria nivea L.*) is fiber crops which has excellent fiber characteristics and high cellulose content that abundantly planted in the world including Indonesia, China, India, Japan, and South America. The use of chemical batteries cause thermal runaway and danger disposal, EDLC is the alternative. In this research, first ramie fiber was degummed to obtain pure cellulose. Pyrolysis of celluloses was conducted at temperature of 800°C for 2 hours under the nitrogen or nitrogen followed by ammonia gases. The surface area was determined using the Brunauer Emmett Teller (BET). The electrodes were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrodes were arranged into EDLC sheets with addition of Na_2SO_4. The electrochemical properties were determined with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The result shown that the surface area of carbon using N_2in its pyrolysis process is 119m²/g, while that of $NH_3$is 144m²/g. The obtained capacitance of the material is 0.27mF/g and exhibited a high stability in cyclic test (charge-discharge).**

***Index Terms*—ammonia, carbon, capacitor, electrode, etchant, ramie**

I. Introduction

Ramie (*Boehmeria nivea Gaud.*) is one of the oldest bast fiber of plant origin ruled the textile world as king of natural fibers [1] , which is cultivated on 146.6 thousand hectares of land in almost all region in China, most of countries in Asia and Americas especially in South America [2]. Indonesia is one of countries that have the historical story of ramie plant. Pujon 10 clone is one of the best varieties of ramie plant in the world that planted in Malang city, Indonesia [3]. It is not surprisingly if Indonesia has high production of ramie fiber. Therefore, the world production of ramie fiber reached 193.8 thousand tons in 2010 [2]. Besides, ramie is one of the strongest, lustrous, excellent microbial resistances, softer and finer among bas fibers which possess valuable hygienic properties to a large extent, generally not found in other textile fibers [4]. Ramie contains 68-91% of cellulose, 5-17% of hemicelluloses and only 0.6-0.7% of lignin [5]-[7]. Those contents are potential to be processed as carbon EDLC material.

Yet, the use of energy storage technologies today brings environment in danger because of its excessive use of chemical substances [8]. Moreover, increasing ecological consciousness has accelerated interest in ramie originating from plants that can be recycled, more environmentally friendly, potentially abundant, less costly and green composites [9]. The great increasing of battery temperature until reach the melting point of lithium is called by thermal runaway. Battery cell will explode if ventilation system does not conduct well [10]. The excessive use of chemical substance inside the battery can put the environment in danger. It causes land and water pollution in the earth. Therefore, developing EDLC (electric double layer capacitor) through ramie fiber is potentially used as green energy storage device.

In the pyrolysis process to obtain carbon fibers, N_2 gases are commonly used [11] Nitrogen is a stable and nonreactive gas which causes the material having degradation stage without oxidation [12]. This process results carbon with C-C bonding that can be used for electrode material. Several ways are conducted by using chemical substances to produce carbon with better characteristics in terms of higher porosity and surface area [8]. However, the use of chemical substance to increase the carbon characteristic is time consuming, costly and hazardous for the environment. The use of NH_3 in pyrolysis process is a breakthrough to answer those problems. NH_3 contains nitrogen and hydrogen atoms which are abundant in the earth [13]. Its characteristics can be utilized to improve the features of carbon. As a result, processing ramie fiber into EDLC

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material by using NH_3 gas pyrolysis is promising to produce green energy storage technology.

II. EXPERIMENTAL

A. Degumming Ramie

Before Ramie plant was processed by degumming method, firstly ramie's stem must be decorticated using decorticating machine to obtain its fiber. Degumming process aims to obtain the cellulose and hemicelluloses of ramie fiber. In the other hand, lignin and gum that contained in ramie fiber will reduced. Lignin and gum will produce sticky brown liquid during pyrolysis process and affect the furnace tube. Decorticated ramie fiber was soaked in 5% NaOH solution then heated using hot plate at temperature 90-95^{o}C during 2-3 hours. After that, degummed ramie fiber was rinsed with water then dried in oven during 24 hours.

B. Cellulose Characterization

Obtained degummed ramie fiber was characterized using FTIR (Fourier Transform Infrared Spectroscopy) to analyze organic carbon functional group and XRD (X-Ray Diffraction) to analyze material structure.

C. Pyrolysis

Pyrolysis process is a process to carbonize the celluloses of ramie fiber using furnace. Conventional way to carbonized cellulose is using inert gas such as nitrogen (N_2) and Argon (Ar). Yet, ammonia gas (NH_3) is potential to use due to its etchant characteristic. To compare two gases, nitrogen and ammonia, pyrolysis process was conducted into two atmospheres. 20 grams of degummed ramie fiber was prepared in combustion boat. Pyrolysis under nitrogen (N_2) gas only was conducted at temperature 800^{o}C during 2 hours with gas rate of 5 ml/min. However, pyrolysis under ammonia (NH_3) gas was also conducted at temperature 800^{o}C during 2 hours with gas rate of 1 ml/min, but it needed nitrogen gas at both of begin and end of reaction to avoid direct reaction between ammonia (NH_3) gas and air. Then, those two pyrolysis process were resulted two kinds of carbon that need to be pondered.

D. Carbon Characterization

Carbon that resulted from pyrolysis using nitrogen (N_2) gas treatment (C-N_2) and carbon that resulted from pyrolysis using ammonia (NH_3) and nitrogen (N_2) gas treatment (C-NH_3) were characterized using BET (Brunauer Emmet and Teller) to know the surface area of both of carbon and FTIR (Fourier Transform Infrared Spectroscopy) to analyze organic carbon functional group.

E. Electrode Experiment

Carbon C-N_2 and C-NH_3 were processed become electrodes. 5 ml-beaker of glass and stirrer were needed and prepared above hot plate. 2 ml of DMAc (N,N Dimethylacetamide) was poured into beaker. DMAc (N, N Dimethylacetamide) was used as solvent because of its volatiles, it would be easier to evaporate the solvent and obtain the electrode only. After that, PVDF (Polyvinylidine) as the polymer was poured into beaker then stirred with speed of 200-250 rpm at temperature +/- 80 ^{O}C until it seen fully colorless. Carbon were poured into beaker and stirred until mixed into slurry. Aluminum oil needed to be prepared as electric current. Then, carbon slurry was poured into aluminum foil, after that it was dried and flattened out with certain thickness using dry box.

F. Performance Testing

To determine the capabilities of electrode C-N_2 and C-NH_3, each of electrodes must be arranged into EDLC (Electric Double Layer Capacitor). Two kinds EDLC were made by arranging the electrodes with sandwich arrangement.

TABEL I. ELECTRODE COMPOSITION

Sample	Electrode 1	Electrode 2
EDLC C-N_2	100% Carbon (N_2 treatment)	90% Carbon (N_2 treatment) + graphite 10%
EDLC C-NH_3	100% Carbon (N_2 and NH_3 treatment)	90% Carbon (N_2 and NH_3 treatment) + graphite 10%

The samples were arranged then stacked with separator in the middle then gave a few drops of $Na_2SO_{4(aq)}$ as electrolyte. EDLC C-N_2 and EDLC C-NH_3 were analyzed using CV (cyclic voltamettry) and EIS (Electrochemical Impedance Spectroscopy).

III. EXPERIMENTAL RESU LT AND ANALYSIS

A. Cellulose of Ramie Fiber

As the objective of degumming process to obtain cellulose and hemicelluloses of ramie fiber and reduce lignin and gum, those contents were evidenced using FTIR.

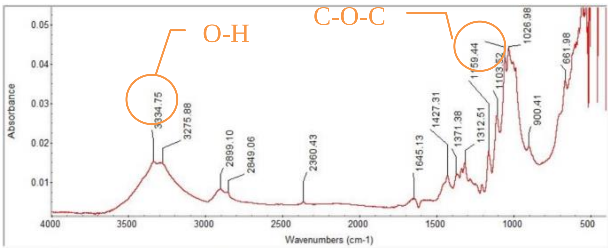

Figure 1. Analysis of degummed ramie fiber using FTIR

Shown on the Fig. 1, most of bonds are showing cellulose content. O-H bonding on 3334^{-1} cm; C-O-C bonding on 1159^{-1} cm; indicates that the result of degumming process contains cellulose that include on hydrocarbon compound. Lignin has absorbance level above cellulose and hemicelluloses which is 0.8 or more. The compounds which have absorbance level under 0.8 are cellulose and hemicelluloses with main bonding C-O, C-H, C-O-C and O-H. Besides using FTIR, XRD in Fig. 2 analysis also has been conducted to analyze material structure of sample. In X–absis with 2θ (deg), 2θ = 16.42(10) deg; 2θ = 22.83(2) deg; indicates that degumming produces ammonia cellulose (C6H14N2O5) that can be good source of carbon.

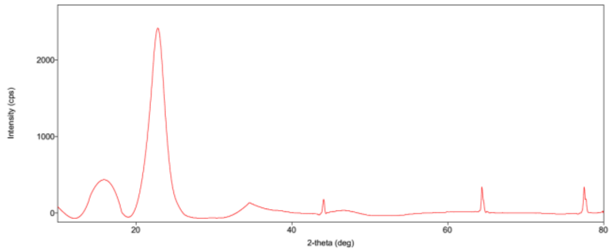

Figure 2. Material structure analysis of degummed ramie fiber using XRD

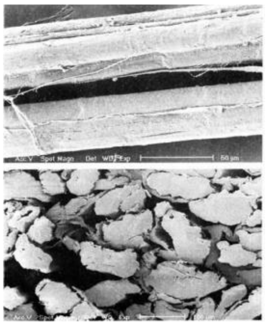

Figure 3. SEM photographs depicting longitudinal and cross sectional views of decorticated ramie fibers

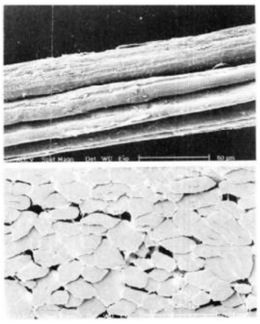

Figure 4. SEM photographs depicting longitudinal and cross sectional views of degummed ramie fibers [14]

Decorticated ramie fiber was shown on Fig. 3 and degummed ramie fiber was shown on the Fig.4. Decorticated ramie fiber is the bark of ramie that processed using decorticating machine to obtain the fiber only. Degumming reduces the lignin and gum as the pre-treatment for pyrolysis process. There was physical difference between decorticated and degummed rami fiber. Degummed ramie fiber has softer fiber and smaller fiber than decorticated ramie. Decorticated ramie fiber has brown color; however degummed ramie fiber has brownish-white color. It indicates that the gum has been shed.

B. Carbon Characteristics

Carbon C-N_2 and C-NH_3 were analyzed to compare surface areas. This analysis proves that pyrolysis process using ammonia NH_3 gas could etchant the surface of carbon, so that the surface area of C-NH_3 was larger than C-N_2. Surface area of carbon C-N_2 (pyrolysis using nitrogen N_2) is 119,098m^2/g, however surface area of C-NH_3 (pyrolysis using ammonia NH_3) is 143,791m^2/g.

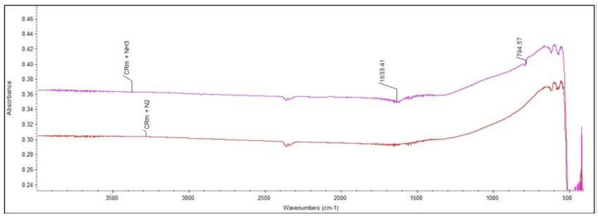

Figure 5. FTIR Comparison of C-N_2 and C-NH_3

There are two graphs shown on Fig.5, the red one shows the result of C-N_2 sample however the purple shows the result of C-N_2 sample. They were treated in the same temperature and time but different gases were used. In fact, their FTIR show different result. The result shows C-NH_3 has peak in wave number 1633cm^{-1} and 794 cm^{-1}. However, wave number 1633 cm^{-1} shows C-N bonding.

C. Electrodes Capabilities

In order to analysis the capabilities of the electrodes, CV (Cyclic Voltametry), SEM (Scanning Electron Spectroscopy) and EIS (Electrochemical Impedance Spectrometry) were used in this experiment.

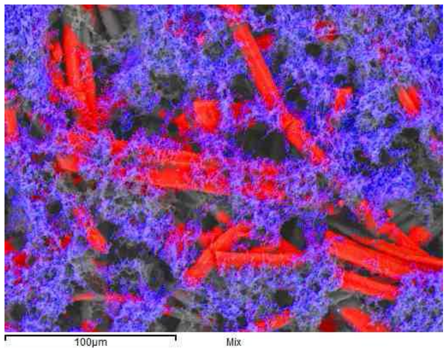

Figure 6. SEM – the electrode of C-N_2 sample

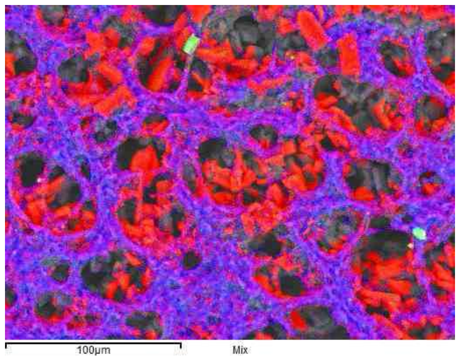

Figure 7. SEM-the electrode of C-NH_3 sample

Shown on the Fig. 6 and Fig. 7, the mapping of the electrodes sample shows the red color as the carbon and the purple as the polymer. These electrodes were prepared from carbonized degummed ramie fiber. The electrode of C-NH_3 (Fig. 7) shows smaller and more homogenous carbon than the electrode of C-N_2 (Fig. 6). The using of ammonia gas NH_3 in the pyrolisis process could increase the physical characteristic of the carbon. In the other hand, the electrochemical characteristic which was analyzed using CV, shown as figure below:

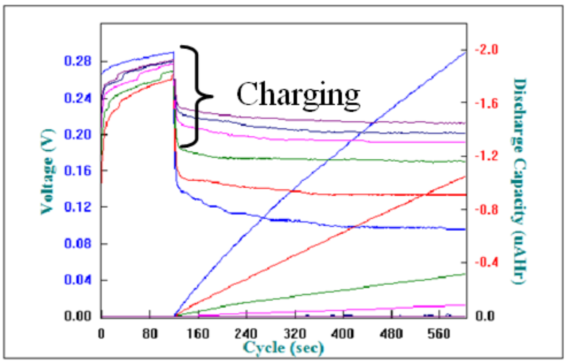

Figure 8. Charging-discharging electrode C-N_2

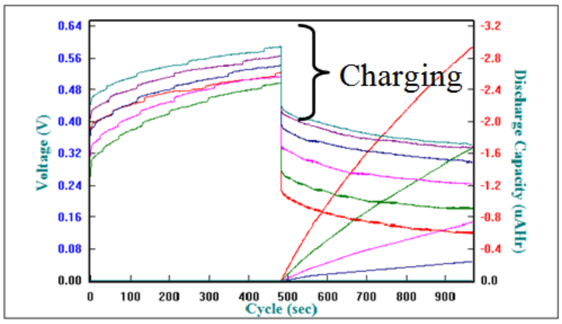

Figure 9. Charging-discharging electrode C-NH_3

Charging and discharging of electrode from carbon NH_3 was better than those of carbon N_2 with the same current load. The results were showed on the Fig.8 and Fig.9, electrode C-N_2 could charge until 0.28V and having discharge capacity 2.0 µAHr. However, electrode C-NH_3 could charge higher which reached 0.48V and having discharge capacity 2.8µAHr. The voltage reached of electrode from carbon NH_3 was 2-3 times higher than carbon N_2

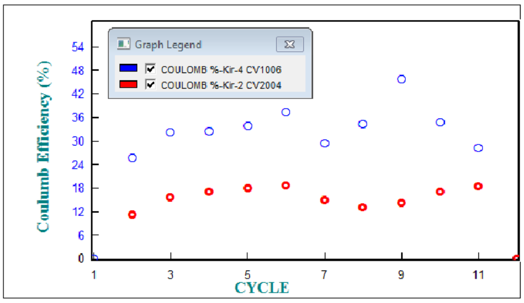

Figure 10. couloumbic efficiency of electrode C-N_2 and C-NH_3

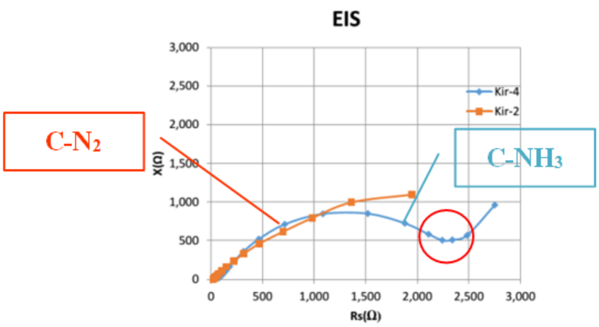

Figure 11. impedance of electrode C-N_2 and C-NH_3

Shown on the Fig. 10, the electrode from carbon NH_3 has higher columbic efficiency than carbon N_2, it reaches 24-45% however carbon N_2 reaches 12-18%. As the result we can conclude that the use of ammonia gas can improve the columbic efficiency until 2-3 times. The ionic and electron movements inside an energy storage device can be observed using EIS analysis (Electrochemical Impedance Spectrometry).

Electrochemical impedance can be measured using AC voltage. The result of EIS analysis is shown on the Fig. 11. Graph on the Fig. 11 called by *Nyquist* graph. Red circle is shown Warburg impedance that caused by electron transfer from an electrode into another electrode [15]. The blue *nyquist* graph is the result of EIS analysis of C-NH_3 electrode. It shows Warburg impedance around 2500Ω and creates extrapolation showed by semicircle graph. However, the orange graph shows the result analysis of C-N_2 electrode which has not reached the Warburg impedance yet. So, the electrode from carbon NH_3 was qualified as EDLC however carbon N_2 was not yet due to Warburg impedance. The capacitance value of electrode from carbon NH_3 using EIS experiment was 0.27mF/g. However, the electrode from carbon N_2 has capacitance value of 0.17mF/g.

The function of ammonia gas to etchant the surface of the carbon was physically increasing the surface area of the carbon. The increased surface area causes greater contact between the electrode and the ions. As a result, there was higher number of electrons transfers inside the EDLC. It was proved by the result of capacitance value of EDLC carbon NH_3 was higher than EDLC carbon N_2.

IV. Future Research

Improving the characteristic of Electric Double Layer Capacitor in the terms of surface are by using higher rate gas (NH_3) supply and longer time of pyrolysis process to increase the capacitance, stability and efficiency of EDLC material.

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