Investigation of Different Carbon Materials with Different Coating Methods as Micro Porous Layer for Proton Exchange Membrane Fuel Cells

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Abstract: In this work, two types of carbon - Vulcan XC-72R, and vapor-grown carbon fiber (VGCF, $7\mu m$ in length and 100 nm in diameter) were investigated as materials composing a micro porous layer (MPL). These carbon materials were either sprayed or doctor bladed on commercial carbon paper (GDS 340, CeTech Co., Ltd., Taiwan) to form an MPL with various carbon loadings and various polytetrafluoroethene (PTFE) contain ratio. All of the home-made GDLs were assembly with commercial catalyst coated membranes (CCMs, General Optics Corp., Taiwan) for fuel cell performance test. All of the membrane electrode assembly (MEA) samples were investigated by the polarization curve and Electrochemical Impedance Spectroscopy (EIS).

1. INTRODUCTION

Due to their high power density, high efficiency, nonexistent emissions, high-quality power, scalability, and fast start-up, proton exchange membrane fuel cells (PEMFCs) are a promising future power source [1-4]. Membrane electrode assemblies (MEAs) play an important role in the performance of PEMFCs. An MEA is composed of two gas diffusion layers (GDLs), two catalyst layers, and a proton exchange membrane (PEM). GDLs permit gas transport from a flow field to the catalyst layer, and conduct electrons from the catalyst to a flow field plate. GDLs should therefore be a conductive porous material. The GDL strongly affects mass transport and water management, which also affects performance.

Typically, a GDL has a dual-layer, composed of a gas diffusion substrate (GDS) and a micro-porous layer (MPL). Generally, the GDS is a carbon-fiber cloth or paper. While carbon cloth may present higher power performance than carbon paper, the use of carbon paper as a GDS is still widespread due to an advantageous cost and more convenient MPL fabrication [5]. Extensive research into the MPL has been performed, such as investigation into the effects of carbon powder types [6-11], hydrophobic reagents (e.g. fluorinated ethylene propylene (FEP), polytetrafluoroethylene (PTFE)), content ratio [11-13], and coating technique [11]. GDL 10 BC is a well-known

commercial GDL product from SIGRACET Corp. (USA), and consists of carbon powder and carbon paper as the MPL and GDS, respectively. The GDL 10 BC is used for comparisons in this study.

Jordan *et al.* [6,7] demonstrated that heat treatment by sintering of the carbon powder and PTFE resulted in better fuel cell performance for both carbon powder types studied (Vulcan XC-72R and Acetylene Black). Subjecting the carbon powder to a milling process decreased the particle size and fuel cell performance [7]. Yan *et al.* [11] found an optimal FEP content ratio for screen printing and spraying coating techniques. Yan *et al.* [11] also demonstrated that an MPL fabricated by spraying presented about twice the Darcy permeability constant than the screen-printed equivalent. Using air as the oxidant, the optimal FEP content ratio was 40 and 30 wt% for MPL fabricated by screen printing and spraying, respectively. The MPL fabricated by spraying showed lower fuel cell performance than screen printing, for both high and low FEP content ratios using air oxidant. For pure oxygen oxidant, the optimal FEP content ratio was 30 and 50 wt% for MPL fabricated by screen printing and spraying, respectively, and the two optimized MPLs performed at similar levels. These results by Yan *et al.* [11] imply that an optimal FEP content ratio correlates with fuel cell operating conditions. Chang *et al.* [13] investigated MEA compression ratios in concert with various GDS and MPL PTFE content ratios. Typically, an increased PTFE content ratio retarded water flooding but increased ohmic resistance. Therefore, the PTFE content ratio should be set at an optimized value. The optimal compression ratio and PTFE content for an

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MPL were both found to be 30% [13]. However, the experiments of Park *et al.* [12] found an optimal MPL PTFE content of 20%. Therefore, the optimal MPL PTFE content should be dependent upon the coating method, operating conditions, hydrophobic reagents, and so on.

Wang *et al.* [10] fabricated MPL with two types of carbon – Black Pearls 2000 (BP) and Acetylene Black (AB) – and indicated that BP and AB were hydrophilic and hydrophobic, respectively. The results demonstrated that an MPL fabricated with AB performed better than BP, while AB combined with BP in a certain ratio yielded the best performance. These results imply that the hydrophilic/hydrophobic structure can be tuned not only with hydrophobic reagents but also with different carbon types. The hydrophobicity can thus be maintained at an optimal value even without the use of a non-conductive hydrophobic reagent (i.e. PTFE). Four types of carbon have been tested as MPL: Shawinigan Acetylene Black (SAB), Vulcan XC-72, Asbury graphite 850, and Mogul L [8]. The fuel cell performance from best to worst was SAB, Vulcan XC-72, Asbury graphite 850, and Mogul L. Yu *et al.* [9] showed that MPL fabricated with Ketjenblack EC-600JD produced lower ohmic resistance and higher fuel cell performance than MPL using Vulcan XC-72R. Jordan *et al.* [7] found the optimized loading of AB at 1.25 and 1.9 mg-cm^{-2} for air and oxygen oxidants, respectively. However, these results were entirely different to Park's work, which found an optimal AB loading of 0.5 mg-cm^{-2} [12]. Passalacquaet *et al.* indicate that the carbon loading optimization depends on the material characteristics [8]. In our opinion, the optimized loading is not only dependent on the material characteristics but also the operating conditions, compression ratio [14], and so on. Ge *et al.* [14] concluded that the optimal compression ratio of GDL varied based on the material and should be ascertained to enable maximum stable performance. Very few studies into the coupling of the MPL carbon loading and PTFE loading have been undertaken. Therefore, various loadings of carbon powder XC-72R coupled with a range of PTFE loading were investigated in this work. In addition, two different methods- spraying and doctor blading of the MPL on GDS has been prepared for further comparison. Carbon nanotubes (CNTs) have become a high durable carbon material for fuel cell application. In recent years, CNTs was utilized as an MPL material in this work in addition to the traditional carbon powder XC-72R. VGCF has similar properties and structure

with CNTs. The main difference of VGCF and CNTs is VGCF a little longer than CNTs, but VGCF is much shooter than typical carbon fibers. The price of VGCF is 30 times less than CNTs. Thus, a GDL with VGCF MPL could be high performance and low cost GDL.

2. EXPERIMENTAL

### 2.1. MPL Fabrication on GDS with Spraying

Vulcan XC-72R, and long vapor-grown carbon fiber (VGCF, 7μm in length and 100 nm in diameter, Unitetek international Co., Ltd., Taiwan) were each combined with an appropriate amount of ethanol (without or with specific PTFE amount) and mixed using an ultrasonic bath to produce MPL inks. The MPL inks were sprayed with an air gun onto carbon paper of type GDS (GDS 340, CeTech Co., Ltd., Taiwan).

2.2. MPL Fabrication on GDS with Doctor Blade (DB)

A slurry was formed by mixing carbon material (VGCF) with ethanol, and depending on experimental requirements, a solution of PTFE was added. The mixture was then sonicated using an ultrasonicator for 1 hour, followed by the addition of glycerin and magnetic stirring for one hour. In order to create a slurry with the correct viscosity for use with the doctor blade, excess moisture was removed using a rotary evaporator. The carbon slurry was coated onto GDS340, where coating thickness was controlled using the doctor blade method. The coated substrates were then placed into a high-temperature furnace with a multistage heating element reaching up to 350°C treatment temperature, which is the glass transition temperature (T_g) for PTFE, as well as to remove excess solvent.

2.3. Performance and Electrochemical Impedance Spectroscopy Test

Commercial catalyst coated membranes (CCMs, General Optics Corp., Taiwan) were used in the performance assessment of fuel cells incorporating the homemade (XC-72R, VGCF) or commercially available (SGL 10 BC) GDL. The anode and cathode Pt loading of the CCM was 0.2 and 0.4 mgPt-cm^{-2}, respectively, and the membrane material was Nafion 211 (25 μm). The catalyst layer (CL) active area was 23 x 23 mm^2 and the GDL was 25 x 25 mm^2. Each CCM was sandwiched between two GDLs and assembled into a single cell without hot pressing for the fuel cell performance test.
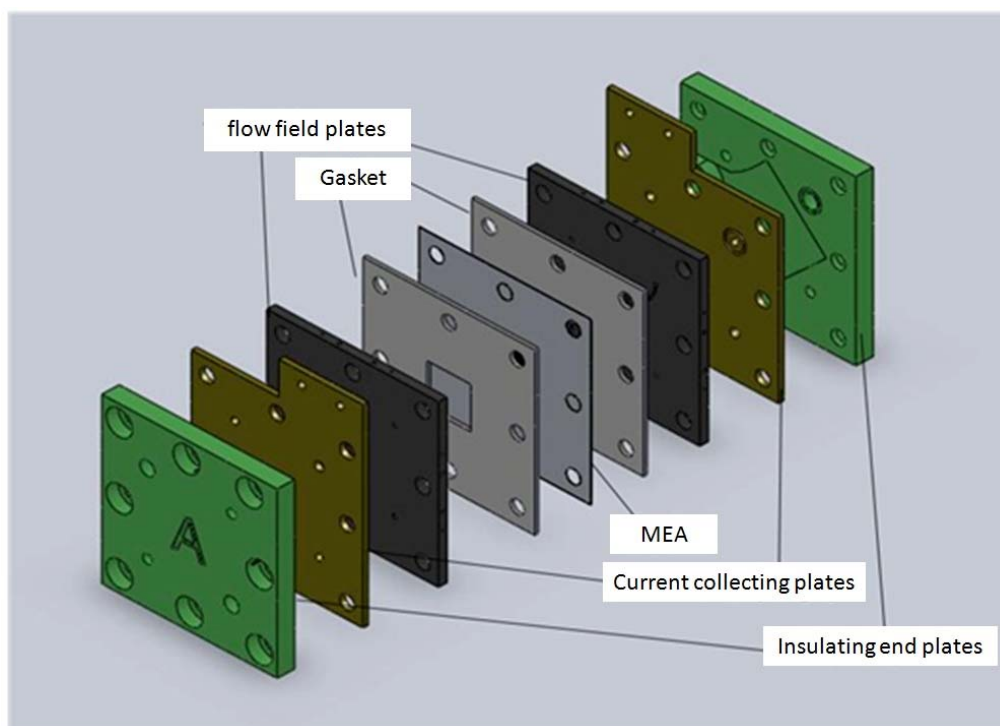
Figure 1: Schematic of single cell.

In this study, a homemade single cell was utilized which consisted of three components: two insulating end plates, two current collecting plates, and two flow field plates as shown in Figure **1**. The component materials were glass fiber, gold-coated brass, and graphite, respectively. The channel depth, channel width, and rib width of the serpentine flow field plate were all 1 mm. The compress ratio of each samples were fix at 30% which based on the previous research [15]. Polarization test measurements were conducted using a Fuel Cell Test System 850C (Scribner Associates Incorporated, USA).

Once a pair of GDLs were assembled with fresh commercial CCMs, an activation process was undertaken prior to the performance test. The activation process consisted of open circuit for 3 seconds, then constant 0.2 V for 30 minutes, repeated twelve times. Conditions during the activation process were a temperature of 65 °C with relative humidity (RH) 100%, 100 sccm hydrogen flow rate, and 250 sccm air flow rate. The operating conditions during polarization measurements were the same as for the activation process, but with a lower air flow rate of 150 sccm in order to emphasize the mass transport effect. No back pressure was used during any portion of the experiment. Electrochemical impedance spectroscopy (EIS) was carried out with a constant current of 0.5 A-cm^{-2}, and a frequency range of 1 - 1000 Hz.

3. RESULTS AND DISCUSSION

3.1. MPL Preparation with Spray Method

3.1.1. Effect of Carbon Loading

An appropriate carbon loading within the MEA can reduce contact resistance, however, carbon overloading will reduce gas diffusion, thus decrease fuel cell performance. As shown in Figure **2a**, a carbon loading of 3.0 mg-cm^{-2} at 0.6 V resulted in a rapid decline in fuel cell performance. This is attributed to the microporous layer (MPL) becoming too thick. The too thick MPL causes two effects to decline the performance. The first effect of too thick MPL is inhibiting gas flow, thus reducing the amount of gas available to the catalyst during the reaction. The second effect of too thick MPL is increasing the ohmic resistance due to longer electron transport path. Compare to other carbon loading in this study, 3.0 mg-cm^{-2} MPL was too thick, obviously. The polarization curves indicate a carbon loading of 2.0 mg-cm^{-2} MPL performs the best performance. A suitable carbon loading can reduces contact resistance and not increases so much electron resistance and gas transport resistance. As a result, a carbon loading of 2.0 mg-cm^{-2} MPL was found to produce a more favorable current limit value and exhibited better performance overall, as shown in Figure **2b**. Where the

i_{lim} was fitting result of polarization curves fit with the following equations by software FCView.

$$V = E_a - b \cdot \log(i) - i \cdot R_{ohm} + C \cdot \log\left(\frac{i_{lim} - i}{i_{lim}}\right) \qquad (1)$$

Here, $E_a = E_{theor} + b \log i_o$ where E_{theor} is the theoretical (or reversible) potential and i_o is the exchange current density, and b is the Tafel slope. Therefore, E_a and b parameters describe the Tafel behavior of a system. The Rohm parameter is the ohmic resistance of a cell. C and i_{lim} are an empirical description of a mass transport limiting condition.
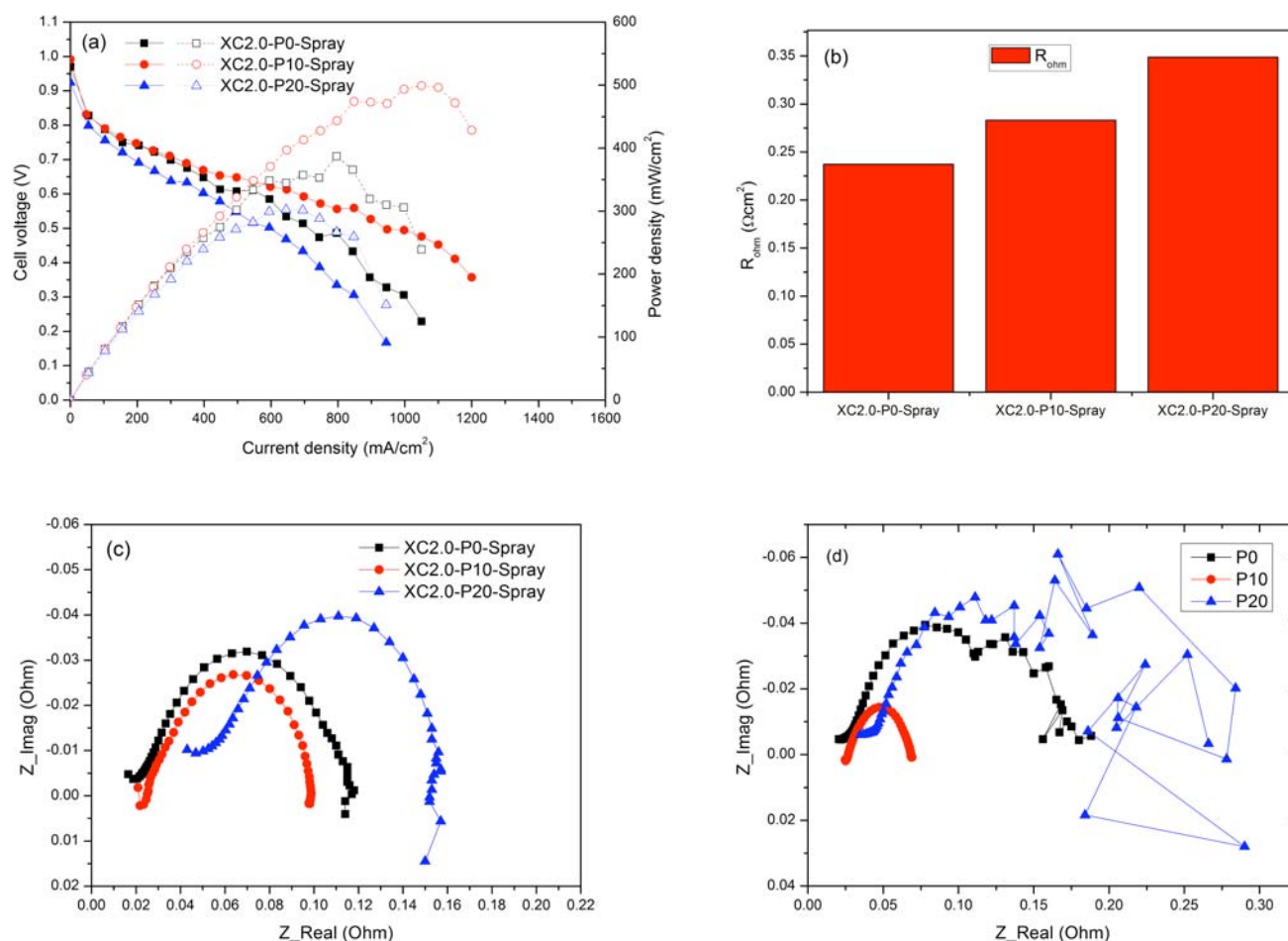
3.1.2. Effect of PTFE Content Ratio

PTFE is a non-conductive and hydrophobic polymer material. Adding PTFE can combat the water flooding phenomenon in the MEAs, and can enhance the mechanical strength of the microporous layer (MPL). However, too much PTFE could increase the thickness of MPL and decrease the electron conductivity. The carbon material used in this series of experiments was XC-72R, where P0 denotes no addition of PTFE, and P10 denotes a 10 wt% addition of PTFE. When the cathode air flow rate was set at 150 sccm, the performance of the fuel cell at low current density (100 mA-cm^{-2}) is, as shown in Figure **2a** for various content ratio of PTFE: 0.788 V (P0) = 0.790 V (P10) > 0.756 V (P20). The polarization curves were fitting with equation (1) to get the R_{ohm} as shown in Figure **2b**. The R_{ohm} increased with increasing PTFE content ratio. The whole experimental use the same model of CCMs as well as GDS, thus the difference of R_{ohm} was cause by

MPL. The R_{ohm} of P20 increased significantly due to PTFE overload and increasing electron resistance, thus reducing performance. The R_{ohm} of P0, P10 and P20 was 0.24 Ohm-cm^{-2}, 0.28 Ohm-cm^{-2} and 0.35 Ohm-cm^{-2}, respectively. The higher R_{ohm} of P10 should lead lower performance, however, when the current density was increased to 400 mA-cm^{-2} or greater, P10 (0.669 V) outperformed P0 (0.648 V). The heavier current load the higher performance of P10 compare to P0. P10 perform better performance than P0 implies the 10% PTFE content not only has bad effect on R_{ohm} but some benefits in somewhere else. The benefits could be analyzed by AC impedance measurements shown in Figure **3c** and **d**. The higher performance of P10 was attributed to the fact that in the presence of PTFE at high current densities, gas and water permeability is higher, which prevents water accumulation so that charge and mass transfer impedance is lowered, resulting in improved performance.

This section focuses on the carbon material VGCF at a cathode air flow rate of 150 sccm. Figure **4a** shown the polarization curves of VGCF MPLs with various PTFE content ratio, the differences in performance between P0 and P10 might be negligible. As shown in Figure **4a**, whereas the performance of P20 was slightly poorer at the ohmic polarization domain and significantly decrease at the mass transport domain. The polarization curves were fitting with equation (1) to get the Rohm as shown in Figure **4b**. The Rohm increased with increasing PTFE content ratio, this trend as well as Vulcan-XC72R constituted MPL. But the Rohm value of VGCF constituted MPL is slight lower than Vulcan XC-72R one due to the intrinsic resistance
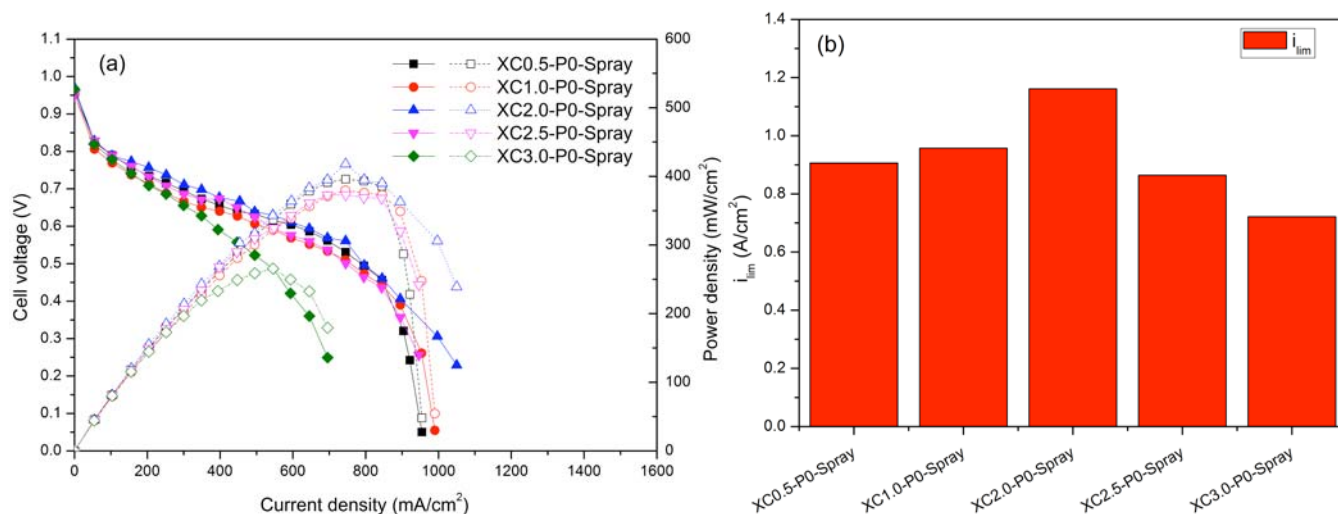
Figure 2: Dependence of carbon loading on (**a**) polarization curves, and (**b**) limiting current densities of various Vulcan XC-72R constituted MPLs. (XC0.5-P0-Spray: MPL constituted by Vulcan XC-72R carbon with 0.5 mg/cm^2; 0 wt% of PTFE contain in the ink/slurry and coated by spray method).

Figure 3: The dependence of PTFE content ratio of Vulcan XC-72R constituted MPL, with air flow rate 150 sccm to cathode. (**a**) polarization curves (**b**) R_{ohm} and (**c**) EIS with current density 200 mA-cm^{-2} and (**d**) EIS with current density 800 mA-cm^{-2}.

of VGCF is lower. Figure **4c** and **d** shown the EIS with 500 mA-cm^{-2} and 800 mA-cm^{-2}, respectively. The overload PTFE might induce micro-structural changes and reduce pore size, thereby P20 has higher mass transport resistance. Due to P0 performs higher charge transfer resistance and mass transfer resistance than P10, thus 10% PTFE is the best formula for VGCF constitute MPL by spray method.

The addition of an appropriate amount of PTFE can effectively enhance charge transfer, and reduce mass transfer impedance, thereby enhancing performance. The effect of the addition of PTFE in Vulcan XC-72R is more apparent, which could be attributed to Vulcan XC-72R constituted MPL has different pore size and more hydrophilic than VGCF one. Thus Vulcan XC-72R constituted MPL need PTFE to solve water management issue then enhance the accessibility of fuel on the catalyst layer. Generally, the performance of VGCF constituted MPL is superior to that of Vulcan XC-72R constituted MPL. Besides, VGCF constituted MPL is not so sensitive with PTFE content ratio which

implies much easier to control the quality during mass production.

3.2. MPL Preparation with Doctor Blade Method

3.2.1. Effect of Carbon Load

Utilizing the optimized parameters for the spraying method outlined in section 3.1, the carbon material used and PTFE loading used to investigate the effect of carbon load was VGCF and 10 wt%, respectively. Figure **5a** shows the polarization curve as a function of carbon load in the MPL. In the figure, the "20" of VGCF20-P10-DB denotes the distance between the doctor blade and the substrate as 20 μm, with a carbon loading of 1.7 mg-cm^{-2}, whereas 30 (μm) and 50 (μm) possess a carbon loading of 2.0 and 3.7 mg-cm^{-2}, respectively. At low current density, the 20 MPL exhibited poor performance. According to Figure **5b**, this could be attributed to the insufficient carbon loading in VGCF20-P10-DB, thereby resulting in higher ohmic resistance and higher charger transfer resistance. The higher ohimic resistance implies the
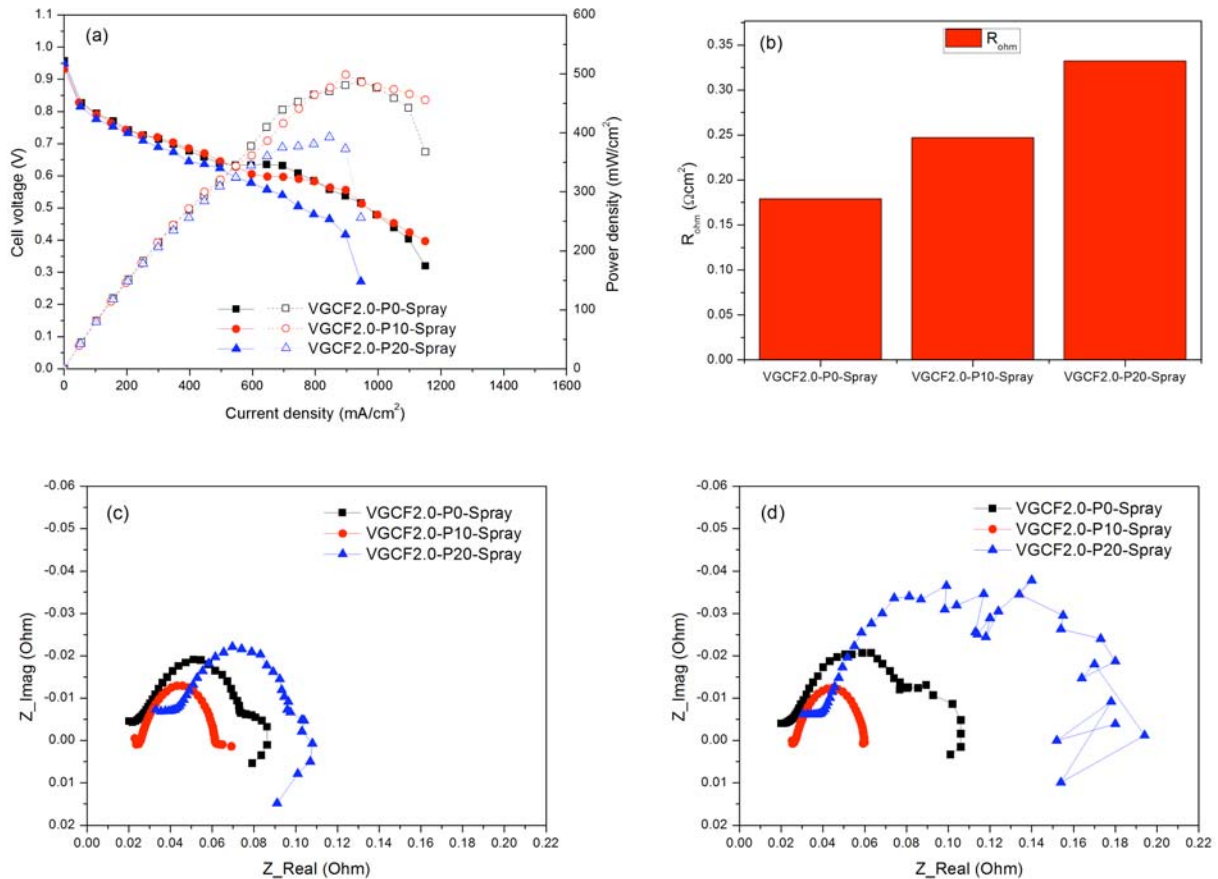
Figure 4: The dependence of PTFE content ratio of VGCF constituted MPL, with air flow rate 150 sccm to cathode. (**a**) polarization curves (**b**) R_{ohm}, (**c**) EIS with current density 500 mA-cm^{-2} and (**d**) EIS with current density 800 mA-cm^{-2}.

insufficient carbon loading in VGCF20-P10-DB was caused by poor contact between the MPL and the catalyst layer. This increases contact resistance, resulting in the loss of ohmic polarization characteristics, as shown in Figure **5a**. The higher charger transfer resistance implies the insufficient carbon loading in VGCF20-P10-DB might caused by poor gas distribution. The poor gas distribution performs slighter lower performance at the activation polarization domain, and significant performance decay at the mass transport domain.

While the performance of the VGCF50-P10-DB MPL is superior to that of VGCF20-P10-DB, it is still lower than VGCF30-P10-DB. This may be due to the
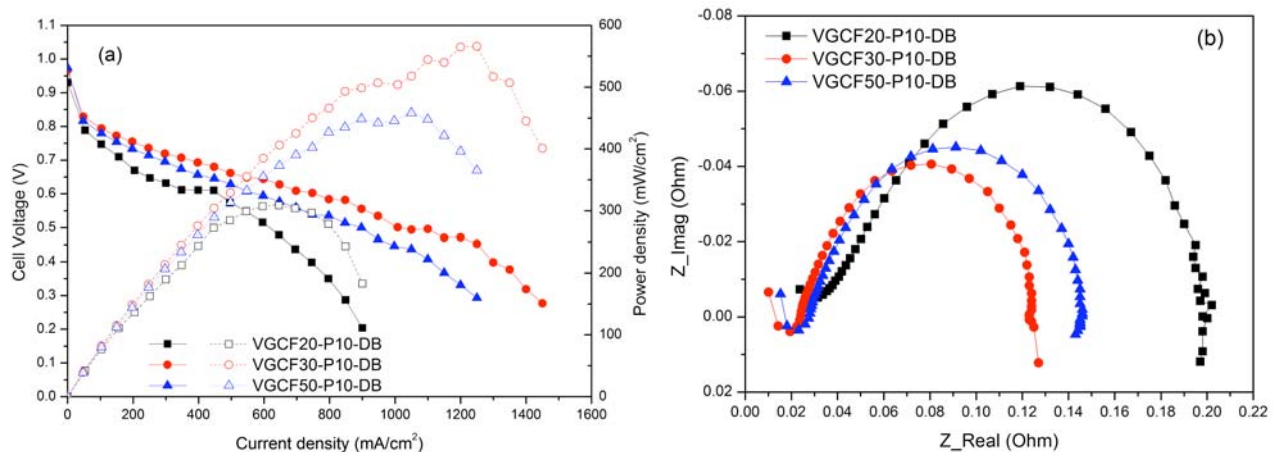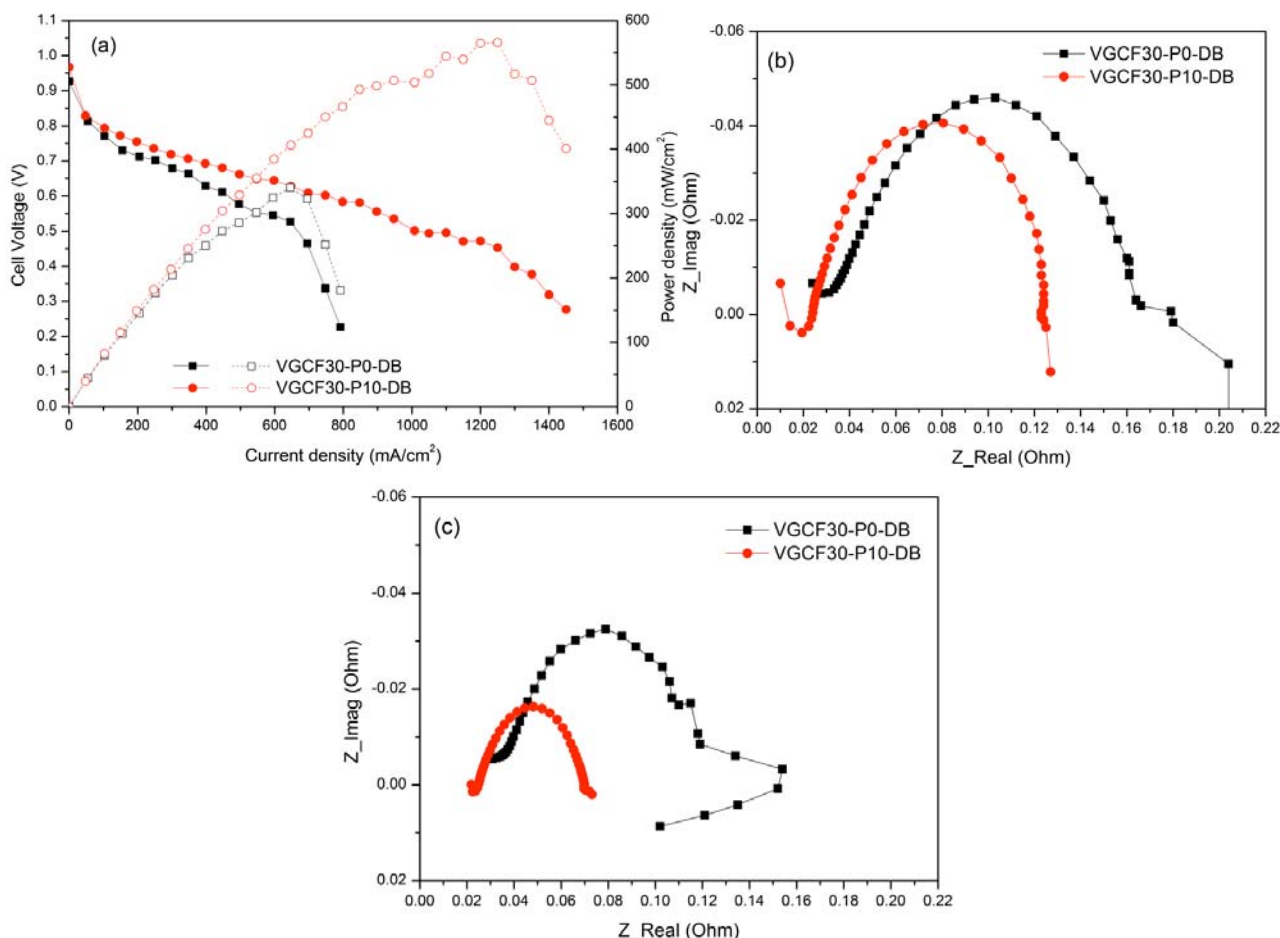

Figure 5: Dependence of VGCF carbon loading on (**a**) polarization curves and (**b**) EIS with current density 100 mA-cm^{-2} with MPL fabricated using doctor blade.

fact that the MPL is too thick, even though contact resistance has decreased, the thickness of the MPL increased the overall resistance of the layer. Furthermore, the gas permeation through this layer is hindered, leading to a poor charge transfer resistance, thereby decreasing performance. From these results, it can be seen that VGCF30-P10-DB is the optimum thickness (carbon loading), which possess low contact resistance and low charge transfer resistance.

3.2.2. Effect of PTFE Content

Figure **6a** shows polarization curves of the VGCF MPL with various PTFE content. According to previous studies into spraying method, the performance of the MPL with either 0 wt% or 10 wt% PTFE content is reasonably high if the carbon material used is VGCF. Therefore, this section will investigate whether a MPL prepared using the doctor blade method also possesses good performance characteristics without the addition of PTFE. Figure **6a** shows that a significant difference is observed for samples with PTFE (0.771 V) and without PTFE (0.794 V) under low current density

(100 mA-cm^{-2}) conditions. The AC impedance analysis shown in Figure **6b** demonstrates that samples without PTFE at low current densities (100 mA-cm^{-2}) exhibited higher charge transfer resistance. From Figure **6c**, it is apparent that the charge and mass transfer resistance is higher for P0 samples. Thus, at moderate current densities (500 mA-cm^{-2}) or higher, the performance difference becomes even more apparent (P0 = 0.577 V, P10 = 0.662 V). The results suggest that MPL fabricated using the doctor blade method result in a denser structure, resulting in poor accessibility of gas to reaction sites, as well as poor expulsion of water from reaction sites. This effectively increases charge and mass transfer resistance, which suggests that an appropriate level of PTFE must be added to the doctor blade method to maximize gas and water permeation. Compare Figure **4a** and Figure **6a**, the VGCF30-P10-DB performs higher maximum power density than VGCF2.0-P10-Spray which indicate VGCF-MPL fabricated by doctor blade might be batter. But PTFE content ratio plays an important role for VGCF-MPL fabricate by doctor blade method.

Figure 6: Dependence of PTFE loading on (**a**) polarization curves, (**b**) EIS with current density 100 mA-cm^{-2}, and (**c**) EIS with current density 500 mA-cm^{-2} with LVGCF constituted MPL fabricated using doctor blade method.

4. CONCLUSIONS

(1)   An appropriate level of carbon loading can reduce the contact resistance. Insufficient carbon loading results in higher contact resistance, whereas overloading will lead to higher internal resistance and mass transfer polarization.

(2)   The addition of an appropriate amount of PTFE can facilitate the expulsion of water, and prevents water flooding, thereby increasing performance. However, excessive PTFE loading can result in the increase in internal resistance, and may induce micro-structural changes that results in poor mass transfer.

(3)   Due to VGCF-MPL is not very sensitive with PTFE content ratio, thus VGCF constituted MPL is easier to control quality than Vulcan XC-72R constituted MPL, by using spray method.

(4)   The VGCF-MPL fabricated by doctor blade method performs better performance than spray method one. But PTFE content ratio plays an important role for VGCF-MPL fabricate by doctor blade method.

ACKNOWLEDGEMENTS

APPENDIX

Nomenclature

E_{theor} = theoretical potential

b = Tafel slope

I = current density

R_{ohm} = ohmic resistance

i_0 = exchange current density

i_{lim} = limiting current density

C = empirical factor of mass transport

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