Fabrication of gas diffusion layer from carbon ramie fiber by hot press method

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Abstract. Polymer exchange membrane fuel cell (PEMFC) is an electrical energy-generating device that is renewable and environmentally friendly. However, the price of components in PEMFC is still relatively expensive and more studies are needed on making cheaper components in terms of methods and raw materials. In this research, the fabrication of gas diffusion layer (GDL) which is a component of PEMFC made from ramie fiber was investigated. The processes of preparing GDL in this research were divided into two parts: the process of making carbon from ramie fiber through pyrolysis process and fabrication of composite from carbon ramie fiber and urea formaldehyde resin (UFR) by hot press method. The carbon results from the process of pyrolysis of degummed ramie fiber with variations in pyrolysis temperature of 500 °C, 900 °C, 1100 °C and 1300 °C yield electrical conductivity values of 8.7 x 10⁻⁷ S/cm, 0.84 S/cm, 3.72 S/cm and 4.6 S/cm, respectively. The electrical conductivity of carbon ramie fiber was increased by degumming and increasing pyrolysis temperature. The 1300 °C carbon composite with a hydrophobic coating 10 wt.% FEP has an electrical conductivity of 0.25 S/cm and a water droplet angle of 133° (hydrophobic). Composites of carbon ramie fiber have potential as GDL in PEMFC.

1. Introduction
The Proton Exchange Membrane Fuel Cell (PEMFC) is a device that converts chemical energy directly into electrical energy [1]. One of the important components in PEMFC is the Gas Diffusion Layer (GDL). A GDL main functions are to distribute the fuel gas, to eliminate water produced from the cell and electrical pathway. In order for the GDL to perform these functions, it has to have electrical conductivity-, porous and hydrophobic characteristics [2]. Research trends in the use of natural fibers as carbon fiber-based GDL are on the rise, some of which involve coconut fiber [3] and oil palm fiber [4]. The electrical conductivity of carbon is affected by the cellulose composition of the natural fibers [5] and the pyrolysis temperature [6].

One of the promising materials for carbon conductive is Ramie fiber (Boehmeria nivea). The Ramie fiber has higher cellulose content of about 68.6 – 76.2%[7–9] than natural fibers in the previous study i.e. coconut [3] and oil palm fiber [4]. With the higher content of cellulose, carbon ramie fiber is predicted to have higher electrical conductivity [5] that makes it a suitable material for GDL in PEMFC.
In this research, the authors’ objective is to look for a method to process the ramie fibers to become carbon composite that has good characteristics similar to that of GDL in PEMFC. The hot press method was chosen to produce GDL from carbon. This method is a simple and inexpensive process. Three treatment were selected to achieve the goals; the degumming process to increase the content of cellulose, pyrolysis temperature to produce higher electrical conductivity carbon and the optimum composition of carbon composite to produce a good solid layer.

2. Experimental
This research was divided into two stages. The first stage was the process of producing carbon from ramie fiber through pyrolysis process. Prior to the pyrolysis process, ramie fiber was applied to initial treatment with the degumming process to remove hemicellulose/gum so that cellulose content increases [10][11]. The degumming process was carried out by soaking the ramie fiber in 10%NaOH solution for 3 hours at 95 °C. Then the ramie fibers were washed with water and dried in the oven. The pyrolysis temperature used to convert ramie fiber to carbon fiber was based on the results of the thermal analysis (TGA). The resulting carbon fibers were then polycyclicized at the higher pyrolysis temperature (900 °C, 1100 °C, 1300 °C). This re-pyrolysis treatment aims to increase the value of electrical conductivity [12]. The electrical resistance of carbon ramie was measured using LCR-meter.

The second stage was the fabrication of composite using hot press method. The composite is the mixture of carbon ramie and urea formaldehyde resin. The hot press was applied at the temperature of 150 °C, the pressure of 200 kg/cm² and for 30 min. In this process, carbon ramie content was varied between 70%, 75%, and 80%. Afterwards, the composite product was coated with hydrophobic coating 10 wt.% FEP solution. For characterization, the properties of samples were evaluated by electrical conductivity, porosity, contact angle and surface morphology. The electrical conductivity of carbon composite was measured using LCR-meter Hiochi 3522. The porosity was measured using pycnometer (BS 1902: Part 1A; 1966). The measurement of the contact angle with water droplet using Bashforth and Adams 1883 Table [13]. The surface morphology was observed using scanning electron microscope SEM HITACHI SU-3500.

3. Results and discussion
3.1. Thermal analysis of ramie fiber
Figure 1(a) shows the results of Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements for ramie fiber without degumming. It shows three intervals of mass loss. The first interval occurred at the temperature of 50 °C – 260 °C, the second interval occurred at the temperature of 260 °C – 370 °C and the third interval at 370 °C – 600 °C. At the first interval, relative mass decreases about 10% due to hemicellulose decomposition of the ramie fibers. This process took place at the temperature between 200 °C – 260 °C [14]. The second interval shows the occurrence of cellulose decomposition at temperature of 260 °C – 370 °C with a total mass loss about 47%. The decrease in mass resulting from the release of NO, ClH2, ClH4, ClH6, ClH8, components of ramie fiber material [14]. At the third interval, the mass decrease of 10% from temperature of 400 °C – 600 °C due to the decomposition of lignin. In the other hand, the DSC curve shows two endothermic peaks at 370 °C – 400 °C indicates cellulosic decomposition. Another endothermic peak temperature range of 770 °C – 780 °C, it was suggested due to the melting of KCl mineral, that occurred at 772 °C [4].

Figure 1(b) shows the results of TGA and DSC for the degummed ramie fiber. It was identified that the results have the same intervals as those of non-degummed fibers. The differences are in terms of the relative magnitude of the mass drop. In the interval two of degummed ramie fibers, the decomposition of cellulose has a relative mass decrease of 58%. There is an increase by 11% of the mass loss. This proves the increased cellulose content in the degummed ramie fibers. Based on these TGA result, the first pyrolysis temperature to convert ramie fibers to carbon is at 500 °C.
Figure 1. TGA and DSC of ramie fibers (a) without degumming process and (b) with degumming process.

3.2. Effect of pyrolysis temperature on electrical conductivity of carbon from ramie fiber

The results of carbon pyrolysis temperature at 500 °C, 900 °C, 1100 °C and 1300 °C at 30 kgf.cm on the electrical conductivity are $8.7 \times 10^{-7}$, 0.84, 3.72 and 4.6 S/cm, respectively. This result is shown in Figure 2. The electrical conductivity of carbon is closely related to the structure of carbon material. The electrical conductivity increases significantly by rising the temperature of pyrolysis, which causes the growth of the carbon structure with turbostratic crystallites structure in the form of irregular graphene sheets [6]. The electrical conductivity of carbon with pyrolysis temperature at 1300 °C is 4.60 S/cm, this result is higher than the electrical conductivity of other natural fibers at the same pyrolysis temperature i.e oil palm fibers of 0.14 – 0.17 S/cm [4] and coconut fibers of 0.12 - 0.18 S/cm[15]. The ramie fiber has a higher cellulose content of about 68.6 - 76.2% [7–9] than the cellulose content of the coconut fiber of 23-43%, and the result of pyrolysis process of cellulose produces a more orderly carbon structure so that the electrical conductivity of carbon ramie is higher [5].
3.3. Carbon composite from ramie fiber

3.3.1. Effect of initial treatment (degumming process) and carbon composition on the through-plane electrical conductivity of the composite. Figure 3 shows the electrical conductivity of carbon composites at the pyrolysis temperature of 900 °C with initial treatment (degumming process) of ramie fibers and carbon compositions variations. The electrical conductivity of carbon composites with carbon compositions variations of 70%, 75%, and 80% is 0.03 S/cm, 0.11 S/cm and 0.26 S/cm respectively. Increasing the percentage of conductive carbon increases the electrical conductivity. The increase in electrical conductivity has proceeded constantly as an increase in the percentage of carbon to a point where the increase in the amount of carbon has increased dramatically, a point called a percolation threshold. The addition of carbon after the percolation threshold does not significantly affect the electrical conductivity. However, it affects the decreasing mechanical properties of the composite [12].

Figure 3. The electrical conductivity of carbon composite.

The through-plane laminar electrical conductivity of the carbon degummed ramie composite is nearly ten times than the electrical conductivity of carbon ramie composite without degumming. The result shows 0.26 S/cm for degummed ramie versus 0.03 S/cm for non-degumming. Higher cellulose content in degummed ramie fiber produces more electrically conductive carbon [5].

3.3.2. Carbon composite with optimum variables. After investigations of the effect of degumming treatment, the increase of pyrolysis temperature, and the composition of carbon ramie fibers in the
composite on the electrical conductivity, the experimental works are continued with the composing of the composites by using the optimum result of those variables.

Based on the results of the research, the degumming treatment and the increase of pyrolysis temperature increases the electrical conductivity of carbon with a yield of 4.6 S/cm for pyrolysis at 1300°C and the optimum composition of carbon fiber in the composite is 80%. The electrical conductivity of composite of the above three variables has an electrical conductivity of 2.85 S/cm. The result has a higher value than the electrical conductivity of coconut fiber that has an electrical conductivity of 2.22 S/cm [16]. But GDL from coconut fiber uses carbon with an electrical conductivity of 0.18 S/cm. There was an increase in the electrical conductivity by a factor of 12 if one uses the casting process to produce GDL from carbon coconut fiber [16]. Using hot press method with carbon ramie and urea formaldehyde resin produces a lower electrical conductivity value than the original electrical conductivity of carbon ramie fiber itself. There is expected that fabrication GDL from carbon ramie fiber using the same method as the previous study [16] can produce GDL with higher electrical conductivity than GDL using hot press method. But with hot press method result, carbon ramie fiber composite using hot press method has good potential for GDL in PEMFC.

3.3.3. Hydrophobic coating on carbon composite. The hydrophobic coating is used to support GDL capability in avoiding the occurrence of water flooding at the GDL-catalyst layer in the cathode area [2]. The hydrophobic coating used was 10 wt.% FEP. This content was chosen because from the study conducted by Chan Lim and C.Y. Wang on the effect of FEP content used in GDL with the content variation of 10-40%. The GDL with 10 wt.% FEP has higher current density and relatively similar contact angle than higher content [17].

Figure 4 shows water droplets on carbon composite without a hydrophobic coating and Figure 5 water droplets on the composites coated by 10 wt.% FEP over time of 0-60 min observation. The contact angle of the composite without coating is below 90° while the composite after coating of 10 wt.% FEP layer is 133° which is hydrophobic.

![Figure 4. Water droplet on carbon composite.](image)

![Figure 5. Water droplet on carbon composite with hydrophobic coating.](image)

3.3.4. Effect of hydrophobic coating on the porosity of carbon composite. The porosity of the GDL has an effect on PEMFC performance. High porosity has an impact so that GDL is capable of supplying more reactant gases [18]. The porosity of the composite before and after hydrophobic coating decreased from 53.53% to 52.23%. This decrease results from the narrowing of the pores in composite with a hydrophobic coating. However, the porosity of carbon composite after hydrophobic coating is still in the range of porosity characteristics required by GDL in PEMFC that is between 50% - 90% [19].

3.3.5. Effect of hydrophobic coating on the electrical conductivity of carbon composite. The electrical conductivity of the carbon composite with hydrophobic is 0.25 S/cm has a one-order difference with a
commercial GDL of 5.10 S/cm under the same measurement conditions. Hydrophobic coating with FEP on carbon ramie composite decreases the carbon composite electrical conductivity from 2.85 S/cm to 0.25 S/cm. The value of this decrease is higher than the effect of PTFE coating which has the same electrical resistance value as FEP> 1018 Ohm.cm. Carbon coconut composite fiber coated with 10 wt.% PTFE decreased the electrical conductivity value from 2.22 S/cm to 2.09 S/cm [16].

Figure 6 shows the surface morphology of the carbon composite from ramie fiber and coconut fiber. The two composites show the size of carbon fiber particles of ramie fiber is smaller than the carbon size in the coconut fiber coconut composite so that the surface area of the carbon ramie fiber composite is greater than carbon coconut composite. The coating of hydrophobic materials on the carbon ramie fiber composite has the higher percentage of hydrophobic content than on carbon coconut fiber composite. So that the coating of hydrophobic materials on carbon ramie fiber composite produces a significant decrease in electrical conductivity.

4. Conclusion
The initial treatment with the degumming process of ramie fiber produces carbon composites with higher electrical conductivity than carbon composites of ramie fiber without degumming treatment. Increased pyrolysis temperature in second stage pyrolysis of carbon ramie fiber leads to increase in electrical conductivity of carbon. In the first-stage pyrolysis with the temperature of 500 °C, the conversion process from ramie fiber to carbon has the electrical conductivity of 8.7 x 10⁻⁷ S/cm with measured pressure at 30 kgf.cm (maximum pressure given during measurement). Then in the second stage pyrolysis of carbon at 900 °C, 1100 °C and 1300 °C produce carbon with the increased electrical conductivity of 0.84 S/cm, 3.72 S/cm, and 4.6 S/cm. The optimum composition of carbon content in the composite is 80%, that has good electrical conductivity and compact. The composites with carbon content above 80% yield a fragile composite. Carbon ramie composite has the electrical conductivity of 0.25 S/cm, the porosity of 52.23% and hydrophobicity properties. Therefore carbon ramie composite has good potential for GDL in PEMFC.

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