The influences of catalyst combination on the high temperature proton exchange membrane fuel cell

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Abstract. High temperature proton exchange membrane fuel cell (HT-PEMFC) is a green device which converts chemical energy to the electricity directly. A redox reaction occurs at the catalyst layers of fuel cell, where electrons separate from hydrogen molecule through the help of catalyst. The structure of catalyst is an important factor that affects the cell performance due to the consequences of chemical reaction area and thickness of the catalyst layer. SEM was used for structure investigating of different platinum and carbon ratios (Pt/C). At 0.7mg/cm² Pt loading, 3 weight percentages, 10%, 20%, and 40% were compared to see the thickness differences of catalyst layer. The catalyst binder can affect the fuel cell performance as well. PTFE and PVDF were tested, and the results showed the former provided 50% higher current density than the latter at the same voltage output. The uniformity of catalyst layer provided better contact with the gas diffusion layer. It also induced thicker CL which results in more surface area for the chemical reactions. A catalyst combination of 10wt.% Pt/C and PTFE was able to reach 0.58A/cm² at 0.278V.

1. Introduction
PEMFC has been considered as one of the promising future power sources because of distinguished characteristics, such as compact size, quiet operation and low emissions. It can be applied to vehicle, portable devices and auxiliary power unit. Hydrogen and air are fed in and converted to electricity, meanwhile, water and heat are produced. There are two types of PEMFCs which are categorized by working temperature. Low temperature one is the early generation, it is named LT-PEMFC. The system of LT-PEMFC is complicated because of those necessary parts, i.e. balance of plant (BOP), humidifier, reformer, CO cleaner and water management system. High temperature PEMFC (HT-PEMFC) is one of the new generation of fuel cells. With the working temperature at about 160°C, water will become vapour, hence, the system can be very simple compared to the LT-PEMFC. In contrast to the conventional LT-PEMFC which the CO tolerance is less than 30ppm, HT-PEMFC can still survive even the concentration of CO in the fuel goes up to 30,000ppm [1].The outgrowth of high working temperature is the better quality waste heat, which can be applied to many applications including preheating the inlet fuel.

Membrane electrode assembly (MEA) is the core component of the PEMFC. It consists of the gas diffusion layer (GDL), microporous layer (MPL), catalyst layer (CL), and membrane. The gas diffusion layer is the outmost layer of MEA, and functions to diffuse the fuel gasses in both cathode and anode sides. It also acts as the electron transporter which transfers the electron from the catalyst layer to the outer system[2]. Normally, the GDL is made of the flexible carbon material. It is coated by
the MPL which is a layer of Polytetrafluoroethylene (PTFE) material. For HT-PEMFC, the function of MPL is not only increasing the gas dispersion by small pore size of the structure, but also prevents the extinction of phosphoric acid due to the hydrophobic character. However, PTFE is an insulating material. High content of PTFE increases internal cell resistance[3]. The interface between MPL and CL is the region the chemical reaction taking place. There are many techniques to deposit CL on MPL, e.g., brushing, spraying, doctor blading, etc. The CL is an important unit that affects the cell performance. It is a combination of catalyst material, catalyst support material, and catalyst binder. For HT-PEMFC, platinum (Pt) is the main catalyst material. Carbon powder is used as support material of catalyst because of the following properties: excellent bonding with the micro porous layer since they are the same materials compound, high electrical conductivity, high stability against the chemical reaction, high surface area etc. The reasons to mix binder with the catalyst, is not only for preventing the loss of Pt catalyst during operating, but also retaining the phosphoric acid in the membrane. A proper combination of catalyst, carbon supporter and binder will consequently engender a high performance and stable fuel cells.

There are two common types of the binder used for preparing the catalyst layer. PTFE, known in the common name of Teflon, is a plastic compound which can resist chemical corrosion and also can be used in the high temperature condition. Polyvinylidene difluoride (PVDF) is a thermoplastic which can also cope with high-temperature and strong acid conditions. Liang et al.[4] investigated the effects of different binder mixtures with PTFE, PVDF and Polybenzimidazoles (PBI). The experiments showed PVDF binder mixture resulted in the best performance of a single HT-PEMFC. At 0.4V, the current output of using PVDF binder compared with PTFE and PBI were 24% and 77% higher respectively. A conflict result was shown by Su et al.[5], who also did the tests with different binder, i.e. PVDF, PTFE, PBI and Nafion. At 0.4V, the MEA generated highest current density with PTFE binder. It was 15%, 88% and 150% higher than PVDF, PBI and Nafion, respectively. Since the chemical reactions of fuel cell occur in the catalyst layer, the influence of CL on fuel cell performance was investigated. Carbon powder is used as the catalyst support material, there are various Pt loading on carbon available in the market. The loading number represents the percentage of Pt to the total mixture in weight. The 10wt.% Pt/C, 20wt.% Pt/C and 40wt.% Pt/C were used as the catalyst materials in this study. The lower Pt percentage results in a higher carbon content in the Pt/C mixture. With the same loading of Pt, different weight percentage of Pt/C will cause different thickness of CL. The effects of CL on the performance of HT-PEMFC were evaluated by structure characterization, electrochemical analysis, and cell polarization tests.

2. Experimental

2.1. Preparation of the GDEs

In this study, the effect of the catalyst layer on the performance of fuel cell was investigated. For preparing the CL, the platinum on Vulcan XC72 graphitized carbon with 10wt.% Pt/C, 20wt.% Pt/C and 40wt.% Pt/C from Sigma-Aldrich were used as the catalyst material. The catalyst inks were prepared by mixing Millipore water, 60wt.% PTFE-dispersed water, and Pt/C. Isopropyl alcohol was the solvent for PTFE. Another type of the catalyst inks consisted of Pt/C catalyst, Poly(1,1-difluoroethylene) (PVDF), and organic compound N, N-Dimethylacetamide (DMAc). The catalyst inks were homogeneously mixed by using an ultrasonic bath for 1 hour. A treated carbon cloth with Teflon MPL were used to form the gas diffusion layer. The gas diffusion electrodes were prepared by depositing the prepared catalyst inks on microporous layer. The brushing technique was used for coating the inks. The deposited GDLs were left in a vacuum oven overnight for removing the solvent under 160°C temperature. The Pt loading was measured after the oven process, the default Pt loading of all tests was controlled at 0.7mg/cm².
2.2. Preparation of the MEAs
The Advent TPS HT membrane was used in this study. The nominal dry thickness is about 60-65μm. The commercial membranes were immersed in 85wt.% phosphoric acids (PA) for 9 hours. The temperature of PA was controlled at 90℃. The doped membrane was sandwiched between prepared GDEs without hot-press process. The flow field plate with semi serpentine-parallel channel was used in this study. The graphite plates were machined by computer numerical control machine to gain 5cm² working area. The high-temperature gaskets were used for preventing gasses from leakage on both sides of the cell. The H₂ and the air were controlled and supplied to the cell at atmosphere pressure. The ceramic heating pads were attached to both sides of the cell to maintain the cell temperature at 160℃ for all tests.

2.3. Fuel cell performance tests
A polarization curve is an ordinary measurement for investigating fuel cell performance. An ITECH IT8512A+ DC electronic load was used to obtain the results of electrochemical reaction by adjusting the cell outputs. The performance tests were proceeded by increasing the current density from the open circuit (0 A/cm²) until the cell voltage suddenly dropped. The characteristic of polarization curve can be explained by an irreversible equation [6] as follows:

\[
V = E - A \ln\left(\frac{i}{i_0}\right) - ir - m \cdot \exp(ni)
\]

where E is the reversible open circuit voltage (V)
A is the slope of the Tafel line
\(i_0\) is the internal and fuel crossover equivalent current density (A/cm²)
\(i_0\) is the exchange current density (A/cm²)
m and n are the constants in the mass-transfer overvoltage equation
r is the area-specific resistance (kΩcm²)

There are four terms on the right hand side of equation. E represents the theoretical potential of the cell. The activation losses of the cell are explained by the second term, which represents the kinetic reaction at low current region. The third term stands for the Ohmics losses. The resistance is caused by the conductivity and interconnection of components of fuel cell, and presented by the slope of the linear variation section of performance curve. The last term explains the effect of the Mass transport losses.

2.4. Catalyst layer characterization
CL consists of Pt catalyst, graphite carbon support, and catalyst binder. The Pt/C particles are in nanoscale size. A scanning electron microscope (SEM, JEOL JSM-7610F) was used for observing the physical properties of CL. The result images and Energy-dispersive X-ray spectroscopy (EDS) results were taken with an accelerating voltage between 0 and 20kV. The cross-sections of MEAs were investigated for observing the thicknesses of CLs, GDEs, and membrane.

3. Results
3.1 Catalyst layer structure
The structure characters of CL were investigated by SEM. The effects of Pt content on carbon were illustrated in terms of the thickness of catalyst layer. At 0.7mg/cm² Pt loading, Figure 1(a), 1(b) and 1(c) show the thicknesses of 10wt.% Pt/C, 20wt.% Pt/C and 40wt.% Pt/C as 282µm, 136µm and 58µm, respectively. The lowest percentage of Pt content (10wt.% Pt/C) resulted in the thickest catalyst layer compared with the other two. As a catalyst binder, PTFE can provide more uniform structure than PVDF did. Different contents of Pt/C with PVDF binder all evinced a fragmented CL. The SEM
image also revealed the expansion of TPS membrane. The membrane thickness was increased from 65µm to 110µm after phosphoric acid doping process.

**Figure 1.** Cross-section images of MEAs interfaces: (a) 10wt.% Pt/C with PTFE binder; (b) 10wt.% Pt/C with PVDF binder; (c) 20wt.% Pt/C with PTFE binder; (d) 20wt.% Pt/C with PVDF binder; (e) 40wt.% Pt/C with PTFE binder and (f) 40wt.% Pt/C with PVDF binder.

EDS can present information of the elemental composition and show the energy intensity graph. Figure 2 shows the EDS result of the CL with different Pt/C concentrations. The 10wt.% Pt/C (highest carbon concentration) presents the highest intensity peak at carbon energy section. It is 50% and 156% higher than the 20wt.% Pt/C and 40wt.% Pt/C, respectively.
3.2 Cell performance

Figure 3 provides the relationship between Pt concentration and the open circuit voltage (OCV). The results show that, the lowest weight percentage of Pt on carbon (10wt.% Pt/C) with PTFE catalyst binder provides the lowest OCV as 0.885V. The OCV of PTFE and PVDF catalyst binder were increased 5.8% and 5.2% when the weight percentage of Pt was changed to 20% to 40%. The CL thickness represents the amount of binder, the thicker CL consists of higher binder amount since both PTFE and PVDF are the insulating materials, higher content of PVDF or PTFE will cause lower OCV of the fuel cell.

The relationships between current density and single cell voltage of different types of CL are shown in figure 4. The results show that the varying weight percentage of Pt on carbon affect the cell performance. A lower Pt content of Pt/C, i.e. higher content of carbon, provides better performance than the higher Pt content. Because high content of Pt causes thinner layer of CL and limited area for taking place the chemical reaction, which results in poor performance. The 10 wt.% Pt/C with PTFE catalyst binder shows the best performance. It can reach the maximum current density of 0.58A/cm$^2$ at 0.278V. At 0.4V, the current density is 52.7% and 147.1% higher than 20wt.% and 40wt.% Pt/C.
respectively. The comparison of 2 types of catalyst binder also shown in figure 4. PTFE shows better performance than PVDF as catalyst binder. PTFE binder consists of Teflon, which is the same material of MPL, a lower resistance between these two layers is presumed. The similar result has also been observed by other research group [7]. The PTFE coated carbon paper with PTFE catalyst binder shows the better cell performance than PVDF, PBI, and Nafion catalyst binder.

4 Conclusions
The influences of catalyst combination on HT-PEMFC have been investigated in this study. Different weight percentages of Pt/C, 10wt.%, 20wt.% and 40wt.%, were used for investigating the proper CL combination. At the same loading of Pt, 0.7mg/cm², the 10wt.% Pt/C consists the thickest layer as 282μm. It is 107% and 386% thicker than 20wt.% Pt/C and 40wt.% Pt/C, respectively. EDS results confirmed that 10wt.% Pt/C consists the highest energy intensity in the carbon energy range due to the high content of carbon. It is 50% and 156% higher than the 20wt.% and 40wt.% Pt/C, respectively. In terms of cell performance, the 10wt.% Pt/C presented the maximum current density of 0.58A/cm² at 0.278V. At 0.4V, it can provide higher current density than 20wt% and 40wt% Pt/C as 52.7% and 147.1%, respectively. The types of catalyst binder are one of the important factors which affect the cell performance as well. With 10wt.% Pt/C catalyst, the PTFE catalyst binder performs 50% higher current density than PVDF catalyst binder at 0.4V cell voltage. The best CL combination in this study was 10wt.% Pt/C with PTFE catalyst binder, both best cell performance and good contact with GDE were observed. It also provided a thicker CL which results in higher surface area for having the chemical reactions in the cell.

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