Fabrication of GDL microporous layer using PVDF for PEMFCs

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Abstract. The Gas Diffusion Layer(GDL) of fuel cell, are required to provide both delivery of reactant gases to the catalyst layer and removal of water in either vapor or liquid form in typical PEMFCs. In this study, the fabrication of GDL containing Micro Porous Layer(MPL) made of the slurry of PVDF mixed with carbon black is investigated in detail. Physical properties of GDL containing MPL, such as electrical resistance, gas permeability and microstructure were examined, and the performance of the cell using developed GDL with MPL was evaluated. The results show that MPL with PVDF binder demonstrated uniformly distributed microstructure without large cracks and pores, which resulted in better electrical conductivity. The fuel cell performance test demonstrates that the developed GDL with MPL has a great potential due to enhanced mass transport property due to its porous structure and small pore size.

1. Introduction

In proton-exchange membrane fuel cells(PEMFC), gas diffusion layer(GDL) serves as current collectors that allow ready access of fuel and oxidant to the anode and the cathode catalyst surface.

Usually, the catalyst layer is reinforced by a thick porous electrode support layer. In PEM fuel cell, this electrode support layer is called a gas diffusion layer(GDL). The GDL protects the delicate catalyst structure, provides mechanical strength, allows easy gas access to the catalyst, and enhances electrical conductivity[1,2]. The gas Diffusion Layers (GDLs) of fuel cell are required to provide both delivery of reactant gases to the catalyst layer and removal of water in either vapor or liquid from in typical PEMFCs. A Microporous layer (MPL) reduces the contact resistance between catalyst layer and macroporous substrate [3,4]. Primary purpose of MPL is water management, as they provide effective wicking of liquid water from the cathode catalyst layer into the diffusion media. It also may have utility in reducing electrical contact resistance with the adjacent catalyst layer. The properties of microporous layers can be adjusted by changing the carbon, specifically the particle and agglomerate structure, and the hydrophobicity. Owing to its superior thermal ability and resistance to chemical degradation, PTFE is used in majority of gas diffusion electrodes as a hydrophobic binder. Though, PTFE is insoluble in any known solvent; it can be prepared at high temperature sintering processes from powder or suspension, which results in increase in the cost of PEMFC. With the aim of producing a low-cost, easy to prepare gas diffusion electrodes with favorable chemical and electrical properties, a method for obtaining gas diffusion electrodes based on poly(vinylidene fluoride) (PVDF)-carbon blends via phase inversion was firstly detailed by Cabasso et al.[5] PVDF matrix demonstrates lower physical and chemical properties than PTFE; especially PVDF has lower melting temperature (160–180 °C) than PTFE(327 °C). Also, it was proved that PVDF coated on carbon cloth
shows good impact and compressive strength, as well as improved wear resistance and higher thermal conductivity. Besides, PVDF has more advantages than PTFE, including low cost, easy processing property and etc.

In this study, the fabrication of GDL containing Micro Porous Layer(MPL) made from the slurry of PVDF(Polyvinyliden Fluoride) mixed with carbon black is investigated in detail. The microstructure of the developed GDL containing MPL was analyzed by SEM/EDX by observing the surface and cross section of the specimen. The properties, such as electric conductivity, permeability and porosity were measured. The amount of carbon loading to get optimum thickness was defined, and the performance of the fuel cell using developed GDL with MPL was evaluated.

2. Experimental procedure

Commercial carbon cloth was cut out into pieces and washed in acetone to remove dust or undesirable matters. Later, the washed carbon cloths were dried at 50°C for 2hours. 30wt% of PTFE emulsion (Du Pont) was diluted to make 3wt% aqueous solutions. The dried carbon cloths were dipped entirely in the different PTFE solutions for 30 seconds and dried again at room temperature for 5hours. After then, the samples were heat-treated in 350°C at air.

In order to prepare carbon slurry for MPL, carbon powder (Vulcan XC-72R) was mixed with PVDF in the ultrasonic bath for 2hours. The obtained carbon slurry was coated onto one side of woven carbon cloth gas diffusion-backing layer(E-TEK Division) by doctor blade method, and successively dried at 80°C for 30min. The MPL coated GDL sample was heat treated at 180°C for 1hours to distribute PVDF homogeneously through the MPL. The microstructure of the developed GDL containing MPL was analyzed in SEM/EDX by observing the surface and cross section of the specimen. The properties such as electric conductivity and pore size were measured. The bubble point method using a capillary flow porometer CFP-1500AEL (PMI, USA) was selected for the measurement of the mean flow pore diameter. The amount of carbon loading to get optimum thickness was defined, and the performance of the fuel cell using developed GDL with MPL was evaluated. The performance of the developed single cell was evaluated at 80°C in a fuel cell test station, using H₂ and O₂ gases as fuel gas with 500 sccm and 300 sccm flow rates, respectively. Nafion® 117 with 5 x 5cm² was used as a membrane and the active area of electrode was 5cm².

3. Results and Discussion

Figure 1. Scanning Electrode Microscopy(SEM) images of the commercial PTFE MPL-coated GDL(a-b) and PVDF-based MPL-coated GDL. (c-d))

SEM photographs of the surface morphology of a microporous layer with PTFE and PVDF binders are shown in Figure 1. The microstructure of the microporous layer with PTFE binder was characterized by a large number of coarse cracks and pores on the surfaces (Figure 1(a-b)).

The presence of large cracks and open pores on the surface of diffusion layer isn’t desirable because they lead to poor electrical conductivity. Besides, the Pt catalyst particles might fall into the open cracks and pores which results in reduced support for the catalyst.

In the case of the microporous layer with PVDF binder, the microstructure of the diffusion layer was uniformly distributed on the layer (Figure 1(c-d)). The microstructure with uniform distribution and without large crack and pore was desirable to get better electrical conductivity, as well as good support of the Pt catalyst.
Figure 2 shows the MPL resistance and gas permeability as a function of PVDF concentration. As it can be seen that the conductivity and gas permeability were increased with decreasing the PVDF contents. It was observed that the MPL on carbon cloth change the physical properties of GDL and changed the cell performance. The analysis of results proved that the lower ratio of PVDF resulted in lower resistance. However, a steady increase in the gas permeability values was observed with decreased ratio of PVDF. This phenomena could be explained by low porosity due to small amount of PVDF binder. Thus, it can be assumed that the further decrease of PVDF ratio would result on lower resistance, but in higher gas permeability values.

![Figure 2](image-url)

**Figure 2.** Effect of PVDF concentration on MPL surface resistance and gas permeability.

The pore size distribution in PTFE-based MPL and PVDF-based MPL is illustrated in Figure 3(a) and summarized in table shown in Figure 3(b). The pore size of commercial non-treated carbon cloth was 81.40 μm. The analysis showed that using traditional PTFE binder resulted in considerable decrease of pore size distribution down to 48.97 μm. However, there are some drawbacks of using PTFE binder, such as relatively higher surface resistance and lower gas permeability values. These drawbacks can be eliminated by using PVDF binder instead. The results indicate that the concentration ratio of PVDF/Vulcan was key parameter for controlling the pore size distribution. When using high concentration of PVDF, the pore size could be successfully decreased down to 67.30 μm. Though, as shown in Figure 2, high concentration of PVDF resulted in relatively higher surface resistance and lower gas permeability, which were undesirable for fuel cell performance. Decreasing the PVDF concentration to 40% allowed to decrease the pore size as low as 53.73 μm, which was close to one of traditional PTFE-based MPL.

![Figure 3](image-url)

**Figure 3.** The diagram (a) and table (b) of pore size distribution measured in PTFE-based MPL and PVDF-based MPL with different PVDF concentration.

| Sample Description                                      | Average Pore Size (μm) |
|---------------------------------------------------------|------------------------|
| 1. Non treated carbon cloth                             | 81.402                 |
| 2. PTFE-based Microporous layer (3wt.% PTFE treated carbon cloth) | 48.9753                |
| 3. PVDF-based Microporous layer (PVDF/Vulcan=6/4) (3wt.% PTFE treated carbon cloth) | 67.3055                |
| 4. PVDF-based Microporous layer (PVDF/Vulcan=5/5) (3wt.% PTFE treated carbon cloth) | 59.7666                |
| 5. PVDF-based Microporous layer (PVDF/Vulcan=4/6) (3wt.% PTFE treated carbon cloth) | 53.735                 |
During the cell operation, gas mixture is delivered by convention from cathode towards catalyst through GDL. Therefore, good mass transportation is very important to enhance the cell performance. In order to examine the effect of binder type on fuel cell performance, different types of gas diffusion layers were prepared. Figure 4 shows cell potential-current density plots and power density plots of non-treated carbon cloth GDL, PTFE MPL-coated GDL and PVDF-based MPL coated GDL. From the plots it can clearly be observed that the cell performance varied with different microporous layer. Fuel cell performance analysis showed that PVDF-based MPL demonstrated considerably higher power density values than those of other samples. This phenomenon could be explained by appropriate in-plane and through-plane microstructure of PVDF-MPL coated GDL. Due to symmetric porous structure and small pore size, the in-plane and through-plane mass transport in PVDF-MPL coated GDL could be enhanced.

![Figure 4. Potential-current density plots and power density plots of non-treated carbon cloth GDL, PTFE MPL-coated GDL and PVDF-based MPL coated GDL.](image)

4. Conclusions

Different types of GDL containing Microporous layer have been prepared from slurries. The effect of binder type and PVDF concentration ratio on resistance, gas permeability and cell performance has been investigated. The PEM fuel cell performance test demonstrated that the presence of PVDF-based MPL potentially reduced mass transport losses within the GDL at current densities, thus, resulted in enhancement of the cell performance.

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