CHAPTER 1

Introduction

1.1. Rationale

Currently, the demand for electrical consumption in Thailand is continuously increasing every year [1] against the depletion of energy resources. Of the fossil fuels for electrical generation in Thailand, around 50% (78,077 thousand tons of oil equivalent, ktoe) is provided in the country and around 47% (70,232 ktoe) is imported from elsewhere [2]. Therefore, the development and research of alternative energy are necessary to mitigate energy issues in the country.

Fuel cells are an alternative energy technology that can directly generate electricity by converting the electrochemical reaction from their fuels. Since fuel cells generate electricity without the processes of combustion and mechanical works, compared with conventional methods, they provide high efficiency and low pollution. Typically, fuel cells comprise an electrolyte layer sandwiched by a positive electrode (cathode) and a negative electrode (anode). Although the fuel cell components are similar to those of a battery, they can generate electricity as long as sufficient fuel is supplied, unlike a battery. When the charged ions are completely consumed during electrochemical reaction, a battery cannot generate electricity.

Among the many types of fuel cells, PEMFCs operate at the lowest temperature because their reactant gases (hydrogen and oxygen or air) require low heat for driving the electrochemical reaction. This means that PEMFCs have low heat loss and provide high efficiency, as well as fast startup and shutdown. Moreover, PEMFCs can operate at atmospheric pressure. With these advantages, they are promising power sources that can be widely applied for transportation, residential use, industry and electrical appliances.

The single cell of the PEMFC comprises three main components that each play related roles. The typical electrolyte polymer membrane sandwiched by the anode and cathode electrodes is called a MEA. This is set up at the center and consequently sandwiched by gas diffusion layers (GDLs) and flow field plates. These components are connected together by a tightening force to prevent fluid leakage. The roles and principle of each component can be briefly explained as follows. The reactant gases are fed through the anode and cathode flow field plates having flow channels as the fluid guideline. As they flow, the reactant gases simultaneously diffuse through the GDLs toward the electrochemically active area at the MEA. At the anode electrode, hydrogen is oxidized and then releases positive (proton) and negative (electron) ions. The polymer electrolyte membrane allows only protons to pass, thus electrons are conducted and travel to the conductors, such as the catalyst cluster, GDLs and flow field plate, to be utilized as electricity. At the cathode electrode, oxygen is reduced and combined with protons and electrons of hydrogen to produce water as a byproduct of this system.

It can be seen that the MEA is a key component where the electrochemical reaction takes place for generating electricity. Normally, the MEA can be fabricated by coating electrocatalysts (generally prepared as catalyst ink) on both sides of the polymer electrolyte membrane to form anode and cathode electrodes or catalyst layers. There are two coating methods, the catalyst-coated membrane (CCM) and the catalyst-coated substrate (CCS). The CCM has directly coated catalyst on the membrane surface whereas the CCS has the coating catalyst on a substrate, typically the GDL and then pressing on the membrane surface. The CCM method yields better performance than the CCS method due to the better contact between the electrodes and membrane, resulting in lower ionic resistance and better durability [3]–[5]. However, during the coating processes, with CCM there usually occurs the issue of membrane swelling and deformation [6], which are a cause of catalyst layers cracking and being lost.

Improvement of the catalyst utilization in electrochemically active areas or in catalyst layers leads to the maximum PEMFC performance. There are many ways to improve catalyst utilization such as development of the catalyst coating technique [7]–[11], optimization of catalyst ink formulas, improvement of specific areas of catalyst particles

by synthesizing the catalyst on any supported elements, etc. Examples of improving catalyst utilization by different coating techniques were illustrated in the following studies. Benitez *et al*. [9] compared the Pt utilization from three coating methods for MEA fabrications: impregnation, spray and electrospray methods. They reported that the MEA fabricated by the impregnation method provided the best Pt utilization (80%) followed by the electrospray method (40%) and the spray method (25%). Hwang *et al*. [10] proved that the ECSAs of MEA electrodes prepared by the screen-coating technique (CCS method) were greater than those of MEA electrodes prepared by the spray-coating technique (CCM method). Z. Wang *et al*. [11] reported that the catalyst utilization of MEA electrodes fabricated by the inkjet printing method was higher than that by the spray-painting method (8.3% vs. 3.9%).

Catalyst inks are the input material in many types of coating processes. After the coating processes, they form catalyst layers. The optimization of catalyst ink formulas can be performed by determining the most suitable catalyst ink composition. Normally, catalyst ink is composed of three main compositions: catalyst powder, ionomer and solvent. In any coating processes, it is difficult to transfer or coat the catalyst in solid state. Thus, the solvent and ionomer (liquid state) are mixed with catalyst powder to become slurry or ink that is easy to transfer.

When catalyst ink is coated on the membrane surface (CCM method) or other substrates (CCS method), solvent is evaporated out of other compositions and the pores remaining in the catalyst layer. Therefore, there are three regions – pores, catalyst clusters and ionomer – residing together in the catalyst layer. These regions are very important for the electrochemical reaction. Pore regions are the pathway for reactant gases reaching the active area and water draining out of the system. Catalyst cluster regions are the conductor of electrons, whereas ionomer is the conductor of protons released from the electrochemical reaction. The existence of each region should be of an appropriate scale, because the excessive expanse of one region could have the effect of reducing the other regions, resulting in ineffective catalyst utilization.

It can be seen that the solvent plays a significant role in determining the catalyst layers morphology, and especially the formation of catalyst particles and ionomer, which also relate to the ECSAs. Many types of solvent are used to produce catalyst inks, such as water, alcohol, ethylene glycol, glycerol, etc. The solvent properties, such as the evaporation point, dielectric constant and solubility (δ), are the main factors affecting the catalyst layer morphology. The different values of the dielectric constant affect whether the catalyst ink becomes one of three states, solution, colloid or precipitate. Solvents having a dielectric constant in the range of 0–3, 3–10 and more than 10 result in catalyst inks that become precipitate, solution and colloid, respectively [12]–[16]. Shin *et al*. [13] and Saha *et al*. [15] reported that the catalyst cluster sizes and the catalyst layer thickness formed by colloidal ink were larger than those formed by solution ink. Moreover, the ECSAs and cell performance of the MEA made by the colloidal ink was also higher than that made by the solution ink. The evaporation point value of solvent relates to the solvent remaining in catalyst layers. Solvent having a low evaporation rate is easier to evaporate out of catalyst layers compared with a high evaporation rate solvent. Solvent remaining in catalyst layers might be the cause of mass transport resistance and reduce the ECSAs in the catalyst layers [16]. Ngo *et al*. [17],[18] found that the δ of the solvent affects the formation of the ionomer. Normally, an ionomer molecule consists of a backbone structure, typically of perfluorocarbon, surrounded by a side-chain structure, typically sulfonated vinylether. The perfluorocarbon and sulfonated vinylether have δ of 9.7 $cal^{0.5}cm^{-1.5}$ and 17.3 $cal^{0.5}cm^{-1.5}$, respectively. When a solvent having δ close to the δ of the backbone structure was mixed with Nafion, the side-chain structure was dissociated and then formed negative charge ($–SO_3^-$) surrounding the backbone structure. This is beneficial for ion transfer in the catalyst layers.

Not only the solvent but also the ionomer plays many significant roles in the catalyst layers. Normally, the ionomer is well known under the commercial name of Nafion solution. Its chemical structure is similar to electrolyte membrane so it can be a proton conductor. Moreover, it acts as a binder between the catalyst particles and membrane to improve the MEA durability. Nafion is a hydrophilic material that favors water absorption and thus it also acts as a moisture conservator in the catalyst layers. Proton

conductivity is also improved when moisture is retained in the MEA. Although the existence of Nafion in catalyst layers is useful for the electrochemical reaction, an excessive amount is not beneficial. For example, Nafion is a proton conductor but electron insulator, thus increase of the Nafion content in catalyst layers results in a decrease of the electron conductive areas. Some catalyst particles which are completely covered by Nafion film also cannot participate in the electrochemical reaction. This indicates ineffective utilization of the catalyst. Moreover, Nafion texture may penetrate and fill the pores in the catalyst layers, resulting in hindering the pathway of reactant gas reaching the active area [19]–[35]. Although the water capture ability of Nafion can encourage moisture conservation and improve the proton conductivity, too much captured water could be the cause of water flooding and a hindrance for reactant gas transportation. It can be seen that there are advantages and disadvantages of Nafion existing in catalyst layers. Thus, control of the Nafion in catalyst layers to maintain the optimum content is very important to maximize MEA performance. Much research has been done to determine the optimum Nafion content, as shown in Table 1.1

Table 1.1 Comparison of the optimum Nafion content in literature

References	MEA fabrication	Catalyst type	Pt loading (mg/cm^2)	Optimum Nafion content (wt.%)
S.J. Lee 1998 [19]	CCS, Rolling technique	20%Pt/C	0.400	23.1 48.7[a]
E. Antolini 1999 [20]	CCS, Brushing	20%Pt/C	0.200	40.1
E. Passalacqua 2001 [21]	CCS, Spraying	20%Pt/C	0.100	33.0
P. Gode 2003 [22]	CCS, Spraying	20%Pt/C	0.100	40.0
Z. Qi 2003 [23]	CCS, Spraying	20%Pt/C 40%Pt/C	0.120 0.350	30.0
G. Sasikuma 2004 [24]	CCS, Brushing	20%Pt/C	0.100 0.250 0.500	50.0 40.0 20.0

Table 1.1 (continued)

References	MEA fabrication	Catalyst type	Pt loading (mg/cm^2)	Optimum Nafion content (wt.%)
D. Lee 2008 [25]	CCS, Brushing	20%Pt/C	0.400	33.0 42.8[b]
A.M. Chapparro 2009 [26]	CCS, Electro spraying	20%Pt/C	0.170	15.0
S. Martin 2010 [27]	CCS, Electro spraying	10%Pt/C	0.025 0.050 0.100	50.0 40.0 30.0
R.R. Possos 2006 [28]	CCM, Paint	20%Pt/C	0.300 0.400	15.0
L. Sun 2008 [29]	CCM Spraying	40%Pt/C	0.150	33.0
K. Kim 2010 [30]	CCM, Spraying	45.5%Pt/C	0.400	25.0 30.0[c]
H.N. Su 2010 [31]	CCM, Spraying	40%Pt/C	0.120	25.0
J. Xie 2010 [32]	CCM, Decal (brush paint)	20% Pt_3Cr/C	0.200	27.0
T.H. Huang 2012 [33]	CCM, Ultrasonic spraying	40%Pt/C	0.155 0.194 0.232 0.271	20.0
			0.310 0.348	33.0
S. Mu 2012 [34]	CCM, Decal	60%Pt/C	0.150 0.350 0.500	25.0 30.0[d]

[a] The optimum Nafion content of 21.1 and 48.7 wt.% are obtained from using air and oxygen as cathode reactance, respectively.

[b] The optimum Nafion content of 33 wt.% is obtained from Nafion–mixed catalyst layers, whereas the 42.8 wt.% optimum Nafion content is obtained from the Nafion–filmed GDL combined with Nafion–mixed catalyst layers.

[c] The optimum Nafion content of 25 wt.% is provided by controlling the Nafion content as equivalent in the anode and cathode, whereas the 30 wt.% optimum Nafion content is provided by maintaining the anode Nafion content of 25 wt.% and various cathode Nafion content.

[d] The suitable Nafion contents of 25 and 30 wt.% are obtained from low and high current density, respectively.

It can be observed that the suitable Nafion contents reported in each study are not consistent, and depend on the MEA fabrication technique, catalyst loading and catalyst types. For example, when considering fixed conditions of the same catalyst type (20% Pt/C) and Pt loading (0.4 mg/cm^2) [19],[25],[28], MEA fabricated by different coating techniques provides different optimum Nafion contents. When focusing on MEAs fabricated by the same coating technique, the ultrasonic spray from Huang [33] and the decal transfer from Mu [34] required a higher Nafion content when the Pt loading was increased. On the other hand, MEA fabricated by brushing from Sasikuma [24] and electro spraying from Martin [27] required lower Nafion content when the Pt loading was increased.

The catalyst, another important composition of catalyst ink, also acts to increase the reaction rate and as an electron conductor. It resides with the other compositions in three regions, and works together with them. As previously explained, the varying amount of catalyst affects the optimum Nafion content. In fact, the amount of catalyst also depends on the Pt/C concentration (weight percentage of Pt on supported C). At the same Pt loading, increase in the Pt/C concentration leads to a decrease of the amount of catalyst [23],[36]. However, there is no research to compare the effects of various Pt/C concentrations on the Nafion content. Although different Pt/C concentrations are selected to produce the catalyst ink in many studies, such as 20%Pt/C [19]–[26],[28],

[32], 10%Pt/C [27], 40%Pt/C [23],[29],[31],[33], 45.5%Pt/C [37], 46.1%Pt/C [35] and 60%Pt/C [34], they are not comparable due to the different MEA fabrication methods. There is little research comparing the performance of MEA fabricated by various Pt/C concentrations [23],[38]–[40]. Among these works, the optimum Nafion content was examined at one Pt/C concentration [23],[38] and then it was selected to represent the Nafion content for other Pt/C concentrations. The varied Pt/C concentrations affect not only the amount of catalyst but also the ECSAs [36]. Therefore, it is hypothesized that the optimum Nafion content should be different with varying Pt/C concentrations.

The above information leads to the objective of this experiment. MEA fabrication by the CCM method will be applied in this work since it provides catalyst layer– membrane connection, longer durability and lower internal resistance than MEA fabrication by the CCS method. Although several coating methods were used to fabricate the MEA, there is no method that comprehensively studies the combined effects of the main compositions of catalyst ink on MEA performance. Thus, catalyst inks which are formulated by varying the three compositions – solvent types, Nafion contents and Pt/C concentration – will be used to fabricate MEAs and then examine the best catalyst ink formulas. The optimum Nafion content with various Pt/C concentrations will be focused on especially due to the lack of research studying this effect. In addition, the catalyst-coated membrane (CCM) with the low frequency ultrasonic spray technique will be used to fabricate the MEAs for the first time in this research.

1.2. Literature reviews

1.2.1. Comparison of different coating method

Chaparro *et al*. [5] compared the performance of MEAs fabricated by the CCM and CCS methods by electrospraying. The catalyst inks were prepared from catalyst (Pt/C, E-TEK, 20 Pt), Nafion solution (Aldrich, 5 wt.%), and isopropanol (IPA). The Pt loading was 0.21 mg/cm^2 and the Nafion content was 15 wt.%. Typical electrolyte membranes of Nafion 212 were used for MEA fabrication by the CCM method and GDLs (ELAT E-TEK, LT1200W) were used for MEA fabrication by the CCS method. The coating

area or catalyst active area was 16 cm^2. To characterize the morphology of the catalyst layers, the scanning electron microscope (SEM) technique was used. The results show that the catalyst layers formed by the CCM method have a globular morphology while those formed by the CCS method have a dendritic morphology. The MEA fabricated by the CCM method also provides lower internal cell resistance compared with the CCS method because of better contact between the catalyst layer and membrane.

Prasanna *et al*. [4] studied the durability of MEA fabricated by three methods, CCS, CCM, and a CCM-hot pressed method. The three different MEAs were made from the same catalyst ink formula and membrane (Nafion 112). The catalyst inks were prepared by mixing catalyst powder (40 wt.% Pt/C, E-TEK), IPA and 5 wt.% Nafion solution (Du Pont, Inc.). All MEAs were fabricated by the spraying technique with Pt loading of 0.3 and 0.4 mg/cm^2 for anode and cathode, respectively. The H_2 and air stoichiometry of 1.5:3, the cell relative humidity of 55% and the cell temperature of 80°C were conditioned. The experiment was performed at a constant current density of 600 mA/cm^2 to investigate the voltage drop and durability in each MEA. The results show that CCM and CCS MEAs can be run for 1000 hours, whereas the CCM-hot pressed MEA can be run for only 500 hours. The CCM MEA exhibits the lowest degradation rate and the highest initial performance. The cell voltage of the CCM-hot pressed MEA decreases fastest, followed by the CCS and CCM MEAs, because the hot-pressed process is the cause of a decrease in porosity in the catalyst layers, resulting in more severe water accumulation in the CCM-hot pressed MEA than in the other MEAs.

Xiong *et al*. [3] studied the effects of the CCM and CCS methods on MEAs fabrication. The catalyst ink comprised a catalyst (20 wt.% Pt/C, Alfa Aesar), 5 wt.% Nafion solution, and DI water. The weight ratio of Pt/C to Nafion was set as 7:3. All MEAs were fabricated from Nafion 115 membrane with the printing technique. The Pt loading was varied as 0.1, 0.2

and 0.4 mg/cm^2 for the CCS MEA, whereas the Pt loadings of 0.05, 0.1, 0.2 and 0.25 mg/cm^2 were used for the CCM MEA. The results show that at entire Pt loading, the performance of the CCM MEAs was better than that of the CCS MEAs due to better contact between the catalyst layers and membrane, leading to the improvement of ion transportation and less mass transport resistance. Moreover, the CCM MEAs showed a significantly higher ECSA compared with the CCS MEAs, resulting in better performance and stability. The cross-section images of the catalyst layer were also investigated by SEM. The catalyst layers of the CCM MEA present a continuous interface, uniform thickness about 3 μm, and no gap with the membrane, whereas the catalyst layers of the CCS MEA show some gaps with the membrane. The CCM MEA fabricated with the Pt loading of 0.1 mg/cm^2 provides the optimal catalyst thickness and best performance. When the Pt loading is excessive, the performance is decreased due to increase of the mass transfer resistance from the thicker catalyst layers. In contrast, when the Pt loading is less than 0.1 mg/cm^2, the electrode kinetics is too slow to increase in the reaction, causing a decrease in performance.

Millington *et al*. [41] compared the performance of CCS MEAs fabricated by the hand-printing and ultrasonic spray techniques. The catalyst inks were prepared by mixing catalyst powder (20 wt.% Pt/C), Nafion solution (10 wt.%) and THF. The Pt loading was varied as 0.4, 0.15 and 0.05 mg/cm^2. The results showed that the MEAs prepared by the ultrasonic-spray technique yield better performance than those prepared by the hand-painting technique, especially at low Pt loading. The ultrasonic spray offers a better distribution of the catalyst ink on the catalyst layer, resulting in better Pt utilization. Furthermore, it offers minimal bounce-back and low overspray of the catalyst ink onto the substrate. The cavitation phenomenon from the nozzle's high frequency vibration is the cause of non-clogging issues at the nozzle tip and de-agglomeration of the catalyst ink.

1.2.2. Effects of various solvent types on catalyst ink formulas for MEA fabrication

Shin *et al.* [13] compared the performance of MEAs produced by catalyst inks formulated by different solvents, IPA and n-Butyl acetate (NBA). The other catalyst ink compositions were catalyst powder (40 % Pt/C) and Nafion solution. All the MEAs were fabricated by the CCS method with the airbrush technique on the membrane (Nafion 115) with an active area of 25 cm^2. The cell temperature of 80°C and the hydrogen/oxygen flow rate of 270 cm^3/min were set as the operating condition. The results show that the catalyst ink performs as colloidal ink when it was prepared by IPA whereas it also performs as a solution ink when NBA was used as the catalyst ink mixture. The cell performance and ECSA of the MEA made by colloidal ink are higher than that made by solution ink, with 30% and 20%, respectively. The resistance of the MEA due to colloidal ink is also diminished by 7 Ω cm^2 when compared with a MEA made by solution ink. The catalyst agglomerate sizes and the catalyst layer thickness formed by colloidal ink are larger than those formed by solution ink. These larger catalyst agglomerates of colloidal ink have difficulty penetrating into the GDL pores, resulting in a good bond between the catalyst layer and membrane. Furthermore, the reactant gases easily reach into the active area, confirming the improvement of mass transfer limitation. When investigating the solution ink, the Nafion texture diffuses into secondary pores and covers the catalyst surfaces, resulting in high mass transport resistance and reducing catalyst utilization. In the case of colloidal ink, the Nafion texture continuously forms as the networks that exist outside the catalyst agglomerate. They do not penetrate into secondary pores, leading to improved proton conductivity.

Saha *et al*. [15] studied the effects of solution and colloidal catalyst inks on MEAs performance. The catalyst inks were prepared by mixing catalyst powder (40 wt.% Pt/C, E-TEK) and 5 wt.% Nafion solution. The CCM by the decal spraying technique was applied to fabricate MEAs. The catalyst

layers were deposited on the membrane (Nafion 112) with an active area of 5 cm^2. The Pt loading was controlled as 0.20 mg/cm^2. The SEM technique was used to image the catalyst layer morphology. The results show that the pores and catalyst clusters in the catalyst layers formed by the colloidal ink are larger than those by the solution ink. This is the reason for the higher mass transport in the catalyst layers formed by colloidal ink. The ECSA of the MEA made by the colloidal ink is also 20% higher than that made by solution ink. The Nafion texture in the solution ink covers the catalyst surface, causing increasing electron insulation and decreasing the ECSA. For these reasons, the current and power density obtained from the MEA produced by colloidal ink are 45% higher than those by solution ink.

Millington *et al*. [16] studied the effect of various solvents which were used in the catalyst ink mixture on MEA performance. The catalyst inks were prepared by mixing the catalyst powder (20 wt.% Pt/C), 10 wt.% Nafion solution and four different solvents, THF, IPA, ethylene glycol (EG) and glycerol (G). CCS by the painting technique on the membrane (Nafion 212) was used for MEA fabrication. The Pt loading was controlled as 0.4 mg/cm^2. The operating conditions of 70°C cell temperature, 50% relative humidity, and 2 bar back pressure were set in this experiment. The stoichiometry of H_2 : air was 1.2 : 2.2. The results show that THF, having a dielectric constant of 7, makes the catalyst ink act as colloidal ink, whereas the other solvents having dielectric constants greater than 10 make the catalyst inks perform as solution inks. The MEA fabricated by THF catalyst ink provides the best performance, followed by the IPA catalyst ink, because the THF and IPA are evaporated out of the catalyst layers more rapidly at room temperature when compared with EG and glycerol. Therefore, the remaining solvents, EG and glycerol, in the catalyst layers could reduce the effectiveness of the three regions, leading to poor performance.

Ngo *et al*. [18] investigated the morphology of Nafion agglomerates in the mixtures of IPA (isopropyl alcohol) diluted in water with IPA/water concentrations varying from 20 to 100 wt.%. The experiments were carried out in two parts. The first was investigation of the Nafion morphologies in each concentration of IPA/water without adding catalyst. These morphologies were observed by transmission electron microscopy (TEM) and dynamic light scattering (DLS). The second was the observation of the Nafion morphologies in the electrodes of the MEA. The mixture of IPA/water in each concentration was mixed with a constant loading of catalyst of 38 wt.% Pt/C, 0.4 mg/cm^2 and Nafion content (Nafion/Pt) of 30 wt.% to produce catalyst inks. This was used to fabricate the MEA with CCS by ultrasonic spraying. The author reported that the formation of Nafion agglomerates depends on the δ and dielectric constant value of the IPA/water solution. Normally, the chemical structure of Nafion consists of a backbone structure called a perfluorocarbon (–[(CF_2–CF_2)x–(CF_2–CF)y]–) and a side-chain structure called sulfonated vinylether (–OCF_2–$CF(CF_3)$–O–CF_2–SO_3H). Each structure has an individual property of δ ($\delta_{backbone}$ = 9.7 cal$^{0.5}$cm$^{-1.5}$ and $\delta_{side\ chain}$ = 17.3 cal$^{0.5}$cm$^{-1.5}$). The compatibility between the chemical structures of Nafion (backbone and side-chains) and the IPA/water solution depends on the difference of δ. A smaller difference in δ between the solution and Nafion indicates greater compatibility. The IPA/water concentration of 55 wt.% provided the δ of 17.3 cal$^{0.5}$cm$^{-1.5}$, which is closest to the δ of the side-chain structure of Nafion. This meant the greatest compatibility between the Nafion side-chains and solution. In this case, the solvents were in contact with the side-chain groups which are associated with the backbone. This makes Nafion agglomerate like rods. The high dielectric constant value of this solvent makes side-chain (–SO_3H) groups dissociate into negatively charged (–SO_3^-) groups on the surfaces of the Nafion agglomerates. In the case of an IPA/water concentration less than 55 wt.% (increasing molar ratio of water/IPA), the excessive H_2O molecules bond with the H^+ ions detached from the side-chain (–SO_3H) groups and then form H_3O^+ ions such as (–

$SO_3^-\cdots[H_3O^+]\cdots-O_3S-$). Moreover, the dielectric constant values are also increased with increase of the water/IPA molar ratios, resulting in increasingly negatively charged ($-SO_3^-$) groups surrounding the Nafion backbone. This is also the cause of higher negative charge repulsion between the side-chains and backbone. Therefore, the Nafion agglomerates are smaller when the IPA/water concentrations are decreased. When the IPA/water concentration is higher than 55 wt.% (decreasing molar ratio of water/IPA), the δ of the IPA/water solution is decreased and closer to that of the backbone structure of Nafion, resulting in better compatibility between the solution and Nafion backbone. The Nafion backbone which is in contact with the solution appears like coiled particles having Nafion side-chains impregnated inside. In this case, the Nafion agglomerates are also smaller, with low negative charges ($-SO_3^-$). Nafion morphologies which were agglomerated by the lowest IPA/water concentration provided the best MEA performance because of the highest negative charges and smallest agglomeration.

1.2.3. Effects of Nafion content and Pt loading on catalyst layers

Passalacqua *et al*. [21] researched the influence of the Nafion content on MEA fabrications. The catalyst inks were prepared using catalyst powder (20 wt.% Pt/C, E-TEK) mixed with glycerol, ethanol and various contents of Nafion (Aldrich, 5 wt.%) in the range of 14 to 66 wt.%. The MEAs were produced by CCS, having an active area of 50 cm^2, and then deposited on the membrane (Nafion 117). The spraying technique was applied to coat the catalyst layers. The Pt loading was maintained as 0.1 mg/cm^2 for both anode and cathode. The experiment was performed under the following conditions: reactant gas temperatures of 85:80°C, absolute gas pressures of 2.5:3.0 bar and stoichiometry of 2.5:1.5 for hydrogen and air respectively. The results demonstrate that the most suitable Nafion contents are 30–35 wt.% because they enable a compromise between the maximum Pt utilization and minimum mass transport limitations, resulting in the maximum MEA performance. However, in the case of insufficient Nafion content (14%),

although the reactant gases easily reach the reaction sites and the catalyst particles allow a good electron conduction, the real active areas in contact with Nafion are poor. Thus, the Nafion is insufficient to provide proton conductivity inside the catalyst layers and the catalyst utilization is low. In the case of excessive Nafion content (greater than 33%), the total specific pore volume and the ECSAs of the catalyst are decreased because the Nafion penetrates and then fills the secondary pores, resulting in a decrease of the pore volumes and catalyst surfaces. The excessive Nafion content also cuts off the percolation path of reactant gases reaching toward the reaction sites.

Qi *et al*. [23] compared the performance of MEAs fabricated by catalyst inks which were formed with different Pt/C concentrations. The catalyst inks were prepared by mixing various Pt/C concentrations (20%Pt/C and 40%Pt/C) and Nafion solution (5 wt.%, DuPont). The Pt loading of 20%Pt/C was varied in the range of 0.022–0.332 mg/cm^2, while the Pt loading of 40%Pt/C was varied in the range of 0.074–0.387 mg/cm^2. The optimum Nafion content was examined among various contents of 20 to 40 wt.% under the conditions of 0.1 mg/cm^2 Pt loading of 20%Pt/C. The results show that the Nafion content of 30 wt.% exhibits the best performance. This was then used as the content for the second part of the experiments, the effects of various Pt loadings of 20 and 40%Pt/C concentration on MEA performance. The results show that the best performance is achieved at the Pt loading of 0.14–0.25 mg/cm^2 for 20% Pt/C. For 40% Pt/C, the best performance is at a Pt loading around 0.35±0.05 mg/cm^2. It was also observed that the use of 40%Pt/C performs better than 20%Pt/C at higher Pt loading (0.20–0.40 mg/cm^2) because the Pt particle size of 40%Pt/C is about two times larger than 20%Pt/C (3.9 and 2.0 nm for 40% Pt/C and 20% Pt/C, respectively). The larger particle size corresponds to a smaller surface area (72 m^2/g for 40% Pt/C and 112 m^2/g for 20% Pt/C) [42]. This is beneficial to utilize the surface area at high Pt loading.

Sasikumar *et al*. [24] examined the optimum Nafion content with various Pt loadings of 0.5, 0.25 and 0.1 mg/cm^2 to produce catalyst inks. The main compositions of the catalyst inks were catalyst powder (20% Pt/C, E-TEK), Nafion solution (5 wt.%, DuPont) and IPA. The prepared catalyst inks were coated by the CCS method on 5 cm^2 membrane with the brushing technique to make the MEAs. The results indicate that the optimum Nafion content depends on the Pt loading. The optimum Nafion contents increase with decrease of the Pt loading. The Nafion contents of 20 wt.%, 40 wt.%, and 50 wt.% are suitable with Pt loadings of 0.5, 0.25 and 0.1 mg/cm^2 respectively. The optimum Nafion content affects the increasing three phase regions of catalytic activity, Pt utilization and high performance. It also retains moisture and prevents membrane dehydration, especially at high current densities. In contrast, too low Nafion contents lead to low electrochemically active sites and a decrease in MEA performances. Excessive Nafion contents result in blocking catalyst sites, reducing gas permeability and increasing mass transfer resistance.

Passos *et al*. [28] investigated the combined effects of various Nafion contents and Pt loadings on MEA performance. The MEAs were produced by the CCM method for the cathode side and the CCS method for the anode side. The coating technique of painting was applied to form the catalyst layers. The catalyst inks were composed of catalyst powder (20%Pt/C, E-TEK), polytetrafluorethylene suspension (PTFE, TE-306A, DuPont), Nafion solution (5 wt.%, Aldrich) and IPA. The cathode Pt loading was varied from 0.05 to 0.4 mg/cm^2 and the Nafion content was varied from 10 to 40 wt.% in each Pt loading. The Pt loading and Nafion content at the anode remained at 0.4 and 1.1 mg/cm^2 respectively. The morphology of the catalyst layers was observed by the SEM technique. The anode catalyst layer shows no uniformity because the catalysts strongly penetrate into the GDL, resulting in a loss of contact with the membrane. This makes it hard to facilitate the electrode reaction. The cathode catalyst layer shows uniformity, resulting in better contact between the catalyst layers and membrane and higher catalyst

utilization. When considering the effects of the Nafion contents, it was found that when the Nafion contents are increased, the ECSAs are also increased. This trend is not significant at excessive Nafion contents (above 30%) because the reactant gas has difficulty penetrating toward the active site, causing high mass transport resistance. Excessive Nafion is also the cause of increasing internal ionic resistance. The effect of various Pt loadings on the cathode with a constant Nafion content of 15 wt.% was also investigated. The increase of Pt loading leads to closer contact of the Pt/C particles, an increase in the reaction rate, initial improvement of the electronic conductivity and an increase of the catalyst active area. However, the higher Pt loading results in thicker catalyst layers or a longer pathway for mass transport. This causes mass transport limitations. For example, it is hard for the reactant gas to diffuse and for the water to drain out of the catalyst layers, causing a flooding phenomenon.

Kim *et al*. [30] studied the effects of various Nafion contents in the catalyst inks for MEAs fabrication. The catalyst inks were prepared by mixing a catalyst (Pt/C, 45.5 wt.%), IPA and a Nafion solution (5 wt.%, DuPont). The Nafion content was varied between 20, 25, 30, and 35 wt.%. The Pt loading was controlled at 0.4 mg/cm^2 for both the anode and cathode. The catalyst ink was coated on a membrane (CCM) with an active area of 25 cm^2. The results show that when the Nafion content is increased from 20% to 30%, the ECSAs increased, resulting in a gradually increasing cell voltage. When the Nafion content is increased to 35%, the ECSAs and cell voltage decrease slightly since the excessive Nafion is percolated into the pores and covers the surface of the catalyst. Moreover, the excessive Nafion provides thicker catalyst layers that affect high ionic resistance and gas transport resistance. Increase of the Nafion content also leads to an increase of the water capture ability since Nafion favors water absorption. This is the cause of the flooding issue. To prove that the flooding phenomenon occurs at a Nafion content of 35 wt.%, all the MEAs were tested under the condition of changing the cathode stoichiometry from 1.5 to 2.5. The results showed that

at high current density (1.2 A/cm^2), when the stoichiometry is increased, the MEA made with 35% of Nafion content shows greater potential than the others. This clearly proves that the enhancement of the cathode stoichiometry can improve the mass transport that is caused by excessive Nafion content.

Martin *et al*. [27] studied the combined effects of various Nafion contents and Pt loadings on MEA performance. The catalyst inks were formed by mixing catalyst powder (10% Pt/C), ethanol and Nafion (5 wt.%, Aldrich). The electro-spraying technique was used to fabricate the MEA with the CCS method. The results show that when varying the Nafion content, each Pt loading requires the optimum Nafion content to maximize the MEA performance. Pt loadings of 0.1, 0.05, and 0.025 mg/cm^2 are appropriate for Nafion contents of 30%, 40% and 50% respectively. However, the optimal Nafion content is not stable (20–40 %) when insufficient Pt loading (0.0125 mg/cm^2) is used, because the amount of deposited catalysts is not enough to form a thick and continuous entire catalyst layer. In the case of too low Nafion content, the Nafion is not enough to link the catalyst layer and membrane, resulting in low Pt utilization. A loss of performance also occurs when the Nafion content is excessive because of increased thickness and decreased porosity of the catalyst layers. This results in a lower permeability of reactant gases diffusing through the Nafion toward the catalyst site. Furthermore, the utilization of catalyst is decreased because the catalyst particles are isolated by the Nafion.

Huang *et al*. [33] investigated the effects of various Nafion contents in each Pt loading on the MEA performance. The catalyst inks were prepared by mixing the catalyst powder (40 wt.% Pt/C, Johnson Matthey), Nafion solution (5 wt.%), DI water, and ethanol. The catalyst ink was coated by ultrasonic spraying (48 kHz) with a flow rate of 0.125 ml/min onto the 25 cm^2 membrane (Nafion 212). The experiment was operated under the following conditions: cell temperature of 90°C, cell relative humidity of

50%. The results show that each Pt loading provides the maximum MEA performance when the proper Nafion content is determined. A Nafion content of 20% is suitable with a Pt loading lower than 0.232 mg/cm^2, whereas 33% Nafion content is appropriate with Pt loadings higher than 0.310 mg/cm^2. The 40 wt.% Nafion exhibits poor performance when mixed with all Pt loadings. These results may indicate that too high a Nafion content in the catalyst layer will seriously decrease the performance because of the thicker catalyst layer, lower electronic conductivity, poor pore volumes and flooding phenomena in the catalyst layers. An investigation of the effect of various Pt loadings on MEA performance was also performed. The MEA produced by a Pt loading of 0.232–0.271 mg/cm^2 shows the best performance. The most suitable Pt loading leads to the highest mass power density because it provides the highest Pt utilization and an increase of the total volume of TPB. However, excessive Pt loading forms thicker catalyst layers, causing higher mass resistance and lower performance.

Su *et al*. [31] studied the effects of various ultra-low Pt loadings on MEA performance. Moreover, the influence of Nafion content varied for each Pt loading was also studied. The catalyst inks were prepared by dispersing catalyst powder (40 wt.% Pt/C, Johnson Matthey) into a mixture of IPA and Nafion solution (5 wt.%, DuPont). The Pt loadings on the cathode and anode were varied as follows: 0.3:0.2 mg/cm^2, 0.2:0.08 mg/cm^2, 0.12:0.04 mg/cm^2 and 0.09:0.03 mg/cm^2. The Nafion content was varied as 15, 20, 25, 30 and 35 wt.%. MEAs were fabricated by spraying catalyst ink using the CCM method. The cell operating conditions were set with the hydrogen and air flow rates of 300 and 1000 cm^3/min, respectively. The cell temperature was 60°C and the humidifying temperature was 65°C. The results show that MEA 0.12:0.04 provides the best performance and slightly higher than MEA 0.3:0.2 and MEA 0.2:0.08, because its thinner catalyst layers result in improved mass transport, the compromise of TPB, high Pt utilization and easy diffusion of reactant gases, especially at high current densities. The MEA for 0.09:0.03 mg/cm^2 provides a much lower performance than the

others due to insufficient catalyst, which is not enough to activate the reaction in the active sides, resulting in poor ORR kinetics and the largest cell resistance. When considering the effect of Nafion content at each Pt loading, the results show that at the Pt loading of 0.12:0.04 mg/cm^2, the Nafion content of 25 wt.% provides the best performance because the Nafion facilitates proton conductivity in the catalyst layer. However, when the Nafion content is higher than 25 wt.%, the performance decreases sharply because the Nafion fills some of the electrode pores, leading to a reduction of reactant gas permeability and the mass transportation problem. Moreover, some catalyst sites are covered by Nafion, leading to ineffective catalyst utilization.

1.3. Research objectives

1.3.1. To determine the solvent and Nafion contents which give the best performance of the membrane electrode assembly (MEA)

1.3.2. To study the influence of the Pt/C concentration on PEM fuel cell performance

1.3.3. To study the morphology and electrochemical properties of the catalyst layers

1.4. Scopes of research

1.4.1. The solvents used in this work are ethanol, IPA and THF.

1.4.2. The ionomer is Nafion (5% v/v DuPont).

1.4.3. The catalysts are commercial catalyst (10%, 20% and 40% Pt/C, Premetek Co.).

1.4.4. The coating method is ultrasonic spraying with a frequency of 20 kHz.

1.4.5. The catalyst ink flow rate is controlled in the range of 0.12 cm^3/min.

1.4.6. The fabricated MEAs have an active area of 23 cm^2.

1.4.7. A Fuel Cell Test Station (Model 890E, Scribner Associated Inc.) is used to test single PEMFCs.

1.4.8. The Pt loading is controlled at 0.3 mg/cm^2.

1.4.9. The physical structure of the catalyst layers by SEM techniques.

1.4.10. Cyclic voltammetry technique is used to determine ECSA of catalyst layer.

1.5. Significance of research

1.5.1. The application of appropriate types or amounts of catalyst ink components will lead to an effective utilization of the catalyst and the best PEMFC performance.

1.5.2. Currently, many Pt/C concentrations are widely applied for MEA fabrication, thus the study of the electrochemical and physical behavior of each type of Pt/C will be useful for suitable application for MEA fabrication.

1.5.3. The MEA is the most important component of the PEM fuel cell; therefore the fabrication of MEA by ourselves will enhance our own know-how and technology.