CHAPTER 4

Various Nafion contents in Pt/C concentration for MEA fabrications

4.1. Introduction

MEA is the most important part of a PEMFC [50]–[53]. The electrochemical reaction technically takes place in the MEA, where hydrogen is oxidized at the anode and oxygen is reduced at the cathode. At the MEA, the charges and electrons transfer simultaneously, generating heat and water as the products [54], [55]. The electrochemical reaction occurs at low temperatures in a PEMFC due to the use of electrocatalysts such as Pt/C [56]–[58]. The electrocatalysts are coated on either a GDL or the electrolyte membrane using various techniques. The most well – known technique is the catalyst-coated membrane (CCM), where the electrocatalyst is deposited directly onto the electrolyte membrane producing catalyst layers or electrodes [59]–[63].

The CCM fabrication technique normally uses Nafion as an ionomer allowing H^+ ions transfer to and from the reaction zone. It has been observed that fuel cell performance is considerably dependent on Nafion content in the catalyst layers. The Nafion content in the CCM method has been optimized by a large number of studies. For example, Passos *et al.* [64] painted Pt/C 20 wt.% onto the electrolyte membrane at the cathode and found the optimal Nafion content depending on current densities. At high current densities, a Nafion content of 15 wt.% gave the best performance, while the performance was better with higher Nafion content at low current densities. Sun *et al.* [65] directly sprayed catalyst inks (with 40 wt.% Pt/C) onto both sides of electrolyte membranes, and observed that the optimum Nafion was in the range of 33.3 to 50 wt.%. Using the same approach, but higher a Pt/C concentration, (45.5 wt.% Pt/C), Kim *et al.* [30] investigated the effect of Nafion with symmetric MEAs and found that the most suitable Nafion content was 25 wt.%. Su *et al.* [66] studied ultralow platinum loading and reported that MEA with 25 wt.% Nafion showed the best performance with a Pt loading of 0.04 mg/cm^2 and 0.12 mg/cm^2 at the anode and cathode, respectively. Moreover, Xie *et al.* [67] used the decal method and reported that the optimal Nafion content at the cathode was 27 ±6 wt.%, where the Nafion content at the anode was fixed at 28.8 wt.%. Similarly, Mu and Tian [34] showed that the optimal Nafion content for the decal technique was between 25 and 30 wt.% for the cathode, and about 30 wt.% for the anode, using a Pt/C catalyst with a concentration of 60 wt.%. Recently, Huang *et al.* [33] reported that the optimal Nafion content was from 20 to 33 wt.%, depending on Pt loading at the cathode, by using an ultrasonic spray-coater. They found that a lower Pt loading preferred a lower Nafion content.

Table 1.1 shows a summary of those works, which reported the optimum Nafion content using CCM fabrication. It indicates that the optimal Nafion content ranges from 15 to 33 wt.% depending on the fabrication method, catalyst concentration, and Pt loading. Table 1.1 shows that catalysts are usually only used at one concentration, such as 60 wt.%, 40 wt.% or 20 wt.%. However, it is hypothesized that the optimal Nafion content may depend on the Pt/C concentration, but this has not been widely studied. This work aims to investigate the effect of various Nafion contents in each the Pt/C concentration for MEA fabrication by using the same Pt loading and fabrication method. The images of catalyst layers of MEAs from different Pt/C concentrations are also examined. The Pt active surface areas and polarization curves are measured, and by considering both the percentage by mass of Pt/C catalyst and Nafion simultaneously, the production of MEA can be effectively optimized.

4.2. Experiments

4.2.1. MEA fabrication

The MEAs were fabricated using commercial Pt/C catalysts with 10 wt.%, 20 wt.% and 40 wt.% (Premetek Co.). The catalyst inks were formulated with proper compositions of ethanol (99% v/v, RCI Labscan Limited), 5% v/v Nafion solution in isopropanol alcohol (DuPont Inc., EW1100), and the Pt/C catalysts. The catalyst inks were sonicated for 30 minutes at room temperature before the fabrication of the MEAs. The ultrasonic spraying technique was used to fabricate both the anode and cathode with a frequency of 20 kHz. The catalyst inks were coated directly onto the electrolyte membrane (XL 100, DuPont Inc.) with the rate of 0.12 cm^3/min. After spraying on both sides of the electrode, the MEAs were cured at 70 °C in the oven for about 2 hours to evaporate the solvents and contaminants. The catalyst loading on the MEAs was kept identical on both the anode and cathode at 0.3 mg/cm^2 with a reactive area of 23 cm^2. The Nafion composition in the catalyst ink was varied by a ratio of the dry weight of Nafion to the dry weight of Pt/C catalysts and Nafion, and the ratios were 15%, 20%, 25%, 30%, and 35%.

4.2.2. Single cell assembly and electrochemical testing

A single cell was assembled using fuel cell hardware from Fuel Cell Technologies Inc. A MEA was sandwiched with carbon cloth GDLs (W1S1005, CeTech) without hot pressing, and followed by attaching fiberglass – silicone composite gaskets. The graphite flow field, with 3-channel serpentine, was used as the polar plate. A distribution load of 50 lb/in^2 (344.75 kN/m^2) was applied by tightening a single cell as presented in Figure 3.1. A fuel cell was conditioned by using a potential swing method for two hours. The polarization data were obtained using Fuel Cell Test Station (Model 890E, Scribner Associated Inc.), using the constant potential mode (Figure 3.2). The cell resistances were also recorded during polarization. The cell temperature was set at 75 °C, while the stoichiometry of hydrogen to air was regulated at 1.2:2.0 respectively. Both the anode and cathode had back pressures of atmospheric pressure. The relative humidity was set as 65% and 95% RH to observe mass transport behavior.

The ECSAs of the MEAs were investigated using the cyclic voltammetry (CV) technique by Princeton Applied Research potentiostat/galvanostat model 263A (Figure 4.1). Hydrogen, with a flow rate of 300 sccm, was fed into the anode as a reference electrode, whereas nitrogen, with a flow rate of

300 sccm, was supplied into the cathode as a working electrode. The potential was scanned from 0.05 V to 1.20 V (SHE) with a scanning rate of 50 mV/sec. The data were reproduced 10 times to obtain the stable profiles. The peak at the hydrogen desorption was obtained and used to calculated the ECSAs of the MEAs.

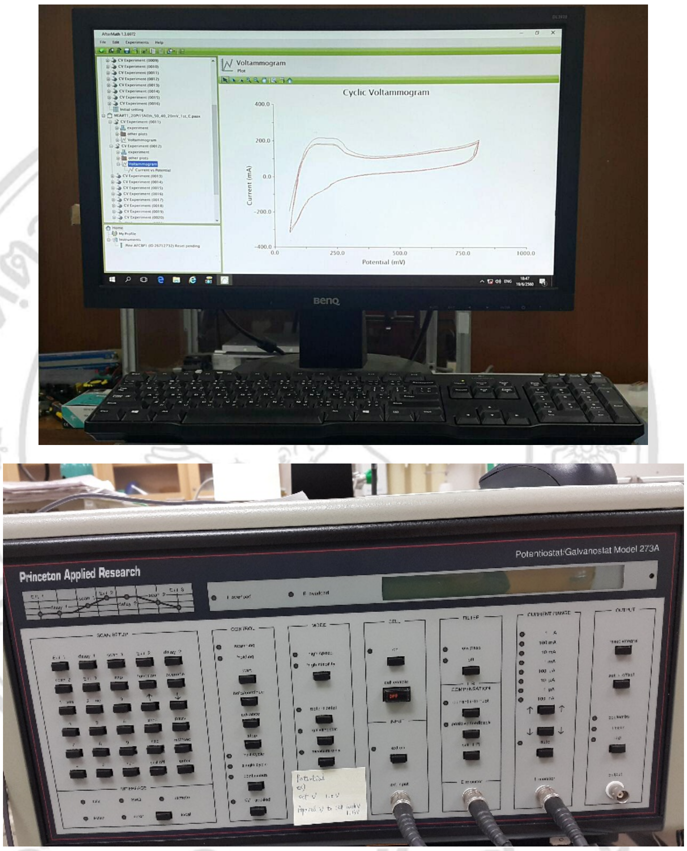

Figure 4.1 CV testing by Princeton Applied Research potentiostat/galvanostat model 263A

4.2.3. Scanning electron microscopy

SEM with cold cathode field emission (JEOL JSM 6335F) was used to characterize the physical structures and morphologies of the catalyst layer. The electron potential was between 0.5 and 30.0 kV. The element analysis in catalyst layer was analyzed using an energy – dispersive X – ray microanalyser. The MEAs were cut into small pieces about 0.5 cm × 0.5 cm, for planar images. Additionally, the MEAs were also broken under a liquid nitrogen environment, to prepare the samples for visualizing the cross-section images.

4.3. Results and discussions

4.3.1. Morphology of catalyst layer with varying Pt/C concentration and Nafion contents

MEAs in this work had an identical platinum loading of about 0.3 mg/cm^2 for both the anode and the cathode. In order to examine the effect of Pt/C concentrations and the Nafion ionomer content (NI), MEA fabrications were prepared in batches. The catalyst inks were mixed with different Nafion contents, whereby the weight percentage of dry Nafion per the total weight of dry Pt/C catalyst and Nafion was described as a percentage of Nafion. For example, 20 wt.% of the Pt/C catalyst has approximately 34.5 mg and a reactive area of 23 cm^2. Therefore, at the Nafion content of 25% by weight, the dry weight of Nafion needed is about 11.5 mg. Table 4.1 describes the mass of Pt/C catalyst, dry mass of Nafion corresponding to particular Pt/C concentrations and Nafion contents.

At the same catalyst concentration, the increase in percentage of Nafion content (the second column) corresponds to the increase of Nafion required in the catalyst ink (the fourth column). On the other hand, when the concentration of Pt onto the supported carbon (the first column) increases, for example from 10 wt.% to 20 wt.%, the mass of the Pt/C catalysts (the third column) used, is reduced by about half (i.e. from 69.0 mg to 34.5 mg). This is due to the fact that the platinum loading on the MEAs is controlled at about 0.3 mg/cm^2, when the platinum concentration on Pt/C catalysts is increased. As a result of this, when the same Nafion content is considered, the dry mass of Nafion decreases with the increasing of platinum concentration in the Pt/C catalysts. MEAs with Pt/C concentration of 10 wt.%, 20 wt.% and 40 wt.% were fabricated and examined by SEM, while the Nafion ionomer content was kept constant at 30%. The physical morphology of the catalyst layers in those MEAs was evaluated and the in – plane and cross – section images are shown in Figure 4.2.

Table 4.1 percentage of Nafion contents in catalyst inks for Pt/C catalysts of 10wt.%, 20wt.% and 40wt.% are described. Mass of Pt/C catalysts and dry mass of Nafion are calculated according to the percentage of Nafion contents, where the Pt loading was controlled at 0.3 mg/cm^2 and the The reactive area of MEA was 23 cm^2.

Pt/C catalysts	Nafion contents (%)	Mass of Pt/C catalysts (mg)	Dry mass of Nafion (mg)
10wt.%	15	69.0	12.2
	20	69.0	17.3
	25	69.0	23.0
	30	69.0	29.6
	35	69.0	37.2
20wt.%	15	34.5	6.1
	20	34.5	8.6
	25	34.5	11.5
	30	34.5	14.8
	35	34.5	18.6
40wt.%	15	17.3	3.0
	20	17.3	4.3
	25	17.3	5.8
	30	17.3	7.4
	35	17.3	9.3

From the in – plane images in Figure 4.2(a), the microstructures of the catalyst layers show that the pores are due to the agglomeration of Pt/C catalysts, facilitated by the Nafion ionomer acting as a binder. Uchida *et al.* [68] reported that the pores located between agglomerations are the secondary pores, which have a pore size greater than 0.040 µm. At the same Nafion content of 30%, the secondary pore size of the catalyst layer was observed in these images, where 10 wt.% Pt/C exhibited the largest pore, followed by the pore from 20 wt.% Pt/C, and the smallest pore is from 40 wt.% Pt/C. The cross-section images in Figure 4.2(b) shows that the thickness of the catalyst layer depends on the Pt/C concentration.

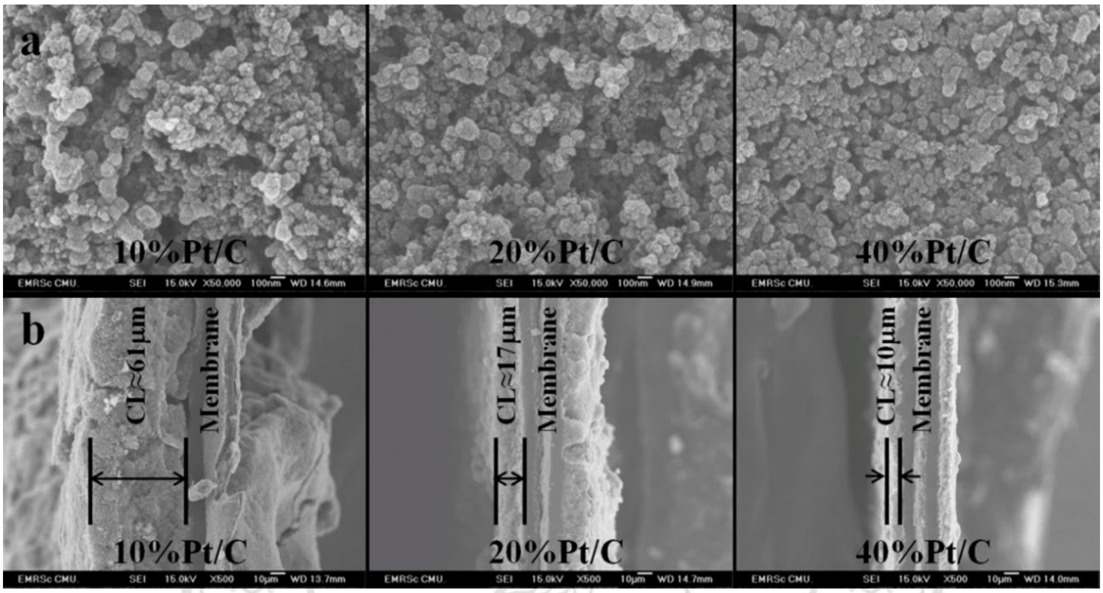

Figure 4.2 The SEM images of catalyst layer of MEAs with Pt/C concentration of 10wt.%, 20wt.% and 40wt.% at the Nafion content of 30%, (a) the in-plane image with magnification of 50,000 times; (b) the cross-section images with magnification of 500 times

The Pt/C concentration increases from 10% to 20% and 40%, and the resulting the thickness of catalyst layer decreases from about 61 μm to 17 μm and 10 μm, respectively. This is because the Pt/C catalysts with smaller Pt/C concentration also have less bulk density. At the same Pt loading, the smaller Pt/C concentration requires a greater amount of Pt/C catalysts. Consequently, the Pt/C concentration yields a different physical morphology of MEAs giving different thicknesses and porosity. For other Nafion contents, the morphology images are identical and show similar tendencies.

4.3.2. Electrochemical surface areas

MEAs with Pt/C concentrations and Nafion contents were fabricated and investigated for ECSA by cyclic voltammetry (CV) as shown in Figure

4.3(a), 2(b) and 2(c). The hydrogen desorption profile represents H^+ ions oxidized at the Pt surface. The coulombic charges of hydrogen oxidation after subtraction of the charges associated with the double layer were considered. The ECSAs can be calculated by assuming one H^+ ion desorbed from one Pt surface site, as shown in Figure 4.3(d).

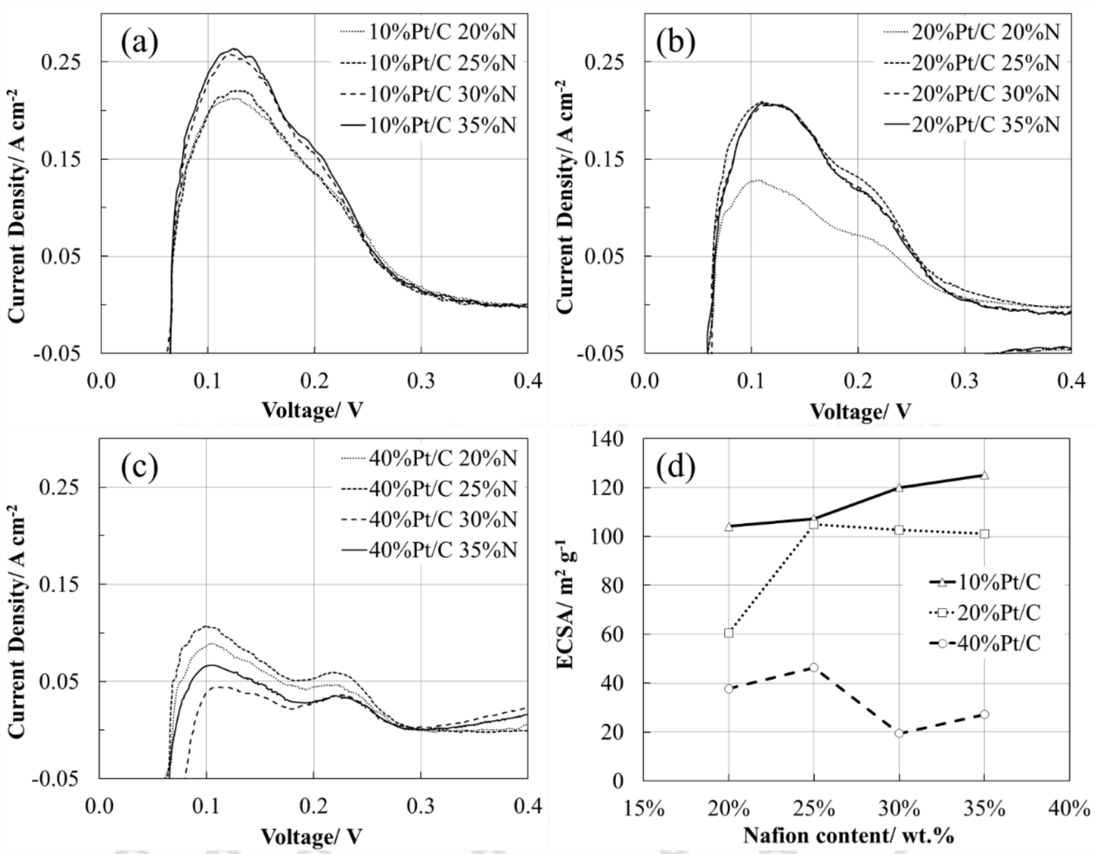

Figure 4.3 Cyclic voltammogram of MEAs fabricated from various Nafion contents in each Pt/C concentration; (a) 10wt.% (b) 20wt.%, and (c) 40wt.% and the ECSAs versus Nafion contents of MEAs fabricated from each Pt/C concentration (d)

In Figure 4.3, the CV results show that 10% of Pt/C catalyst yields the highest peak and has the highest ECSA (Figure 4.3(d)) for all ranges of Nafion content. This is because the 10% Pt/C concentration has the highest carbon portion. Therefore, the coverage of Nafion is mostly coated onto the supporting carbon, exposing the Pt surfaces to the electrochemical reactions.

This explanation also describes why an ECSA of 20% Pt/C concentration gives a higher Pt surface than 40% Pt/C concentration for all ranges of Nafion, as shown in Figure 4.3(d). Moreover, the ECSAs of Pt 20% and 40% have the maximum surface area when Nafion content attains at 25%. This indicates the optimum Nafion content facilitating the charge and electron transfer during electrochemical reactions. On the other hand, the ECSA of 10% Pt/C concentration increases when the Nafion content increases. It can be extrapolated that the optimal Nafion for Pt/C10% is greater than 35 wt.%.

Cyclic voltammetry measurements were made on these ECSAs using a current density of between 50 and 250 mA/cm^2. This corresponds to the kinetic region (i.e. activation loss) in the polarization curve, where the cell potential is in between the open circuit voltage (OCV) and 0.75 V. For all ranges of polarization, different results may be given, particularly at the higher current density.

4.3.3. Polarization curves

The polarization curves and cell resistance of identical MEAs were investigated, as shown in Figure 4.4. The cell resistances for all MEAs had a similar average value of about 70 mΩ/cm^2, since they used the same electrolyte membrane. However, when the cell resistance distribution, regardless of Nafion content, is considered, it is observed that 10wt.% Pt/C gave the broadest distribution, followed by the Pt/C of 20 wt.%, and the narrowest distribution was with a catalyst of 40 wt.% Pt/C. This distribution possibly relates to the variation in catalyst layer thicknesses causing small deviations in cell resistance. The polarization curves were considered in three different potentials: 0.4 V, 0.6 V, and 0.8 V. These are indicative of mass transport, ohmic, and kinetic regions, respectively. The current densities obtained from the polarization curve (Figure 4.4) were plotted against Nafion contents, as shown in Figure 4.5. The profiles of 0.4 and 0.6 V for and Pt/C catalyst represent the same tendency. This indicates that the effect of Nafion on Pt/C concentration is analogous for the mass transport and ohmic region, respectively.

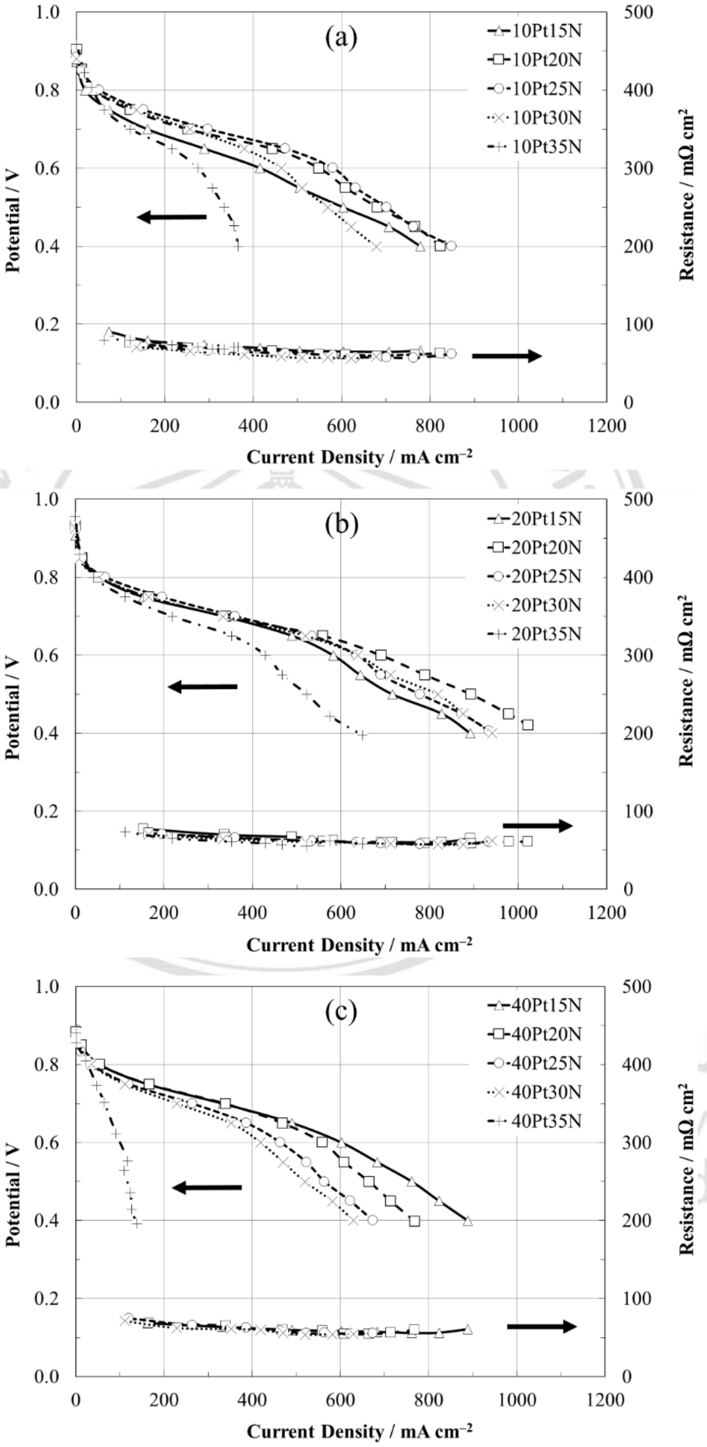

Figure 4.4 Polarization curves and cell resistances of Pt/C concentration of (a) 10%Pt/C, (b) 20%Pt/C and (c) 40%Pt/C for MEAs fabricated by various Nafion contents

For each Pt/C concentration in Figure 4.5, at cell potentials of 0.4 and 0.6 V, the current density drops when the Nafion contents are greater than the optimum amount. This is due to excess Nafion covering the Pt surface site, and consequently reducing the fuel cell performance. Moreover, at the transport region (0.4 V cell potential), current density dropped dramatically compared to 0.6 V, probably due to the accumulation of water from the electrochemical reactions taking place in hydrophilic Nafion, causing cell flooding (as shown in Figure 4.4 and Figure 4.5). When Nafion contents are lower than the optimum point, the current density also decreases owing to the inadequate proton pathway facilitating hydrogen ions transportation to and from the reaction zone. Therefore, the optimum Nafion content balances the amount of Pt surface sites and the mass transportation (including hydrogen, oxygen, charges and electrons) that yields the best performance. However, there is no optimum point for 40wt.% Pt/C in Figure 4.5(c) for both 0.4 and 0.6 V. The current density decreases with the increment of Nafion content. This indicates the excess Nafion, where Pt sites are covered by Nafion causing the lower fuel cell performance. In this case, it is able to extrapolate that the optimal Nafion for 40 wt% Pt/C is probably at 15wt.% or less than 15 wt.%. However, it was quite difficult to prepare MEA with very low Nafion content especially lower than 15wt%, since the catalyst layer was not able to form as a thin film causing the cracks and peeling out of the membrane. Therefore, the 15wt.% is the minimum Nafion content in this report.

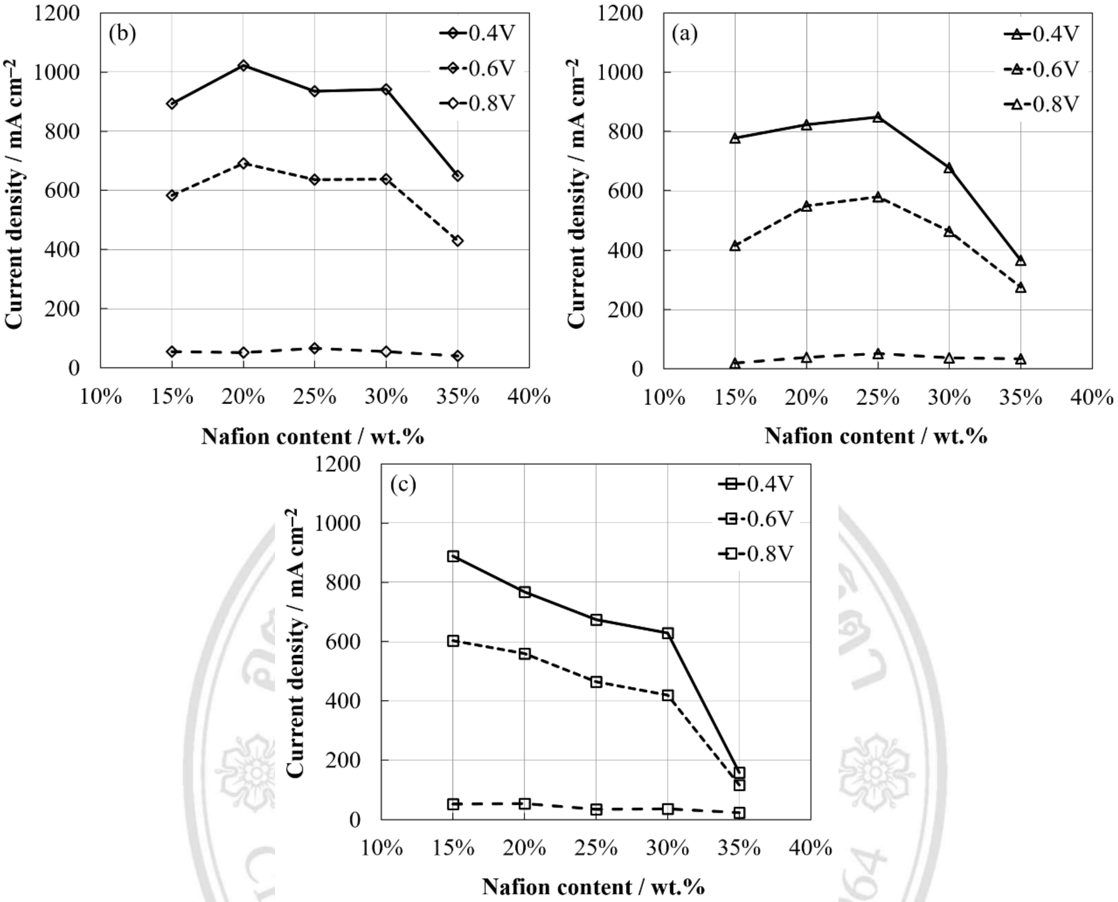

Figure 4.5 Current density versus Nafion contents at cell potential of 0.4, 0.6 and 0.8 V for MEAs fabricated from Pt/C concentration of (a) 10%, (b) 20%, and (c) 40%

The results show that a Nafion content of 25%, 20%, and 15% yielded the best performance for Pt/C catalysts of 10 wt.%, 20 wt.%, and 40 wt.%, respectively. Amongst these, a catalyst with 20 wt.% Pt/C fabricated with Nafion content of 20% yields the highest performance, as shown in Figure 4.6. It is observed that lower Pt/C concentration (i.e. 10 wt.% Pt/C catalyst) required more Nafion content than higher Pt/C concentration (i.e. 20 wt.% or 40 wt.% Pt/C catalysts). This is because of the higher volume of supported carbon at lower Pt/C concentrations. Moreover, the catalysts with lower Pt/C concentrations also have lower Pt surface densities than those with higher Pt/C concentrations. Consequently, the lower Pt/C concentrations need more ionomer than the higher ones in order to connect platinum active sites, and transfer protons to and from the reaction zone and the electrolyte membrane.

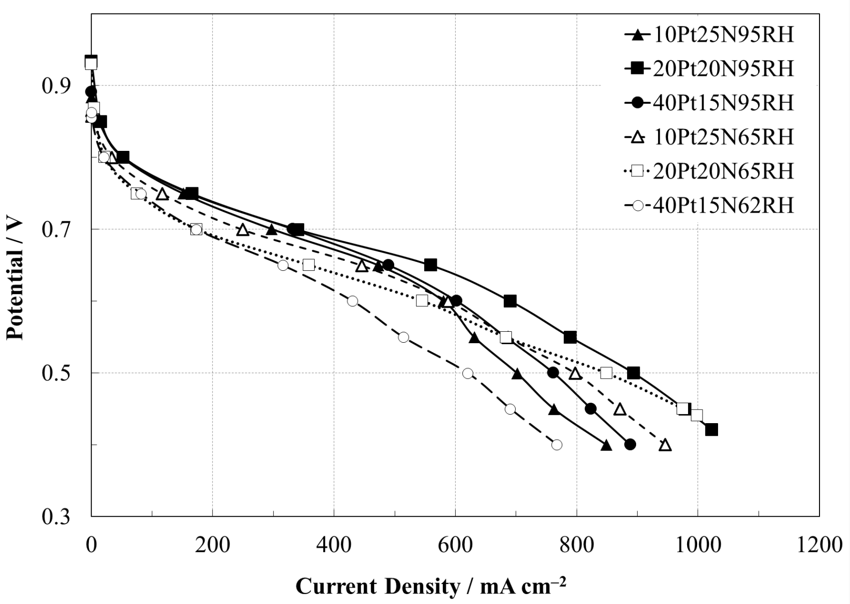

Figure 4.6 The best performance comparison of MEA fabricated from 10% Pt/C, 20% Pt/C and 40%Pt/C at the relative humidity of 65% and 95%

The best performance of 10 wt.% Pt/C was smaller than the best performance of 20 wt.% Pt/C particularly at a current density larger than 500 mA/cm^2, whereas their performances were almost identical at a current density lower than 500 mA/cm^2. This suggests that the mass transportation of reactant gases (i.e. hydrogen and oxygen) and produced water is more influential. Since the catalyst layer of 10 wt.% Pt/C has a thickness 3 times larger than that of 20 wt.% Pt/C (Figure 4.2), then the diffusion rate of those transportations are hindered due to the thicker catalyst layer. On the other hand, the best polarization curve with 20 wt.% Pt/C was higher than that of the best of 40 wt.% Pt/C, although 20 wt.% Pt/C had a slightly thicker catalyst layer (about 1.7 times). This is mainly due to the much lower Pt surface area (Figure 4.3(d)). Our previous work also confirmed that Pt/C 40 wt.% had a larger average particle size and lower Pt surface sites than the Pt/C 20 wt.% [36].

To prove that the issue of mass transport in catalyst layer of 10%Pt/C was more severe than that of others, the performance testing at the relative humidity of 65% was also performed as shown in Figure 4.6. Normally, Nafion or electrolyte membrane likes to absorb moisture and it can excellently conduct proton at high moisture [45], [69], [70]. The reduction of RH in the operation is the cause of reducing proton conductivity. Therefore, the best performance of MEAs fabricated by 20%Pt/C and 40%Pt/C were decreased with reducing RH from 95% to 65%. In contrast, the performance of MEA made 10%Pt/C was improved when RH was reduced to 65%RH because at 95%RH, it occurred the water flooding at the too thick catalyst layer of 10%Pt/C. Thus, at the operation of 65%RH, the amount of generated and accumulated water in catalyst layers of 10%Pt/C can compensate the moisture that was reduced from 95%RH.

Additionally, Figure 4.7 represents the optimal Nafion contents when various Pt/C concentrations were used. This data shows that regardless of fabrication methods, Pt loadings, and fuel cell operating conditions, most of the time a single Pt/C concentration can be used. It shows that the optimal Nafion content depends on Pt/C concentration, and verifies that the higher Pt/C concentration requires lower Nafion content. The results from this work show a lower optimal Nafion than the average, probably due to the fabrication technique.

The current density at a 0.8 V cell potential (the activation or kinetic region) was plotted against Nafion contents and compared with the ECSA, as shown in Figure 4.8. The profiles of the ECSA and current density have similar shapes for all Pt/C concentrations and all ranges of Nafion contents. During cyclic voltammetry, the ohmic and transportation losses are very small due to the low current density. Therefore, the active Pt surface area during the CV technique is applicable only when it is at a low current density.

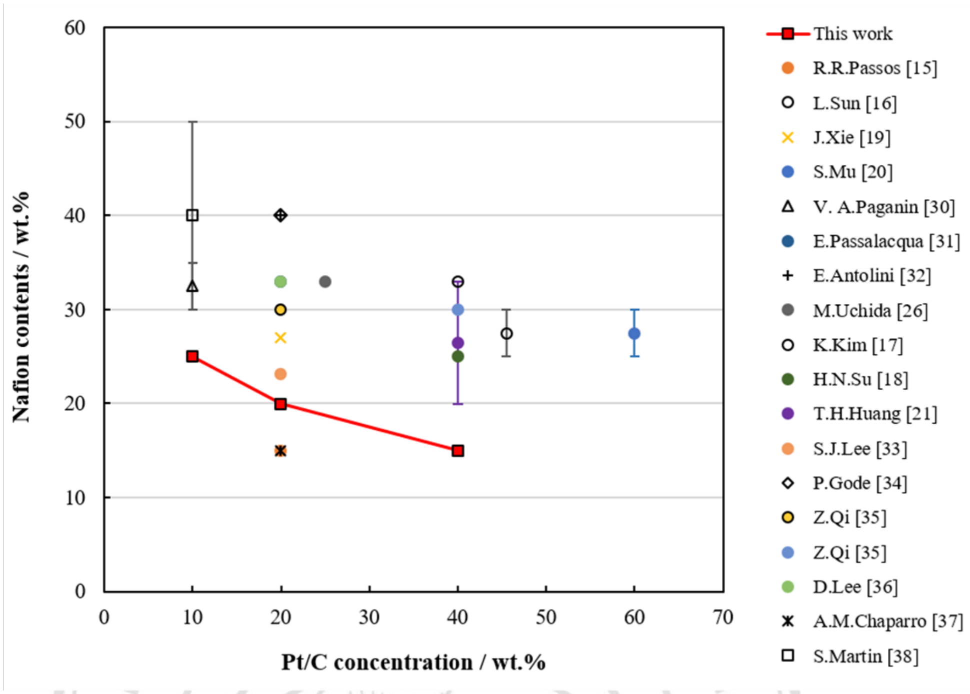

Figure 4.7 The correlation between Pt/C concentration and optimal Nafion contents regardless of fabrication techniques, Pt loadings and operating conditions

At higher current density (above 100 mA/cm^2), the ohmic resistance from the membrane, MEA and transportation from all the species in the anode and cathode are more significant. Consequently, the ECSA might not be used to relate the active surface area with the polarization in the entire current density range. Thus, the optimal Nafion contents for each Pt/C concentration from polarization curves does not agree with those from the ECSA results. This observation agrees with Kim *et al.* [30], who reported that the optimum Nafion content of Pt/C 45 wt.% taken from the polarization curve was not the same value of that from the ECSA. They explained that when the ionic resistance in the catalyst layer was significant, the ECSA measured by CV could not be fully utilized as the active sites for electrochemical reactions [71]. Therefore, it is only useful to use the results from the polarization to correlate the Nafion contents and Pt/C concentration.

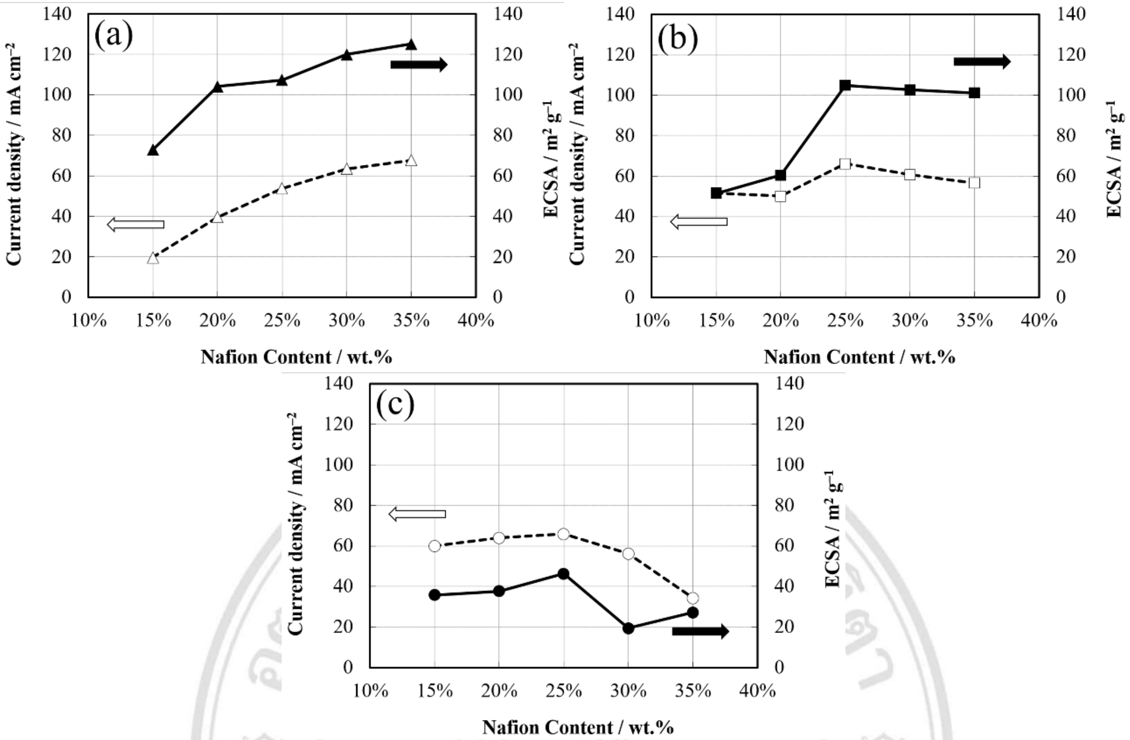

Figure 4.8 Current density at cell potential of 0.8 V versus Nafion content, and ECSA versus Nafion content from cyclic voltammetry of Pt/C concentration 10wt.% (a), 20wt.% (b), and 40wt.% (c)