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Material processing of oil palm empty fruit bunches for use as raw material of conductive carbon paper

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Abstract. Empty fruit bunches of oil palm is a by-product of the palm oil industry that contains a high element of carbon. This by-product can be processed into a conductive carbon paper that could be applied as fuel cell electrodes. Carbon paper for this application must be conductive, porous, and hydrophobic. Utilization of oil palm empty fruit bunches begins with the carbonization process at a temperature of 500°C that produced charcoal. It is followed by heating at temperature of 900°C and 1300°C. To obtain the carbon paper, powdered charcoal with polymer binder (PEG and EVA) were mixed in solvent and molded using tape casting method. This process successfully produced carbon paper with dimensions of ±(20x20) cm² and a thickness of 0.1-0.3 mm. Properties of carbon paper were characterized and analyzed in terms of electrical conductivity, porosity, hydrophobic property, and microstructure. Polytetrafluoroethylene (PTFE), a hydrophobic agent, was treated on carbon paper to enhance the hydrophobicity of the carbon paper. PTFE coating on the surface of the carbon paper could change their physical properties. Carbon paper shows excellent properties in terms of porosity and hydrophobicity. Whereas, its electrical property needs to be improved further by increasing the pyrolysis temperature. But overall, this might show a potential GDL material for PEMFC.

1. Introduction
A proton-exchange membrane fuel cell (PEMFC) is an electrochemical cell that is fed with hydrogen and oxygen. The hydrogen is oxidized at the anode; while the oxygen is reduced at the cathode. The protons released during the oxidation reaction of hydrogen and passed through proton exchange membrane to the cathode side, while the electrons travel through an external circuit to provide an electric current [1]. Electrode is one of the main components of PEMFC, it consists of a gas diffusion layer (GDL) and the catalyst. GDL acts as gas diffusion media, provides mechanical support, an electrical pathway, and also helps to remove by-produced water outside of the catalyst layer. The GDL must be porous, high conductivity, appropriate hydrophobic, high air permeability and sufficient mechanical strength. GDLs are typically carbon-based materials, and usually in cloth or paper form [2-3]. Generally, GDL are composed of commercial carbon materials, which is produced from non-renewable resources such as carbon nano-tube (CNT) [4], polyacrylonitrile (PAN)-based carbon fibre [5], carbon black [6], etc. It could raise the sustainability issues.

Carbon material can be obtained by a simple carbonization process of natural fibers. Natural fibers are renewable resources and abundant. These resources consist of complex organic compounds namely hemicellulose, cellulose and lignin. Each of these compounds decomposes at different
temperatures and produces charcoal as a residue with high carbon content (± 50% to 90%) and porous
[7-10]. Hemicellulose is polymers of several monosaccharides such as pentosan and heksosan. The
earliest decomposed at temperatures of 200°C to 260°C, followed by decomposition of cellulose at
temperatures of 240°C to 350°C, and lignin decomposed at 280°C to 500°C [11]. Oil palm empty fruit
bunches (EFB) is one example of natural fibers that can be used. It is a waste of the palm oil industry
that has not been utilized optimally. Pyrolysis process at a temperature of 1300°C produced carbon
material with electrical conductivity of (1.4x10) S/m to (1.7x10) S/m [12]. Thus, if the EFB can be
utilized as a base material for GDL, it will be able to resolve the issue of sustainability.

The present study describes the preparation of conductive carbon paper with the carbon material
from EFB. And the objective of this study is to produce conductive carbon paper by using EFB
carbon. Carbon material from EFB was used to replace commercial carbon, which has been used as
raw materials of carbon paper production. Conductive carbon paper could be applied as GDL for
PEMFC electrode. In addition, by using natural fiber materials, it can be resolved the sustainability
issues due to the renewable nature of oil palm.

2. Material and method

2.1. Material
Carbon materials were prepared from pyrolysis products of oil palm empty fruit bunches (EFB) fibers.
Ethylene vinyl acetate (EVA) and Polyethylene glycol (PEG) obtained from Aldrich Chemical Co.,
Inc. (St. Lois, MO, USA) were used as binder. Xylene obtained from Brataco Chemika was used as solvent.
Teflon emulsion PTFE 30 obtained from Fuel Cell Earth LLC was used as hydrophobic agent
of carbon paper. Teflon emulsion PTFE 30 should be diluted to a concentration of 10% before treated
on the surface of the carbon paper. For comparison, a commercially available carbon paper, TGP-H-
090 (5% wet-proofed) Toray carbon paper, was obtained from Fuel Cell Earth and was used as received.

2.2. Preparation of carbon materials
The carbon materials were prepared from EFB fibers by a two stage process: carbonization at 500°C
and pyrolysis at 900°C followed 1300°C. In the carbonization process, the EFB fibers was heated at
500°C for an hour under N₂ atmosphere and cooled down to room temperature. The carbonization
process produced charcoal from EFB with high carbon content. Then the EFB charcoal was subjected
to pyrolysis at 900°C then 1300°C. In the pyrolysis process, the EFB charcoal was heated at 900°C for
an hour under N₂ atmosphere and cooled down to room temperature. It was followed by the pyrolysis
process with the same conditions at a temperature of 1300°C. These process produced EFB carbon
materials. Pyrolysis processes were carried out to improve the electrical conductivity, eliminate
impurities, and improve other properties of carbon.

2.3. Preparation of carbon paper
To prepare the conductive carbon paper, EFB carbon was used as raw materials. First, polymer EVA
and PEG were dissolved in xylene as solvents. The solution was stirred and heated at 90°C for 20
minutes. After the polymer dissolved perfectly, then EFB carbon was added. The mixture consisted of
EFB carbon, EVA, and PEG with a mass ratio of 80:14:6 in 46 ml solvent. The mixture was continuously stirred and heated at 90°C for 80 minutes to make slurry, and then casted on glass mold
with dimension of 20 cm x 20 cm. The carbon paper sheet was dried at room temperature for 24 h to
evaporate the solvent. The carbon paper thickness ranged from 0.2 to 0.4 mm.

Hydrophobic coating was made to enhance the hydrophobic property of carbon paper. It was
immersed in 10 % PTFE suspension for 10 minutes and dried at room temperature for 24 hours. Then,
it was heated at 150°C in an oven for 30 minutes to evaporate the remaining solvent, and then heated
at 350°C for 30 minutes under N₂ atmosphere.
2.4. Characterization of composite carbon paper

Characterization was carried out on carbon paper before and after PTFE coating, as well as commercial carbon paper as a comparison. Through-plane electrical conductivity was measured using HIOKI 3522-50 HITESTER LCR-meter. Porosity was determined by the kerosene density method using Archimedes principle in accordance with BS 1902: Part 1A standard. Hydrophobic properties are determined by the value of the contact angle using sessile drop test. For each measurement, a 50 µL water droplet was placed on the carbon paper surfaces by placing the tip of the syringe close to the sample surface, and images were captured. Furthermore, the droplet shape was analyzed using Bashforth and Adams tables [13] to determine the contact angle of the samples. Scanning electron microscope (JEOL JSM-6390 Series) was used to observe the morphology of the carbon paper before and after PTFE coating. Energy-dispersive spectroscopy (EDS) mapping was carried out to analyze the PTFE distribution in the carbon paper.

3. Result and discussion

3.1. Electrical conductivity

Carbon materials in powder form that had been prepared from EFB at different carbonization temperatures were characterized for their electrical conductivity. As shown in figure 1, with increase in the carbonization temperatures from 500°C to 1300°C, the electrical conductivity of the carbon materials increased from a value of 0.8x10^-3 to 0.8x10^1 S/cm. The increase in carbonization temperature leads to an increase in the crystallinity degree of carbon materials that derived from natural fibers [12]. In other words, higher carbonization temperatures enhance amount of the conductive phase in the carbonized natural fibers [14]. The property of EFB carbon changed from an insulating material into conductive material. Therefore, EFB carbon was treated under 1300°C used as raw materials of carbon paper production. Figure 2 shows the electrical conductivity of differentially prepared carbon paper in the through-plane direction.

![Figure 1. Electrical conductivity of carbon powder from EFB as the function of carbonization temperature](image1)

![Figure 2. Electrical conductivity of untreated carbon paper, PTFE-treated carbon paper and commercial carbon paper](image2)

The conductivity value of un-treated carbon paper decreased approximately 94.5% compared to that of EFB carbon as its raw material. It was due to the presence of non-conductive polymer (EVA and PEG) as binder which may interrupt the formation of the conductive network in carbon paper. Moreover, the presence of non-conductive PTFE particles in the carbon paper resulted further decrease in the electrical conductivity up to 50% compared to the un-treated carbon paper. And, it was also found that the electrical conductivity of the 10% PTFE-treated carbon paper from EFB carbon was still lower than commercial carbon paper (TGP-H-090 Toray and GDL LT 1200-W carbon paper). However, this electrical property could be improved further by increasing the pyrolysis temperature in the production of carbon materials from EFB to enhance the amount of conductive phase.
3.2. Porosity

The porosity of the composite carbon paper from EFB was measured and compared to commercial carbon paper. As shown in figure 3, the porosity of carbon paper decreased from 73.01% to 68.73% with the wet-proofing treatment of 10% PTFE. The decrease in porosity is mainly due to the blockage and narrowing of the pores by PTFE particles. PTFE particles deposited onto the surface and filled the open pores of carbon paper, as a consequence, reduces the overall porosity. Even though the porosity of carbon paper from EFB is slightly lower than the commercial carbon paper, this value still within the allowable range of porosity values as GDL of PEMFC. As GDL, carbon paper has functions to allow the reactant gases to reach the reaction zones and the product water moves out. To perform these functions effectively, carbon paper should have high porosity from 50 to 90% [15].

![Figure 3. Porosity of un-treated carbon paper, PTFE treated carbon paper and commercial carbon paper](image)

3.3. Hydrophobic property

Hydrophobic property is required by carbon paper as the GDL for the removal of product water from catalyst-layer area to flow-field channels in the PEMFC stack. Hence, carbon paper was water-proofed by introducing PTFE in this work. Furthermore, water contact angles on carbon paper were measured to determine the hydrophobic properties. The photographs and contact angles of water droplet on the surface of each carbon paper sample are presented in figure 4. As shown, the untreated carbon paper did not exhibit the hydrophobicity with low value of contact angle (less than 90°). When the carbon paper was treated with PTFE, the contact angle greatly increased to 117° and displayed the hydrophobic property. The contact angle value of both carbon paper were greater than 90° indicating that the PTFE treated carbon paper from EFB are resistant to wetting as well as the commercial products of Toray TGP-H-090.

![Figure 4. Water drops photographs and contact angle of (a) un-treated carbon paper, (b) PTFE treated carbon paper, and (c) TGP-H-090 Toray carbon paper](image)

3.4. Morphologies and elemental analysis

The surface and cross section morphologies of the untreated, PTFE treated and commercial carbon paper used in this work are shown in figure 5(a) to figure 5(f). The gray-colored regions and dark regions are assigned to the the carbon materials and the pores, respectively. As can be seen in figure 5(a) and figure 5(b), the pores are spread evenly on the untreated carbon paper surface and that of the PTFE treated. As pointed out previously, PTFE particles were deposited onto the untreated carbon paper surface and this reduces the overall porosity. This phenomenon is reflected in the SEM micrographs. Meanwhile, the SEM micrographs in figure 5(d) and figure 5(e) show the cross-sections of the untreated and PTFE treated carbon paper, respectively. It can be observed the porous morphology of carbon paper with thickness approximately from 0.40 to 0.50 mm. Whereas the surface and cross-section morphologies of commercial carbon paper are slightly different compared to carbon
paper from EFB. As shown in figure 5(c) and figure 5(f), this is composed of carbon fibers arranged randomly.

Figure 6(a) and 6(b) show the elemental F distribution (represented by pink dots) of cross section of PTFE-treated and commercial carbon paper, respectively. It is clearly observed that the PTFE particles successfully deposited onto the surface of both carbon paper, and some of them penetrated through the carbon paper.
4. Conclusion
In the present work, conductive carbon paper was successfully prepared by utilizing oil palm empty fruit bunches through the process of carbonization, pyrolysis, tape casting, and hydrophobic treatment. Carbon paper was shown to have excellent properties in terms of porosity and hydrophobicity. Whereas, its electrical property needs to be improved further by increasing the pyrolysis temperature. But overall, this can prove as a potential GDL material for PEMFC.

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