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# Effect of Gas Diffusion Layer With Double-Side Microporous Layer Coating on Proton Exchange Membrane Fuel Cell Performance Under Different Air Inlet Relative Humidity

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The effects of cathode gas diffusion layer (GDL) with double-side microporous layer (MPL) coating on the performance of a proton exchange membrane fuel cell (PEMFC) are tested under different relative humidity (RH) at air inlet. Standard commercial SGL® 10BA carbon paper is used as the substrate of GDL and it is coated with MPL on both sides of the paper with different carbon loadings and polytetrafluoroethylene (PTFE) contents. Acetylene black is used as the carbon powder in the MPL composition. A single cell testing apparatus with adjustable RH at air inlet is constructed to measure the cell performance. The results show that the cell performance could be enhanced greatly under low air RH conditions by the employment of such a GDL with double-side MPL coating. The peak power density obtained at extremely low air RH condition may be increased more than 85% in comparison with that of conventional GDL with single-side MPL coating. The optimal compositions of MPL on the surfaces facing to the catalyst layer and flow-channel plate are found to be 1.2 mg/cm$^2$ and 0.3 mg/cm$^2$, respectively, with the same PTFE content of 20 wt.% in both the MPLs.

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**Keywords:** double-side microporous layer, carbon loading, PTFE content, air relative humidity

## 1. INTRODUCTION

The air humidity is an important factor affecting the performance of a proton exchange membrane fuel cell (PEMFC). In order to increase the volumetric power density, one developing trend of PEMFC design is to remove the complicated humidification system and make the Membrane-Electrode-Assembly (MEA) to be able to work normally under low air relative humidity (RH) conditions. To fulfill this requirement, it is important to maintain the water content in the polymer electrolyte membrane at low air RH conditions. Thus, the microporous layer (MPL) plays an important role especially in the cathode site since it is a key component for the water balance in the MEA [1-2].

The MPL is a thin layer coated on the gas diffusion layer (GDL) surface facing to the catalyst layer, which generally consists of carbon powder and hydrophobic agent like polytetrafluoroethylene (PTFE) or fluorinated ethylene propylene (FEP). It has been found that the employment of MPL may lower the liquid water saturation in the cathode gas diffusion media and improve the water transport performance in the adjacent catalyst layer [3]. However, it also may lower the gas permeability due to the micro pores in MPL structure and thus cause higher gas transport resistance [4]. Therefore, it is essential to explore the effect of MPL design on the cell performance in order to operate a PEMFC at low air RH conditions.

Numerous investigations have been devoted to the research of gas diffusion media and explored its influence on fuel cell performance. Detailed reviews for the materials, designs, and characterization techniques for gas diffusion layers in PEMFCs have been reported recently [5-7]. Most these studies generally considered the conventional situation that the MPL is coated on the side of GDL next to catalyst layer and air stream is fully humidified. The effect of different carbon powders for MPL on cell performance had been tested in the studies [8-9], in which acetylene black was found to present the better cell performance. In the works of Wang et al. [10-11], they proposed a novel MPL made with composite carbon powder of acetylene black carbon and Black Pearls 2000 carbon by adding different MPLs on each side of carbon paper. Their results show that such a MPL design can reach a bi-functional structure which maintains good transportation of both reactant gases and liquid water. Recently, the effect of double-side MPL coating has been evaluated further by considering different kinds of carbon black [12]. Acetylene black was also found to give the best cell performance with appropriate amount carbon loadings on both sides of GDL. However, it is still unclear whether such a gas diffusion media design is beneficial to improve the cell performance under low air RH conditions, which motivates the present study. Several investigations focusing on the degree of humidification in air stream and its influence on cell performance have been proposed in the literature [13-18]. A detailed discussion for these investigations could be found in the work [18].

In the present study, the effect of cathode GDL with double-side MPL coating on the performance of a PEMFC is evaluated under different RH in air stream. Acetylene black is employed in the experiments and the optimal carbon loading on each side of GDL is tested in order to enhance the cell performance under insufficient air humidification. The optimal loading of hydrophobic agent PTFE in the MPL on each side of GDL is also evaluated. The technique of electrochemical impedance spectroscopy (EIS) is used to measure the variations of ohmic losses, charge transfer losses, and mass transfer losses with different gas diffusion media fabricated by a double-side MPL coating. The results clarify the possibility for the improvement of PEMFC performance at low air RH conditions by a novel GDL design with double-side MPL coating and benefit the optimization of cathode MPL structure.

## 2. EXPERIMENTAL

### *2.1 Preparation of microporous layer and MEA*

The commercial carbon paper SGL® 10BA with 5 wt% PTFE content was used as the substrate for GDL in the cathode side. MPL was coated on both sides of the carbon paper, which consists of carbon black and PTFE. Acetylene black was used in all the experiments as the carbon black in MPL. The detailed specification of acetylene black could be found in the works [10-11]. The carbon paper was first washed by acetone before the coating of MPL on its surface in order to remove possible surface contaminants. Carbon slurry was prepared from a mixture of carbon powder and ethylene glycol with a pre-assigned weight percentage of PTFE. The mixture was sonicated in an ultrasonic cleaner and then agitated by a dispersing instrument for 1 h in each process to ensure sufficient mixing of the carbon powder and PTFE. Next, the carbon slurry was sprayed uniformly on the surface of the carbon paper and then dried in a convection oven at 90 °C. This spraying and drying process repeated several times until the carbon loading reaches the assigned value to form the MPL. The same procedures were applied on the other surface of the GDL. Finally, the carbon paper with double-side MPL coating was drying further at 240 °C for 30 min and then sintered in a high-temperature oven at 350 °C to complete the MPL coating processes. The MEA was made by a catalyst-coated proton exchange membrane (CCM) with two GDLs on opposite sides of the CCM. The GDL with double-side MPL coating was used in the cathode side to test its effect on fuel cell performance. The commercial carbon paper SGL® 10BC was used in all the experiments as the GDL in the anode side. The CCM was produced by Nan-Ya® with series number bMEA5. Both GDLs were attached to the CCM directly to form the MEA. The dimensions of reaction area on the CCM are 5 cm×5 cm.

### *2.2 Fuel cell performance test*

A single cell was constructed to test the fuel cell performance, which comprise the MEA, graphite flow field plates, current collectors, and end plates. The flow field plates were made of Poco graphite material AXF-5QC with a two-parallel serpentine channel design. The current collectors were made of copper with a coating of pure gold on their surfaces. The border of the MEA was surrounded by gaskets which were made of soft polymer material in order to prevent possible leakage of reaction gases. A Hephas® P-300 fuel cell test station was used to measure the cell performance and acquire the polarization curves. Pure hydrogen and compressed air were employed respectively as the fuel and the oxidant and both reactant gases were humidified by bubbling through distilled water tanks held at a pre-assigned temperature. The temperature of water tank for hydrogen gas was held constantly at 70 °C, while the temperature of water tank for air was adjustable in order to obtain the desired RH at the air inlet of fuel cell. Both hydrogen and air streams flow through an electrical heating pipeline before entering the fuel cell and the heating power is adjustable to make sure the reactant gases enter the fuel cell at 70 °C. The temperatures were all monitored by burying thermocouples at the exits of water tanks and the gas inlets of fuel cell. In order to obtain steady gas temperature at the inlets of fuel cell, humidified hydrogen and air were delivered at constant flow rates of 600 and 2000 sccm, respectively, in all the tests. The RH of air at the exit of water tank was calibrated under various temperatures to ensure the air stream was fully humidified after bubbling through the tank. Therefore, the RH of air at the inlet of fuel cell can be determined based on the temperature difference. By adjusting the air humidification temperature in the range of 30-70 °C, the RH at the inlet may vary between 13.6-100%. The fuel cell temperature also keeps at 70 °C by electrical pipe heaters.

The cell potential was recorded from open circuit voltage (OCV) to 0.3V by increasing the current density to obtain the polarization curve. The individual contribution of the cell resistance was further analyzed by a frequency response analyzer (FRA) module added to an Autolab PGSTAT 302N potentiostat to perform the EIS measurement. The impedance spectra were recorded by scanning frequencies over the range of 10 $\mu$Hz to 1MHz, in which the amplitude of the AC current was held at 5% of that of the DC current. An equivalent circuit was further employed to analyze the obtained spectra in order to clarify the influence of double-side MPL coating on the ohmic resistance, charge transfer resistance, and gas transfer resistance under various air RH conditions.

## 3. RESULTS AND DISCUSSION

### *3.1 Effect of carbon loading on the double-side MPLs*

We first pay attention to the effect of carbon loading and then evaluate the influence of PTFE content in the MPLs coated on both sides of cathode GDL.

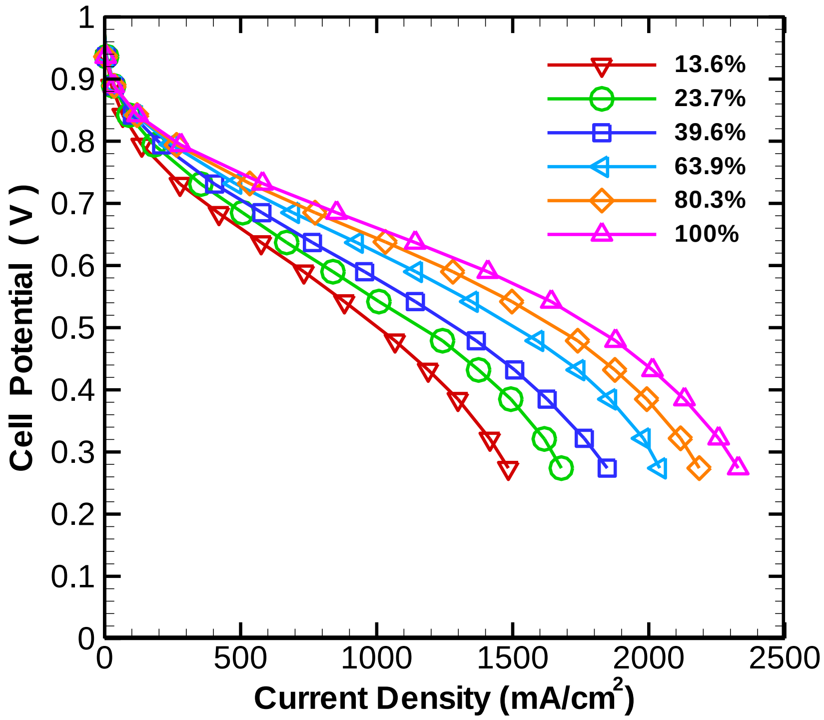


**Figure 1.** Polarization curves at different air RH. The carbon loadings are 1.2/0.3 mg/cm$^2$ on both sides of GDL facing to the catalyst layer/flow channel, respectively.

Figure 1 shows the polarization curves at different air RH for the typical case with carbon loadings 1.2/0.3 mg/cm$^2$ on the surfaces facing to the catalyst layer/flow channel, respectively. The PTFE content is fixed at 20 wt.% in both the MPLs. Obviously, the cell performance depends significantly on the degree of humidification in the air stream. The best cell performance was observed at fully humidification condition. Once the air RH decreases, the cell performance degrades gradually. Similar results also can be observed at the other cases with different combinations of carbon loading in the double-side MPLs. The results are summarized as illustrated in Fig. 2(a) by the variations of peak power density with air RH and in Fig. 2(b) by the variations of limiting current density measured at cell voltage 0.3V with air RH. The total carbon loading of both the MPLs is fixed at 1.5 mg/cm$^2$ in all the tests. It is found that the double-side MPL coating on the cathode GDL surfaces indeed can effectively enhance the fuel cell performance especially when the humidification in air stream is insufficient.

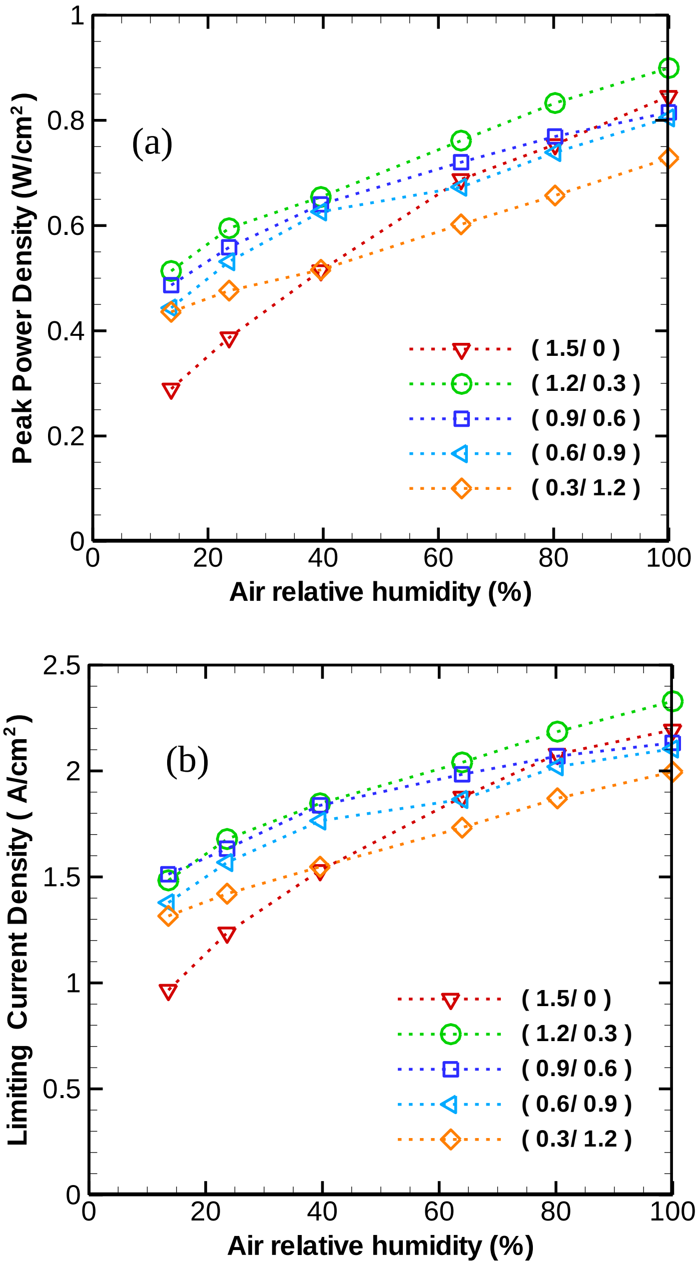


**Figure 2.** Variations of (a) peak power density and (b) limiting current density with air RH at different carbon loadings on both sides of GDL facing to catalyst layer/flow channel in unit of mg/cm$^2$. The total carbon loading is fixed at 1.5 mg/cm$^2$.

For example, under the condition of extremely low air RH 13.6%, the peak power density is only approximately 0.28 W/cm$^2$ for the case of traditional single-side MPL coating with carbon loading 1.5 mg/cm$^2$ on the surface of GDL facing to the catalyst layer, which is the general structure of gas diffusion media in PEM fuel cells. When a small amount of MPL is coated on the other side of GDL facing to the flow channel, the cell performance is improved significantly and the peak power density is almost double which increases dramatically to about 0.52 W/cm$^2$ as shown in the case of 1.2/0.3 mg/cm$^2$. However, once the amount of carbon loading on the flow-channel side increases further, the cell performance begins to degrade gradually. But even the case of carbon loading combination 0.3/1.2 mg/cm$^2$ still possesses higher peak power density than the case of single-side MPL coating. These results indicate that an additional MPL coating on the other side of GDL facing to the flow channel is helpful for the enhancement of fuel cell performance at low air RH condition, and a small amount of carbon loading in this MPL is favorable since an over amount of carbon loading results in worse cell performance. When the air RH increases, the peak power density in each case rises gradually. Particularly, the case of single-side MPL coating with carbon loading 1.5/0 mg/cm$^2$ exhibits the highest increasing rate than the other cases. However, the case of carbon loading 1.2/0.3 mg/cm$^2$ still gives the highest peak power density when the air stream is fully humidified with 100% RH. That is, a double-side MPL coating with appropriate carbon loadings on both sides of GDL not only benefits the improvement of cell performance at low air RH situations but also enhances the cell performance even though the air humidification is sufficient. The variations of limiting current density with air RH are similar as shown in Fig. 2(b). One can see that the case of carbon loading 1.2/0.3 mg/cm$^2$ presents the highest limiting current density at 100% RH. If the degree of humidification decreases, all the cases with double-side MPL coating still can provide limiting current densities over 1.3 A/cm$^2$ at extremely low air RH 13.6%. In contrast, the limiting current density of the case with single-side MPL coating declines more rapidly and just can reach 0.96 A/cm$^2$.

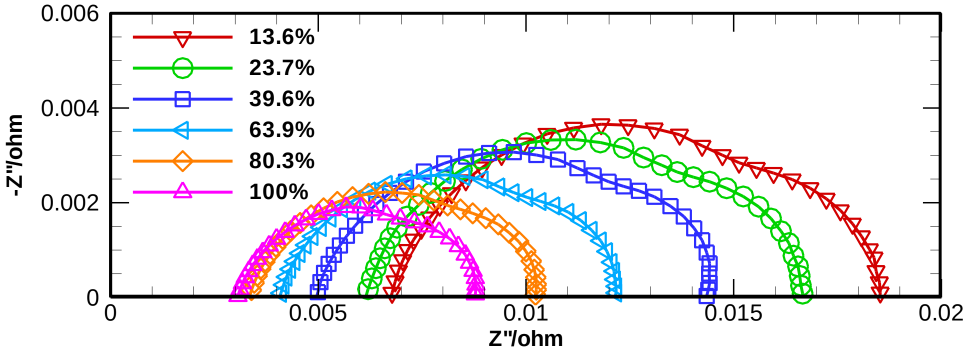
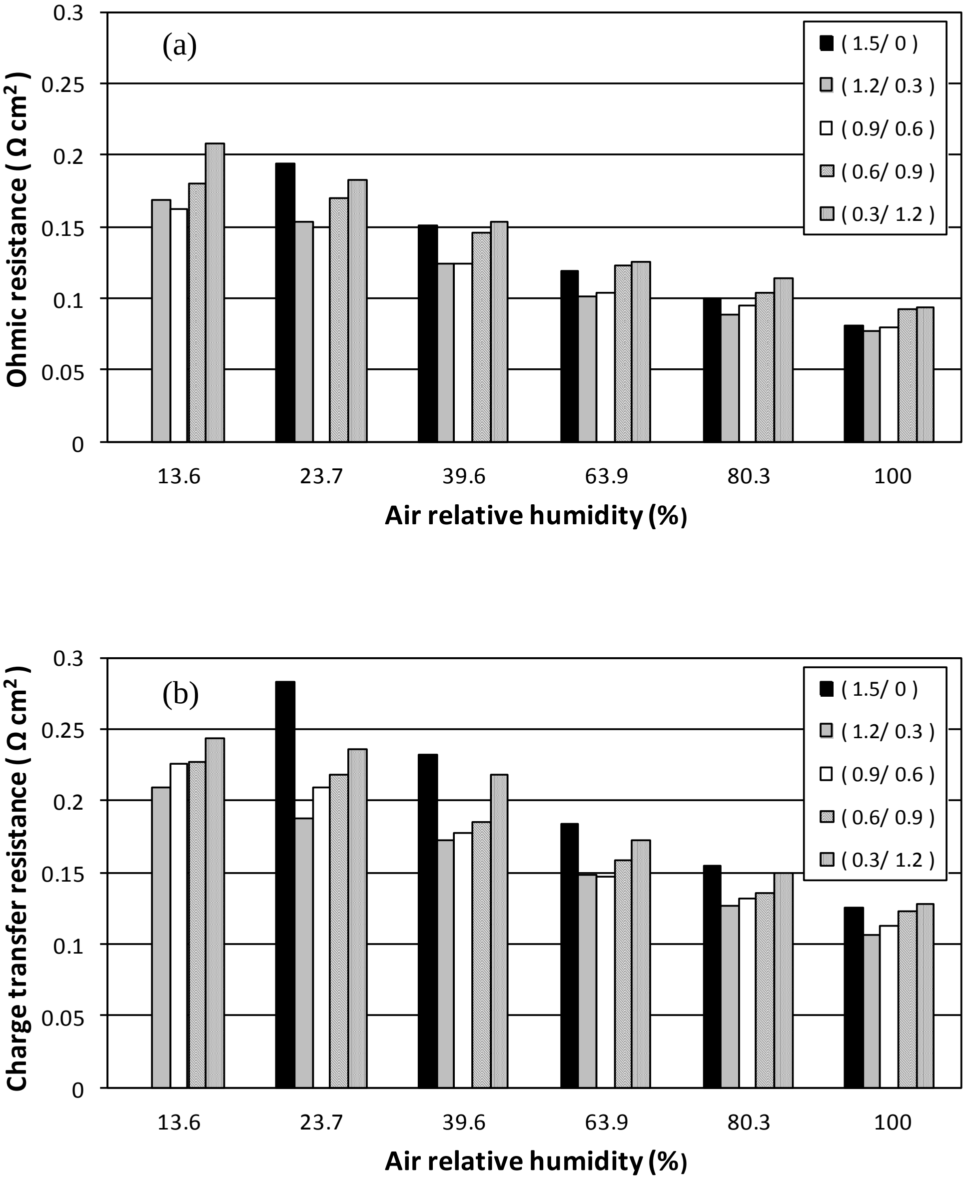


**Figure 3.** Impedance spectra at different air RH measured at current density 1 A/cm$^2$ for the case of carbon loadings 1.2/0.3 mg/cm$^2$ on both sides of GDL facing to catalyst layer/flow channel, respectively.

The effect of double-side MPL coating under various air RH conditions is further characterized by the EIS technique. The obtained spectra are analyzed further to explore the variations in charge transfer resistance, ohmic resistance, and gas transfer resistance. A typical test result is shown in Fig. 3 at current density 1 A/cm$^2$ for the case of carbon loadings 1.2/0.3 mg/cm$^2$. Two distinct arcs can be observed in each spectrum corresponding to a designated air RH condition. The horizontal real axis intercept of the impedance spectrum at the end of the left arc represents the ohmic resistance of the fuel cell. The high-frequency arc on the left mainly reflects the effective charge transfer resistance for the oxygen reduction reaction in the catalyst layer, and the low-frequency arc on the right is attributed to the transport resistance of air within the GDL. As demonstrated in Fig. 3, the ohmic resistance decreases and shifts gradually to the left with increasing air RH. Note that the ohmic resistance in a PEM fuel cell primarily arises from the transport of proton through the electrolyte membrane.



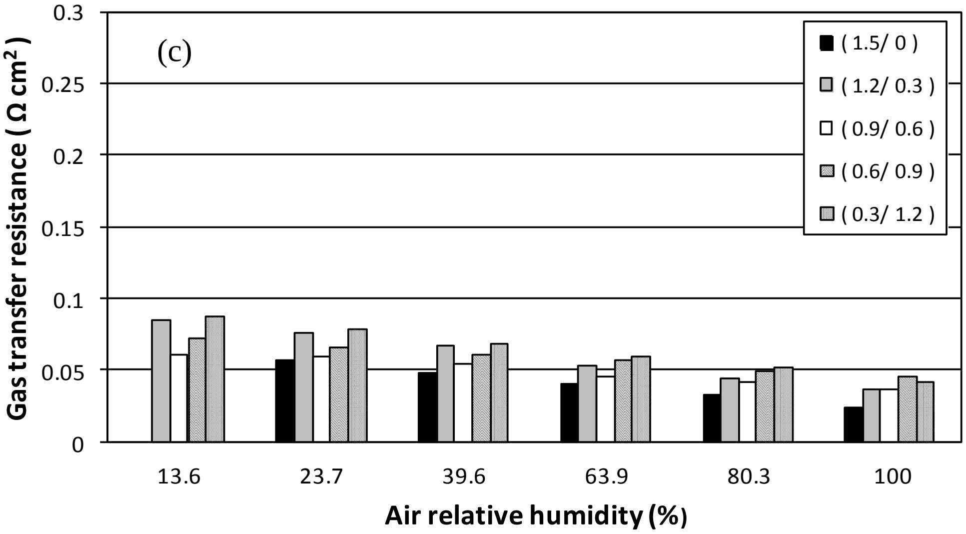


**Figure 4.** Variations in (a) ohmic resistance, (b) charge transfer resistance, and (c) gas transfer resistance with air RH at different carbon loadings on both sides of GDL facing to catalyst layer/flow channel in unit of mg/cm$^2$.

Hence, this result is expectable because higher air RH is beneficial for the maintenance of water content in the membrane, improves the proton conductivity, and reduces the ohmic resistance accordingly. The overall cell impedance measured by the right intercept with the horizontal axis in each spectrum also appears to decrease quickly as air RH increases.

Similar spectra were also obtained for the other cases with different combinations of carbon loading. A generally proposed equivalent circuit for a hydrogen/air PEM fuel cell [19] was used to simulate the impedance data. The results are summarized and illustrated in Fig. 4 (a)-(c). As shown in Fig. 4(a), the ohmic resistance in each case of combination of carbon loading always increases with decreasing air RH. Especially, the increasing rate of the case with shingle-side MPL coating is faster than the other cases with double-side MPL coating. The corresponding data for the case 1.5/0 mg/cm$^2$ is missing at air RH 13.6% because the limiting current density is less than the assigned test point 1 A/cm$^2$. On the contrary, the increasing rates for the other cases with double-side MPL coating is relatively slower and both the cases 1.2/0.3 and 0.9/0.6 mg/cm$^2$ generally have comparable values when air RH is less than 63.9% and determine the lowest ohmic resistance. Similar variations also can be observed in Fig. 4(b) for charge transfer resistance. The charge transfer resistance of the case 1.2/0.3 mg/cm$^2$ is significantly less than that of the case 1.5/0 mg/cm$^2$ and gives the lowest value generally in all the assigned air RH conditions. These results indicate that the cathode GDL with double-side MPL coating indeed can benefit the proton conduction membrane to improve water content and proton conductivity under low air RH conditions in comparison with the common GDL with single-side MPL coating only, and achieve a lower charge transfer resistance. However, a small amount carbon loading on the surface facing to the flow channel is preferable, an excess of carbon loading on this surface will make both the ohmic and charge transfer resistances increase again. The magnitude of gas transfer resistance as shown in Fig. 4(c) is apparently less than ohmic or charge transfer resistance. It is noticed that the case of single-side MPL coating always presents the lowest gas transfer resistance in each case of assigned air RH. This result is reasonable because an additional MPL coating on the other side of GDL may increase the transport difficulty of reactant gas through the gas diffusion media. However, the influence of double-side MPL coating on both ohmic and charge transfer resistances seems to be more crucial and predominates the overall cell performance.

### *3.2 Effect of PTFE content on the double-side MPLs*

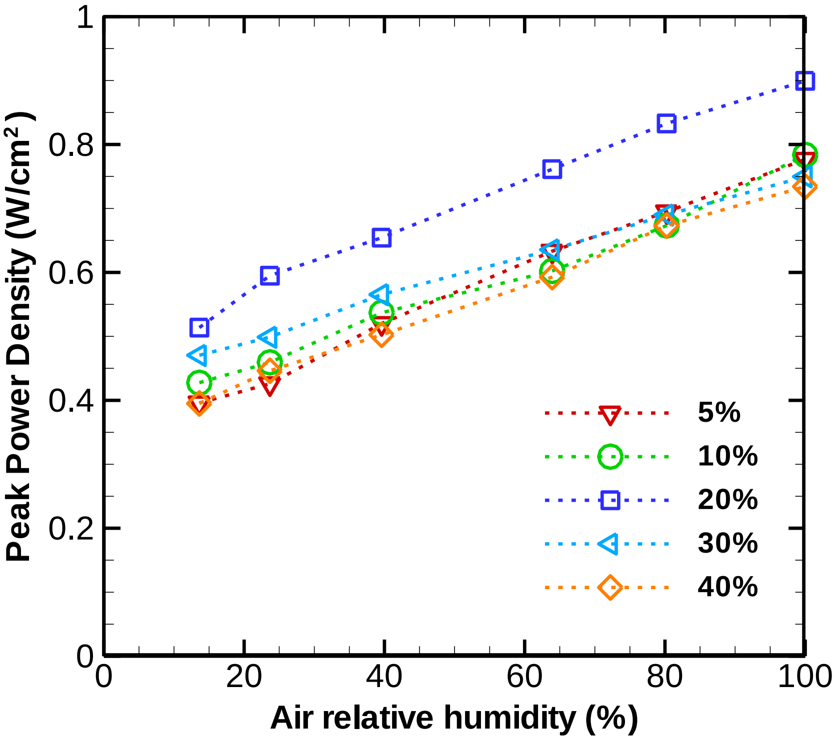


**Figure 5.** Variations of peak power density with air RH at different PTFE contents in the MPL on the side of GDL facing to catalyst layer.

The composition of MPL consists of carbon powder and PTFE. Therefore, the PTFE content in MPL is also an important factor which may influence the cell performance profoundly. In order to explore the effect of PTFE content on the double-side MPLs, we first pay attention to the MPL on the side facing to the catalyst layer and fix the PTFE content on the opposite side at 20 wt.%. The carbon loadings in all the following tests are fixed at 1.2/0.3 mg/cm$^2$ since it demonstrated the best cell performance as discussed in previous subsection. The test results are summarized in Fig. 5 by showing the variations of peak power density with PTFE content at various air RH situations. Obviously, the case of 20 wt.% PTFE always presents the best cell performance with highest peak power density in each assigned air RH condition. The influence of PTFE loading in MPL had been studied previously by Park et al. [2] for the common structure with single-side MPL coating. They found that the MPL porosity decreases with increasing PTFE loading, and a higher pressure is necessary to force the liquid water to penetrate through the gas diffusion media. Hence, a higher PTFE loading in the MPL may impede the water transport from the catalyst layer to the GDL and result in water flooding phenomenon in the catalyst layer, whereas a lower PTFE loading may reduce the hydrophobicity of the MPL and cause water flooding in the gas diffusion media. Consequently, there exists an optimal PTFE content in the MPL for effective transport of reactant gas and liquid water. Here we also find the same result for a GDL with double-side MPL coating that the optimal PTFE content is 20 wt.% in the MPL next to the catalyst layer. As shown in Fig. 5, the optimal PTFE content is invariable with the variation of air RH, which means that an appropriate PTFE content is still quite important for the balance of water saturation in the catalyst layer and gas diffusion media under low air RH conditions.

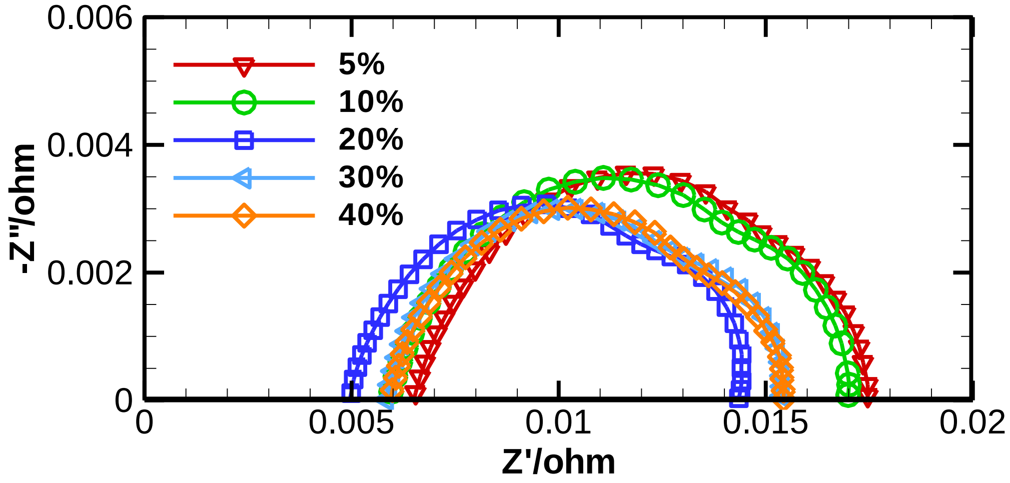
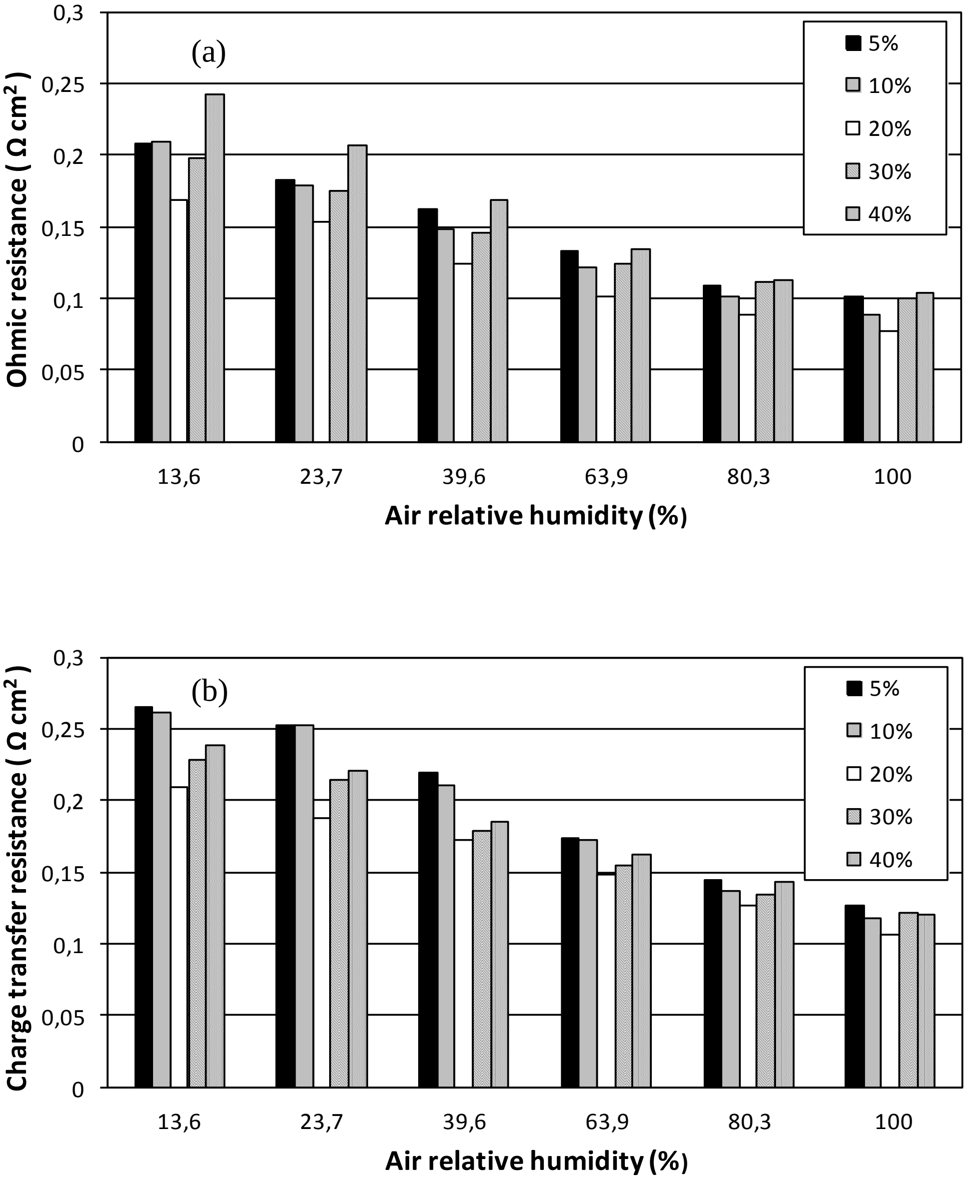


**Figure 6.** Variation of impedance spectra with PTFE content in the MPL next to catalyst layer at air RH 39.6% measured at current density 1 A/cm$^2$.

Figure 6 illustrates the corresponding impedance spectra measured at 1 A/cm$^2$ for the assigned PTFE contents at air RH 39.6%. One can see that the case of 20 wt.% exhibits the lowest ohmic resistance and overall cell impedance. This result indicates that a proper PTFE content in the MPL is crucial for the membrane to maintain water content and proton conductivity when the humidification in air stream is insufficient. All the impedance spectra measured at various air RH conditions with different PTFE contents were further analyzed to examine the variations of ohmic, charge transfer, and gas transfer resistances. The results are respectively illustrated in Fig. 7(a)-(c). It is apparent that the case of 20 wt.% PTFE loading always gives the lowest ohmic resistance and charge transfer resistance in each assigned air RH condition. Similar to the results shown in Fig. 4, the contribution of gas transfer resistance is relatively less significant in comparison with the ohmic and charge transfer resistances. It is also noted that an excessive PTFE loading seems to lower the water content in the membrane and result in higher ohmic resistance especially at low air RH condition. On the contrary, a lower PTFE loading tends to reduce the reaction kinetics in the catalyst layer and cause higher charge transfer resistance particularly when the humidification of air stream is insufficient.

We also have explored the effect of PTFE content in the MPL coated on the other side of GDL facing to the flow channel. The results are similar to those demonstrated in Figs. 5–7. Accordingly, we may conclude that the GDL with double-side MPL coating loaded with the same PTFE content 20 wt.% leads to the best cell performance. Besides, the optimal PTFE loading is independent of the RH in air stream.



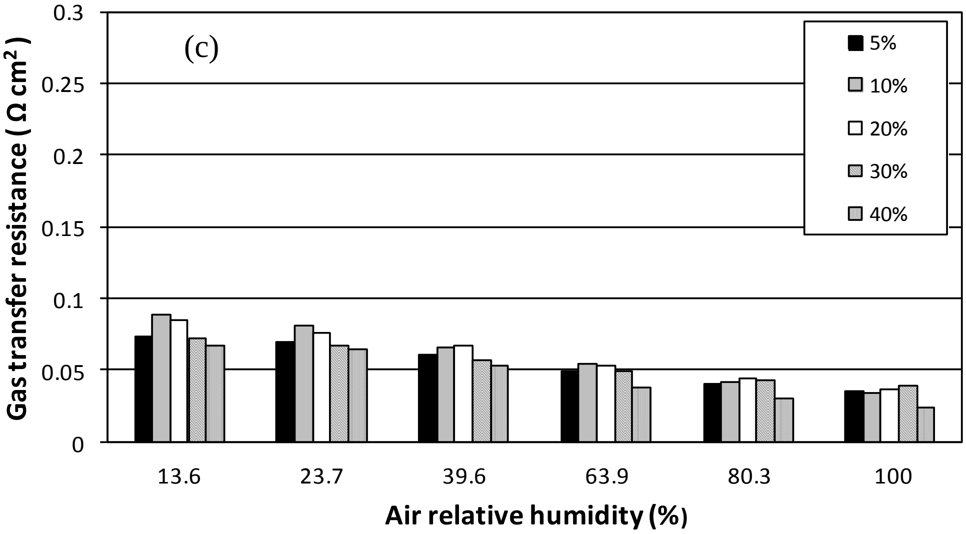


**Figure 7.** Variations in (a) ohmic resistance, (b) charge transfer resistance, and (c) gas transfer resistance with air RH at different PTFE contents in the MPL next to catalyst layer at current density 1 A/$cm^2$.

## 4. CONCLUSIONS

The effect of cathode GDL with double-side MPL coating on the PEM fuel cell performance has been tested under different air RH conditions. The purpose is to evaluate whether it is possible to improve the cell performance by employing a GDL with double-side MPL coating at low degree of humidification in the air stream. Comparing with the traditional GDL with single-side MPL coating, the present results show that a GDL with double-side MPL coating indeed can enhance the cell performance significantly under insufficient air humidification circumstances. Different amounts of carbon loading in the MPLs on both sides of GDL were tested and the influence of PTFE content was also examined. The results show that an appropriate combination of carbon loading is quite important and the set of carbon loadings 1.2/0.3 mg/$cm^2$ always gives the optimal cell performance under various air RH conditions. That is, a small amount of MPL coating on the side of GDL next to the flow-channel plate is particularly beneficial for the improvement of fuel cell performance not only at low air RH situations but also when the air flow is fully humidified. The influence of PTFE content is also quite significant and the optimal PTFE loadings are found to be the same in both the MPLs as 20 wt.%. EIS analyses show that the double-side MPLs with such a composition always exhibit the lowest ohmic resistance and charge transfer resistance. According to the test results, we may conclude that the structure of gas diffusion media plays an important role in the attempt to remove the air humidification device from a PEM fuel cell system and raise the volumetric power density. However, it is worth noting that the fuel cell assembly processes may potentially destroy the brittle MPL structure coated on the surface of GDL facing to the flow channel, and cause the occurrence of carbon particles in the water product and air stream especially after long-term operation. Therefore, it is quite important to avoid possible damage to the double-side MPL structure during assembly procedures and investigate how to improve the stability of MPL structure in the future.

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