CHAPTER 3

Variation of Nafion content and solvent types for MEA fabrication

3.1. Introduction

PEMFCs are a promising and environmentally friendly technology. Since PEMFC products are the electricity and water generated from the electrochemical reaction between the supplied reactant gases (H_2 and O_2 or air), PEMFCs provide high efficiency and low noise. Moreover they are also operated at low temperature and pressure [43].

The electrochemical reactions in PEMFCs take place at MEA, the most vital component. Normally, the MEA can be fabricated by coating the electrode or catalyst layers on both sides of membrane surface. A three region boundaries (TRB), comprising of pores, ionomer, and catalyst regions, are the key factors determining the mass and ion transport and consequently the PEMFC performance. The parameters influencing the catalyst layer morphology and TRB are the catalyst coating technique and the catalyst ink components, which normally comprise the solvent, ionomer, and catalyst. The solvent plays the role as determinant of pore shape (the first region of the TRB) in catalyst layers [13], [15] because while the catalyst ink is deposited on the membrane surface, the solvent suddenly evaporates out of the catalyst layer. The areas where solvent evaporates become to pores. The amount of Nafion solution and catalyst also affects the second and the third regions of the TRB. Although the catalyst is an electron conductor and is beneficial for increasing the kinetic reaction rate, an excessive amount of Nafion leads to mass transport problems in catalyst layers [33], [45]. Nafion residing in catalyst layers facilitates proton conductivity and retains moisture. But the excessive Nafion is the cause of mass transport resistance [25], [28], [33], [35], [46]. Therefore, the balance of TRB by varying the proportions of catalyst ink compositions is very important in order to obtain the highest catalyst utilization and PEMFC performance. When different types of solvent are mixed with Nafion, the catalyst inks can become to one in three states, which are solution, colloid, and precipitate states. These states depends on the dielectric constant of the solvent [13], [14]. Each state affects the catalyst layer morphology particularly the agglomeration of catalysts and creating surrounding pores.

It can be seen that the selection of suitable solvents and proper Nafion content determines the catalyst layer morphology and consequently the PEMFC performance. The coating technique typical ultrasonic spraying was applied to fabricate MEA by Pollet [47]. However, the application of ultrasonic coating technique also lacks the information about appropriate solvents with various Nafion contents. Therefore, this research aims to optimize the MEA performance by determining a suitable solvent with various Nafion contents for MEA fabrication by using the ultrasonic spray technique.

3.2. Experiments

3.2.1. MEA fabrication

The catalyst inks were prepared by mixing 20% Pt/C (Premetek), Nafion solution (5% v/v, DuPont), and three types of solvents; ethanol, THF, and IPA. The different types of solvents were selected by considering the solvent properties such as; boiling point and dielectric constant. The rational for selecting solvents in this experiment is applied from Ref. [13]–[16]. For example, Millington [16] informed that the solvents having high boiling point are bad result for PEMFC performance due to the mass transport obstacle from remaining texture of these solvents in catalyst layer. Thus, the boiling point of the selected solvents this experiment is not exceeded 100°C. Moreover, the solvents having various properties of dielectric constant are also selected to provide various states of catalyst inks as reported by Ref. [13]–[15]. Dielectric constant values between 3.0 and 10.0 makes the catalyst inks become colloid, whereas those values more than 10 makes catalyst inks behave as solution inks, as shown in Table 3.1. The Nafion contents were varied as 20, 25, 30, and 35 wt.% in each solvent type. The Pt loading was controlled at 0.3 mg/cm^2. Each MEA was fabricated by following processes. All catalyst ink compositions were put into a beaker and then sonicated for 30 minutes.

Table 3.1 The physical properties of solvents

Solvents	**Dielectric constant**	**Boiling point**	**Catalyst ink state**
Ethanol	24.3	78°C	Solution ink
IPA	18.3	82°C	Solution ink
THF	7.0	65°C	Colloid ink

The catalyst ink was contained in syringe pump and then was fed at the flow rate of 0.12 cm^2/min though an ultrasonic nozzle that vibrates at a frequency of 25 kHz. The catalyst ink was directly sprayed onto the electrolyte membrane (XL 100, DuPont), which had a reactive area of 23 cm^2. These processes were performed in the same way for another side of membrane to complete MEA fabrication. After the spraying processes, MEAs were put into the oven at 85 ºC for 2 hours to completely evaporate the solvents and contaminants.

3.2.2. Single cell assembly and testing

To assemble single PEMFC (Figure 3.1), The MEA was sandwiched in both anode and cathode by carbon cloth gas diffusion layers (W1S1005, CeTech) followed by fiberglass – silicone composite gaskets, and the flow field plates typical three – channel serpentine. A fuel cell test station (Model 890E, Scribner Associated) was used to test the PEMFC performance as shown in Figure 3.2. The polarization curves were obtained by using the constant potential mode. The overall cell resistances were obtained during polarization. The cell temperature and humidity were set at 75 ºC and 95%, respectively. The hydrogen to air stoichiometry was set at 1.2:2.0. To investigate the catalyst layer morphology of MEAs, the surface and cross – sectional images of catalyst layers formed by Nafion content of 30 wt.% and various solvent types; THF, ethanol, and IPA were photographed by SEM.

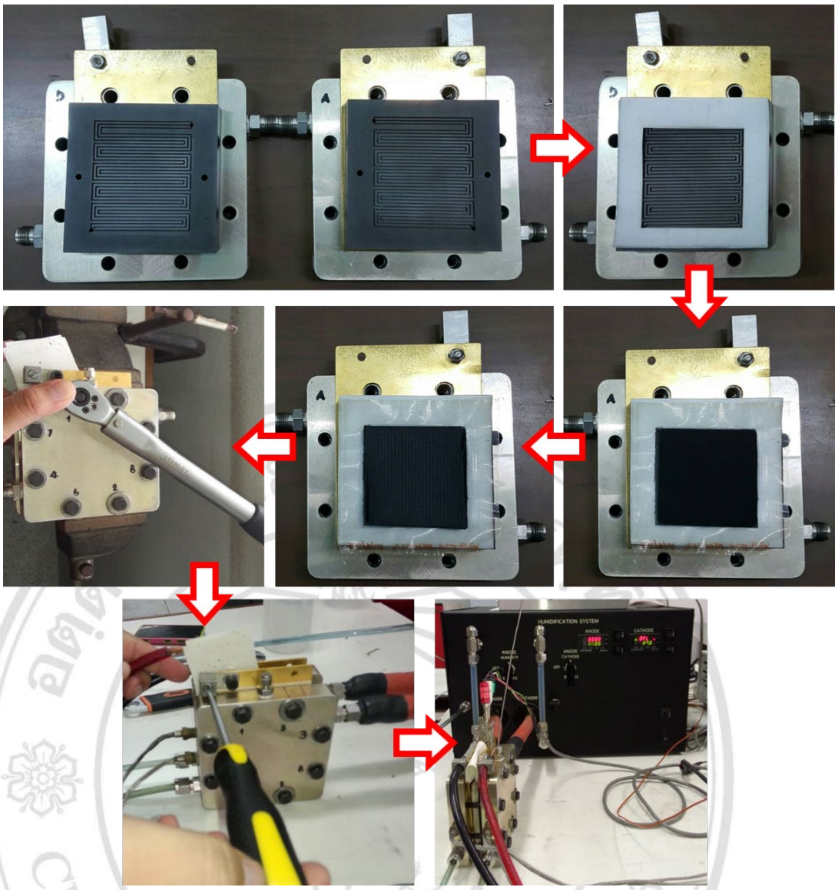

Figure 3.1 The assembly procedural of single PEMFC

Figure 3.2 A fuel cell test station (Model 890E, Scribner Associated)

3.3. Results and discussions

3.3.1. Morphology of catalyst layers

The catalyst layer morphologies from each MEA (Figure 3.3) show that sphere – shaped catalyst agglomerates were formed on the surfaces of catalyst layers. The spherical shape of catalyst clusters is caused from the originated shape of sprayed droplets from ultrasonic spray. Normally, the sprayed droplet sizes of catalyst ink emerged from ultrasonic nozzle is in the range of 10 – 100 μm, as reported by our previous work [48] and Ref. [49]. Figure 3.4 shows the droplet stains of sprayed catalyst ink on glass sheet surface that were obtained in our previous work [48]. Ultrasonic spray can provide the uniform size and distribution of droplet stains.

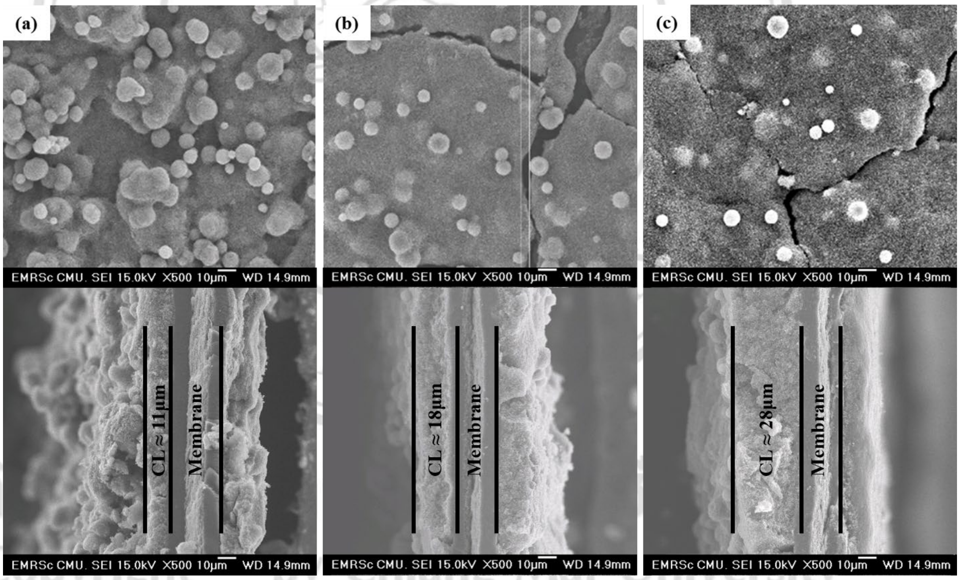

Figure 3.3 SEM image of the surface and cross – section of MEAs formed by the solvents; (a) THF, (b) ethanol, and (c) IPA at 500× magnification.

When considering Figure 3.4 (right), the optical microscopy was magnified to 500 times. It can clearly observe that the droplet stains of catalyst ink which was produced by mixing 20%Pt/C, ethanol and Nafion characterizes as large and small droplets. The small droplet stains are the catalyst clusters. These catalyst clusters originated from sprayed droplets, but the solvent evaporated out of them before reaching the substrate. It is possible that the vibration energy from ultrasonic is strong enough to evaporate solvent of very small droplet. Thus, the large droplets stains are unevaporated solvent during spraying process. The most size distribution of the large and small droplet stains is around 90 µm and 10 µm, respectively. This is the reason why the normal droplet sizes of catalyst ink from ultrasonic spray is in the range of 10-100 µm.

The size of catalyst agglomerates formed by THF is higher than that formed by IPA and ethanol inks. The catalyst layer surface from THF is also rougher than that from ethanol and IPA. As shown in Table 3.1, the catalyst inks that composes of THF is colloid ink. The catalyst clusters formed by colloid inks are larger than those formed by solution inks as described by Ref. [13], [15]. The agglomeration of catalyst was produced, where THF had greatest size of the agglomeration.

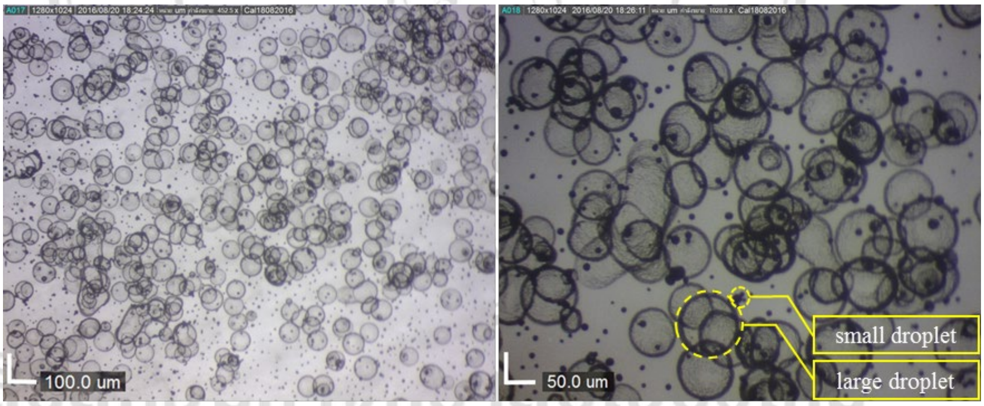

Figure 3.4 The optical microscopy images of catalyst ink droplet stains which are sprayed on cover glass at the magnification of ×270 (left) and ×530 (right) [48]

The cross – sectional images of MEAs fabricated by the IPA, ethanol, and THF solvents are shown in Figure 3.3 (bottom). The catalyst layer thickness formed by IPA is highest (28 µm) followed by that formed by ethanol (18 µm) and THF (11 µm). The thinnest catalyst layer of is due to higher density of catalysts and the colloid property from THF. On the other hand, the catalyst inks from ethanol and IPA, which have a solution property, facilitated the distribution of catalysts during spraying and consequently generated thicker catalyst layers. With this, the catalyst layers from ethanol and IPA are thicker than those from THF. Furthermore, the good catalyst distribution indicates a higher void space in the catalyst layers. This is directly related to the mass transport of reactant gases and water in catalyst layers. However, the excessive thickness of the catalyst layers may not be beneficial, because it has the longer pathway for transporting reactive gases and draining water in the catalyst layers. However, excessive thinness of the catalyst layers could be a drawback for the overall performance because the amount of void spaces will be too small for transportation of reactant gas.

3.3.2. Performance testing

Figure 3.5 shows the polarization curves of MEAs fabricated by (a) IPA, (b) THF, and (d) ethanol with various Nafion contents of 20, 25, 30, and 35 wt.%. The performances were plotted on the left hand scale while the overall cell resistances were also recorded and plotted against the right hand scale. For all MEAs, the additional Nafion contents were the cause of slightly decreasing overall resistances. It is due to the improvement of proton conductivity with increase of Nafion.

The polarization curves of MEAs fabricated by IPA in Figure 3.5(a) show that the increase in Nafion content from 20 to 25 wt.% affected the increasing current density from 528.69 to 591.03 mA/cm^2. On the other hand, the additional Nafion contents of 30 and 35 wt.% resulted in decreasing current densities of 498.33 and 407.26 mA/cm^2 (at 0.6 V), respectively. When considering the MEA made by THF as shown in Figure 3.5(b), the increase in Nafion contents of 20, 25 and 30 wt.% rose up current density of 467.27, 481.27 and 505.18 mA/cm^2, respectively. On further increasing Nafion content to 35 wt.%, the current density dropped to 430.57 mA/cm^2 (at 0.6 V). In Figure 3.5(c), MEAs produced by ethanol yielded the maximum current density of 697.02 mA/cm^2 at a Nafion content of 20%, followed by current densities of 638.14, 636.43, and 429.62 mA/cm^2 (at 06.V) at Nafion contents of 25, 30, and 35 wt.%, respectively.

The effects of Nafion in catalyst layer was explained by many researchers [25], [28], [33], [35], [46]. The insufficient Nafion content in the catalyst layers results in insufficient proton conductors and low catalyst utilization. The excessive Nafion content leads to two possible problems, the mass transport problem, and the reduced catalyst utilization. In the case of the mass transport problem, the additional Nafion content leads to an increase in the hydrophilic capability causing water flooding in the catalyst layers. In the case of the reduced catalyst utilization, the excessive Nafion content can cover and reduce the active surface areas of the catalyst. Since Nafion is an electron insulator, its excessive content is the cause of increasing electron resistance. Therefore, maintaining the proper content of Nafion leads to the highest performance by balancing the charge, electron, and mass transportation. From these results, it can see that the variation of Nafion contents in each solvent for MEA fabrication results in various PEM fuel cell performance. The MEA fabricated in each solvent requires different suitable Nafion content to perform the best performances. The solvents typical IPA, THF, and ethanol require the suitable Nafion contents of 25, 30, and 20 wt.%, respectively.

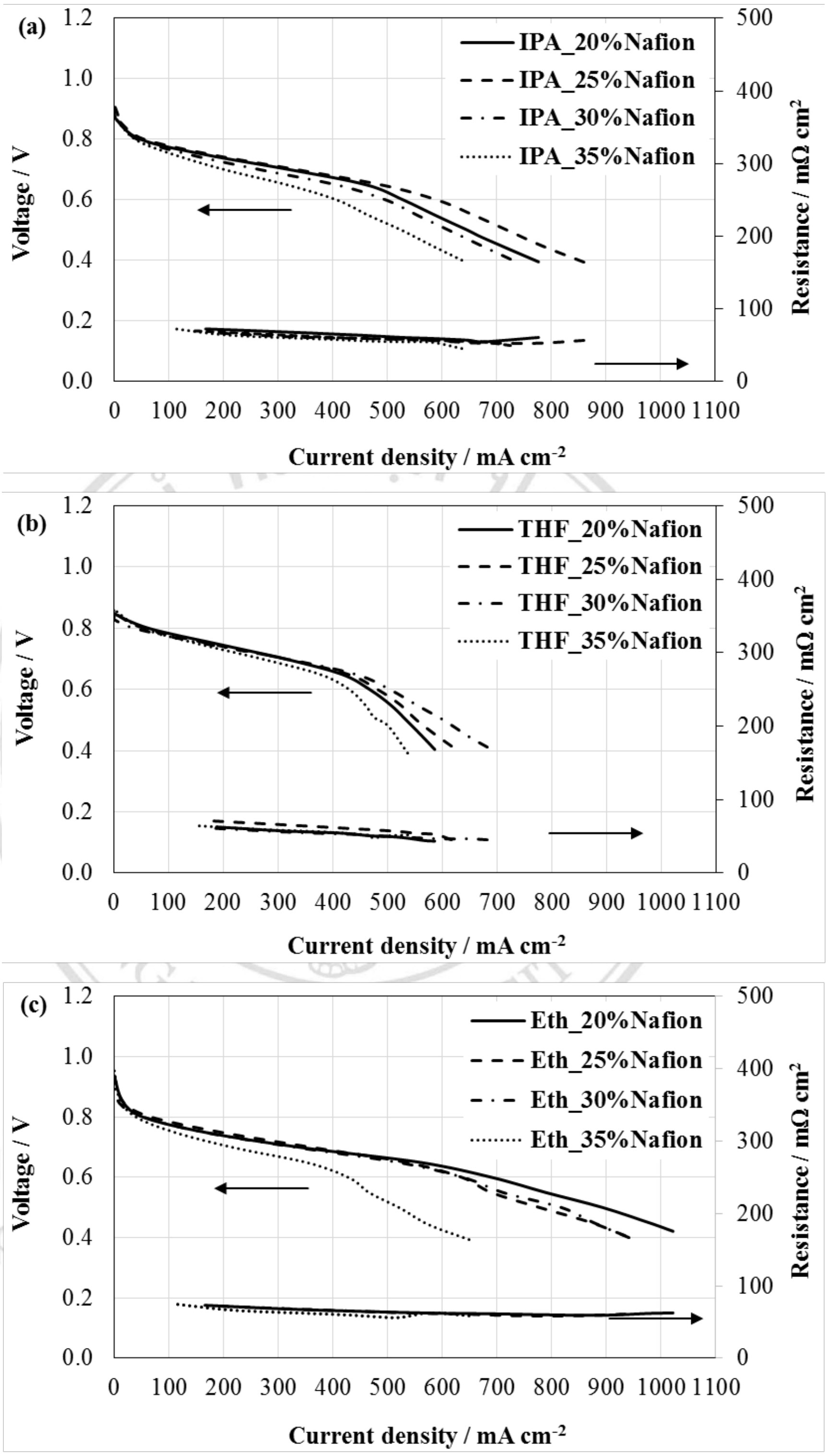

Figure 3.5 Polarization curves of MEAs fabricated by various Nafion contents and solvents; (a) IPA (b) THF, and (c) ethanol.

When comparing the best MEA performances in each solvent as shown in Figure 3.6 (a), it was found that the fuel cell performance of MEA made from THF was worse compared to that from IPA and ethanol. This agrees well with the SEM results, which show that greater catalyst agglomeration occurred in THF due to the colloid property. Catalyst agglomeration reduced the Pt surface area, leading to lower fuel cell performance, while solution inks (IPA and ethanol solvent) gave a higher Pt surface area and better performance due to the greater catalyst distribution. To support these results, the simulation of polarization curve was fitted by using equation (53) against the experimental polarization curve as shown in Figure 3.6 (b). As descripted in the topic 2.6 (Fuel cell performance), there are three typical losses affecting in PEMFC performance; activation, ohmic and concentration losses. Activation losses relate with the kinetic rate of electrochemical reaction. And the parameters directly affecting activation losses are i_0 and Tafel slope as shown in Equation (40).

$$\Delta V_{act} = 2.3\frac{RT}{\alpha F}\log i - 2.3\frac{RT}{\alpha F}\log i_0 \qquad (40)$$

When plotting the relationship between voltage and log i at low current density region of polarization curve (Figure 3.6 (c)), the parameters of i_0 and Tafel slope ($2.3RT/\alpha F$) were obtained as presented in Table 3.2.
It can see that i_0 of MEA fabricated by ethanol is highest (0.065 mA/cm^2) followed by that IPA (0.050 mA/cm^2) and THF (0.004 mA/cm^2). This means that the catalyst specific area (a_c) of catalyst layer formed by ethanol is highest because i_0 directly relate with a_c as shown in Equation (3.5)

$$i_0 = i_0^{ref} a_c L_c \left(\frac{P_r}{P_r^{ref}}\right)^{\gamma} exp\left[-\frac{E_C}{RT}\left(1-\frac{T}{T_{ref}}\right)\right] \qquad (35)$$

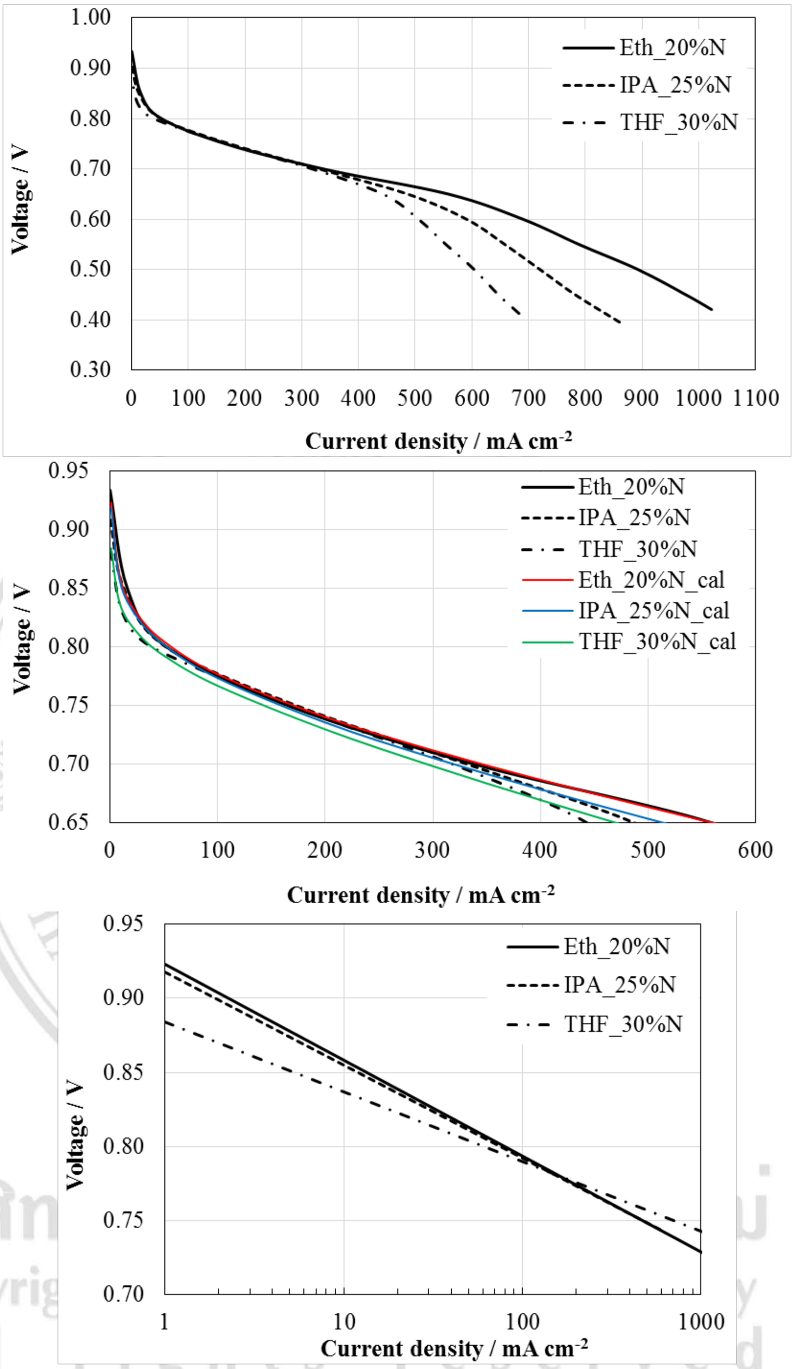

Figure 3.6 (a) Comparison of best MEA performances in each solvent (b) the fitting polarization curve from the experimental polarization curve by using equation (53) and (c) Tafel plot from activation region of polarization curve

Table 3.2 Kinetic parameters calculated from fitting polarization curve in Figure 3.6

MEA	i_0 (mA/cm^2)	Tafel slope (mV/dec)	R (Ω cm^2)
MEA$_{Ethanol}$	0.065	64.703	0.170
MEA$_{IPA}$	0.050	62.854	0.190
MEA$_{THF}$	0.004	47.141	0.230

Moreover, the analysis of PEMFC performance at medium current density region was also observed. It was found that the overall resistance of MEA fabricated by THF is highest followed by that IPA and ethanol, respectively. From above analysis by using pitting polarization curve, it well agrees that thinnest catalyst layer thickness from THF provides the highest compactness of catalyst and Nafion. This affects lowest electrochemical active areas meaning lowest areas to conduct electron and consequently highest overall resistance.

On comparing IPA and ethanol, catalyst ink with ethanol had higher performance, particularly at high current densities (greater than 600 mA/cm^2). This indicates that the mass transport issue in catalyst layer formed by IPA is more efficient than that formed by ethanol due to thicker catalyst layer from IPA. Moreover, the dielectric constant value of IPA is lower than that of ethanol. This also affected the morphology of Nafion in catalyst layer. As descripted by Ngo *et al.* [17], when mixing Nafion with any solvent types, the morphology of Nafion agglomerates depends on not only dielectric constant but also δ of solvent. When plotting the relationship between dielectric constant and δ of many solvent types from Ngo *et al.* [17], it was found that dielectric constant linearly relates with δ as shown in Figure 3.7.

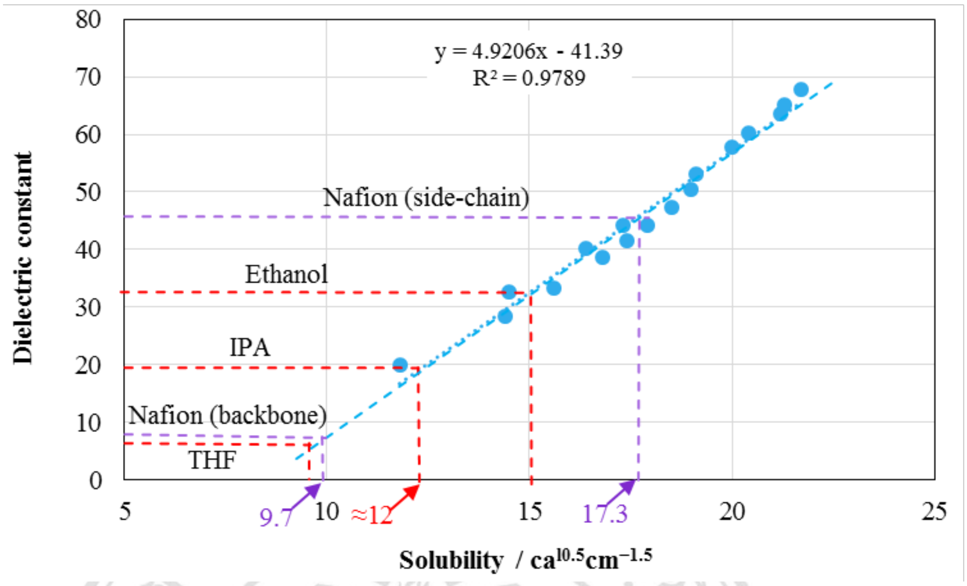

Figure 3.7 Relationship between dielectric constant and δ of the solvents from Ngo *et al.* [17]

Thus, this relationship was used to approximate δ of each solvent in this work by using dielectric constant values of the THF IPA and ethanol from Table. 3.1. 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) as shown in Figure 3.8. Each structure has an individual property of δ ($\delta_{backbone}$ = 9.7 $cal^{0.5}cm^{-1.5}$ and $\delta_{side\text{-}chain}$ = 17.3 $cal^{0.5}cm^{-1.5}$).

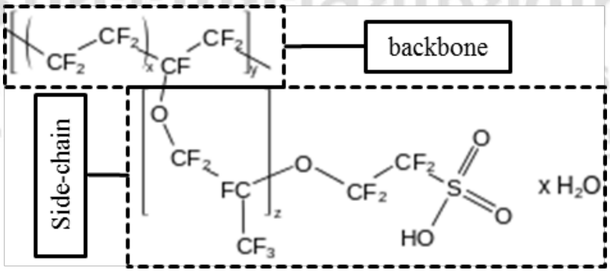

Figure 3.8 Chemical structure of Nafion

From Figure 3.7, it can see that the difference between δIPA and δbackbone is smaller than that between δIPA and δside-chain of Nafion. This means that the compatibility between the IPA and Nafion backbone is greater than that between the IPA and Nafion side-chain structure. Ngo *et al* explained that in the case of δ of the solvents is close to δ of the backbone structure of Nafion, the dielectric constant values is also low. The solvent molecules is not enough to dissociate the Nafion $–SO_3H$ groups into negative charge as $–SO_3^-$ groups. Thus, the Nafion backbones contact with the solvent and the Nafion side-chains impregnated inside the Nafion molecules.

In contrast, when δ of the solvent is close to δ of the side-chain structure of Nafion. This means higher compatibility between the solvent and Nafion side-chain. In the case, there are two possible morphologies of Nafion. Firstly, when the solvent is alcohol, the alcohol molecules may react with H^+ dissociated from side-chain ($–SO_3H$) groups of Nafion and form $C_xH_y\text{-}OH_2^+$ as ($–SO_3^-\cdots[C_xH_y\text{-}OH_2^+]\cdots{}^-O_3S–$). Secondly, the molecules of water, byproduct of PEMFC, may 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 higher value of dielectric constant results 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 resulting in higher agglomerate size of Nafion. As shown in Figure 3.9 (upper), the Nafion morphology was simulated to better understanding. When δ of the solvent is close to δ of Nafion backbones, Nafion agglomerates are smaller because of low negative charges ($–SO_3^-$) in Nafion molecules. When δ of the solvent is close to δ of Nafion side-chain, the negative charges ($–SO_3^-$) from Nafion side-chain are continuously increasing and the size of Nafion agglomeration is also increase. In our experiment, the difference between δ of ethanol solvent and δ of Nafion side-chain is closer to than that of IPA solvent and δ of Nafion side-chain. Thus, the negative charges ($–SO_3^-$) of Nafion molecules formed by ethanol is more than that by IPA. The higher negative charges mean higher possibility to conduct proton in catalyst layer and consequently higher PEMFC performance.

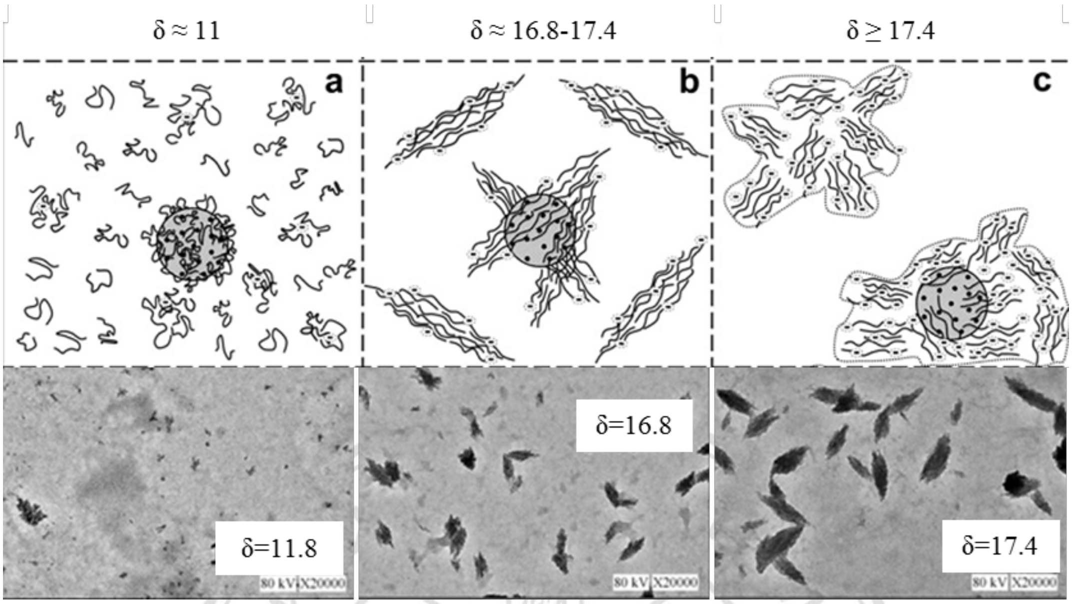

Figure 3.9 Morphology of Nafion agglomerates at different δ values of the solvent, (upper) simulation images and (lower) TEM images [17]

In summary, the polarization of fuel cells fabricated from ethanol solvent had the highest current density of 697.02 mA/cm^2 at a cell potential of 0.6 V under H_2/air operation. And it indicates that ethanol solvent demonstrated the most optimization, where the balance of charge, electron, and gas transfer were taken during electrochemical reaction in the PEM fuel cell.