

Molecular Conformation of Nafion Ionomer on Electrocatalyst Layer Prepared by Screen Printing Technique

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Preparations of Pt/CNT electrocatalyst layer in colloidal and solution state by screen printing techniques gave different molecular conformation of nafion ionomer. By this technique, low Pt-loaded ($0.07\text{-}0.1\text{ mg/cm}^2$) and thin electrocatalyst were produced with different microstructural surface and electrochemical properties depending on organic solvents used. Interaction of nafion ionomer and organic solvents (isopropanol, tetrahydrofuran and normal-butyl acetate) promote importantly different performance in the electrode system. Material analysis relevance to electrocatalyst performance was further carried out. Physical properties examination, electrochemical analysis, and performance evaluation reveal that the best performance of electrocatalyst was produced in the solution state whereas well-define CNT individually wrapped by ionomer in a homogeneous fashion was produced. In colloidal state, molecular conformation of nafion ionomer form continuity three dimensional network and blocking pore structure on carbon surface providing low electron conductivity and high mass transfer resistance.

Keywords: Pt/CNT electrocatalyst, colloidal state, solution state, screen-printing technique

1. INTRODUCTION

Manufacturing of electrocatalyst layer constitute important phase for determining the whole performance of Proton Exchange Membrane Fuel Cell (PEMFC). The electrocatalyst layer is key component in Gas Diffusion Electrode (GDE) where electrochemical reaction takes place. Most popular manufacturing techniques of electrocatalyst layer were developed for preparing the catalyst layer of MEA. They are catalyst coated membrane (CCM), [1,2,3] catalyst coated GDL (CCG), [4] and decal method. [5,6,7] In the decal method, the catalyst ink is coated on a teflon sheet and then transferred to the membrane by hot press. In the CCM process, the catalyst ink is sprayed or casted directly onto the membrane. Last is the CCG process whereas catalyst ink is spread on a carbon

substrate. In the preparing, proper dispersion of nafion ionomer and catalyst particle is one of the critical factors for the MEA power density and catalyst utilization. Therefore some compounds should be present in the system as electron and proton conductor.

Carbon nanotubes (CNT) constitute a suitable support for an electrocatalyst which have high surface area, good electrical properties, and high electrochemical stability under PEM fuel cell operating conditions. Carbon nanotubes (CNTs) potentially match these requirements including a wide electrochemical potential window, good chemical stability, and large surface area which make them attractive as electrode material candidates. [8] Self-hydrophobic characteristic present in CNT causes it is being utilized as potential supported carbon for electrocatalytic materials because of their relatively high electrical conductivity which facilitate water removal within the electrode, thereby improving mass transport in PEMFC. The properties potentially prevent hydrophobic treatment that improve resistance of mass transfer.

One key factor in the preparation of electrocatalyst layer (CL) is the selection of solvents. Homogeneous catalyst ink is generally prepared by dispersing the catalyst with a mixture of nafion ionomer solution, the solvents, and deionized (DI) water. In the preparing CL many commercial electrocatalyst layer coated on gas diffusion layer (GDL) is being prepared by utilization of solvent to disperse a mixture of catalyst particle, nafion ionomer and PTFE or FEP as hydrophobic agent. In addition to physical binder and proton conductor in CL, nafion ionomer in CL also helps to increase three-dimensional zone of catalytic activity as well as the proton conductor which highly required for high performance MEA in the final microstructure as well as electrochemical properties of CL. [9]

In the recent study, manufacturing low Pt-loaded CL was carried out by screen printing techniques of electrocatalyst ink onto gas diffusion layer (GDL). The GDE preparation route have significant effects on the microstructure even in the electrochemical properties. Effect of organic solvents i.e. isopropanol (IPA), tetrahydrofuran (THF), and normal butyl acetate (n-BA) on the performance of electrocatalyst was further evaluated in formation of nafion molecular conformation. Investigation on final microstructure due to molecular interaction between nafion ionomer and solvent was conducted as critical point. Molecular interaction between nafion ionomer and electrocatalyst particle was deeply evaluated by Transmission Electron Microscope (TEM). Pt distribution and surface active were also observed by Mapping – Scanning Electron Microscope (SEM) and voltametric cyclic, respectively.

2. MATERIAL METHOD

Multi-wall carbon nanotubes (MWCNTs) purchased from Chengdu Alpha Nano Tech. Co. Ltd. with purity level of 95%, outer diameter (OD) of 50 nm and length 5 μm was utilized as electrocatalyst carbon supported. Synthesis of Pt/CNT electrocatalyst was carried out using polyol method according to procedure written by Yudianti (2012). [10] Three organic solvents i.e. isopropil alcohol (IPA), tetrahydrofuran (THF), and n-buthyl acetate (n-BA) were used for making electrocatalyst ink in slow ultrasonic agitation to disperse nafion ionomer in the solution. Nafion solution (5.0% wt) purchased from Fuel Cell Scientific LLC. was used to generate proton conductor in

catalyst layer. Manufacturing of electrocatalyst layer using screen printing technique is currently considered as a suitable techniques for high-scale fabrication.

2.1. Preparation of Microporous and Electrocatalyst Layer

Microporous layer (MPL) was prepared from a mixture of CNT and carbon Vulcan XC-72 with a weight ratio 2 : 3 in distilled water containing triton X-100 and fluorinated ethylene propylene (FEP) as dispersant and hydrophobic agent, respectively. Addition of CNT for preparing MPL was intended to eliminate micro-crack surface that may occur after drying [11] which prepared onto carbon paper directly by using screen printing technique. To prevent micro-crack on the surface, gradual drying was conducted in open air and then at 300°C for 3 h in oven.

Preparation of Pt/CNT catalyst ink was performed by contribution of three main compounds i.e. nafion ionomer, organic solvents and electrocatalyst powder (Pt loading 20.3 wt%). Stirring nafion and solvent for 15 minute, at room temperature was conducted to make homogeneous solution. Subsequently electrocatalyst powder was slowly added under ultrasonic agitation for 2 h. Manufacturing electrocatalyst layer was carried out by screen printing technique of electrocatalyst ink onto MPL layer using nylon screen T114 and then dried at 80°C.

2.2. Morphological Properties of Electrocatalyst

Interaction of ionomer and electrocatalyst in the thin layer was observed by Transmission Electron Microscope (TEM) JEOL, JEM 1200EX, operated at accelerating voltage of 80 kV. Previously sample was prepared by addition of ink solution on the surface of grid sample holder. Morphology of nafion ionomer in the final microstructure of catalyst layer due to different organic solvents determine distribution of Pt nanoparticle. To know the effect of Pt distribution, observation on surface of electrocatalyst layer was conducted by Scanning Electron Microscope (SEM), JEOL JSM-6360LA. Sample 1 cm² was put on sample holder and then coated with gold to get a conductive surface.

2.3. Measurement of Hydrophobic Surface of Electrocatalyst Layer

Hydrophobic surface was known by quantitatively measurement of contact angle formed by a liquid at three phase boundary water and the sample surface by using *Tantec Contac Angle Method* with *Half Angle Technique*. The aquadest was dripped onto the electrocatalyst layer that placed horizontally. Contact angle was observed after 10, 60, 120 and 160 sec. after dripping. Contact angle was measured twice on the different location to know homogeneity of surface.

2.4. Four Point Probe Conductivity Test of Electrocatalyst Layer

Electrical conductivity of sample was measured by four point probe conductivity test instruments using Hewlett Packard 6186C as DC current source, Hewlett Packard 3468A as voltage detector. For each sample, three location was randomly chosen for measurement, in which each location correspond to a single resistance value. This resistance value was obtained by taking the gradient of linear line constructed by three data of voltage-current curve. Sheet resistivity ρ_s and volume resistivity ρ_v is obtained by equations :

$$\rho_s = F \cdot R \quad (Ohm)$$

$$\rho_v = 4.5324 \cdot t \cdot F \cdot R \quad (Ohm\ cm) \dots\dots\dots(1)$$

F : geometrical correction factor

t :sample thickness

Then sheet conductivity (S) and volume conductivity (S/cm) is obtained as the reciprocal value of sheet resistivity and volume conductivity, respectively.

2.5. Electrochemical Properties of Electrocatalyst and Measurement of MEA Performance in Single Cell PEMFC

Cyclic voltametry was performed by Gamry electrochemistry system model (G750) completed with three-electrode system. Three electrodes used in the measurement were platinum wire, saturated calomel electrode (SCE), and glassy carbon as counter, reference, and working electrodes, respectively. The working electrode is electrocatalyst layer put on the glassy carbon with area 40-50 mm². The measurement was conducted in 0.5 M H₂SO₄ at room temperature which scanned in potential range -0.1 and 1.45 V vs SHE at scan rate 20 mV/s. Three electrode cell system was purge with nitrogen gas for 30 min and the potential of the working electrode was cycled 10 times between 0 and 1.2 V vs SHE at 50 mV/s to clean the surface before measurement. The coulombic charge for hydrogen adsorption was used to calculate the electrochemical surface area (ECSA) of platinum in electrocatalyst :

$$ECSA = Q_h / (0.21 \times m) \dots\dots\dots(2)$$

Where m represents the platinum loading in electrode; Q_h is charge for hydrogen desorption (mC/cm²); 0.210 (mC/cm²) represents the charge required to oxidize a monolayer of H₂ from 1 cm² of platinum black; m is Pt loading (mg/cm²).

Prior to measurement of the polarization curve, integration of membrane and electrode was carried out by hot press at 120°C for 3 minutes to get good thermal contact. Measurement of MEA performance was performed in single cell of PEMFC .

3. RESULT AND DISCUSSION

Role of solvent to disperse nafion ionomer in the preparation of electrocatalyst layer give important effect on the final electrocatalyst surface that determines performance of the electrode

system. Previously contribution of nafion ionomer in the performance of electrocatalyst was further evaluated. We compared performance of electrocatalyst with and without nafion ionomer. Voltamograms of those samples are almost similar (Figure 1). Electrochemical surface area (ESCA) of electrocatalys using and without ionomer are significantly different i.e. 75.5 and 120.5 m^2/gram , respectively. Nafion ionomer forms layer on the catalyst surface covering the surface (Figure 1a) and possible limit electrochemical performance for hydrogen desorption. However, nafion ionomer is importantly required to obtain balancing between proton conductive and surface active in the electrocatalyst system of PEMFC. The importance of nafion loading in electrocatalyst layer was also stated by Eguci (2012) that the ionomer causes a increase in the proton conduction and a decrease in cell performance. [12] Low ionomer concentration causes a decrease in the proton conduction and cell performance when below the optimum ionomer and carbon ratio (I/C). An excess ionomer blocks the space volume and decreases the cell performance when over the optimum I/C ratio. Excess ionomer prevents reactant gases from entering, and the product water from leaving. Ionomer block on the surface of electrocatalyst determine simultaneously proton – electron conducting and gas diffusion.

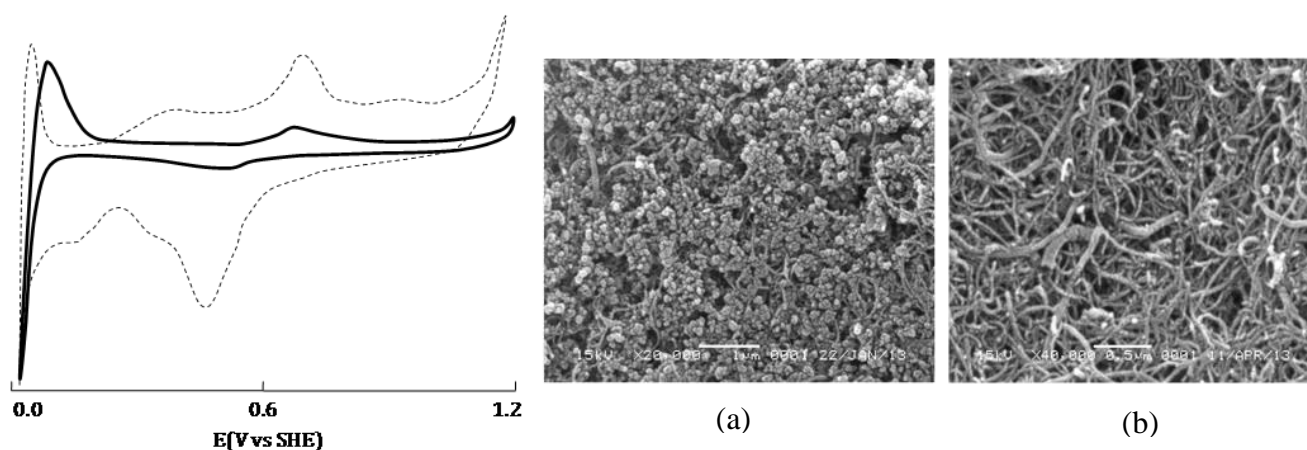


Figure 1. Voltamogram and Morphological Surface of Electrocatalyst Layer on the Effect of Nafion Ionomer (— with Nafion (a) ; ----- without Nafion (b))

Effect of organic solvents i.e. IPA, THF, and n-BA on the performance of electrocatalyst layer in the electrode system was investigated. In Figure 2a and b, solid mass known as nafion ionomer existed as larged aggregated on the surface. Tetrahydrofuran and n-BA with dielectric constant $<3(\epsilon)<10$ generating colloidal state form continued structure on the surface and absorbs the catalyst particles with wider aggregated mass covering electrocatalyst matrix. In meanwhile, IPA with dielectric constant $(\epsilon)>10$ form small agglomerate in the solution state which deeply penetrate into microporous layer. Nafion molecular conformation in colloidal and solution state consequently have different surfacial effect for Pt nanoparticle distribution and size. Molecular interaction of ionomer and solvent control molecular conformation in electrocatalyst layer as also stated by Ngo (2013). [13]

Change in elemental content on the surface was also detected, as given in Table 1. Electrocatalyst layer prepared in the colloidal state have lower Pt loading on the surface (2.9 and 5.9%) than solution state (17.6%). In the condition, F and S element corresponding to nafion ionomer tend to

be lower at Pt/CNT-IPA than those of Pt/CNT-nBA or Pt/CNT-THF. Thick ionomer film on the surface forms large aggregate electrocatalyst and shielding Pt nanoparticle to form cluster-like structure. Deep penetration of ionomer into fiber network CNT Pt/CNT-IPA form thin nafion layer maintaining topological surface and homogeneous morphology.

Table 1. Quantitatif Elemental Analysis on Electrocatalyst Surface

Sample	In Average (%)			
	Pt	C	F	S
Commercial	23.1	56.3	20.1	0.6
Pt/C-IPA	16.3	75.7	8.2	0.8
Pt/CNT-IPA	17.6	76.6	11.1	0.65
Pt/CNT-nBA	5.9	81.8	11.6	0.6
Pt/CNT-THF	2.9	81.9	14.6	0.5

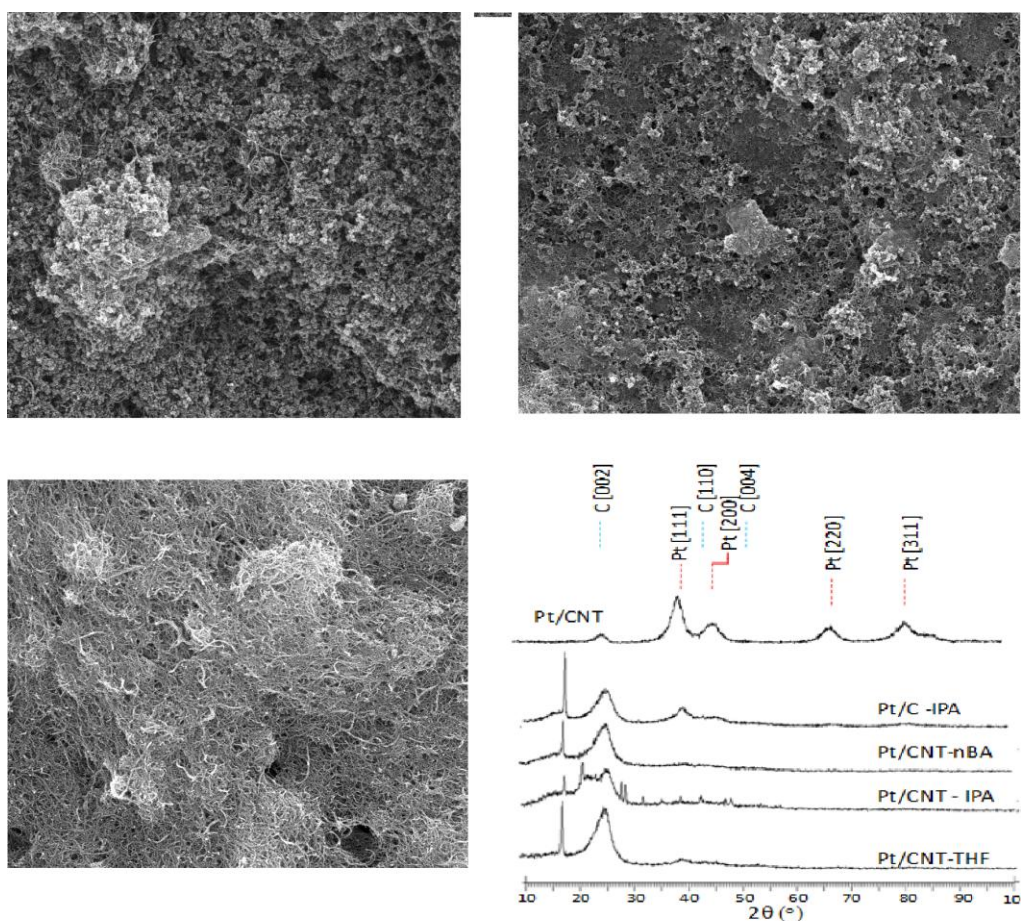


Figure 2. Morphological Surface and X-Ray Diffractogram of Electrocatalyst Layer on The Effect of Organic Solvents (a) Tetrahydrofuran ; (b) Normal-Buthyl Acetate ; (c) Isopropanol

This condition indicates that nafion ionomer play important role for the surface performance of electrocatalyst. Wrapping surface microstructure due to thick continuous network of ionomer identify high ionomer loading on the surface of Pt/CNT-nBA and Pt/CNT-THF.

Comparisons between nafion-coated (NCE) as electrocatalyst layer and nafion-free electrocatalysts (NFE) as electrocatalyst powder are also reported in X-ray diffraction profile (Figure 2). Spectra of NFE powder show evidently major Pt peaks at 39.6, 46.1, 67.4, 81.2 and 85.6 degree corresponding to the reflection planes of (111), (200), (220), and (311). In NCE, ionomer significantly reduce intensity of Pt. In colloidal and solution states, ionomer are also critical parameter affecting the Pt-size. X-ray diffraction profiles show that NCE changes to be more amorphouse due to nafion ionomer contribution. Based on Debye-Scherrer equation, cluster-like Pt structure in NCE shows Pt cluster size 10-16 nm in average and Pt size about 5-6 nm at NFE. Reduction of Pt intensity state that nafion ionomer wrap Pt nanoparticle to be larged aggregate sizes in random arrangements.

Dispersed electrocatalyst in nafion ionomer network was observed by TEM to know the interaction of nafion solution and electrocatalyst (Figure 3). Two key factors, the state of nafion in dispersion and the nafion substrate interaction are dominant in determining the morphological structure of thin film. In colloidal state, extensive swelling form high fiber density as three dimensional network expanding to be swollen network. The condition provide a continuity of the ionomer network that might be resulting in high proton conductivity as well as high mass transfer resistance. Clustering are observed as localized aggregation. In the solution state, interaction of nafion ionomer and solvent disperse electrocatalyst to form thin layer on the fiber surface. The results show that performance of GDE strongly depend on ink solution behavior.

CNTs have an aromatic ring, which allows self-hydrophobic properties. The properties lead to no need additional hydrophobic agent externally. External addition of PTFE or FEP as hydrophobic agent enhance resistance of mass transfer making a decrease in performance.[14] We measured hydrophobicity of electrocatalyst surface by measuring contact angle between a water droplet interface meets electrocatalyst surface. Table 2 gives the hydrophobicity of electrocatalyst layer on the effect of solvent. Hydrophobicity of commercial sample (Pt/C) containing hydrophobic agent (PTFE) and nafion ionomer (0.4 mg/cm^2) is evidently lower than those of Pt/CNT (138 to 145°). Contribution of carbon Vulkan XC-72 importantly influence hydrophilicity of surface in despite of addition of hydrophobic agent was carried out. Inert properties of CNT plays an important role for making hydrophobic surface without hydrophobic agent addition. However, it is slight *difficult* to prepare Pt/C catalyst layer without hydrophobic agent. They look different appearance when made thin layer (Figure 4). Hydrophobic agent in Pt/C-based electrocatalyst plays an important role as binder for the formation of sheet. The PTFE serves as a binder to maintain the integrity of carbon particles and provides high hydrophobicity to avoid water flooding.[15] The optimized value of PTFE content reported in literature [16] varies widely from 10 to 30 wt.%, depending on the MEA structure and the fuel cell operating condition. However, self-hydrophobic properties of CNT provide a critical influence on the appearance and performance of electrocatalyst. Coloidal and solution state essentially affect hydrophobicity of layer. Pt/CNT-IPA has higher hydrophobicity than Pt/CNT-nBA and Pt/CNT-THF due to wrapping fiber in the inner network. Solid mass known as ionomer film on the surface (Figure 2a,b) provide hidropobicity of sample surface in order to provide pathways for proton transport. The localized molecular conformation on the surface allow uneven ionomer distribution into the whole network.

Deep penetration of water into network was readily absorbed by network. The similar trend is also mentioned in the previous study when filtration technique was used for preparing catalyst layer and ionomer coated on the surface. [17] Hydrophilic and hydrophobic characteristics of the catalyst layer are an important aspect in the three-phase interface which might be useful for the water management in PEMFC.

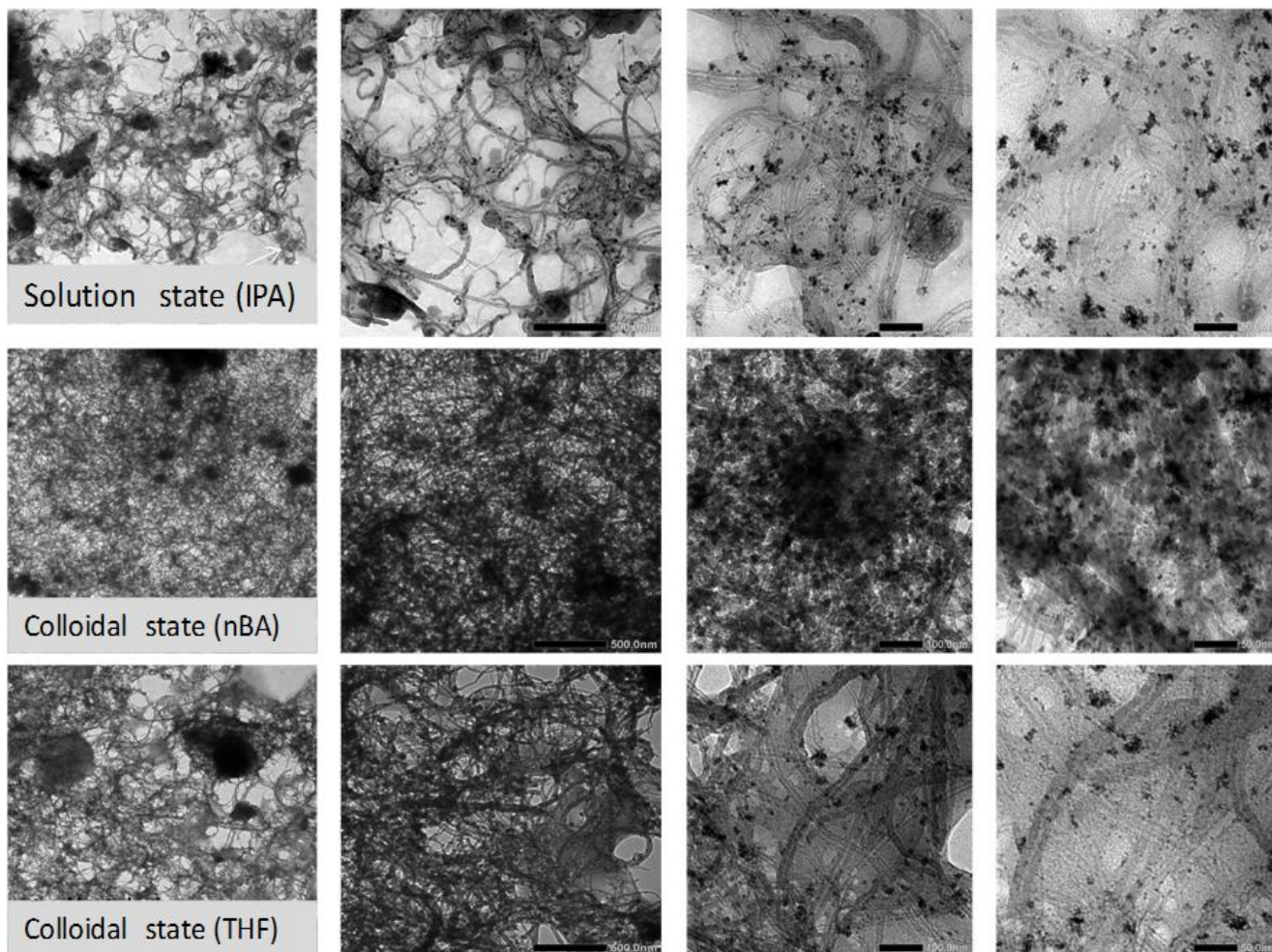


Figure 3. Morphological Structure of Electrocatalyst in Nafion Ionomer-Solvent Solution

Table 2. Characteristic of Electrocatalyst in Different Solvent and Pt Loading

Sample	Pt Loading (mg/cm ²)	Ionomer Loading (mg/cm ²)	Carbon Loading (mg/cm ²)	Pt Loading (%)	Contact Angle (°)	ESCA (m ² /g)
Commercial	0.5	0.6	-	25.8	96	50.3

Pt/C-IPA-PTFE	0.14	0.4	1.3	30.5	91	11.9
Pt/CNT-IPA	0.07	0.2	1.0	27.1	148	90.6
Pt/CNT-nBA	0.07	0.2	1.1	5.7	95	88.2
Pt/CNT-THF	0.1	0.3	1.1	3.7	87	37.2

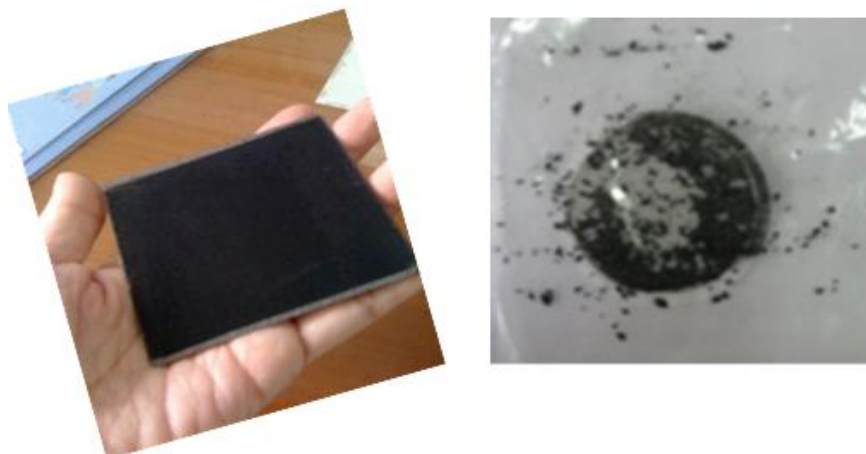


Figure 4. Appearance of Electrocatalyst Layer Without Hydrophobic Agent (a) Pt/CNT ; (b) Commercial Pt/C

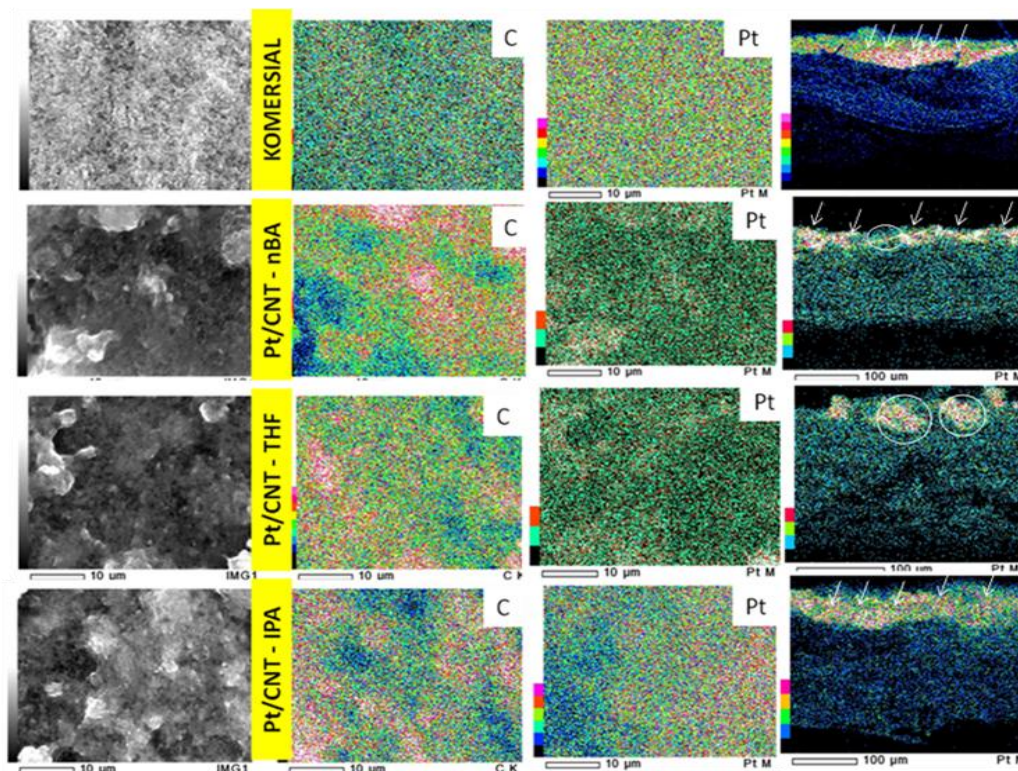


Figure 5. Mapping Platinum and Carbon Distribution on Electrocatalyst Layer Observed by SEM

Preparation of electrocatalyst ink importantly determine Pt distribution on the electrocatalyst surface. Particle mapping analysis was conducted to examine the surface morphology namely to know Pt distribution on the surface (Figure 5). Overall distribution shows that electrocatalyst prepared in the solution state produce uniformly Pt distribution yield. At low Pt loading ($0.07\text{-}0.1\text{ mg/cm}^2$), fine Pt nanoparticle distribution do not clearly detected on the Pt/CNT-nBA and Pt/CNT-THF surface indicating the occurrence of Pt isolation and location within the carbon and ionomer framework with some aggregation. This condition significantly reduce Pt active area. Otherwise, in the solution state, red spot signed as Pt nanoparticle distribution seems clearly on the surface of layer. Pt concentration on the electrocatalyst surface prepared in solution state is efficiently higher (27.1%) than prepared in colloidal state (3.7-5.7%). Pt distribution in commercial sample located on the surface looks uniformly. This condition expectedly generates good performance by high active surface.

For the further analysis, we estimated electrochemical adsorption-desorption of hydrogen on Pt active. The analysis was conducted to reveal that morphological surface of electrocatalyst layer is key factor on the hydrogen adsorption-desorption of Pt nanoparticle loaded on the electrode. We compared electrochemical performance of low Pt-loaded electrocatalyst ($0.07\text{-}0.1\text{ mg/cm}^2$) prepared in different solvents i.e. IPA, nBA and THF with high Pt-loaded commercial electrocatalyst (Pt/C) (0.5 mg/cm^2). The platinized electrode gives a cyclic voltammogram as shown in Fig. 6 with the potential limits are 0 and + 1.2 V. The anodic peak at +0.01V describes weakly bonded hydrogen, is close to the potential which is given for the hydrogen adsorption on a Pt (110) surface. The average Coulombic charge of hydrogen adsorption and desorption was used to calculate the electrochemical active platinum surface area of the electrodes. Electrochemical surface area of electrocatalyst prepared by dispersion of solvent were compared. In the screen printing technique, GDE prepared using IPA had slightly larger ESCA than those prepared using nBA and THF. Correlation analysis of Pt loading and ECSA was performed whereas assumed that all platinum loaded are electrochemically active.

Screen printing technique promote different effect on the thickness of electrocatalyst layer depend on ink characteristic and carbon support shape. Two types of carbon support i.e. spherical and tubular carbon have different characteristics in preparation. Spherical carbon support of Pt/C tend to easily penetrate through woven screen compared to tubular carbon support. It is reasonable that thinner Pt/CNT electrocatalyst layer produced than those of Pt/C. Relationship between thickness and Pt loading is indicated in Figure 6. Thicker layer with high Pt loading contribute in Pt aggregation on the carbon substrate. Aggregate Pt consequently provide a decrease in ECSA and mass transport due to low active surface area. Thin layer forms well-Pt distribution on surface that have great possibility to improve performance. Solution and colloidal ink characteristic also determine role of printing technique to apply ink onto the substrate. In the colloidal state, thicker layer was produced corresponding to ink characteristic. Agglomeration of electrocatalyst particle cover the pore structure of carbon substrate which blocking gas diffusion and electrochemical surface. Therefore thin electrocatalyst layer is most possible condition for having good distribution of Pt.

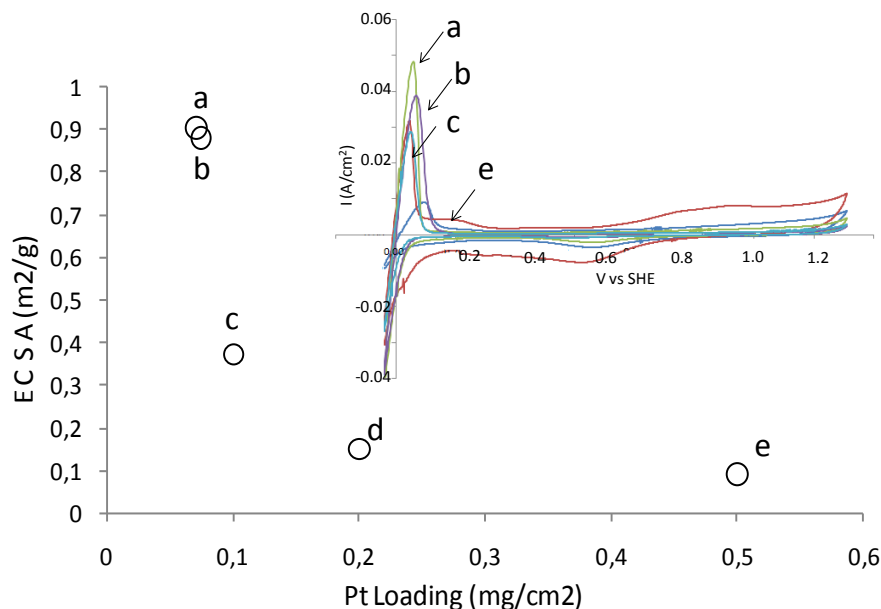


Figure 6. Cyclic Voltamogram at 25°C in the potential range (0-1.4 mV vs SHE) (a) Pt/CNT-IPA ; b. Pt/CNT-nBA ; c. Pt/CNT-THF ; d. Pt/C-IPA ; e. Pt/C commercial)

This study also investigated the performance of membrane electrode assembly (MEA) fabricated with various solvent in electrocatalyst system. The fabricated MEA was tested in a single cell of proton exchange membrane (PEM) fuel cell unit. The results obtained show that the performance of the MEA in the cell improves in CNT-IPA.

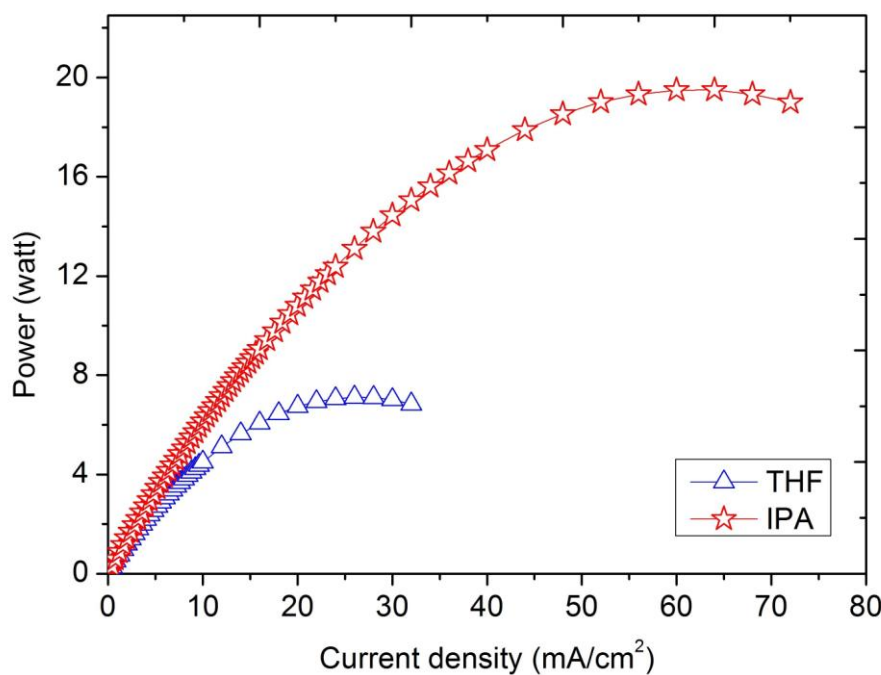


Figure 7. Polarization Curve of Single Cell PEMFC with Different GDE

Figure 7 show MEA performance of single cell for two different solvents whereas THF is representative solvent for colloidal state. In the effects of solvents used for catalyst ink, the electrode with IPA forming ionomer solution had better performance than those with THF forming colloid. Performance of MEA directly describes microstructure of electrocatalyst surface. Continue structure of colloidal ionomer blocked the pore in electrode inhibiting oxygen-hydrogen flow into electrocatalyst surface. Homogeneous surface created by solution ionomer could be able to deeply penetrate into electrocatalyst system to make hydrophobic network. Hydrophobic network support efficient transport of water to prevent flooding of the layer.

4. CONCLUSION

Electrocatalyst characteristic and performance for MEA was successfully investigated in a view of different state of ionomer in electrocatalyst ink as well as for application of CNT as new supported catalyst. Fabrication process using screen printing is most suitable technique for having thin and low Pt-loaded electrocatalyst. During process, solvent plays an important role for molecular conformation of nafion ionomer on the final electrocatalyst surface. In colloidal state, three dimensional network of ionomer on the surface localize Pt nanoparticle in particle cluster and blocking gas diffusion toward electrocatalyst system. Molecular conformation of ionomer inside deeper network form hydrophobic network uniformly with continuously proton movement. The condition suggested that IPA is more suitable solvent for preparing electrocatalyst using screen printing technique than colloidal state.

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