

# An Overview of the Gas Diffusion Layer in Proton Exchange Membrane Fuel Cells: How Its Nano-structural Characteristics Affect Performance

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## Abstract

Gas diffusion layer (GDL) is one of the critical components performing both as the operational as well as the support structure to membrane-electrode assembly (MEA) in the proton exchange membrane (PEM) fuel cell. The role of the GDL is very important in the PEM fuel cell to render it commercially applicable. Structural variations in the GDL can effect physico-chemical and mechanical properties and eventually power performance of the fuel cell. The optimization of the functional features of the GDL is possible just with comprehension the role of its key parameters such as structure, hydrophobicity/hydrophilicity, porosity, gas permeability, electrical conductivity. This paper presents an overview of effects of using nanosize materials to modify GDL structure. In addition, future prospects for new GDL developments are discussed.

**Key words:** Gas diffusion layer, Proton exchange membrane fuel cell, Nano-structure

## 1. Introduction

Due to the growing worries on the exhaustion of fossil based energy resources and climate change, fuel cell technologies have attracted much attention in recent years owing to their high efficiencies and low emissions [1]. Fuel cells are static energy conversion devices that convert chemical energy stored in fuels such as hydrogen directly into electrical energy [2]. Fuel cells are divergent from conventional electro-chemical batteries, rather than repose on static storages of chemicals that must be recharged or renewed at certain intervals, fuel cells necessitate a flow of chemical such as hydrogen, oxygen or air that react in the entity of catalysts. Electricity is generated through the reaction and carried to an external circuit. Fuel cells theoretically can work continuously as long as essential reactants are available [3].

There are various types of fuel cells that identified in the literature such as proton exchange membrane (PEM) fuel cells, alkaline fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells and solid oxide fuel cells. Among them, the PEM fuel cells are attracting significant interest as alternative power sources for several applications due to their higher power densities, lower temperature of operation and effectual environmental profits [4, 5]. However, the power density values are decreased due to mass transport limitations especially at the cathode and its high current density performance is substantially limited by transport of reactants and products [5]. Gas diffusion layer (GDL) is one of the critical components of the PEM fuel cell which main functions are carrying of the reactant gas from flow channels to catalyst layer effectually, conducting electrons with low resistance, pouring liquid water from catalyst layer to flow

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channels and keeping the proton conducting membrane in wet condition at low humidity [6]. Therefore, GDL modification has been paid much attention for the improvement of the physical properties and performance of PEM fuel cells. Generally, a typical GDL is fabricated by coating a macro-porous layer with hydrophobic micro-porous layer. In addition to macro-micro porous layers, nanostructured GDL attracts researchers' attention due to enabling fast electron transfer and high electrocatalytic activity, having properties like high electrical conductivity, high specific surface area and good stability [7].

The GDL is manufactured by using commercially available carbon cloth (woven) or carbon paper (non-woven) made of carbon fiber as macro-porous layer. Carbon-based GDL is widely preferred because (i) procures high gas permeability (ii) has good electronic conductivity (iii) it is stable in acid environment and (iv) is elastic on compression [8]. Unfortunately, carbon is lost from the system through oxidation leading to important losses of carbon over short period of time. The stability of carbon-based GDL affects the loss of platinum surface area following both platinum particle sintering and it releases from carbon based-GDL [9]. To address the corrosion problem in GDL, some alternative materials rather than the traditional carbon-based materials in PEM fuel cells should be explored. For these noncarbon materials for fuel cell GDL, some basic requirements should be met such as high surface area, specific dispersion of catalytic metals, high corrosion resistance under both dry and humid air conditions, low solubility in acidic media, high electrochemical stability under operating conditions and high electrical conductivity. Besides, the noncarbon materials should have a strong physicochemical and electronic interaction with catalysts to enhance their catalytic activity and durability [10].

In this overview, we discuss the performance, potential and issues associated with use of various nano-sized carbon or non-carbon based GDL which are widely investigated for anode and cathode in PEM fuel cell.

## **2. Characteristics of GDL**

The performance of PEM fuel cell is significantly influenced by the structure and morphology of the GDL. As the membrane needs moisture content for ionic conduction, the reactant gases are humidified during the PEM fuel cell operation. However, when the rate and degree of the electrochemical reactions are high at high current densities, excessive amount of water is produced which while effusing of the cell through the GDL, fills the pores of the electrodes with water and thereby limiting the reactant transport to the active catalysts layer. To enhance the performance of PEM fuel cell, it is critical to balance the features of the gas flow characteristics in the GDL. New strategies are recently emerging to design and improve aim-built GDL for operating conditions of fuel cells. This is succeeded though materials and methods for optimum hydrophobic/hydrophilic properties pore size and its distribution, and also electronic conducting network [11, 12].

### **2.1. Hydrophobicity/hydrophilicity**

The hydrophobicity of the GDL should be high to remove water to the flow area effectively and avoid it from building up at the cathode catalyst layer, hence blocking the reactant access to the catalyst. On the other hand, the hydrophilicity of the GDL should be high as to lead to membrane

drying, which would decrease the proton conductivity of the membrane.

## **2.2. Porosity**

The presence of small pores can result in a greater resistance to mass transfer of the reactant gases to the catalyst layer. If pores are too large, the membrane may dehydrate due to excessive water loss. Therefore, the pore size and pore radius distribution are two significant mechanical properties that control fuel cell performance.

## **2.3. Electrical conductivity**

The GDL must be able to conduct electrons generated from the hydrogen to the current collectors. Electrical conductivity of the GDL should be as high as possible to minimize Ohmic losses effectively conducting electrons between the catalyst layer and the current collectors via the bipolar plate.

## **2.4. Thermal conductivity**

Thermal conductivity of the GDL should be high to effectually remove the heat from the membrane electrode assembly (MEA), where it is produced, to the bipolar plates, where cooling is available.

## **2.5. Mechanical supporting**

The GDL must procure robust mechanical support to preserve the membrane and catalyst layers from possible damage during assembly, while protecting good interfacial contact among the MEA layers and to prevent its deflection in the flow area channels during cell compression.

# **3. Materials for GDL**

## **3.1. Nanostructured carbon-based GDLs**

Carbon blacks (CB) are the most widely used supports for catalyst layers for fuel cells in commercial applications (especially Vulcan XC-72). CB comprises of near-spherical particles of graphite, < 50 nm in diameter. These merge into particle aggregates of around 250 nm in diameter. The high surface area ( $\sim 250 \text{ m}^2\text{g}^{-1}$  for Vulcan XC-72), low cost and easy availability of CBs help decrease the overall cost of the fuel cell [13].

Carbon nanotubes (CNTs) are 2D nanostructures, typically tubes occurred by rolled up single sheets of hexagonally regulated carbon atoms. They may be single walled (SWCNT) or multi walled (MWCNT). MWCNTs have been found to be more electronically conductive while SWCNTs procure larger surface areas. CNTs are the best known and the most commonly scouted carbon-based nanostructures for GDL application in fuel cells. For example, Tang et al. nanosized Pt nanodots with 2-3 nm in diameter as catalyst on CNT fabricated in-situ on carbon paper. The combined GDL and catalyst layer exhibited a high maximum power density of  $595 \text{ mW cm}^{-2}$  using a catalyst loading of  $0.04 \text{ mg cm}^{-2}$  Pt on the cathode. This value was substantially higher than the Pt/Vulcan XC 72R-based electrode ( $435 \text{ mW cm}^{-2}$ ) with same Pt loadings [14].

At another example, He et al. synthesised Pt nanoparticles on polyaniline (PANI) functionalized MWCNTs. Here, they used PANI as a bridge between Pt nanoparticles and CNTs. Pt/MWCNT electrodes exhibited high electroactivity and excellent electrochemical stability when compared with commercial CB GDLs [15].

Carbon nanofibers (CNF) have recently attracted interest as catalytic support in GDL mostly due to their negligible micro-porous and crystalline structure, supplying high electrical conductivity with low cost compared to similar nanostructures like CNTs. Padmavathi et al. fabricated electrospun CNF (e-CNF) as supporting material for Pt catalyst and investigated the effect of the functionalization on e-CNF (fe-CNF) samples by using mixtures of conc.  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  solutions. Managing to comparison with commercial Pt/C, 20 wt% Pt loading realized on fe-CNFs. The maximum open circuit potential (OCP) and power density was achieved 0.863 V and  $294.7 \text{ mW cm}^{-2}$  compared to commercial Pt/C electrocatalyst (0.792 V and  $205.2 \text{ mW cm}^{-2}$ ), respectively [16]. At the other study, Hezarjaribi et al. investigated Pani/CNF electrospun nanofibers as both catalyst supports and modification of GDL to improve their properties. Average nanofibers diameter was determined as 100 nm. The cyclic voltammetry (CV) results proved that modified GDL were able to improve higher current density ( $15 \text{ mA cm}^{-2}$ ) compared with commercial Pt/C ( $10 \text{ mA cm}^{-2}$ ) [17].

### **3.2. Nanostructured non-carbon based GDLs**

The usage of nanostructured carbon materials have certainly enhanced the performance of the catalyst support used for GDL in PEM fuel cell as they display strong effect on the catalyst durability and behaviour. Unfortunately, carbon corrosion is still the most important problem for these systems. Therefore, there is immediate necessity to investigate non-carbon supports to overcome these issues.

#### **3.2.1. Inorganic metal oxides-based GDLs**

Titanium oxide or titania materials are potential alternative as catalyst support in fuel cells due to their excellent properties such as high corrosion resistance, high electrochemical stability, cost-effective, non-toxic and easily available. In this direction, Fang et al. have prepared the GDL by coating titanium on an anode side by direct current sputtering to improve durability and performance of PEM fuel cell. The MEA with titanium-coated GDL, with 10 min sputtering time, showed the best performance at  $25 \text{ }^\circ\text{C}$  with corresponding power densities 58.26% higher than that of MEA without titanium coating [18]. At the other work, an oriented ultrathin catalyst layer (UTCL) has been fabricated based on high electrical conductivity  $\text{TiO}_2$  nanotubes (TNTs) for fuel cell application by Zhang et al. The prepared oriented UTCL exhibited a maximum power density of 206 and  $305 \text{ mW cm}^{-2}$  with ultralow Pt loading of 24.8 and  $50.1 \text{ } \mu\text{g cm}^{-2}$ , respectively [19].

The titanium-oxygen system involves sub-stoichiometric composition of the general formula  $\text{Ti}_n\text{O}_{2n-1}$  (magneli phases), where n is a number between 4 and 10. Among the distinct oxides,  $\text{Ti}_4\text{O}_7$  displays the high electrical conductivity and oxidation-resistance properties that would be a possible candidate for GDL material in fuel cells. To this end, Yao et al. reported synthesis of fiber-like nanostructured  $\text{Ti}_4\text{O}_7$  (NS-  $\text{Ti}_4\text{O}_7$ ), which has the specific surface area of  $26 \text{ m}^2/\text{g}$ , to

use as fuel cell catalyst support in oxygen reduction catalysis. The prepared Pt/ NS-  $Ti_4O_7$  catalysts displayed superior durability as well as enhanced Pt mass activity in comparison to commercial Pt/XC-72 [20].

Tungsten oxides ( $WO_x$ ) exhibit significant proton transfer because of the formation of tungsten trioxide hydrates, which is an charming feature in usage for fuel cell catalyst supports. Rajeswari et al. synthesized  $WO_3$  nanorods, which dimensions varied in the ranges of 130-480 nm and 18-56 nm of length and width, respectively. Pt nanoparticles (4-6 nm) were supported on  $WO_3$  nanorods (20 wt% Pt). The activities of Pt/  $WO_3$  nanorods was approximately six times higher than that of Pt/  $WO_3$  bulk, clearly specified that the nanostructure of the catalytic support plays an main role [21].

Zirconia ( $ZrO_2$ ), when modified with anions such as sulfate, forms a highly acidic or super-acidic catalyst that displays superior catalytic activity. Moreover, considering its high hydrophilicity, high proton conductivity, the S- $ZrO_2$  might enhance the cell performance. On this basis, Suzuki et al. examined sulphate zirconia as Pt support for use in PEM fuel cell. The particle size of the S- $ZrO_2$  was approximately 50-100 nm. Pt was deposited on S- $ZrO_2$  nanoparticles by using ultrasonic spray pyrolysis. In the absence of Nafion ionomer, the cell performance of Pt/ S- $ZrO_2$  cathode was higher than that of Pt/C [22].

Silicon dioxide ( $SiO_2$ ) or silica is well known for its hardness and exists in various crystalline as well as amorphous forms. The use of silica as support material for Pt at the cathode electrode in fuel cell has been investigated by Seger et al. [23]. The average size of  $SiO_2$  core was found as 4 nm. The as-prepared  $SiO_2$ -Pt core-shell particle structure was examined as cathode catalyst in MEA. The authors compared the performance of Pt/  $SiO_2$  to that of commercial E-TEK. The best power densities were reported for the sample with Pt:  $SiO_2$  ratio of 2:1. Similar ohmic losses were surveyed in current interrupt (CI) tests for both Pt/  $SiO_2$  and E-TEK samples.

### 3.2.2. Carbides

Carbides are compounds comprised of carbon and a less electro-negative element. Carbides are expected to be used as catalyst supports, which might promote catalytic activity through synergistic effects. More recently, the usage of tungsten carbides as support in GDL for low temperature fuel cells has accepted considerable attention. Zhang et al. compared the electrochemical activity and stability of  $W_xC_y$  supported Pt with that of carbon supported Pt in PEM fuel cell. Electrochemically active surface area (ESA) loss of Pt/  $W_xC_y$  during the stability test in 0.5 M  $H_2SO_4$  at several potentials was much lower than Pt/C. Before stability test, the performance of Pt/C in PEM fuel cell was better than Pt/ $W_xC_y$ . However, after stability test, the single cell prepared with the Pt/ $W_xC_y$  catalyst exhibited a better performance than the cell with Pt/C, denotive of a high oxidation resistance of the Pt/ $W_xC_y$  catalyst [24].

Silicon carbide (SiC) has been proposed to be an interesting possible catalyst support due to its high-temperature stability, hardness and chemical inertness properties. Silicon carbide is low electrically conductive material, therefore in order to further enhance electronic conduction in the fabrication of GDL, a carbon black should be also used with Pt/SiC. Rao et al. attempted to prepare a nano SiC-supported Pt nanoparticle catalyst. Their electrochemical measurements

specified that the oxygen reduction reaction (ORR) activity and degradation of performance of the Pt/SiC catalyst were similar to that of Pt/C (E-TEK) catalyst [25].

### 3.2.3. Electronically conducting polymers (ECPs)

Electronically conducting polymers (ECPs) are significant materials because of their unique chemical, optical, mechanical and electronic features, easy preparation and practicable application in electrochemical energy conversion.

Among ECPs, polyaniline (PANI) is a charming material to be used as catalyst support because of its high electronic conductivity in its partially oxidized state. Chen et al. [26] and Liu et al. [27] have investigated a PANI nanofiber-supported Pt catalyst and a PANI nanowire-supported Pt catalyst, respectively. They found that nanostructured PANI-supported Pt could improved electrochemical active surface area and enhanced catalytic activity when compared to bulk Pt electrodes. According to TEM and XRD analysis, the supported Pt nanoparticles had an average particle size of 1.5-5 nm. In order to improve mechanical properties and electrochemical stability of Pt/PANI electrode, Huang et al. prepared a Pt/PANI-PSS (poly(styrene sulfonic acid)) catalyst on GDL for fuel cell. The Pt/PANI-PSS composite electrode displayed a much higher electrocatalytic activity than Pt/PANI [28]. At the other work, Zamani et al. prepared one-dimensional nanofibers by electrospinning an iron-polyaniline/polyacrylonitrile (Fe-PANI-PAN) metal-polymer blend, followed by subsequent heat treatment. The addition of 10 wt. % PANI to the electrospinning mixture provides 100 and 70 mV improvements to the ORR onset potential and half-wave potential, respectively. The high activity is attributed to the porous structure of the nanofibers, combined with increased nitrogen contents provided by the PANI incorporation [29].

Polypyrrole (PPY) with the high electrical conductivity is a feasible catalyst support for PEM fuel cell applications. Nanostructured PPY materials have also attracted special attention, due to their large surface area, excellent charge transport features and high electronic conductivity. For example, Li and Lin worked the electrocatalytic activity of PPY nanowire/Pt nanocluster composites on a glassy carbon electrode toward the ORR using CV method. This PPY-supported Pt catalyst on the electrode displayed large surface area and higher electrocatalytic activity for the ORR than that for pure Pt modified electrode [30].

## Conclusions

The GDL is a fundamental component of PEM fuel cells. The preference of materials for GDL will depend on the essential multi-functionality of its structure. Nanostructuring (reducing of dimensions) and nano-architecturing (designing nanometer-scale layers) are key points in the improvement of high performance GDL for PEM fuel cells. Development on nanosized materials is vital to overcome the major commercialization barriers of durability and cost.

For nearly two decades, the GDL evidenced great influence on the stability and performance of PEM fuel cells. The recent researches and developments of nanostructured gas diffusion layer materials exhibiting promising performance were overviewed. Various nanomaterials and attempts used for novel GDL development were summarized in the present work.

## Future Prospects

In order to meet some of nanostructured material requirements for new GDL development, the following research area can be recommended:

- Developing novel synthesis methods to modify and originate new nano-materials, which have improved electronic conductivity, insolubility, electrochemical and thermal stabilities, as well as high surface area. For instance, material doping strategies have been tried to be an effective way to enhance conductivity, solubility, and electrochemical and thermal stabilities. Modifying the composition of nano-materials for GDL such as the ratio of components can also develop the GDL's properties and make them feasible GDL materials. Regarding support surface area improvement, synthesis of nanostructured material particles such as nanotubes, nanospheres, nanorods, nanofibers, and nanohierarchical structures should be an effective way to achieve high surface areas and improve the catalytic activity.
- Developing catalyst deposition strategies to make a uniform dispersion of nano-sized Pt or Pt alloy particles on the GDL, and a strong synergistic interaction between the catalyst and GDL structure. This strategy could produce positive electronic and chemical interactions between the catalyst particle and the GDL. Interaction improvement of metals like nano-sized Pt or Pt alloy catalysts with nanostructured noncarbon supports for GDL through various experimental approaches would be an interesting research area in the effort to improve both the stability and the activity of noncarbon-supported Pt-based catalysts in PEM fuel cell applications. The research objectives would be (i) enhancing the electronic conductivity of the GDL, (ii) increasing the surface area of the GDL, (iii) improving the physicochemical stability of the GDL, and (iv) developing catalysts with a highly uniform distribution of nano-sized Pt or Pt alloy.
- Establishing a fundamental understanding of the nanostructured carbon or noncarbon support for GDL through both experimental and modeling approaches, for instance, exploration of morphology effects of nanostructured carbon or noncarbon-supported catalyst on both the catalytic activity and the stability, as well as the interaction between the catalyst and support particles on the GDL for the oxygen reduction reaction. Theoretical modeling such as quantum chemical calculation should supply some guidance for the down-selection of new supports and their supported catalyst designs.
- Optimizing fuel cell design and operation to prevent the catalyst difficulties and encourage the advantages of the nano-sized catalyst material. As mentioned previously, it will be extremely difficult to have a catalyst material that can meet all requirements.

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