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# Effect of Different Types of Microporous Layer Toward the Performance of Direct Formic Acid Fuel Cell

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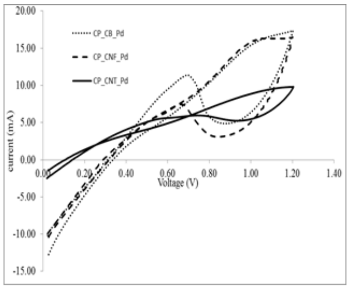
**Graphical abstract**



**Abstract**

Typical electrodes of anode and cathode are supported on macroporous backing layer with additional microporous carbon layer. The effect of the gas diffusion layer (GDL) on the cell performance in a direct formic acid fuel cell (DFAFC) has been characterized. The performance of DFAFC might be hindered by mass transfer limitation due to hydrophilicity properties of the formic acid. By measuring the contact angle and SEM photograph, the physicochemical and surface morphology of different types of GDL can be classified. Meanwhile, the effects of carbon materials such as carbon black, carbon nanofibre and carbon nanotube as a microporous layer on the backing layer of carbon paper were investigated on the basis of the characterization and the performance. From the results, it was obtained that CNF was a good material as microporous layer due to the properties of in plane conductivity, high current in cyclic voltammetry and also had smoother surface on the morphology test.

*Keywords:* Gas diffusion layer; microporous layer; anode electrode; DFAFC

## ■1.0 INTRODUCTION

Direct liquid fuel cells (DLFCs) are promising alternatives power option because they have very high power density relatively lithium ion batteries. Consequently, direct alcohol fuel cells have been extensively investigated (Kamarudin *et al.* 2009; Lamy *et al.* 2002; Vigier *et al.* 2006). Fuel cells generate only heat and water by converting the chemical which is fuel into electricity. Hence, it can be the cleanest renewable energy compare to the combustible engine that may produce harm gas and waste. Among DLFCs, direct formic acid fuel cell (DFAFC) seems to be the encouraging power supply due to several advantages compared to other fuel cells including direct methanol fuel cells (DMFCs). Compared to DMFC, DFAFC have low crossover through the Nafion membrane and ease the water management (Rhee *et al.* 2003). Moreover, DFAFC can run at room temperature like other DLFC with higher power density compared to DMFC. Formic acid also have faster oxidations kinetics on anode catalysts (Uhm, Kwon, *et al.* 2008). This is due to greater mass transfer behavior of formic acid is greatly different from methanol (Cai *et al.* 2013).

The direct formic acid fuel cell (DFAFC) is a promising power supplied since it has theoretically high electromotive force of 1.45 V compares to hydrogen or methanol fuel cell at which 1.23 V and 1.18 V, respectively. (Kim *et al.* 2011; Shuxian Zhang *et al.* 2009). The target application for DFAFC include the low until high power output such as for mobile products up to stationary usage like residential electricity generation (Rees&Compton 2011). Contrasting to internal combustion engines which fueled by diesel, the usage of fuel cell is seem to be more reliable because it can operate in a silent and clean mode (Agnolucci 2007).

Besides the advantageous side of formic acid, DFAFC have several drawbacks; high performance of Pd catalyst cannot sustain for longer time periods mostly due to vulnerability of these catalysts towards uncharacterized intermediate species (Uhm 2008; Uhm, Kwon, *et al.* 2008). In order to improve the DFAFCs' performance, many research in respective fundamental and component are discovered by researcher. Among the research area include the structure of the surface of the GDL either in anode or cathode side (Jordan *et al.* 2000; Uhm, Lee, *et al.* 2008).

For any types of fuel cells, membrane electrode assembly (MEA) is the most significant part since the main reaction to generate electricity take place at the MEA. The membrane electrode assembly (MEA) is the heart of the proton exchange membrane (PEM) fuel cell (Litster&Mclean 2004; Srinivasan&Kirby 2006) and as per other types of fuel cells such as direct methanol fuel cell (DMFC) and DFAFC. It determines the fuel cell performance and durability. An idyllic

MEA allow all active catalyst sites in the catalyst layer to be accessible to the reactant, proton and electrons and would facilitate the effective removal of produced water from the catalyst layer. It also functions as transportation of reactants and liquid water, conduction of electrons and heat, and also as a mechanical support (Zhang *et al.* 2008). In economical and technically aspect, appropriate fabrication of MEA is needed in order to achieve high performance with low costs (Mikołajczuk *et al.* 2011). Normally, MEA is sandwiched by two flow field plates in both sides of anode and cathode. The components for MEA consist of PEM, gas diffusion layer (GDL) and also catalyst layer. All the components are fabricated separately before pressed together at high temperature and pressure (Litster&Mclean 2004).

Since the MEA is a most important component in fuel cell, numerous study were carried out focus on this component into a detail from the method of MEA preparation till the material like types of membrane, macroporous layer , microporous layer and catalyst layer (Gao *et al.* 2010; Park *et al.* 2006, 2008). The electrode properties that can be optimized in order to improve fuel cell performance are ionic and electrical conductivity and also hydrophobicity. The porosity of the GDL will ensures that reactant can easily diffuse to the catalyst layer. GDL plays important role of electrical conductor in transports electrons to and from the catalyst layer (Litster&Mclean 2004). Designed of GDL should be based on two concepts of high electric conductivity and excellent mass transfer ability (Gao *et al.* 2010).

Typically, fuel cell was run by the protons flow from anode to cathode which produces electricity by the change of electromotive force. The electrodes which comprises of anode and cathode are usually supported on macroporous carbon paper or carbon cloth which additional of microporous layer (Uhm, Lee, *et al.* 2008). Macroporous layer is serves as a current collector and a physical support for the catalyst layer (Basri *et al.* 2010). The microporous layer consists of carbon and polymer suspension which forms a hydrophobic diffusion media on which a catalyst is coated (Uhm, Lee, *et al.* 2008). This hydrophobic diffusion media is necessary to apply to force water to penetrate into the pores of these materials (Kamarudin *et al.* 2007). Diffusion media is crucial in the passage of reactant towards the catalyst layer and water/heat/gas product removal towards the flow field channels. It also act as a mechanical support for the protection of the catalyst layer from corrosion or flushing out caused by flow or other factors (Uhm, Lee, *et al.* 2008). In the other hand, microporous layer is function to provide proper pore structure and hydrophobicity to allow a better gas transport and water removal from the catalyst layer hence minimize electric contact resistance with the adjacent catalyst layer (Basri *et al.* 2010). In terms of water management, microporous layer act as water retainer for the water which out from the cathode gas diffusion layer and move it through the anode. According to Park and Popov, severe electronic and ionic contact resistance in the MEA will occur due to the unnecessary liquid water in the gas diffusion electrode (Park & Popov 2009). Improved microporous layer will enhance electrical conductivity or can be said as ohmic behavior and conceivably better catalyst utilization (Weber & Newman 2005). In order to fabricate improved microporous layer, an appropriate macroporous layer should be chosen. Several factor should be took into consideration such as high electrical and thermal conductivity, high porosity, an optimal combination of hydrophobic and hydrophilic properties, good chemical and mechanical durability and low cost.

Here we present our study on the fabrication of the different types of GDL in order to develop anode's electrode. The effects of carbon materials, i.e. carbon black, carbon nanofibre and carbon nanotube, as microporous layer on the backing layer of carbon paper were discussed on the basis of the morphologies and the performances.

## ■2.0 EXPERIMENTAL

The experimental studies focused on the fabrication of the different GDL using three types of carbon structure. Afterward, the GDL will be characterized and went through an electrochemical measurement.

### 2.1 Gas Diffusion Layer Fabrication

Three anode electrodes were prepared by using different structure of carbon as the support to the catalyst layer. 2.5mg/cm$^2$ of carbon with different structure were prepared including carbon black (CB) (Vulcan XC-72), carbon nanotube (CNT) and multiwall carbon nanofibre (CNF). In this work, the carbon paper from Ballard is using as the macroporous layer while the microporous layer were from the composition of Nafion solution 5% wt, 2-propanol and the carbon powder. The composition were ultrasonic to produce a homogenous paste or ink of the GDL before ready for 'direct painting' on the macroporous layer.

The composition of anode ink contains 8 mg/cm$^2$ palladium (Pd) black (Alfa Aesar) as the catalyst, Nafion solution 5% wt and 2-propanol. The ink was ultrasonic until a homogenous solution obtained. After that, the solution is ready for 'direct painting' on the prepared GDL.

### 2.2 Characterization

The physicochemical properties and surface morphology of the GDL were observed with a contact angle measurement (KRÜSS Drop Shape Analysis by Fischer) and screening electron microscopy (SEM,ZEISS). Contact angle measurements were done by using DI water and a range of formic acid concentration (0.5 – 15M). SEM image were taken before the catalyst layer were added to the GDL. Drop shape analysis was used to measure contact angles between water or liquid solution and the carbon backing layer to evaluate the hydrophobicity properties (Lobato *et al.* 2008). Chen *et al.* listed a static contact angle between 0º to 90º was hydrophilic while contact angle above the 90º was hydrophobic. Drop shape and contact angle magnitude is depends on three interaction forces of interfacial tension for each participating phase (gas, liquid and solid) (Chen *et al.* 2011). The wetting of porous solids also involves contact angle phenomena but is complicated by the presence of a porous architecture. Even various methods are employed contact angle are still the primary parameters used to characterize wetting. For solids that have contact angle above than 90 degree will not wet into the liquid.

To evaluate the in plane conductivity of the GDL, a conductivity test was carried out using four-point probe (Jandel Model RM3). This equipment produced electrical resistivity towards the plane of the GDL. From the datas obtained, conductivity of the GDL can be calculated as the conductivity is inversely to the electrical resistivity. For this test, 5 mA current was applied throughout the experiment.

### 2.3 Electrochemical Measurement

The electrochemical reaction mechanism was studied using cyclic voltammetry method. A standard three electrode electrochemical cell with WonATech potentiostat was used for electrochemical measurement. The preparation of the working electrode as mentioned in section 2.1. Meanwhile, the Ag/AgCl and Platinum wire were used as reference electrode and counter electrode. For the electrolyte of the reaction, 0.1 M $H_2SO_4$ was added to 12 M formic acid to maintain a constant pH and stabilize the reference electrode potential (Morgan *et al.* 2010). The scan rate for this electrochemical measurement was 50 mV/s.

## 3.0 RESULTS AND DISCUSSION

Carbon particles are commonly used as catalyst support due to their good electric conductivity, relative stability in both acidic and basic media and high specific surface area (Zainoodin *et al.* 2010). In this study, carbon black, carbon nanotube and carbon nanofibre are used to obtain better perfomance as a support to the anode electrode. The loading of GDL for each sample were kept constant to ensure that only the carbon structure would affect the result as well as to minimize error factors in this study.

The level of hydrophobicity for backing layer were also kept constant throughout this study. Therefore, the commercial carbon paper from Ballard with 20 % wt polytetrafluroethylene (PTFE) was used. Figure 1 shows the SEM images of the in-housed prepared GDL with different carbon structure as catalyst support.

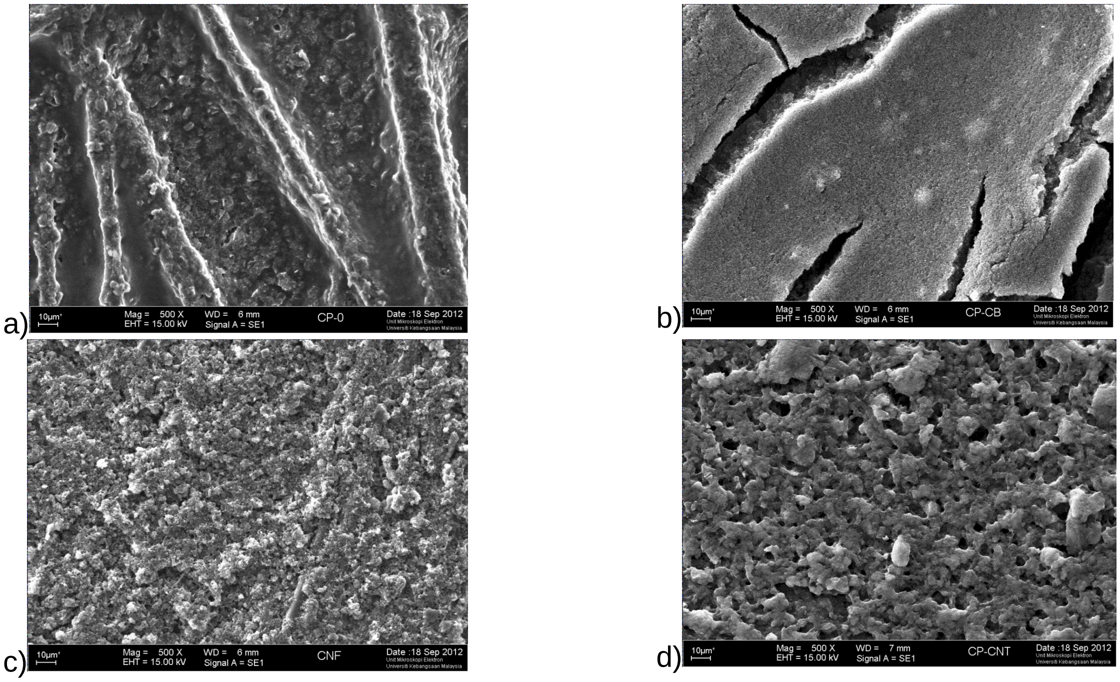


**Figure 1** SEM images of different types of GDL: (a) plain carbon paper (b) carbon paper coated with carbon black microporous layer (c) carbon paper with carbon nanofiber microporous layer (d) carbon paper with carbon nanotube microporous layer

As shown in Figure 1(a), the carbon fibre paper is already layered by the PTFE. It has coarse surface without microporous layer compare to Figure 1(b) which is smoother and less coarse with little crack. Figure 1 (c) and Figure 1(d) have a better surface morphology since they are nanostructured carbon. From the overall Figure 1, carbon black layer have a little crack on the backing layer. This situation is similar to a review by Sundarrajan *et al.* stated that the problem of carbon black as catalyst support. Catalyst particles are trapped in deep cracks of carbon black and not appear on the surface. While carbon nanofibers and carbon nanotubes have higher surface per volume ratio compare to carbon black due to its nanastructure to provide a foundation for catalyst to attach on the GDL . Hence, it will enhanced the catalytic activity compare to carbon black (Sundarrajan *et al.* 2012). Usually, carbon paper has a structure with pore sizes between 20 and 50 µm however, the pore was blocked by some hydrophobic agent (Uhm, Lee, *et al.* 2008) such as PTFE.

In the PEM fuel cells cathode, the contact angle to water can be increase by impregnated GDL with PTFE. In addition, by impregnated PTFE the flooding in the fuel cell can be prevented (Uhm, Lee, *et al.* 2008). Other than PTFE content, the porosity of the sample also lead to a lower contact angle (Weber & Newman 2005). Meanwhile, the comparisons of contact angle with different GDLs were investigated as shown in Fig. 2. GDL is non-wetting hydrophobic surface due to the presence of hydrophobic agent like PTFE. Hence, the contact angle results are expected to be above than 90 degree as shown in Figure 2. However, the degrees of contact angle were different for each GDL as well as different in formic acid concentration from 0 to 15M. The difference of degrees could be due to the effect of hygroscopic characteristic and the point of measurement taken. This is related to the existence of cracking on the GDL and the distribution of pore.

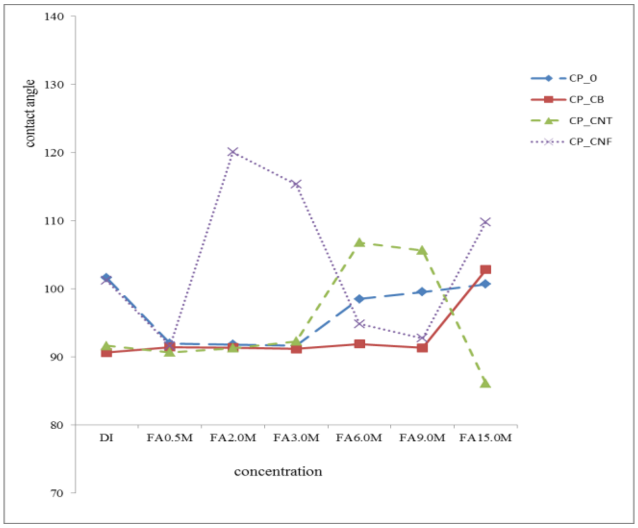


**Figure 2** The comparisons of the contact angle for GDLs

Usually, carbon support will provide electronic conductivity to support catalyst. This is to ensure good contact of most catalyst particles with ionomer material that has ionic contact with the membrane (Zainoodin *et al.* 2010). Figure 3 shows the result of in plane conductivity test that have been carried out. From Figure 3, plain carbon paper has highest in plane conductivity, however in term of water management, microporous layer coated on the carbon support significantly reduce flooding which mean enhance the performance of the cell. Carbon paper coated with CNF as microporous layer seem to have higher conductivity compare to other structure of carbon at which 1.26 S/cm. Basically, the range of electrical conductivity for GDL between 1.64 S/cm and 0.40 S/cm (Litster & Mclean 2004).

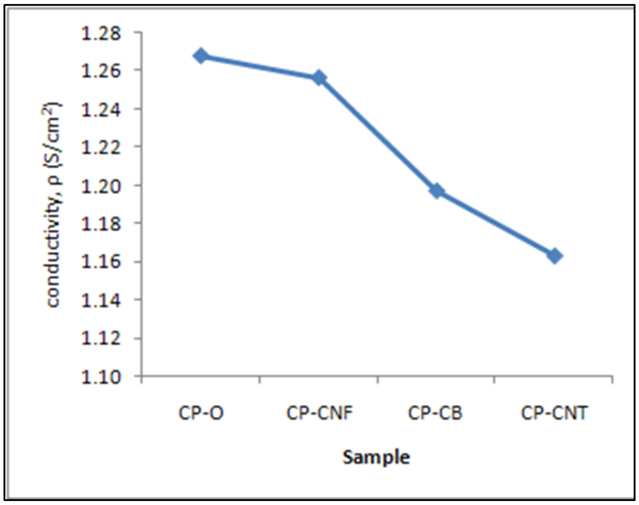


**Figure 3** The in plane conductivity test result for each samples

The activity of electrochemical reaction is measured by the cyclic voltammetry (CV) giving rise to electroanalytical current signals. The general shape of the CV should be unchanged throughout the experiment but the reduction in peak currents can occur (Morgan *et al.* 2010). Figure 4 shows the CV test on anode electrode with different types of GDL. The potential in the CV is measured between the reference and working electrodes and current is measured between the working electrode and counter electrode. In the Figure 4, each reaction activities come out with the same patent of CV test but different in oxidative and reductive power.

Unfortunately, the reaction of Pd with formic acid in DFAFC will produce CO. This poisoning occurred at the Pd surface (Morgan *et al.* 2010). CV test gives much higher mass activity due to the steady state operation and the CO poisons can be oxidized at a higher applied potential (Winjobi *et al.* 2010).

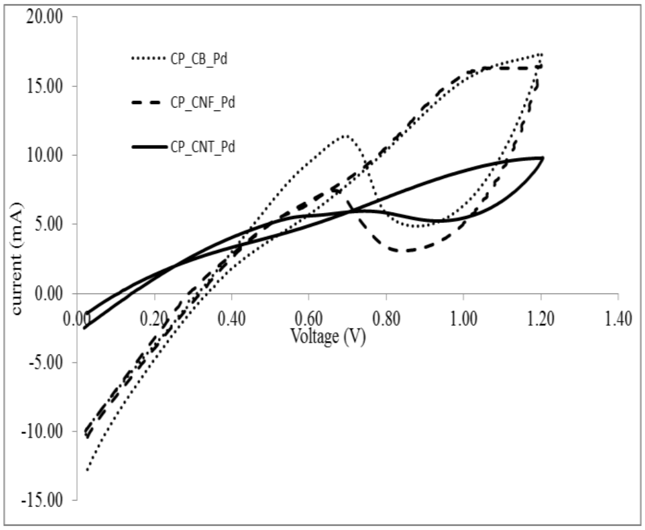


**Figure 4** Cyclic Voltammetric test for different catalyst supports

In this study, CNF and CB microporous layer appear as stronger oxidant compare to CNT microporous layer. However, the CB cycle is smaller compare to CNF cycle and has lower conductivity which may lead to have lower performance on the single cell. Nanostructured carbon support for catalyst layer given high surface area, good electrical conductivity and also fit the porosity to allow good reactant flux and high stability in the fuel cell environment (Zainoodin *et al*. 2010). Apparently, CNF looks suitable to be catalyst support in DFAFC due to good electrical conductivity as well as electrochemical reaction activity.

However, several researchers have considered that CNT as promising catalyst support material. The tubular structure of CNTs makes them unique among different forms of carbons. It also exhibit relatively high surface areas, excellent electronic conductivity and high chemical stability. Catalytic activity of Pd-based is strongly depends on the size, shape and size distribution of the metal particles, in addition to their dispersion on the support (Marinšek *et al.* 2013). From this study, the CNT microporous layer seems to appear a little agglomerate compared to others with uniform structure. This is probably the reason of low performance of the CNT as microporous layer.

## 4.0 CONCLUSIONS

The GDL on the carbon support gives significant benefit on the flooding problem by reducing it and at the meantime enhance the performance of the fuel cell. GDL also effectively inhibit the phenomena of drying of the MEA under low humidity conditions. Nanostructured carbon support is a promising GDL composition due to the characterization and cyclic voltammetry test. The fabrication of GDL with suitable composition and carbon structure should be further discover until obtain high performance in single cell of DFAFC. The results of this study cannot ensure the performance on the single cell but it can be based for the further studies on the nanostructured GDL for DFAFC. This is due to many factors will affect the performance in single cell even the GDL is the best at the preliminary test on each electrode such as cathode and anode.

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