

Design of Highly Efficient Polymer Electrolyte Membrane Fuel Cell Catalyst Layer by Improving Pt Utilization Efficiency via Polymer-Wrapped Carbon Blacks

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**Design of Highly Efficient Polymer Electrolyte
Membrane Fuel Cell Catalyst Layer by Improving Pt
Utilization Efficiency *via* Polymer-Wrapped Carbon
Blacks**

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Table of Contents

Chapter 1	1
Background of the study	1
1.1. Importance of fuel cell technology.....	1
1.1.1. Advantages of fuel cells	1
1.1.2. Applications of fuel cells.....	2
1.2. Fundamentals of fuel cell	5
1.2.1. Working principle of PEMFC	5
1.2.2. Main components and their role in a PEMFC.....	6
1.2.2.1. Electrode.....	6
1.2.2.2. Electrolyte membrane	7
1.2.2.3. Gas diffusion layers (GDL).....	8
1.2.3. Polarization of PEMFC	9
1.3. Cost analysis of fuel cell	11
1.4. The catalyst layer of a PEMFC	12
1.5. Problems in the PEMFC catalyst layer (reduced Pt utilization).....	13
1.6. PBI wrapping approach.....	16
1.7. Objectives of this study	17
1.7.1. Strategy 1.....	18
1.7.2. Strategy 2.....	19
1.7.3. Strategy 3.....	20
1.8. Overview of this dissertation.....	21
References	23
Chapter 2	28
Enhanced Platinum utilization efficiency of polymer-coated Vulcan as an electrocatalyst in polymer electrolyte membrane fuel cells	28
2.1. Introduction	28
2.1. Experimental	30
2.1.1. Materials.....	30
2.1.2. Electrocatalyst preparation.....	30

2.2.3. Material characterization.....	31
2.2.4. Rotating ring disk electrode (REDE)	31
2.2.5. Membrane electrode assemble (MEA) fabrication	32
2.2.6. Fuel cell operation.....	33
2.3. Results and discussion.....	34
2.3.1. Electrocatalyst preparation.....	34
2.3.2. Evaluation of ORR activity by RRDE	37
2.3.3. Evaluation of ECSA	39
2.3.4. Nafion coating on the electrocatalyst	41
2.3.5. Fuel cell characterization	46
2.4. Conclusion.....	50
References	51
Chapter 3	59
Effect of PBI wrapping approach to improve Pt utilization and durability in different types of carbon blacks for polymer electrolyte membrane fuel cells	59
3.1. Introduction	59
3.2. Experimental	60
3.2.1. Materials.....	60
3.2.2. Material characterization.....	60
3.2.3. Electrocatalyst preparation.....	61
3.2.4. Membrane electrode assembly (MEA) preparation	61
3.2.5. Fuel cell operation.....	61
3.2.6. Accelerated durability test (ADT).....	61
3.3. Results and discussion.....	62
3.3.1. PBI wrapping and surface characterization.....	62
3.3.2. Preparation of electrocatalysts and their characteristics	66
3.3.3. Evaluation of electrochemically active surface area (ECSA)	69
3.3.4. Fuel cell performance.....	71
3.3.5. Durability study of AB/Pt and AB/PBI/Pt	80
3.4. Conclusion.....	81
References	82

Chapter 4	86
Design of highly efficient fuel cell catalyst layer by triggering favorable interaction between carbon Support and ionomer	86
4.1. Introduction	86
4.2. Experimental	87
4.2.1. Materials.....	87
4.2.2. Material characterization.....	87
4.2.3. Electrocatalyst preparation.....	88
4.2.4. MEA fabrication.....	88
4.2.5. Fuel cell operation	88
4.3. Results and discussion.....	89
4.3.1. Characterization of catalyst.....	89
4.3.2. Effect of Nafion content on MEA performance	89
4.3.3. Activation over-potential under various Nafion contents	94
4.3.4. Ohmic over-potential under various Nafion contents	96
4.3.5. Concentration over-potential under various Nafion contents	98
4.3.6. Gas diffusion characteristics of catalyst layer.....	101
4.3.7. Fuel cell performance of low loaded Pt catalyst layers.....	106
4.4. Conclusion.....	109
References	111
Chapter 5	114
Conclusions and perspectives.....	114
5.1. Summary of the dissertation.....	114
5.2. Perspective	116
References	117
Chapter 6	118
Acknowledgements	118

Chapter 1

Background of the study

1.1. Importance of fuel cell technology

The combustion of petroleum causes an increased amount of carbon dioxide emissions as well as other greenhouse gases. One of the first studies on the effects of carbon dioxide on climate was in the late 1800s by Swedish Nobel chemist Svante Arrhenius.¹ The **Figure 1-1** shows the global greenhouse gas emission in 2014.² In order to reverse the trend of destroying the environment by burning of petroleum fuel, introduction of more ecologically friendly and cleaner energy sources such as hydrodynamics, geothermal, wind and solar is highly required.³⁻⁵ However, these methods require specific environmental conditions to work effectively. Therefore, the worldwide applications of these methods are limited.

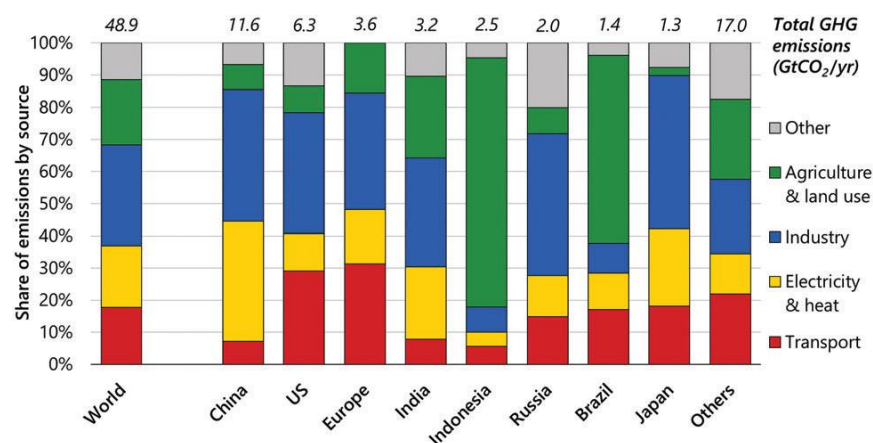


Figure 1-1 Global greenhouse gas emission in 2014, broken down by sector and by major countries. Taken from ref. 2.

1.1.1. Advantages of fuel cells

Hydrogen was recognized as a critical and indispensable element of a decarbonized, sustainable energy system thirty years ago to provide secure and non-pollution energy.⁶ Combination of hydrogen and fuel cell technologies (**Figure 1-2**) offers greater choice in the transition to a low-carbon economy, giving their similar operation and consumer experience to fossil-fueled technologies. Fuel cells can be used in a wide range of applications, including transportation, material handling, stationary, portable, and emergency backup power applications. Fuel cells have several benefits over conventional combustion-based technologies currently used in many power plants and passenger vehicles. Fuel cells can operate at higher efficiencies than

combustion engines, and can convert the chemical energy in the fuel to electrical energy with efficiencies of up to 80 %. Hydrogen fuel cells emit only water, so there are no carbon dioxide emissions and no air pollutants that create smog and cause health problems at the point of operation. Also, fuel cells are quiet during operation as they have fewer moving parts. The **Table 1-1** indicates that fuel cell systems perform with the highest efficiency compared to conventional distributed energy systems.

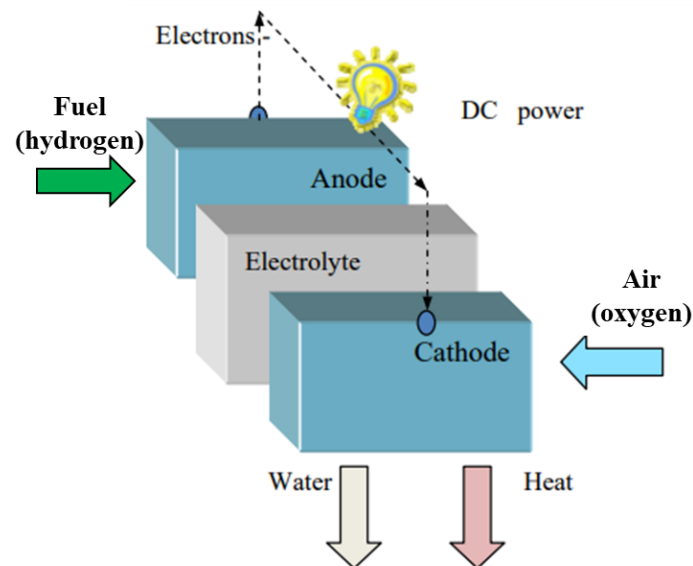


Figure 1-2 Structure of fuel cell.

Table 1-1 Comparison of fuel cell with other power generating systems. Taken from ref. 4.

	Reciprocating engines: diesel	Turbine generator	Photovoltaic	Wind turbine	Fuel cells
Capacity range	500 kW - 50 MW	500 kW – 5 MW	1 kW – 1 MW	10 kW - 1 MW	200 kW - 2 MW
Efficiency	35 %	29 – 42 %	6 – 19 %	25 %	40 – 85 %

1.1.2. Applications of fuel cells

Fuel cells hold promising potential to become competitive energy alternative in a number of markets due to their broad range of applications. Fuel cells have applications ranging from scooters to large cogeneration power plants as fuel cells can theoretically be used for any energy-demanding application. Efforts towards the commercialization of fuel cells in the portable electronics, stationary power generation, and transportation sectors are well underway.

(1). Portable applications

Portable applications in fuel cells are mainly focused on two main markets. The first is the market of portable power generators designed for light outdoor uses such as camping and climbing, light commercial applications such as portable signage and surveillance, and power required for emergency relief efforts. The second is the market of consumer electronic devices such as laptops, cell phones, radios, camcorders, and basically any electronic device that traditionally runs on a battery. Portable fuel cells typically have power ranges between 5 and 500 W, with micro fuel cells having power outputs less than 5 W and more demanding portable electronics reaching the kW-level. Other rapidly growing markets in the portable sector include portable battery chargers in demonstration and educational remote control vehicles, toys, kits, and gadgets by manufacturers such as Horizon and Heliocentris. Unlike stationary fuel cells, portable fuel cells could be carried by an individual and used for a variety of applications. The lower weight, higher energy density and the fact that fuel cells do not require recharging from an electricity source make them more favorable in comparison to batteries in the future portable market. However, their cost and durability are yet to meet set targets.⁷

(2). Stationary applications

Fuel cells can play an essential part in the residential, commercial, and industrial stationary power generation sectors. They are utilized for both grid-independent (also known as stand-alone) and grid-assisted power supply. Stationary fuel cell applications include emergency back-up power supply (EPS) (also known as uninterrupted power supply (UPS)), remote-area power supply (RAPS) and combined heat and power (CHP) generation. The stationary fuel cell market accounts for about 70% of the annual fuel cell shipments on a MW-level. Due to their high energy and power densities, high modularity, longer operation times (2–10 times longer than currently used lead-acid batteries), compact size, and ability to operate under harsh ambient conditions, fuel cells are becoming an encouraging alternative for batteries in the EPS market. Especially in the telecommunication market, polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) are the dominantly-chosen fuel cell types.⁸ Furthermore, fuel cells could serve as the means to make the shift from large centralized power generation to decentralized distributed generation. Due to their static nature, lower emissions, excellent load-following, and high efficiency fuel cells could be used for residential electric power or CHP distributed generation either on a household basis^{9, 10} or a larger residential blocks basis.^{11, 12} The **Figure 1-3** shows the usage of CHP systems by some of the leading countries.

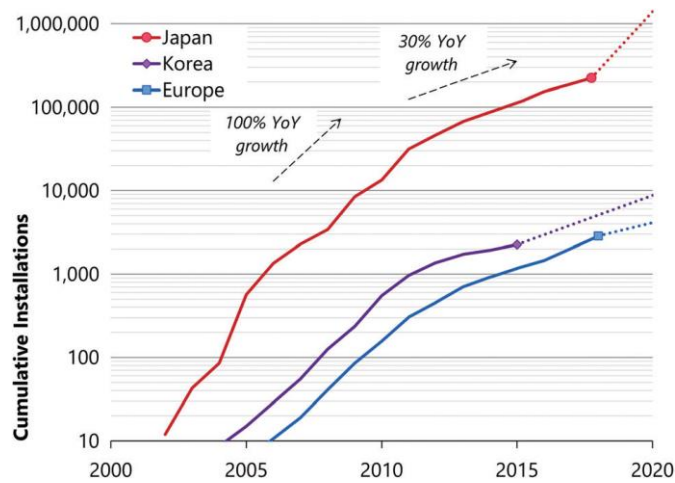


Figure 1-3 Cumulative number of residential micro-CHP systems installed to date (solid line) and near-term projections (dotted line). Taken from ref. 4.

(3). Transportation applications

The transportation industry is one of the main power houses in the development of clean energy technologies. This is due to the fact that the transportation industry is responsible for 17% of the global greenhouse gas emissions every year. Due to the advantages such as static operation, fuel flexibility, modularity, and lower maintenance requirements, fuel cells become an ideal future alternative for current combustion engines. That is, if durability, cost, hydrogen infrastructure, and technical targets are met on-schedule. This is why using fuel cells in various means of transportation, with a focus on light-duty passenger cars, has been one of the main drivers for fuel cell R&D in the past decade. Fuel cell applications in transportation can be classified into following markets: auxiliary power units, light traction vehicles, light-duty fuel cell electric vehicles, heavy-duty fuel cell electric vehicles, aerial propulsion, and marine propulsion. The **Figure 1-4** shows the conceptual design of future fuel cell car based on the Honda 2005 FCX model and fuel cell electronic bus based on the Mercedes-Benz Citaro Fuel Cell EcoBus. Even though the application of fuel cell is promising, the industry still has a long way ahead in order to achieve the long-awaited goal of widespread commercialization.⁷

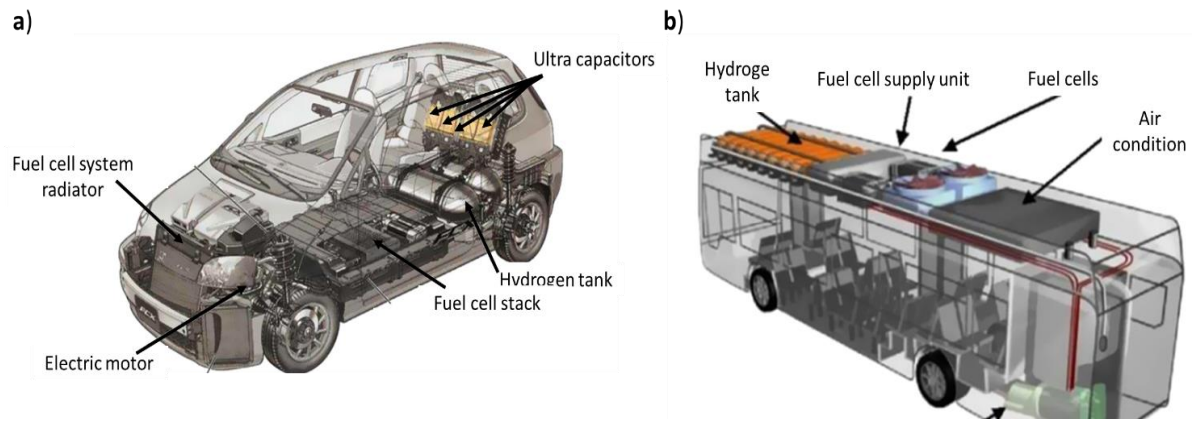


Figure 1-4 Conceptual design of future a) fuel cell car based on the Honda 2005 FCX model and b) fuel cell electronic bus based on the Mercedes-Benz Citaro Fuel Cell EcoBus. Taken from ref. 7.

1.2. Fundamentals of fuel cell

The phenomenon of a fuel cell was identified in 1838 by German chemist Friedrich Schonbein for the first time. After many years back in 1933, Sir Thomas Francis Bacon developed the first fuel cell made of hydrogen and oxygen with practical application using a nickel electrode. Despite their high cost, Bacon's fuel cells proved to be reliable to receive the attention of manufactures.³ Now a days six main types of fuel cells have been used. They are (i) polymer electrolyte membrane fuel cell (PEMFC) including direct methanol fuel cell (DMFC), (ii) alkaline fuel cell (AFC), (iii) phosphoric acid fuel cell (PAFC), (iv) molten carbonate fuel cell (MCFC), (v) solid oxide fuel cell (SOFC) and (vi) microbial fuel cell (MFC).

1.2.1. Working principle of PEMFC

PEMFCs undergo the conversion of chemical energy of fuel into electric energy by hydrogen oxidation (HOR) and oxygen reduction reaction (ORR) using a proper catalyst. The **Figure 1-5** shows schematic illustration including the mechanism of PEMFC. The electrochemical reactions in a PEMFC occur simultaneously at the interface between the cathode and the anode catalyst layers and the electrolyte membrane. There protons travels though the proton conductive membrane from the anode to cathode, while electrons conduct through the external circuit from the anode to cathode to be used in the ORR. It is clear that current of electrons travelling through the external circuit gives us productive electric work. At the cathode, protons passes through the membrane, oxygen (O_2) from the cathodic flow and electrons from the external circuit combine to

form water as the byproduct of PEMFC system.^{7, 13, 14} The overall reaction of the PEMFC system is showing in the **Eq. (1-1)**.

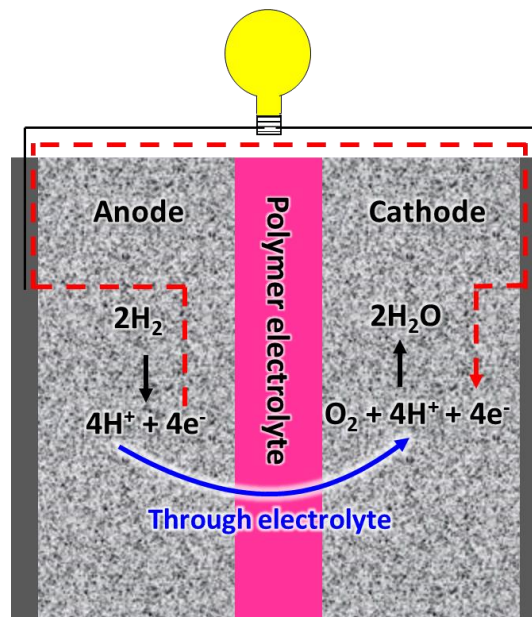


Figure 1-5 Working principle of PEMFC.

1.2.2. Main components and their role in a PEMFC

1.2.2.1. Electrode

The electrode of a PEMFC is the region where the actual electrochemical reactions occur. Basically electrode is composed of carbon supported catalyst blended with protons conductive polymer called ionomer. The widely used ionomer in the field of PEMFC is Nafion. The extensively used carbon supports in PEMFC are carbon blacks (CBs)¹⁵ such as Vulcan XC72R, Ketjen black (KB) and Acetylene black (AB). Platinum (Pt) has been considered to be the best catalyst for both anode and cathode. Because, even at high temperatures like 80 °C both the HOR and the ORR can't occur at a useful rate. Thus a catalyst is needed. According to the volcano plot shown in **Figure 1-6** confirms that Pt works best compared to other metals as a catalyst.¹⁶ The great deal of effort has been made by many researchers toward developing appropriate catalyst materials, especially for the ORR, and Pt is so far still the best option. There are few requirements to be fulfilled by a catalyst to show higher performance in PEMFC system;

- Electrical conductivity
- Good interplay with the ionomer
- Accessible for reactant gases

- Stable while in contact with reactant gases, products and membrane electrolyte

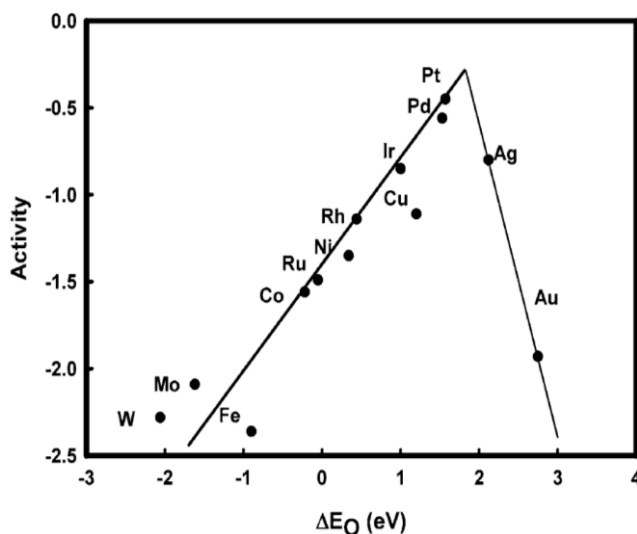


Figure 1-6 Oxygen reduction activity of different metals as a catalyst. Taken from ref. 16.

Pt shows all the requirements mentioned above and thus it is highly active and stable in PEMFC system. Since the reaction takes place at the surface of the catalyst, its active surface area has to be as high as possible. To give high performance the active surface area has to be maximized both per mass of the catalyst and per area of the electrode. Furthermore the limitations on the transport rates of the reactant gases to the catalyst have to be as low as possible.

The key factor of achieving these goals is a perfect catalyst distribution over the electrode. The catalyst particles have to assure for ionic conduction for protons, hydrophobic pathways for gas transport, hydrophilic pathways for the removal of liquid water, and most importantly for good contact to the external electrical circuit, where electrons are transported from the anode to the cathode in order to complete the cell reaction.¹⁷ To be able to match these requirements one has to select specific materials for the different parts of a membrane electrode assembly (MEA).

1.2.2.2. Electrolyte membrane

The main function of the membrane in PEMFC is to transport protons from the anode to the cathode. Therefore, membrane polymers have sulfonic groups to facilitate the transport of protons. The other functions include keeping the fuel and oxidant separated (to prevent mixing of the two gases) and withstanding harsh conditions including active catalysts, high temperatures or temperature fluctuations, strong oxidants, and reactive radicals. Thus, the ideal polymer must have excellent proton conductivity, chemical and thermal stability, strength, flexibility, low gas permeability, low water drag, low cost, and good availability.

Different types of membranes have been tested for use in PEMFC. The membranes are usually polymers modified to include ions, such as sulfonic groups. These hydrophilic ionic moieties are the key for allowing proton transport across the membrane. The favored polymer structure has changed to improve membrane lifetime and slow down membrane degradation. The widely used Nafion contains a polymerized tetrafluoroethylene (PTFE or Teflon) backbone with sulfonic acid groups as side-chains. The sulfonic acid groups are attached to the polymer, but once being hydrated their protons are free to move throughout the electrolyte. A detailed picture of Nafion is shown in **Figure 1-7**.

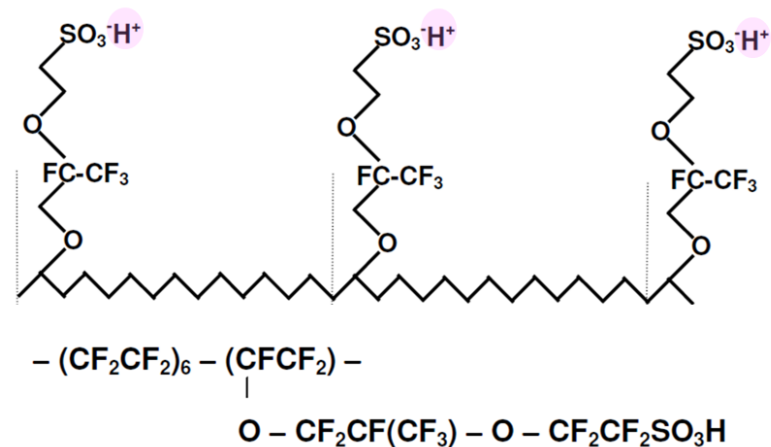


Figure 1-7 Structure and formula of Nafion.

1.2.2.3. Gas diffusion layers (GDLs)

A GDL functions as a supplier of reactant gases to the catalyst layers and as a liquid water evacuator on the cathode side of a PEMFC. Furthermore, GDL has to collect the produced current, be thermally conductive and provide mechanical support to the catalyst layer. Typical GDLs are made of thin porous layers of carbon fibers.^{18, 19} A problem that a GDL might face is accumulation of water in it and thus hinder the gas flow. Therefore, almost all GDLs are wet-proofed, i.e. polytetrafluoroethylene (PTFE) has been added to the GDL. PTFE creates hydrophobic channels in the GDL where water cannot penetrate through. Those pores are then available for reactant gas transport. A further improvement of the standard GDL is a so-called micro-porous layer (MPL).^{20,}

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The **Figure 1-8** shows schematic illustration of MEA containing main components of a PEMFC.

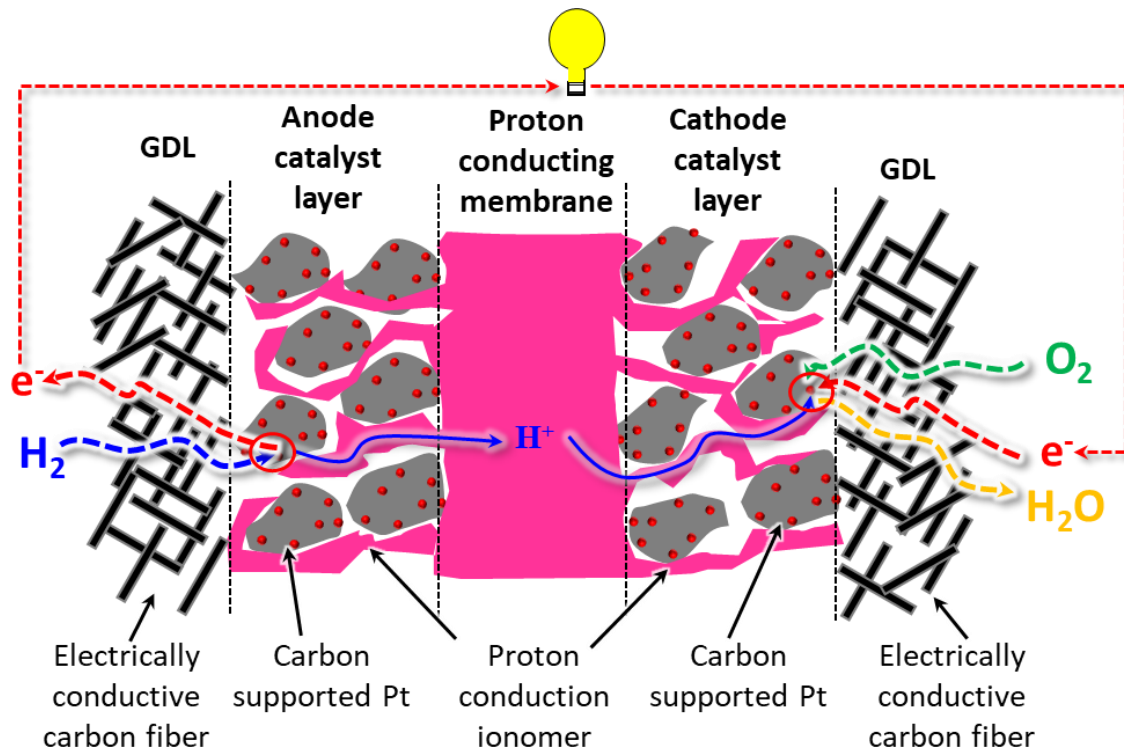


Figure 1-8 A detailed schematic illustration of MEA.

1.2.3. Polarization of PEMFC

In the PEMFC system, if the Gibbs free energy could be converted directly into electrical energy without any losses, the maximum voltage is called reversible cell voltage. However under practical condition, resulting voltage is lower than reversible voltage due to several irreversibilities. These irreversibilities cause reduction of actual voltage as current density increases. Therefore, the performance of the fuel cell can be estimated by plotting cell voltage against current density.⁷ The irreversibilities which causes the reduction of cell voltage are known as cell polarization and could be divided into 3 main polarizations; namely activation, ohmic and concentration losses as shown in **Figure 1-9**. The open circuit voltage is the voltage when no load exists. These polarization sources are active throughout the entire polarization curve. However, they become prominent at a certain segments of the curve.

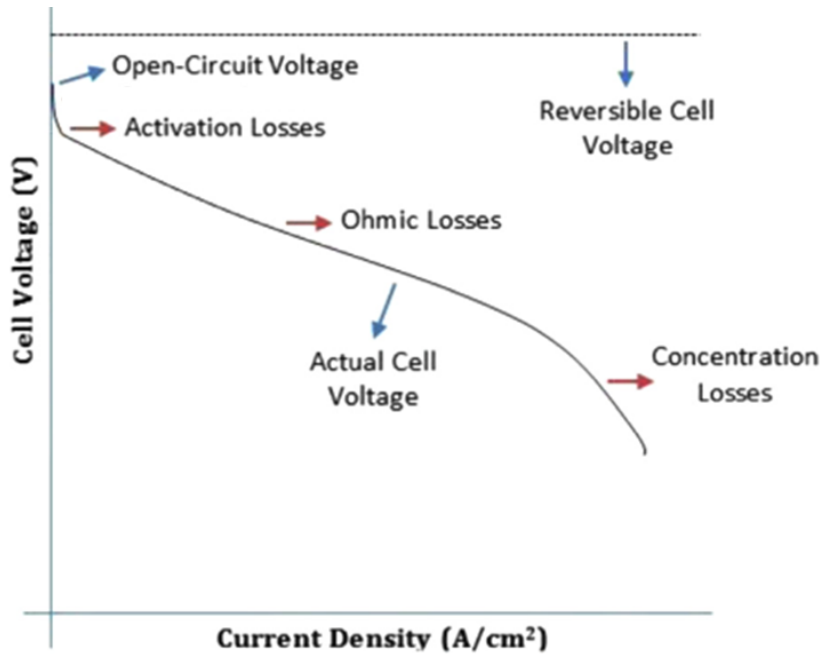


Figure 1-9 Typical polarization curve with voltage losses.

The activation polarization is the main reason for the voltage drop at low current densities and it is due to the sluggish reduction and/or oxidation kinetics at the electrode surface. The energy required for initiating the electrochemical reactions is reflected in the activation voltage drop. In PEMFC system it is well known that ORR is more kinetically sluggish compared to HOR, and thus activation losses are aroused basically due to the ORR in the PEMFC system.

The electronic and ionic resistance of the PEMFC components to the flow of charge result in ohmic polarization and are dominant in middle of the polarization curve. Ohmic voltage losses are due to combination of resistances coming from electrolyte, catalyst layer, GDL, current collectors interfacial contact between components and terminal connections of the PEMFC. The resistivity of the electrically-conductive cell components to the electron flow contributes to the electric resistivity while resistivity of the membrane and the catalyst layer to the ion flow contributes to the ionic resistivity. However, ionic resistivity dominates ohmic losses of the system. Because, the number of charge carriers through the ionic conductor is much less than in the electronic conductor. In an ionic conductors, the ions move through the vacancies in the crystallographic lattice whereas in an electronic conductor, the valence electrons of the atoms become detached and can move freely. Therefore, the electronic resistance is usually insignificant compared to ionic resistance.⁷

The concentration polarization is dominant at high current densities where reduced reactant availability hinders the electronical reactions at reaction sites. Generally, cathode's concentration polarization dominates since water acumination occurs at the cathode side ultimately limiting oxygen diffusion to the reaction sites. It is noted that maximum current density of fuel cell produces when the rate of reactant (i.e., the fuel or the oxidant) consumption is equal to the rate of reactant supply.⁷ The variation of all discussed polarization with increasing current is showing in **Figure 1-10**.

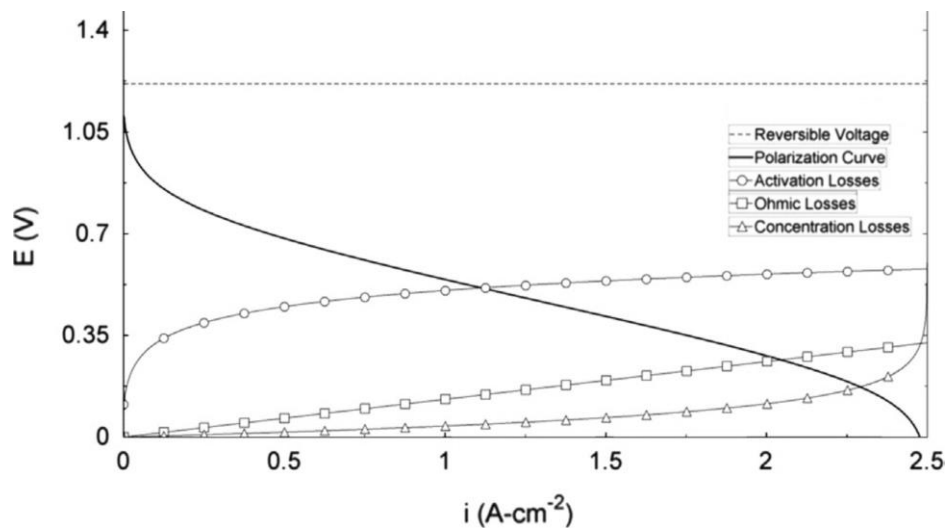


Figure 1-10 PEMFC polarization curve breakdown. Taken from ref. 7.

1.3. Cost analysis of fuel cell

Despite of having promising advantages of fuel cell, the global commercialization of fuel cell is at lower level due to the high cost and durability issues of the system. The **Figure 1-11** shows the cost analysis of fuel cell system by department of energy U.S. (DOE); hydrogen and fuel cells program.

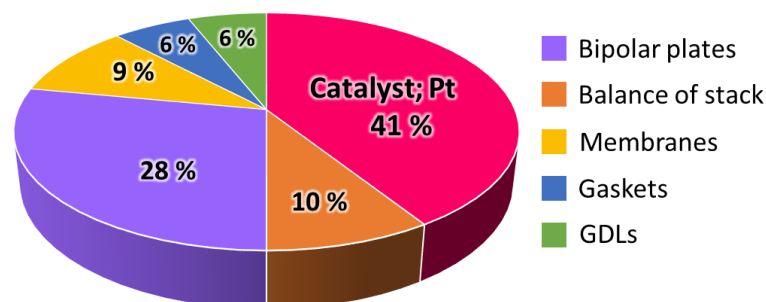


Figure 1-11 Breakdown of projected fuel cell stack cost at 500,000 systems per year, 2017.

Considerably higher percentage of cost is coming from the catalyst application which include both Pt catalyst and the ionomer. However, precious Pt metal cost in the electrocatalysts is the main contributor for the high cost of PEMFC system. DOE fixed the Pt group metal target of 0.125 g kW^{-1} or about $11.3 \text{ g}_{\text{PGM}}$ of Pt per midsize sedan vehicle by the year of 2020.²² However, the current light duty internal combustion engine vehicle catalyst convertor only requires $< 5 \text{ g}_{\text{PGM}}$. Therefore, fuel cell electrical vehicle would remain less than few percentage of global vehicle production, if not the use of Pt is declined to less than $10 \text{ g}_{\text{Pt}} / \text{vehicle}$.²³ **Figure 1-12** shows the relationship between cathode catalyst layer Pt loading where the ORR is taking place with sluggish kinetics and the cost of major stack components. Therefore, decreasing cathode Pt loading is important to alleviate demand on the Pt market and thus allow high penetration of automotive fuel cells.²⁴ Therefore, increasing Pt utilization efficiency in the catalyst layer is an appropriate approach to mitigate the usage of Pt in the fuel cell system.

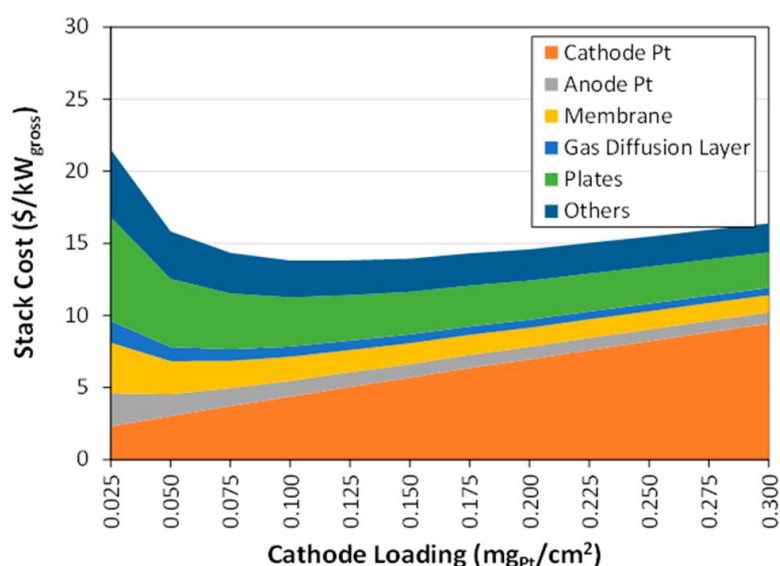


Figure 1-12. Effect of cathode catalyst layer on the stack cost. Taken from ref. 24.

1.4. The catalyst layer of a PEMFC

Even though a lot of research in the field of PEMFCs has been carried out in the last few decades to increase Pt utilization efficiency, there are still some major issues to be solved. Low Pt utilization and thus low energy efficiency keeps the cost of PEMFCs still too high to boost global commercialization. Advances in both materials and structure of the catalyst layer have helped to partly overcome that problem. It has been acknowledge that the performance of the cathode catalyst layer is a major contributor to the overall performance of the PEMFC. To enhance the cathode catalyst layer performance, a number of research groups have been giving efforts to

improve the true activity of electrocatalysts for the ORR to reduce the Pt loading amount, eventually reducing the cost.

One example in increasing specific activity of ORR is alloying Pt with non-precious metals.²⁵⁻³⁰ One of the drawbacks of these Pt alloy is dissolution of non-precious metals under acidic condition, deteriorating efficiency of fuel cell with time.³¹⁻³⁴ Also, some researches decreased the Pt particle size in order to increase the specific surface area of Pt. However, the mass activity reached the maximum at ~ 3 nm³⁵⁻³⁷ and the smaller Pt nanoparticles aggregate hastily compared to the larger Pt particles, subsequently resulting clear degradation of fuel cell performance.³⁸⁻⁴⁰ And also our group reported a new methodology to enhance the Pt utilization efficiency, in which the diameter of the Pt nanoparticles decreased by decreasing the weight ratio between Pt precursor and carbon supporting materials.⁴¹ Moreover an enhancement of catalyst utilization by optimizing the catalyst layer is essential to reduce Pt loading, even though high surface area alloy catalysts are used for the anode and cathode.

Appropriate amount of ionomer is a must to facilitate the proton conduction and O₂ diffusion inside the catalyst layer where ionomer layer should be thick enough for proton conduction and thin enough to reduce O₂ diffusion limitations.⁴²⁻⁴⁶ Not only the amount but also the distribution of ionomer producing connected network within the catalyst layer plays an important role in improving Pt utilization.⁴⁷ The typical catalyst layer is composed with Pt nanoparticles dispersed on high surface area CB agglomerates (CB/Pt) coated with Nafion as mentioned before. Watanabe *et al.*, first highlighted the importance of understanding in two different types of pores in CB/Pt, i.e. primary pores with a diameter $< \text{ca. } 0.1 \mu\text{m}$ and secondary pores with diameter $> \text{ca. } 0.1 \mu\text{m}$.⁴⁸ The primary pore is formed within the CB agglomerates and the secondary pores is formed between the agglomerates.^{48, 49} Watanabe *et al.*, revealed that most of the Pt nanoparticles are ($>85\%$) located on the wall of the primary pores.⁵⁰ Pt particles in these pores do not contact with Nafion and are inaccessible by protons⁵¹ and thus special treatments like auto clave assisted ionomer dispersion is required.⁵⁰

1.5. Problems in the PEMFC catalyst layer (reduced Pt utilization)

It is well known that reduced efficiency in the cathode catalyst layer is the main contributor for the lower PEMFC performance due to sluggish kinetics of ORR as discussed before. Therefore, it is necessary to improve Pt utilization efficiency in cathode side mainly. The **Figure 1-13** shows the schematic illustration of composition and distribution of catalyst components in the cathode catalyst layer. The reduced Pt utilization is expected due to following reasons. Pt nanoparticles has been deposited into the small pores (micropores; < 2 nm) of the CB. If that so,

those Pt nanoparticles are not accessed by gases and ionomer resulting limitations in mass transport for ORR.⁵² And furthermore due to the inhomogeneous distribution of Nafion in the catalyst layer a fraction of Pt nanoparticles even in the outer surface of CB does not connect with Nafion resulting higher proton conduction resistance. Not only distribution but also ionomer thickness plays an important role in O₂ diffusion in the catalyst layer.⁵³ The higher the thickness the higher the O₂ diffusion resistance.²⁴ Furthermore, insufficient pore connectivity limits the effective O₂ diffusion towards reaction sites as well.⁵⁴⁻⁵⁶

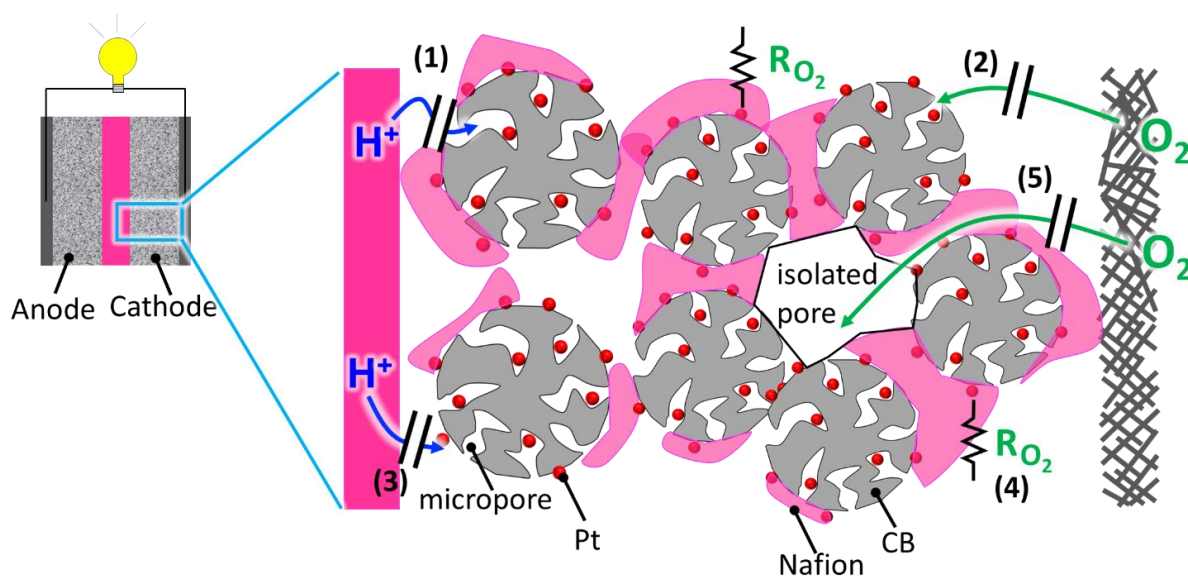


Figure 1-13 Schematic illustration of cathode catalyst layer with reduced Pt utilization.

The identified issues in the cathode catalyst layer can be summarized under five points.

- (1). Reduced proton conduction in the Pt nanoparticles inside the pores
- (2). Reduced O₂ diffusion in the Pt nanoparticles inside the pores
- (3). Reduced proton conduction due to inhomogeneous Nafion dispersion
- (4). Higher local O₂ diffusion resistance due to thicker Nafion layer around Pt nanoparticles
- (5). Higher O₂ diffusion resistance due to disconnected porous structure; presence of isolated pores

The deposition of Pt nanoparticles into pores has been widely investigated using scanning transmission electron microscope (STEM).^{52, 57} Scanning electron microscope (SEM) images of CB supported Pt gives information of Pt nanoparticles on the surface of CB (**Figure 1-14 b**) and while transmission electron microscope (TEM) shows total of Pt nanoparticles in and on the CB

(**Figure 1-14 a**) . Therefore, Pt nanoparticles inside the pores of CB can be determined considering the difference in percentage of Pt nanoparticles on the surface of CB by SEM and total Pt nanoparticles by TEM.

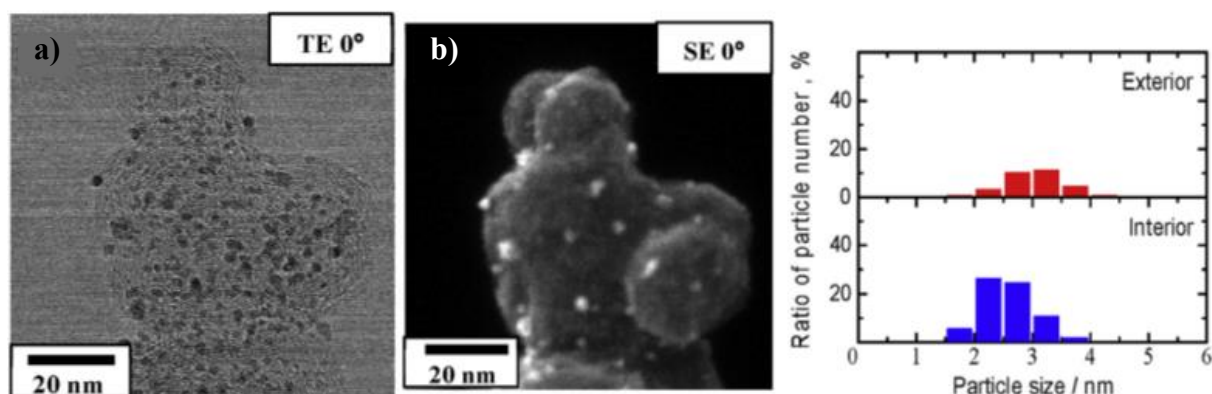


Figure 1-14 a) TEM b) SEM images of CB supported Pt. Taken from ref. 52.

It is reported that nearly half of the mass transport losses are due to the local O_2 diffusion resistance (**Figure 1-15 a**) at the reaction site.²⁴ The **Figure 1-15 b** shows the stimulated mass transport voltage losses coming from local O_2 diffusion resistance (η^{PtO_2}), H^+ conduction resistance in the catalyst layer (η^{CCLH^+}), O_2 diffusion in the GDL ($\eta^{GDL O_2}$) and bulk O_2 diffusion resistance in the catalyst layer ($\eta^{CCL O_2}$) at 1.75 A cm^{-2} . Therefore, it is clear that having a thicker Nafion coverage around Pt catalyst deteriorates the performance at a greater extent due to local O_2 diffusion resistance.

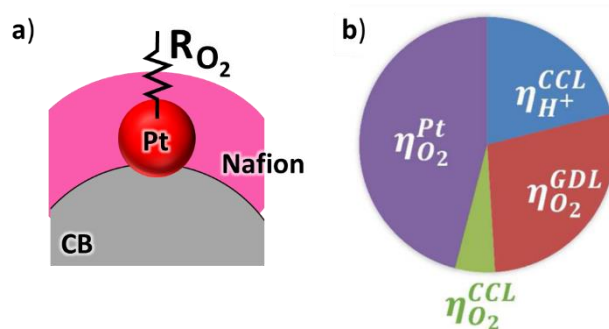


Figure 1-15 a) Schematics of local O_2 transport of Pt nanoparticle through a Nafion film and b) simulate mass transport losses at 1.75 A cm^{-2} . Taken from ref. 24.

Furthermore, Inoue *et al.*,⁵⁶ found that nature of Nafion distribution in the catalyst layer contributed to the pore structure formation in the catalyst layer for gas permeation by analyzing focused ion beam SEM (FIB-SEM) images. The formation of isolated large pores in the catalyst layer is ineffective for gas diffusion (**Figure 1-16 b**) when compared that of with the formation of

connected network of pores like web (**Figure 1-16 a**). Therefore, nature of ionomer distribution plays an important role in pore structure formation in the catalyst layer.

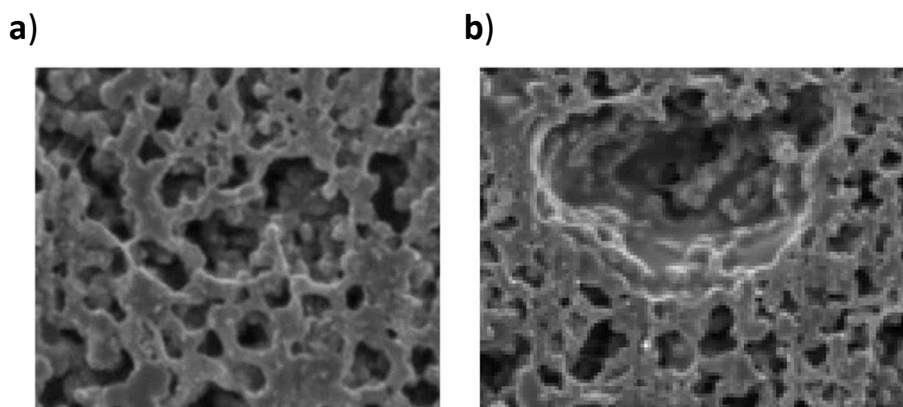


Figure 1-16 Features of catalyst layer structure showing **a)** connected network of pores and **b)** large isolated pores. Taken from ref. 56.

Finally, above discussed reasons for the reduced Pt utilization contribute to the high cost of PEMFC and thus improvement of Pt utilization efficiency in the PEMFC catalyst layer is high required.

1.6. PBI wrapping approach

To overcome the issues discussed above in the catalyst layer, application of polybenzimidazole (PBI) wrapping onto CBs is considered. The structure of PBI is showing in **Figure 1-17 a**. PBI has advantages such as favorable interaction with graphitic surface and functional groups (-COOH, -OH) of CB to form a steady coating layer on the surface of CB⁵⁸ and provide strong interaction with Pt nanoparticles ions via coordination bonding(**Figure 1-17 b**).⁵⁹
⁶⁰ Additionally, PBI is stable in strong acidic conditions and hence able to use in PEMFC system.⁶¹

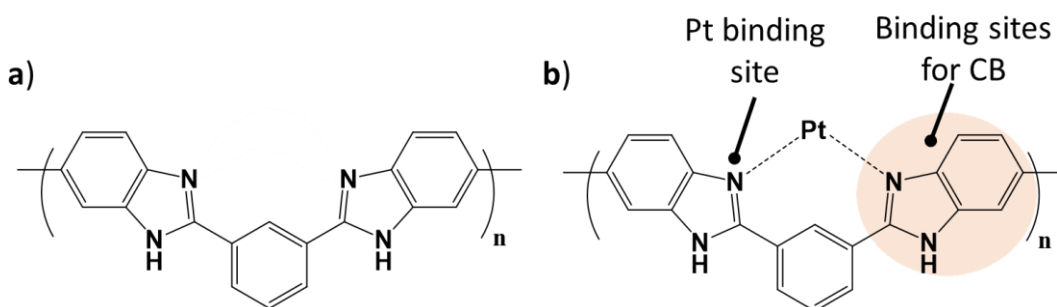


Figure 1-17 a) Structure of PBI and **b)** binding sites for CB surface and Pt nanoparticles.

According to the previous report, it is found that the PBI preferentially coated only outer surface and interior of mesopore surface of CB. Because, after PBI wrapping micropore surface area was significantly reduced. It means after PBI wrapping, micropore surface area became unavailable either because of micropore capping or filling by PBI. However, the important phenomena found in PBI wrapping is reduction of microporous surface.⁵⁸ The expected PBI wrapped CB (CB/PBI) is showing in **Figure 1-18 a**, suggesting that micropore entrance is capped because of PBI wrapping. This phenomena was proved using N₂ adsorption/desorption experiment and pore size distribution was analyzed before and after PBI wrapping (**Figure 1-18 b**). According to that pore analysis data, it is clear that pore size in the range of micropore has been reduced significantly due to PBI wrapping.

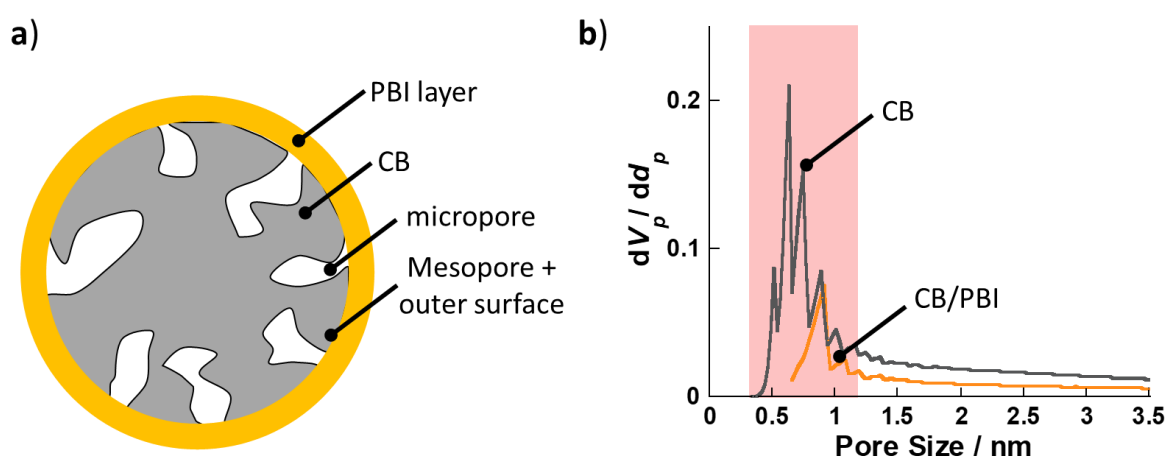


Figure 1-18 a) Schematics of CB/PBI and **b)** pore size distribution of CB (black) and CB/PBI (orange).

1.7. Objectives of this study

The main objective of this study is improving Pt utilization efficiency in the PEMFC catalyst layer in order to reduce the cost of PEMFC system. The total context of this study can be separated into three main parts under three different strategies; 1) improving Pt utilization efficiency in microporous Vulcan, 2) application of PBI wrapping method onto Ketjen black (KB; highly microporous) and Acetylene black (AB; non-microporous) to investigate which type of CB material has high potential of improving Pt utilization by PBI wrapping method and 3) optimizing Nafion content in the catalyst layer to improve Pt utilization efficiency further by improving O₂ diffusion in the catalyst layer and fabrication of low loaded Pt catalyst layers.

1.7.1. Strategy 1

Improving Pt utilization efficiency in microporous Vulcan is the 1st objective of this study. Since PBI wrapping works as either capping of micropore gates or filler of micropores, Pt nanoparticle deposition into smaller pores will be prevented in PBI-wrapped Vulcan supported Pt (Vulcan/PBI/Pt). On the other hand in the conventional Vulcan/Pt a fraction of Pt nanoparticles is still deposited into pores. Thus PBI wrapping is advantageous in improving mass diffusion by prevention of Pt nanoparticles into pore. Furthermore, basic nature of PBI could easily interact with acidic Nafion, ensuring homogeneous Nafion distribution in the catalyst layer. In contrast there is no such preferential interaction between Nafion and Vulcan and thus ensuring homogenous Nafion dispersion is difficult.^{62, 63} Finally, combined effect of micropore capping and homogeneous Nafion distribution in Vulcan/PBI/Pt may have high potential of improving Pt utilization efficiency due to enhanced mass transport within the catalyst layer. The difference in Pt deposition and Nafion distribution in Vulcan/PBI/Pt and Vulcan/Pt is shown in **Figure 1-19**. Performance increment in the means of electrochemical active surface area (ECSA) and polarization curve will be tested in Vulcan/PBI/Pt and will be compared with conventional Vulcan/Pt.

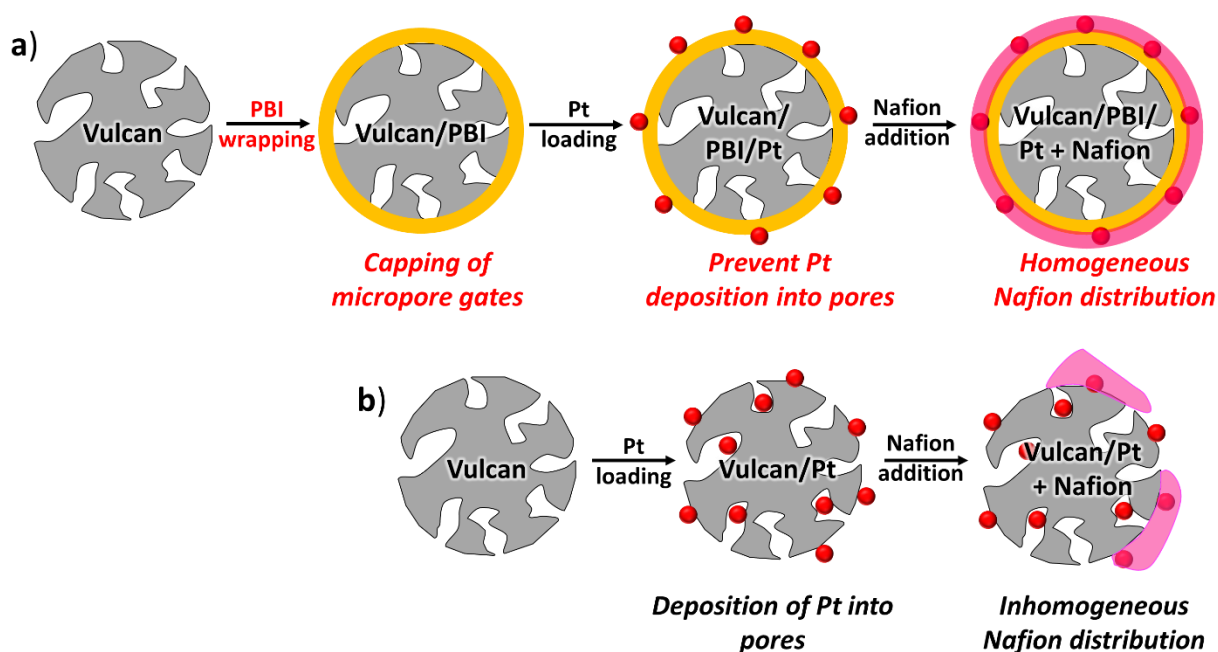


Figure 1-19 Schematics of **a)** PBI wrapping method and **b)** conventional method towards Pt deposition and Nafion distribution.

1.7.2. Strategy 2

Application of PBI wrapping method onto KB (highly microporous) and AB (non-microporous) to investigate which type of CB material has high potential of improving Pt utilization by PBI wrapping method is the 2nd objective of this study. The investigation of broad aspects of PBI wrapping method is expected by choosing two other types of carbon blacks CBs which have different pore size distribution and degree of graphitization. The overview of the strategy 2 is shown in **Figure 1-20**.

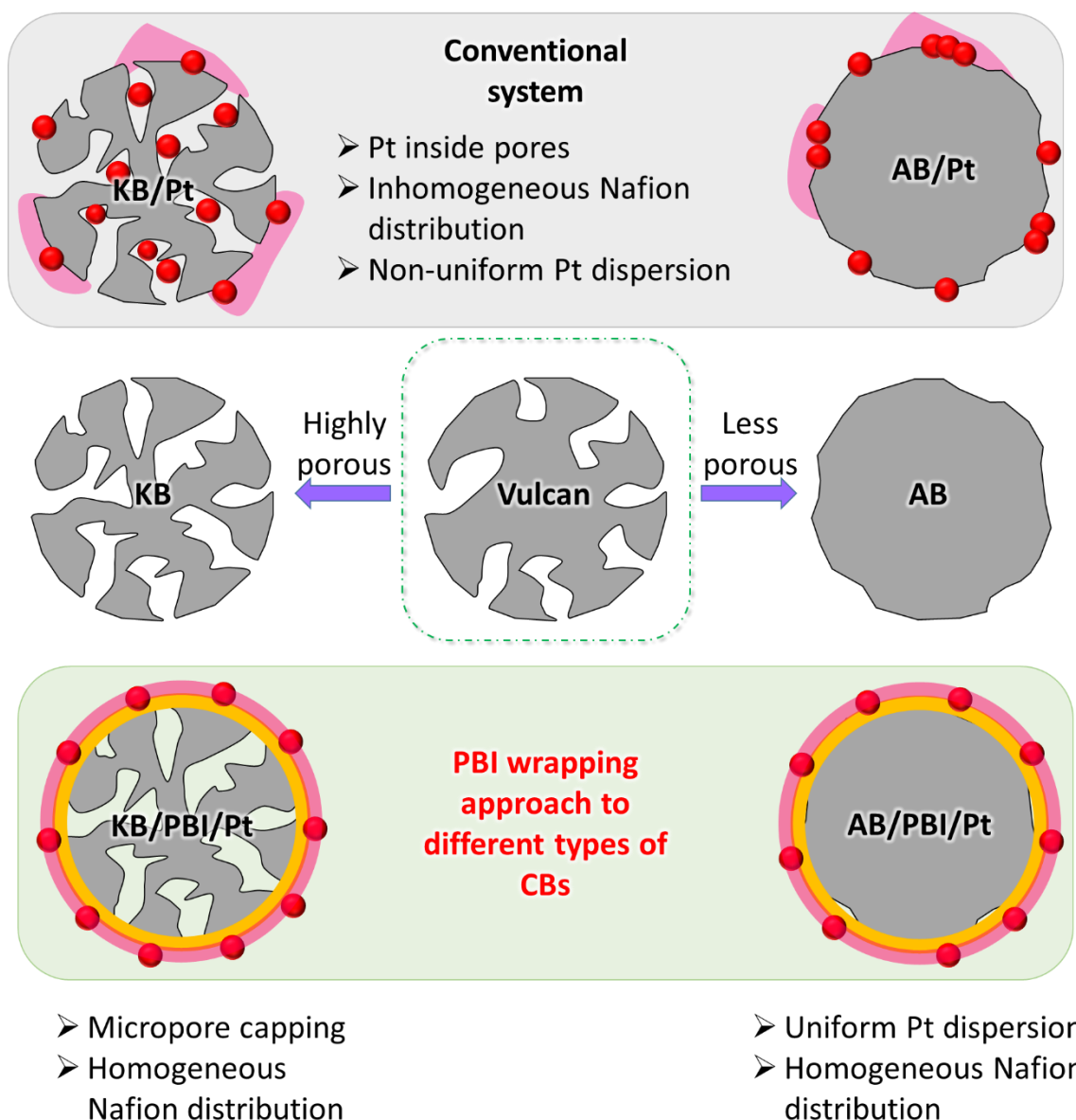


Figure 1-20 Overview of the strategy 2.

KB is highly porous compared to Vulcan and performance improvement in PBI wrapped KB supported Pt (KB/PBI/Pt) mainly will be due to the prevention of Pt nanoparticle deposition into the pores along with the long range proton conduction as mentioned in the Vulcan system.

Since higher fraction of Pt nanoparticles depositing into pores of KB compared to Vulcan as reported by E. Padgett *et al.*, degree of performance improvement in KB/PBI/Pt with similar degree of micropore capping to Vulcan will be higher.⁵⁷

In the case of AB, since it is less porous compared to Vulcan, performance improvement in PBI wrapped AB supported Pt (AB/PBI/Pt) may be due to the effective proton conduction. Furthermore, AB is highly graphitized compared to porous CBs and thus uniform distribution of Pt nanoparticles is quite challenging due to lack of Pt anchoring sites. Therefore, effective surface area of Pt nanoparticles may decreased due to Pt-Pt aggregation. The issue of Pt-Pt aggregation could be eliminated after PBI wrapping owing to Pt anchoring effect of PBI through imidazole groups, resulting uniform Pt nanoparticle distribution on AB/PBI.

1.7.3. Strategy 3

Optimizing Nafion content in the catalyst layer to improve Pt utilization efficiency further by enhancing O₂ diffusion in the catalyst layer is the 3rd objective of this study. Decreasing the amount of Nafion in the catalyst layer is challenging. It is reported that minimum of ionomer/carbon (I/C) ratio should in the range of 0.5 - 0.6 to achieve effective proton conduction in the conventional catalyst layer.⁵³ Because, it is difficult ensure connected network of Nafion with lower I/C due to the absence of preferential interaction between Nafion and Vulcan. In contrast, there is high possibility of decreasing I/C amount in Vulcan/PBI/Pt due to the strong interaction between Nafion and PBI without sabotaging the effective proton conduction in the catalyst layer. Because there is high tendency of forming a connected network of Nafion even with the smaller amount of Nafion in the catalyst layer. In particular, to increase the cell output performance, it is necessary to reduce not only the proton transfer resistance but also O₂ diffusion resistance as shown in **Figure 1-21**. Nafion strongly affects both of these resistances. Therefore, optimization of Nafion in the catalyst layer is highly recommended and possibility of operating PEMFC system with lower amount of ionomer strongly contributes to the cost reduction of PEMFC system as well.⁶⁴

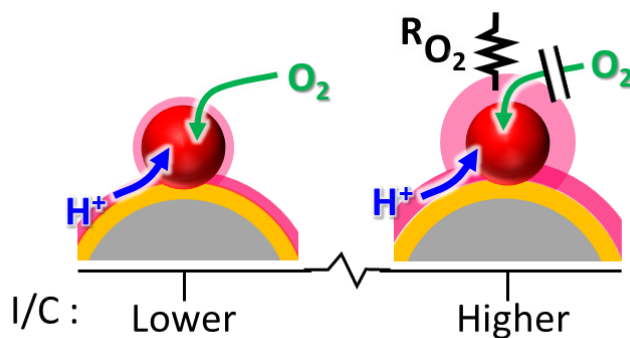


Figure 1-21 Schematics of O_2 diffusion and proton conduction in Vulcan/PBI/Pt with changing I/C.

1.8. Overview of this dissertation

This dissertation describes the methods of improving Pt utilization efficiency in PEMFC.

Chapter 1 outlines a brief introduction on importance, applications and working principle of fuel cells. This chapter describes the reasons for the high cost of PEMFC system which is basically coming from the usage of precious metal Pt as the catalyst of PEMFC. Chapter 1 further introduces the main causes of lower Pt utilization in the typical fuel cell catalyst layer. Finally this chapter outlines the 3 strategies to improve Pt utilization efficiency in the catalyst layer using PBI wrapping method.

Chapter 2 outlines strategy 1. Preparation of PBI-coated Vulcan supported Pt (Vulcan/PBI/Pt) and action of PBI-coating towards enhancing Pt utilization efficiency by comparing performance between Vulcan/PBI/Pt and conventional Vulcan/Pt are discussed. Characterizations of Vulcan/PBI/Pt using transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and X-ray diffraction spectroscopy (XPS) is discussed with procedures. Investigation of Pt utilization efficiency in Vulcan/PBI/Pt and Vulcan/Pt catalyst layers using fuel cell test is discussed. Power density and Pt utilization values of Vulcan/PBI/Pt are calculated and compared with Vulcan/Pt to understand the mechanism behind PBI-wrapping method towards improving Pt utilization efficiency.

Chapter 3 outlines strategy 2. Comparison study between application of PBI coating onto high surface area CB (HSA CB) and low surface area CB (LSA CB) is discussed. Change of surface area characteristics upon PBI wrapping is tested with N_2 gas adsorption measurement and different degree of PBI wrapping onto different types of CBs is identified. Then effect of PBI

wrapping towards improving Pt utilization is discussed using fuel cell measurement. Finally, effect of PBI wrapping on Pt nanoparticle durability is investigated.

Chapter 4 outlines the strategy 3. Optimization of ionomer in the catalyst layer by triggering favorable interaction between ionomer and PBI is explained. Importance of achieving promising proton conduction with lower I/C is investigated and discussed. Contribution of PBI wrapping method on realizing lower I/C is inspected and compared with conventional system. Other advantages such as achieving higher relative conductivity and proper water management in the catalyst layer with lower I/C is investigated. Finally, fabrication of low Pt loaded catalyst layer is endorsed with lower I/C to obtain higher Pt utilization value which is closer/or similar to DOE target.

Chapter 5 explains the general summery of the thesis with perspectives on future works.

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Chapter 2

Enhanced Platinum utilization efficiency of polymer-coated Vulcan as an electrocatalyst in polymer electrolyte membrane fuel cells

2.1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been receiving intense attentions as an efficient and clean power source for stationary and automotive applications.^{1, 2} The efficiency of a PEMFC strongly depends on the nature of the membrane electrode assembly (MEA), especially the structure of the catalyst layer. Platinum (Pt) nanoparticles dispersed on carbon black (CB) with a high surface area, such as Vulcan, have been widely used as the electrocatalyst in PEMFCs because Pt is the most stable and active catalyst for the oxygen reduction reaction (ORR) at the cathode.³ One of the challenges for commercialization of PEMFCs is to minimize the amount of Pt needed to lower the cost of PEMFCs because Pt currently represents more than 40% of the MEA cost.^{4, 5} To lower the amount of Pt in PEMFCs, a number of research groups have been attempting to incorporate non-precious metals such as Fe⁶⁻⁸ Co⁷⁻¹² Cr,⁹⁻¹¹ Ni,^{6, 8-10} and Mn⁸ with Pt to form alloys. One of the drawbacks of these Pt alloys is the dissolution of the non-precious metals under the acidic conditions of PEMFCs, which deteriorates the efficiency of PEMFCs over time.¹³⁻¹⁶ Another approach involves decreasing the Pt particle size to increase the specific surface area of Pt.¹⁷ However, the maximum Pt mass activity is reached at a nanoparticle size of ~3 nm¹⁸⁻²⁰ and smaller Pt nanoparticles aggregate more quickly than larger ones, which degrades PEMFC performance.²¹⁻²³

On the other hand, optimizing the catalyst structure by increasing the number of reaction sites (i.e., triple phase boundaries) is a promising strategy to improve the Pt utilization efficiency of PEMFCs.^{24, 25} One approach to optimize the catalyst structure is to select a better type of CB to increase mass diffusion, which is strongly affected by the CB surface morphology.²⁶⁻²⁸ Since micropores and deep cracks in CB are inaccessible to Nafion and reactants, thus decreasing the triple phase boundary amount,^{29, 30} it is important that all of the Pt nanoparticles are accessible for both proton and oxygen (O₂) on the surface of the carbon support. It was reported that Pt nanoparticles loaded on acetylene black (AB) established favorable supply paths for protons and O₂ because most of the Pt nanoparticles were deposited on the exterior of AB.³¹ However, AB has high crystallinity, which makes it difficult to load the Pt nanoparticles uniformly on the AB surface because of the lack of anchoring sites,³² resulting in decrease of Pt durability and utilization efficiency.³³

The ionomer/Nafion content of the catalyst layer also affects the Pt utilization efficiency and optimization of the Nafion content has been investigated.^{34, 35} In this approach, an increase of Nafion content increased proton conductivity because of the effective connection of the Nafion network, but it also decreased the accessibility of O₂ to the reaction sites.³⁶⁻⁴⁰ Thus, this approach involves a trade-off between proton conductivity and O₂ accessibility to maximize the Pt utilization efficiency. Ideally, the ionomer is covered uniformly and continuously on the surface of carbon support thick enough to deliver the proton but thin enough to supply sufficient amounts of O₂,^{41, 42} in which the interaction between Nafion and the carbon support will strongly affect the Nafion coverage.^{43, 44} However, the recent high resolution transmission microscopy studies suggested ionomer distribution in the catalyst layer is rather inhomogeneous.⁴⁵ Recently, Uchida *et al.* successfully improved the homogeneity of Nafion using electrospray method and obtained the improved Pt utilization efficiency even under the low Nafion content.⁴⁶

In this study, we demonstrate a novel approach to improve the Pt utilization efficiency of PEMFCs by homogeneous Nafion coating. Polybenzimidazole (PBI) is used to support the homogeneous coating of Nafion because it can stably and homogeneously coat carbon materials such as CB,³³ carbon nanotubes (CNTs),⁴⁷ and stacked graphene⁴⁸ via π - π interactions and acid–base reactions. In addition, a PBI layer can provide binding sites for metal nanoparticles including Pt through coordination of metal ions with imidazole groups in the PBI backbone.^{49, 50} It is reported that PBI preferentially coated the outer surface and interior surface of mesopores of Vulcan and blocked the entrance to the micropores, improving the durability of Vulcan.⁵¹ Therefore, a PBI coating is also expected to prevent the deposition of Pt nanoparticles into the small pores of Vulcan. Furthermore, preferential interaction between Nafion and PBI due to acid base interaction could enhance the triple phase boundary condition by proving long range proton conduction. Therefore, coating of PBI on the Vulcan surface is expected to improve the Pt utilization efficiency of PEMFCs because of the combined effects of prevention of deposition of Pt nanoparticles into inaccessible pores and homogeneous Nafion distribution in the catalyst layer, both of which increase the triple phase boundary density.

2.1. Experimental

2.1.1. Materials

Hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), 2-propanol, *N,N*-dimethylacetamide (DMAc), ethylene glycol (EG), and ethanol (99.5%) were purchased from Wako Pure Chemicals, Ltd, Tokyo. Vulcan XC-72R was purchased from Cabot Chemical Co., Ltd. Nafion solution (5%) and Nafion[®] 212 membranes were purchased from Sigma-Aldrich. PBI was provided by Sato Light Industrial Co., Ltd.

2.1.2. Electrocatalyst preparation

Vulcan (20.0 mg) was dispersed in a solution of PBI (13.0 mg) in DMAc (20 mL) by sonication for 15 min using a bath-type sonicator (Branson 5510) followed by 3 hr mechanical shaking (Neo Shaker) to obtain Vulcan/PBI. Then resulted Vulcan/PBI composite was filtered, washed with DMAc, and then dried overnight under vacuum at 80 °C. Vulcan/PBI (100.0 mg) was dispersed in 60% EG aqueous solution (400 mL). $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (4.3 g) dissolved in 60% EG aqueous solution (200 mL) was added and then the mixture was refluxed at 140 °C for 6 hr under nitrogen (N_2) atmosphere. Experimental setup is showing in **Figure 2-1 a**. After cooling, the obtained composite (denoted as Vulcan/PBI/Pt) was collected by filtration, washed several times with Milli-Q water, and then obtained black color product (**Figure 2-1 b**) dried overnight at 60 °C to get well dried Vulcan/PBI/Pt as shown in **Figure 2-1 c**. Vulcan/Pt was prepared in similar manner omitting PBI wrapping step as the test sample.

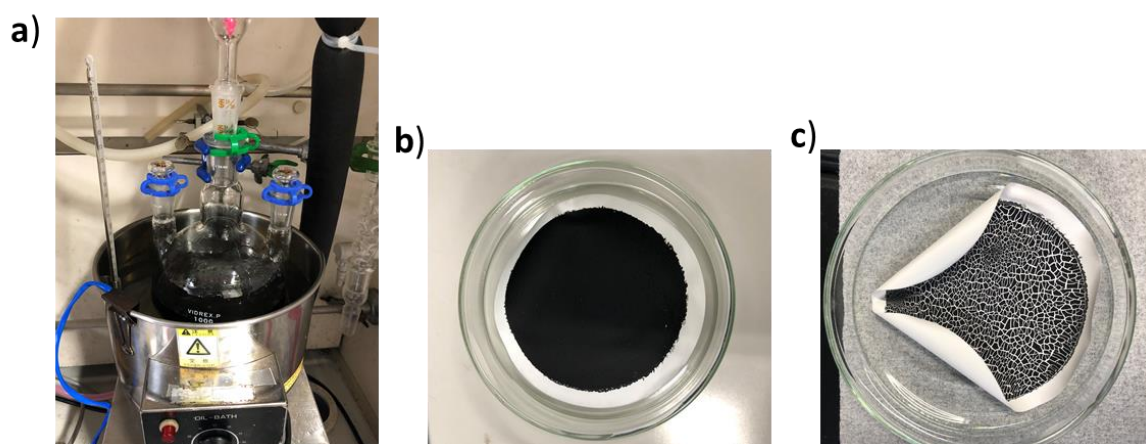


Figure 2-1 Photographs of **a)** refluxing setup and obtained black color Vulcan/PBI/Pt **b)** before and **c)** after drying at 60 °C.

2.2.3. Material characterization

X-ray photoelectron spectroscopy (XPS) was conducted using an AXIS-ULTRADLD spectrometer (Shimadzu). The pressure in the XPS analysis chamber was maintained at 10^{-9} Pa or lower during the measurement. In the calibration process, the binding energy of the core level C1s peak was fixed at 284.5 eV. Elemental analysis was performed based on the regions of the C1s (282-295 eV), N1s (395-407 eV) and Pt4f (68-83 eV) with the pass energy of 40 eV and linear background. The elemental compositions of composites were determined by the ratios of peaks areas. Thermogravimetric analysis (TGA) was performed using an EXSTAR TG/DTA6300 analyzer (Seiko Instruments, Inc.) at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an air flow of 200 mL min^{-1} . Transmission electron microscopy (TEM) was executed using a JEOL 2010 microscope operating at 30 kV. A copper grid with a carbon support (Okenshoji Co., Ltd.) was used for the TEM observations. N₂ adsorption isotherm measurement was conducted using a BELSORP-max (BEL Japan, Inc., 77 K and $1\times 10^{-8} < P/P_0 < 1$). The gas adsorption measurements were conducted after pretreatment at 200 °C for 12 hr under high vacuum condition. Specific surface area of Vulcan and Vulcan/PBI was determined by the Brunauer-Emmett-Teller (BET). CHN elemental analysis of Vulcan/PBI was performed using a CHN Corder MT-6 (Yanaco). The size distribution of the catalyst particles in catalyst ink was investigated by dynamic light scattering (DLS) measurements with a particle size analyzer (DLS, PHOTAL ELS8000, Otsuka Electronics) using spray ink that was diluted four times. The surface charge of composites was determined by zeta-potential measurements on the same instrument. The morphology of the catalyst layer was observed by scanning electron microscopy (SEM) using an SU9000 microscope (Hitachi High-Technologies) operating at 5 kV.

2.2.4. Rotating ring disk electrode (REDE)

The electrochemical measurements were performed with potentiostat (ALS 760D, ALS Co., Ltd.) connected in a three-electrode configuration at room temperature using a Pt and a Ag/AgCl wire as the counter (CE) and reference (RE) electrodes, respectively. All potentials are indicated against RHE. A glassy carbon electrode (GCE) with the surface area of 0.1275 cm^2 was used as the working electrode. To prepare a catalytic suspension (ink), the catalyst composite (2.0 mg) was ultrasonically dispersed in 80% 2-propanol aqueous solution (8.0 ml). A portion of dispersion was cast on the GCE (**Figure 2-2 a**), and then air-dried to provide a uniform layer of catalyst layer on the GCE to prepare the working electrode (WE). The Pt loading amount on the GCE was controlled to be $14\text{ }\mu\text{g cm}^{-2}$. Cyclic voltammetry (CV) was performed by feeding the working electrode in 0.1 M HClO₄ with N₂ for 60 min and then activated by 26 CV cycles, and

then 3 CV cycles were recorded with the scan rate of 50 mV s^{-1} . Linear sweep voltammetry (LSV) for ORR was carried after by purging 0.1 M HClO_4 with O_2 for 30 min. The **Figure 2-2 b** shows the schematics of the experimental setup.

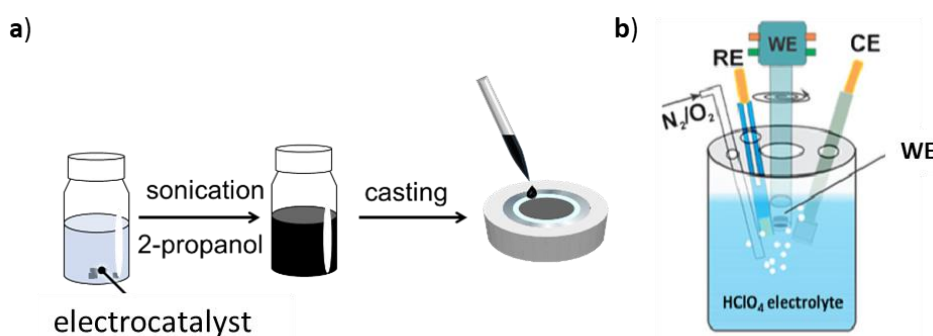


Figure 2-2 Schematics of **a)** GCE casting and **b)** half-cell experiment (three-electrode configuration).

2.2.5. Membrane electrode assemble (MEA) fabrication

The electrocatalyst dispersed in 90% aqueous ethanol solution was cast on a Nafion[®] 212 membrane using a spray coater (PS-1000, Nordson) as shown in schematic (**Figure 2-3 a**).

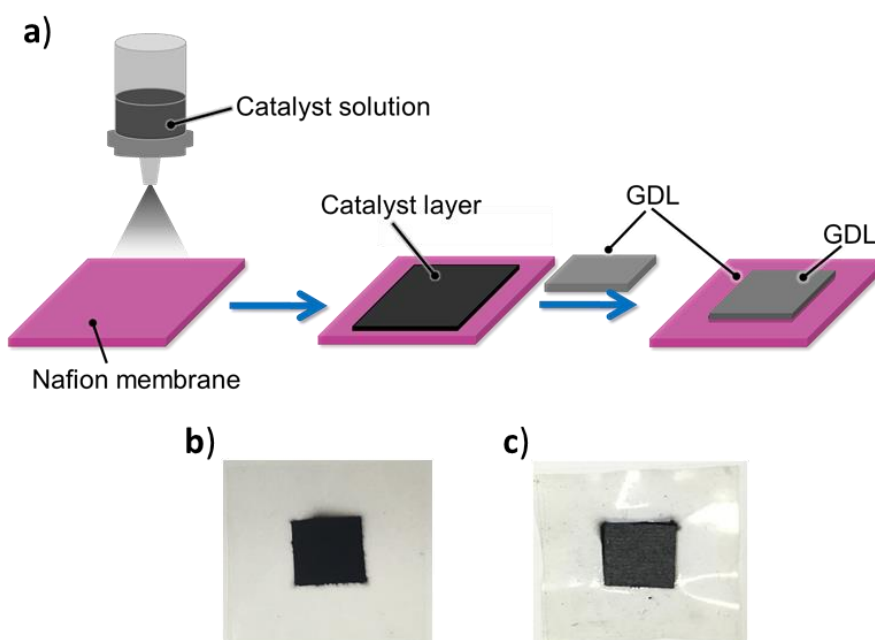


Figure 2-3 **a)** Schematics of spray coating and photographs of **b)** catalyst-coated membrane and **c)** fabricated MEA.

The amount of Nafion ionomer was 28 wt.% (ionomer/carbon; I/C = 0.72). The catalyst-coated membrane (**Figure 2-3 b**) was laminated with two gas diffusion layers (SIGRACET® GDL 25 BC, SGL Group) under 0.6 MPa at 132 °C for 190 s to get a MEA (**Figure 2-3 c**). The Pt loading of the catalyst-coated membrane was 0.3 mg cm⁻² and its geometric area was 1.0 cm².

2.2.6. Fuel cell operation

The electrochemical measurements were performed by feeding with humidified hydrogen (H₂) at a flow rate of 100 mL min⁻¹ and humidified N₂ at a flow rate of 200 mL min⁻¹ at 40 °C at the anode and cathode, respectively, using a fuel cell test system (Auto PEM-ER01, Toyo Corporation). To activate the MEA, 100 potential cycles from 0.1 to 0.9 V vs. RHE at a scan rate of 50 mV s⁻¹ controlled by a ModuLab XM CHAS 08 potentiometer (Solartron Analytical) were carried out. Three cycles were then recorded for data analysis. The electrochemical active surface area (ECSA) was determined using the hydrogen adsorption/desorption (HAD) method and carbon monoxide (CO) stripping method. For CO stripping, humidified H₂ (100 mL min⁻¹) and humidified N₂ (200 mL min⁻¹) were flowed through the MEA at the anode and the cathode, respectively, at 80 °C for 1 h using a fuel cell test system (Mini Test 3000, Toyo Corporation). The gas flow through the cathode was then switched to CO (1% balanced with argon) at a flow rate of 200 mL min⁻¹ for 3 min to completely poison the Pt and then switched back to N₂ (200 mL min⁻¹) to remove free CO in the catalyst layer. Finally, CO stripping voltammograms were obtained by measuring three potential cycles from 0.1 to 0.9 V (vs. RHE) at a scan rate of 50 mV s⁻¹ controlled by a SI 1260 potentiostat (Solartron, Inc.).

The fuel cell tests were performed by feeding with fully humidified H₂ (anode) and air/oxygen (O₂) (cathode) at fixed rates of 100 and 200 mL min⁻¹, respectively, using an in-house single cell system (Auto PEM-ER01). Current–voltage (*I*-*V*) and power density curves were obtained at a scan rate of 50 mA s⁻¹ under atmospheric pressure. The ionic resistance of the cathode catalyst layer was determined by impedance measurements by feeding humidified N₂ and H₂ to the cathode and anode, respectively at a working potential of 0.45 V. Impedance spectra were recorded in the frequency range of 0.1 Hz to 10 kHz with a sinusoidal amplitude of 10% of the applied potential.

2.3. Results and discussion

2.3.1. Electrocatalyst preparation

Vulcan was coated with PBI by mixing Vulcan with PBI solution in DMAc, and then filtrated to obtain the composite ³³(Figure 2-4). Vigorous washing of the composite with DMAc after filtration removed the unbound PBI to leave only the PBI-coated Vulcan (Vulcan/PBI). PBI interact with both graphitic surfaces and hydrophilic functional groups to form a stable layer on the CB surface.⁵¹ The change of surface of Vulcan before and after PBI wrapping was evaluated by BET.

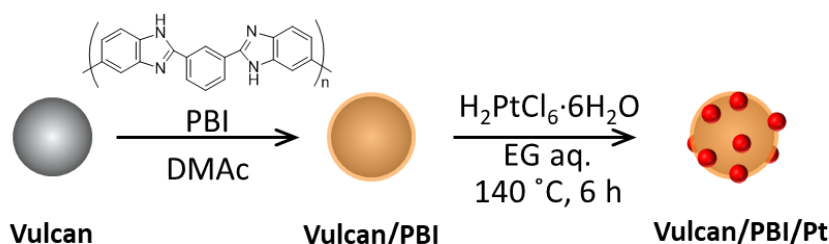


Figure 2-4 Schematic of preparation of Vulcan/PBI and Vulcan/PBI/Pt.

The **Figure 2-5** shows the N₂ adsorption/desorption isotherms of Vulcan and Vulcan/PBI. Ideally, all pores larger than the molecular diameter of N₂ (3.5 Å) can be detected by N₂ adsorption technique. The physical adsorption in micropores (<2 nm) is observable at very low gas partial pressures (<0.01 P/P₀). Concurrent with the filling of micropores, adsorption of the monolayer of N₂ occurs on the pore walls of meso (>2 nm) and on the external surface of the particles.

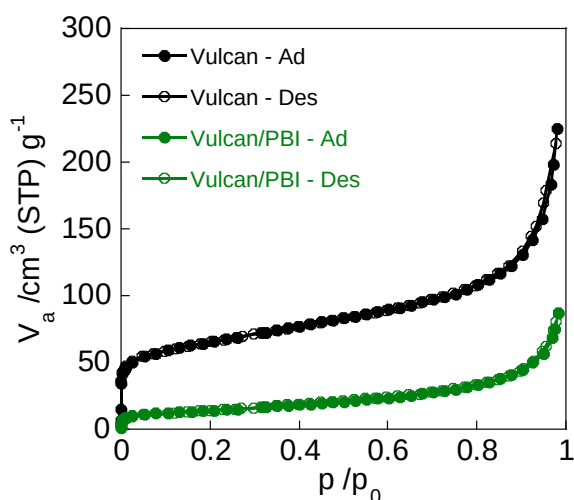


Figure 2-5 N₂ adsorption/desorption isotherm of Vulcan (black) and Vulcan/PBI (green).

Vulcan is type II according to IUPAC classification. Type II isotherms are characteristic of systems containing micropores because they exhibit a strong interaction between adsorbate and adsorbent, which is result in a steep rise in the isotherm under low partial pressures.²⁷ After PBI wrapping adsorption amount of N₂ drastically dropped, indication reduction of surface area.

BET equation⁵² is the most widely used for the calculation of specific surface area of porous materials. Vulcan showed BET surface area reduction from 220 to 113 m² g⁻¹ after PBI wrapping. The quantitative analysis of pore surface area was carried out by t-plot analysis after N₂ adsorption experiment. According to the t-plot, it was found that micropore surface area was significantly reduced compared to mesopores + outer surface due to micropore capping as suggested and calculated micropore capping % in Vulcan/PBI was 84. The difference in surface area is easily visible is bar graph displaying outer + mesopore and micropore surface area (**Figure 2-6**) and **Table 2-1**.

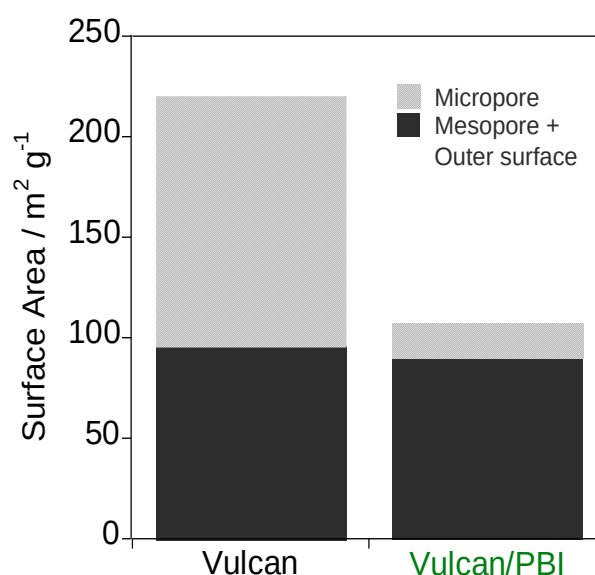


Figure 2-6 Bar graphs displaying outer + mesopore and micropore surface area of Vulcan and Vulcan/PBI.

Table 2-1 Outer + mesopore and micropore surface area of Vulcan and Vulcan/PBI by t-plot analysis.

Composite	Outer + meso surface area / m ² g ⁻¹	Micropore surface area / m ² g ⁻¹
Vulcan	95.6	124.4
Vulcan/PBI	90.5	20.3

To prepare electrocatalysts, Pt nanoparticles were deposited on Vulcan/PBI using the polyol reduction method with EG as the reducing agent to obtain Vulcan/PBI/Pt⁵³ (**Figure 2-4**). PBI provides special binding sites to Pt nanoparticles via imidazole groups.⁵⁴

XPS was used to confirm the presence of PBI in Vulcan/PBI and Pt loading of Vulcan/PBI/Pt. As shown in **Figure 2-7 a**, the N 1s peak around 400 eV originating from the imidazole group of PBI indicated the presence of PBI before and after Pt deposition.^{55, 56} After Pt deposition, the Pt 4f spectrum of Vulcan/PBI/Pt showed two peaks at 71.4 and 75.0 eV attributed to the 4f_{7/2} and 4f_{5/2} signals of Pt metal, respectively (**Figure 2-7 b**), indicating that the dominant valence of the Pt species in the synthesized catalysts was zero.⁵⁷⁻⁶⁰

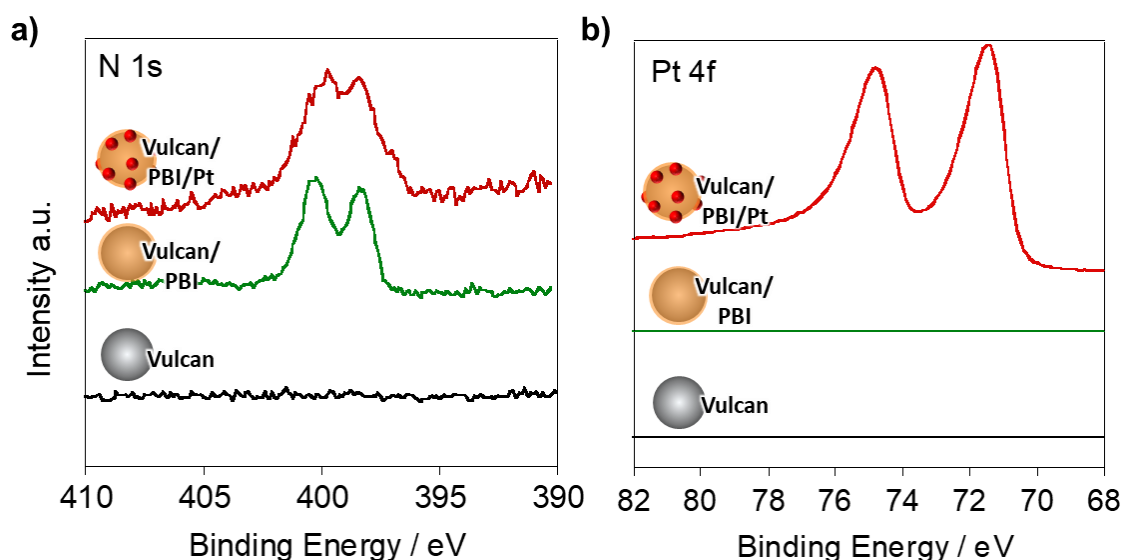


Figure 2-7 a) N_{1s} and b) Pt_{4f} XPS spectra of Vulcan, Vulcan/PBI and Vulcan/PBI/Pt.

The TGA curve of Vulcan/PBI displayed a one-step weight loss similar to that of Vulcan (**Figure 2-8 a**). Therefore, it was difficult to estimate the PBI content of the composite by TGA. Thus, the PBI content of Vulcan/PBI was estimated by CHN elemental analysis, which revealed that its C:H:N atomic ratio was 0.76:93.14:1.22. Considering that nitrogen is originating only from PBI and carbon is from both Vulcan and PBI, the PBI content of Vulcan/PBI was determined to be 7.3 wt.%. The Pt loading of Vulcan/PBI/Pt determined from the TGA weight residue at 900 °C (**Figure 2-8 a**) was 46.5 wt%. In contrast, the Pt loading of Vulcan/Pt was 45.0 wt% (**Figure 2-8 b**). The size of the Pt nanoparticles in both Vulcan/PBI/Pt and Vulcan/Pt was analyzed by TEM, as shown in **Figure 2-8 c** and **2-8 d**, respectively. The determined sizes of the Pt nanoparticles in Vulcan/PBI/Pt and Vulcan/Pt were 3.1 ± 0.6 and 3.2 ± 0.6 nm, respectively. The comparable Pt loading and size of Pt nanoparticles in Vulcan/Pt and Vulcan/PBI/Pt mean that these samples can be used in comparative studies. Moreover, both the types of catalysts showed uniform dispersion of Pt nanoparticles.

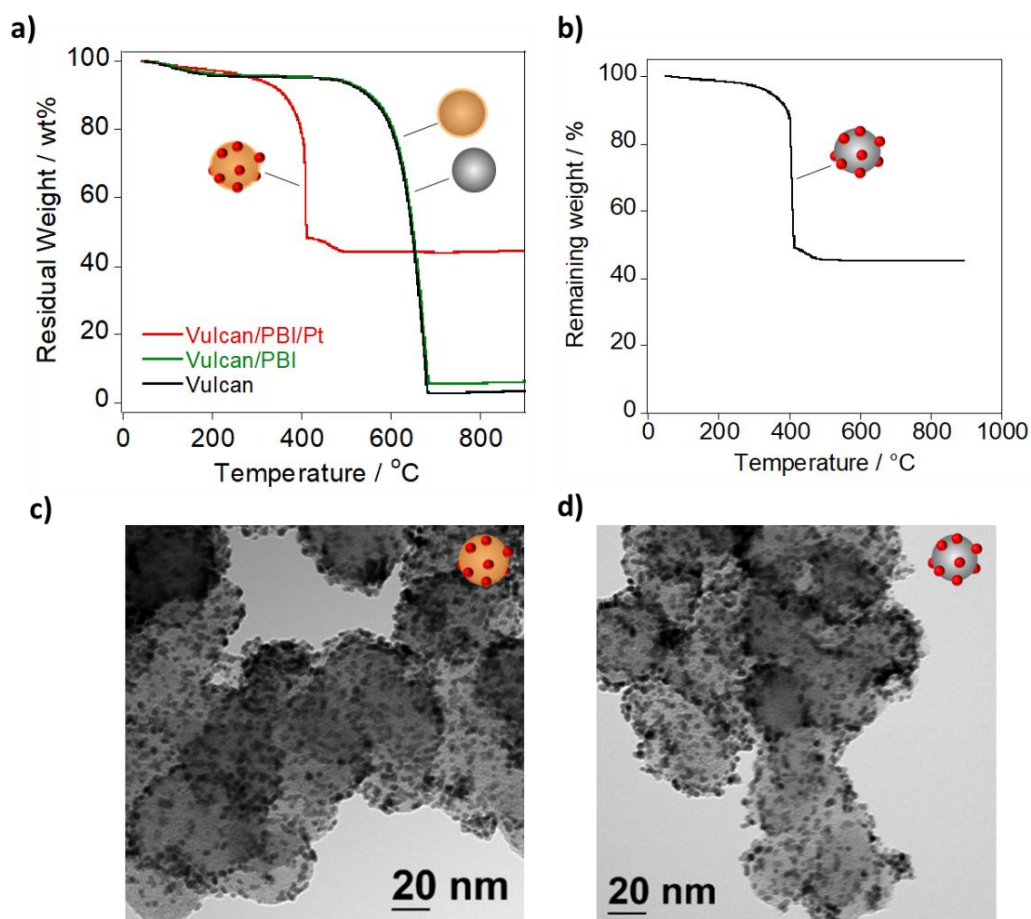


Figure 2-8 TAG curve of **a)** Vulcan, Vulcan/PBI and Vulcan/PBI/Pt and **b)** Vulcan/Pt and TEM images of **c)** Vulcan/PBI/Pt and **d)** Vulcan/Pt.

2.3.2. Evaluation of ORR activity by RRDE

Thin-film RRDE ORR activity measurements were performed on the electrocatalysts as shown in **Figure 2-2 b**. The **Figure 2-9 a** shows LSV curves of Vulcan/PBI/Pt and Vulcan/Pt. The calculated Tafel slopes of Vulcan/PBI/Pt and Vulcan/Pt (**Figure 2-9 b**) were 64 and 66 mV dec⁻¹, respectively. Both of the Tafel slopes are close to their theoretical value of 60 mV dec⁻¹, indicating that PBI wrapping does not affect the mechanism of ORR. However, there is around 50 mV voltage gain in Vulcan/PBI/Pt. The possible explanation of 50 mV gain in half wave potential of Vulcan/PBI/Pt is the difference of the Nafion thickness on Pt nanoparticle surface (**Figure 2-9 c**)⁶¹ and easy accessibility of Pt nanoparticle by O₂ due to the prevention of Pt deposition into pores. It is reported that Nafion has preferred interaction with surface of Pt via sulfonate anion adsorption⁶² compared to that of hydrophobic interaction between Nafion and Vulcan surface. This may result a thicker Nafion layer around Pt nanoparticles in Vulcan/Pt (**Figure 2-9 c upper**). Nevertheless, for Vulcan/PBI/Pt, there is preferential interaction between PBI and Nafion as well,

resulting homogeneous Nafion distribution without deposition of larger amount of Nafion on the Pt surface. Therefore, Vulcan/PBI/Pt may has a thinner Nafion layer around Pt nanoparticles (**Figure 2-9 c lower**), improving ORR performance.

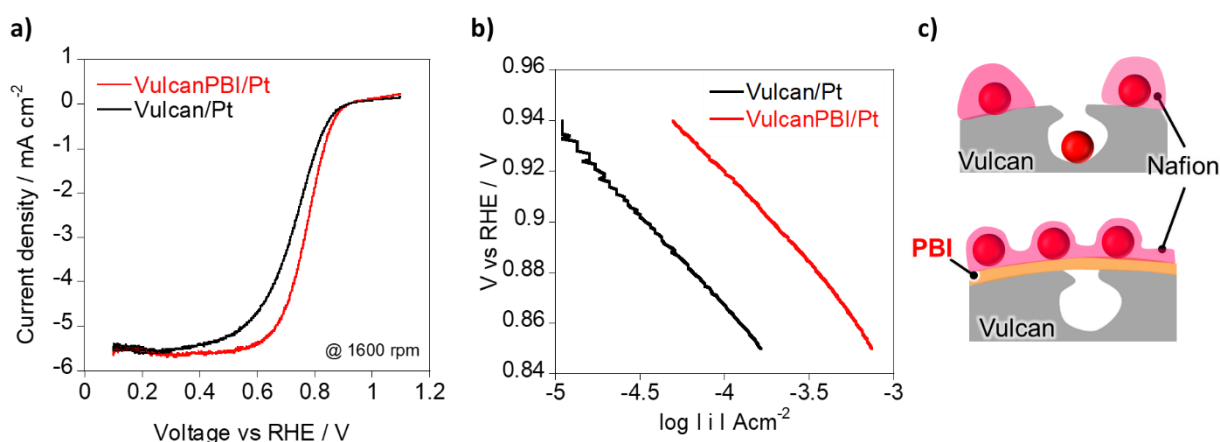


Figure 2-9 a) Linear sweep voltammetry curves, b) Tafel slopes and c) schematics of Nafion deposition on Pt surface of Vulcan/PBI/Pt and Vulcan/Pt.

The mass activity of each catalyst at 0.85 V was calculate by considering kinetically-controlled currents I_k based on the Koutecky-Levich (K-L) equation. The kinetically-controlled currents I_k at a given potential E can be determined based on the K-L **Eq. (2-1)**,

$$1/I = 1/I_k + 1 / (0.62 n F S D^{2/3} CO v^{-1/6} \omega^{1/2}) \dots \dots \dots \text{(Eq. (2-1))}$$

where n is the number of electrons transferred, F is the Faraday constant, S is the effective projected area of the Pt catalyst, D is the diffusion coefficient of O₂, CO is the oxygen concentration, v is the viscosity of the electrolyte and ω is the angular velocity. By extrapolating $\omega^{-1/2}$ to 0 in the graph of $1/I$ vs $1/\sqrt{\omega}$, the value of the kinetically controlled current I_k was calculated for both of the catalysts (**Figure 2-10**). The kinetically-controlled mass activities were calculated based on the amount of Pt initially loaded on the WE. The mass activity of Vulcan/Pt and Vulcan/PBI/Pt at 0.85 V were 33.8 and 95.4 A g⁻¹, respectively. This further confirms that Vulcan/PBI/Pt has easy accessibility of O₂ due to the PBI wrapping application as discussed above.

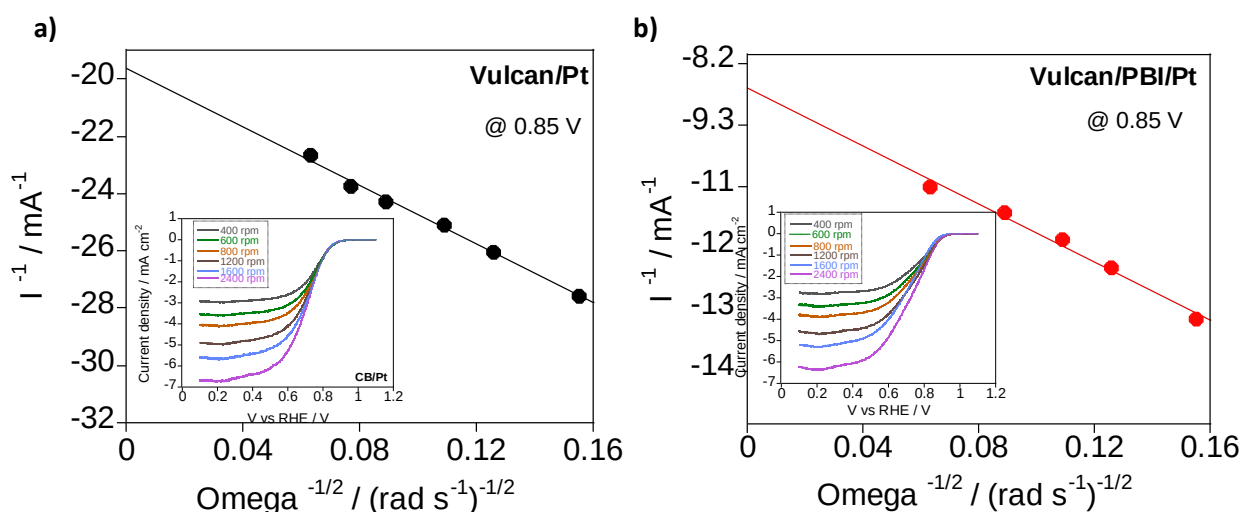


Figure 2-10 K-L plots of **a)** Vulcan/Pt and **b)** Vulcan/PBI/Pt.

2.3.3. Evaluation of ECSA

ECSA is an important parameter demonstrating the accessible Pt surface area in the composites, which can be estimated from the integrated charge in the HAD region of the CV curve. To measure ECSA, MEAs prepared using catalyst ink (composite + Nafion) with the Nafion content of 28 wt. %, as optimized by other researchers⁴¹ was used. As shown in **Figure 2-11 a**, well-defined HAD peaks were observed for both Vulcan/PBI/Pt and Vulcan/Pt MEAs in the range of 0.05–0.4 V (vs. SHE) at 40 °C. Having an insulating polymer layer of PBI on Vulcan (ca. 1 nm)⁵¹ which is thin enough to tunnel electrons⁶³ did not affect the electron conduction between Pt and Vulcan, resulting clear CV signal. Similar electrochemical responses on the carbon surface with a thin insulator coating were observed by other researches^{64, 65} as well as our previous studies.^{47, 48, 50, 66, 67} ECSA values were determined by extrapolation of the double-layer charging current and integrating the charge for hydrogen desorption using the following **Eq. (2-2)**,

$$\text{ECSA}_H = Q_H / 0.210 \times (\text{Pt loading of the MEA}) \dots\dots\dots \text{Eq. (2-2)}$$

where Q_H is the charge exchanged during the hydrogen desorption on Pt and 0.210 mC cm^{-2} is the specific charge for a monolayer of adsorbed hydrogen on Pt.⁶⁸⁻⁷⁰ The determined ECSA of Vulcan/PBI/Pt and Vulcan/Pt at 40 °C were 62.4 and $49.3 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$, respectively. **Figure 2-11 b** shows CO stripping voltammograms of Vulcan/PBI/Pt and Vulcan/Pt in MEAs at 80 °C. In the first scan, no HAD peak was detected but a CO oxidation peak was clearly observed at 0.65 V (vs. SHE). In the second scan, a clear HAD peak was observed at $<0.3 \text{ V}$ but no CO oxidation peak was detected. The CO oxidation peak at 0.65 V agreed well with the reported value for Pt

nanoparticles with the size of 3 nm at 80 °C.⁷¹ These results indicated that accessible Pt nanoparticles were fully covered by CO molecules in the first positive scan and then hydrogen was adsorbed on the bare Pt in the second cycle. Thus, the ECSA could be evaluated from both the CO oxidation peak (ECSA_{CO}) and hydrogen desorption peak (ECSA_H) in the CO stripping voltammograms. ECSA_{CO} was calculated using the following **Eq. (2-3)**,⁷²

$$\text{ECSA}_{\text{CO}} = Q_{\text{CO}}/0.420 \times (\text{Pt loading of the MEA}) \dots\dots\dots \text{Eq. (2-3)}$$

where Q_{CO} is the charge exchanged during the oxidation of CO molecules on Pt and 0.420 is the specific charge (mC cm^{-2}) for the oxidation of CO monolayer.⁷²⁻⁷⁴ ECSA_{CO} of Vulcan/PBI/Pt and Vulcan/Pt were 70.5 and 59.5 $\text{m}^2 \text{g}^{-1}_{\text{Pt}}$, respectively.

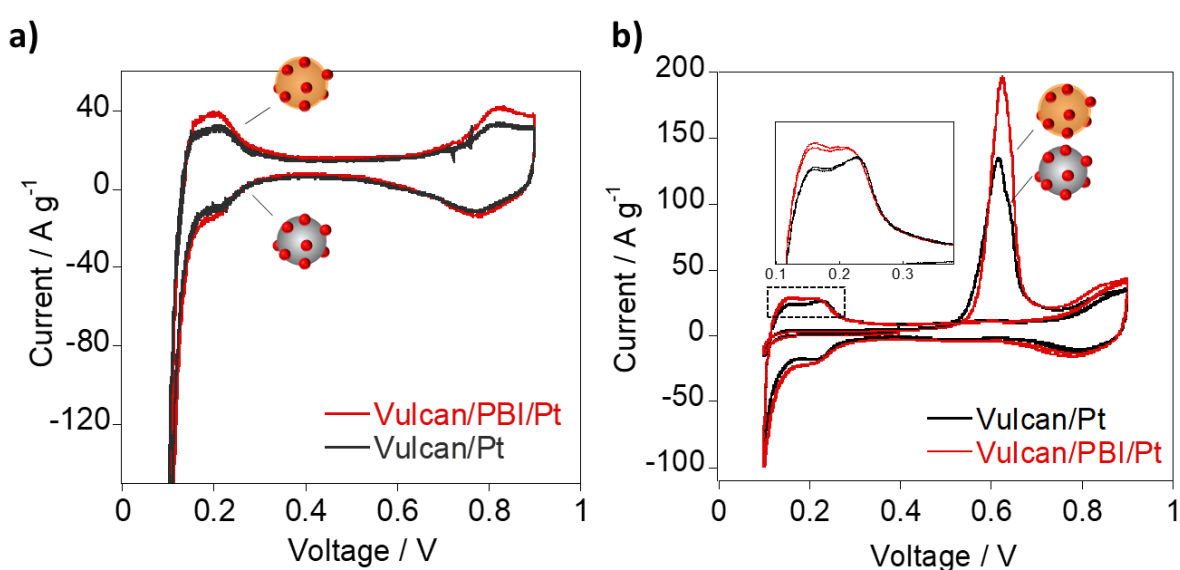


Figure 2-11 a) *In-situ* cyclic voltammograms and b) CO stripping voltammograms of Vulcan/Pt (black line) and Vulcan/PBI/Pt (red line) MEAs.

The ECSA_{CO} values were larger than the ECSA_H values of 41.3 and 36.5 $\text{m}^2 \text{g}^{-1}_{\text{Pt}}$ for Vulcan/PBI/Pt and Vulcan/Pt, respectively as shown in **Figure 2-11 b**. According to Lindstrom *et al.*,⁷¹ the smaller ECSA_H values at 80 °C than those at 40 °C can be explained by the temperature dependence of the HAD region. However, the CO oxidation charge is generally fairly constant as temperature increases.^{75, 76} Therefore, ECSA values determined from the CO oxidation charge are more accurate than those from HAD current, especially at a high temperature like 80 °C. It is assumed that the greater ECSA of Vulcan/PBI/Pt than that of Vulcan/Pt was caused by the preferential deposition of Pt on the accessible Vulcan surface by the capping of the small pores of Vulcan with PBI.³³ It is reported that Pt loaded inside CB micropore was poorly contributed to ECSA due to the low accessibility of protons even in the electrolyte solution^{77, 78} which is

consistence with the observed 18% ECSA increase in Vulcan/PBI/Pt from the three electrode system (**Figure 2-12**). Uchida and colleagues pointed out that Nafion did not penetrate into small pores.⁷⁹ Therefore, Pt deposited in the pores was inaccessible to protons²⁸ and did not contribute to both HAD and CO oxidation current, resulting in the lower ECSA of Vulcan/Pt than that of Vulcan/PBI/Pt.

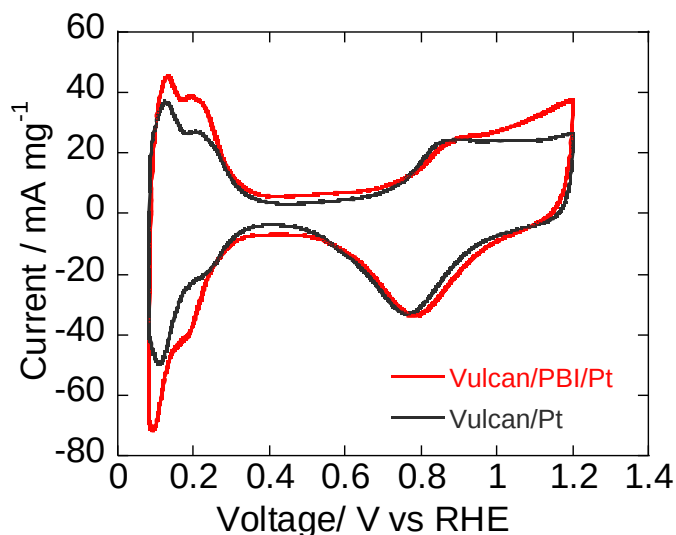


Figure 2-12 *Ex-situ* cyclic voltammograms of Vulcan/Pt (black line) and Vulcan/PBI/Pt (red line) measured by half-cell experiment (three-electrode configuration).

2.3.4. Nafion coating on the electrocatalyst

It is noticed that the Vulcan/Pt ink easily formed aggregates and because of that sedimentation was occurred, whereas the Vulcan/PBI/Pt remained as a very stable dispersion for at least a couple of days as shown in **Figures 2-13 a** and **2-13 b**, respectively.

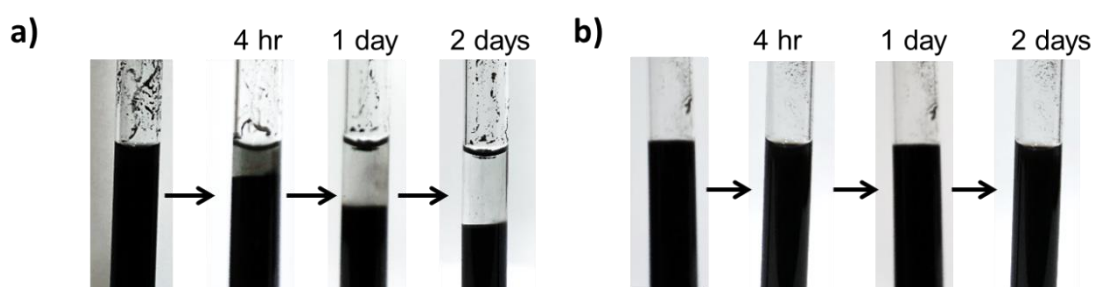


Figure 2-13 Photographs of **a)** Vulcan/Pt and **b)** Vulcan/PBI/Pt catalyst inks after aging for different periods.

In the DLS spectra of the fresh inks, Vulcan/Pt (**Figure 2-14 a**) showed a unimodal peak centered at around 600 nm and Vulcan/PBI/Pt displayed a peak at 420 nm (**Figure 2-14 b**). With time size of Vulcan/PBI/Pt agglomerate did not change while agglomerate size increment in Vulcan/Pt was significant.

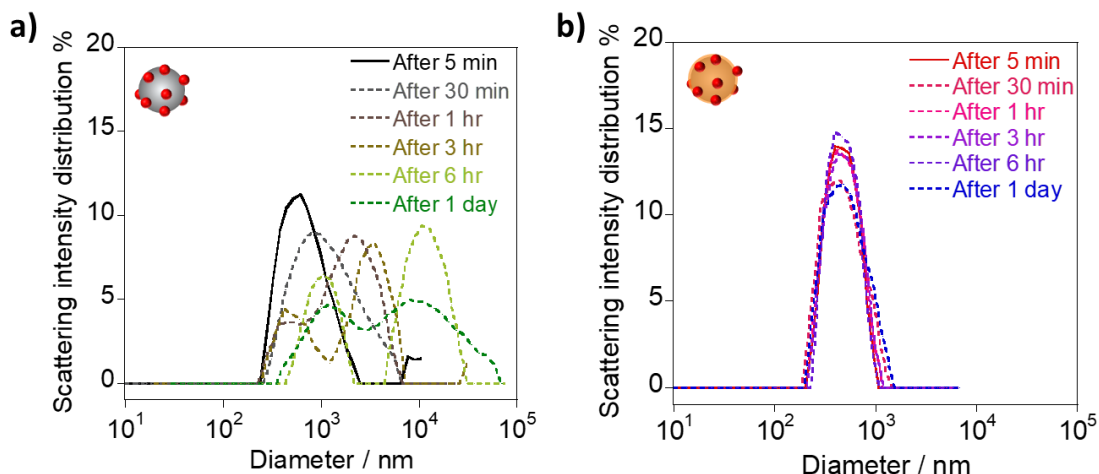


Figure 2-14 Agglomerate size distributions of **a)** Vulcan/Pt and **b)** Vulcan/PBI/Pt inks.

The agglomerate size increment of Vulcan/Pt became bimodal and larger over time compared to Vulcan/PBI/Pt as shown in (**Figure 2-15**).

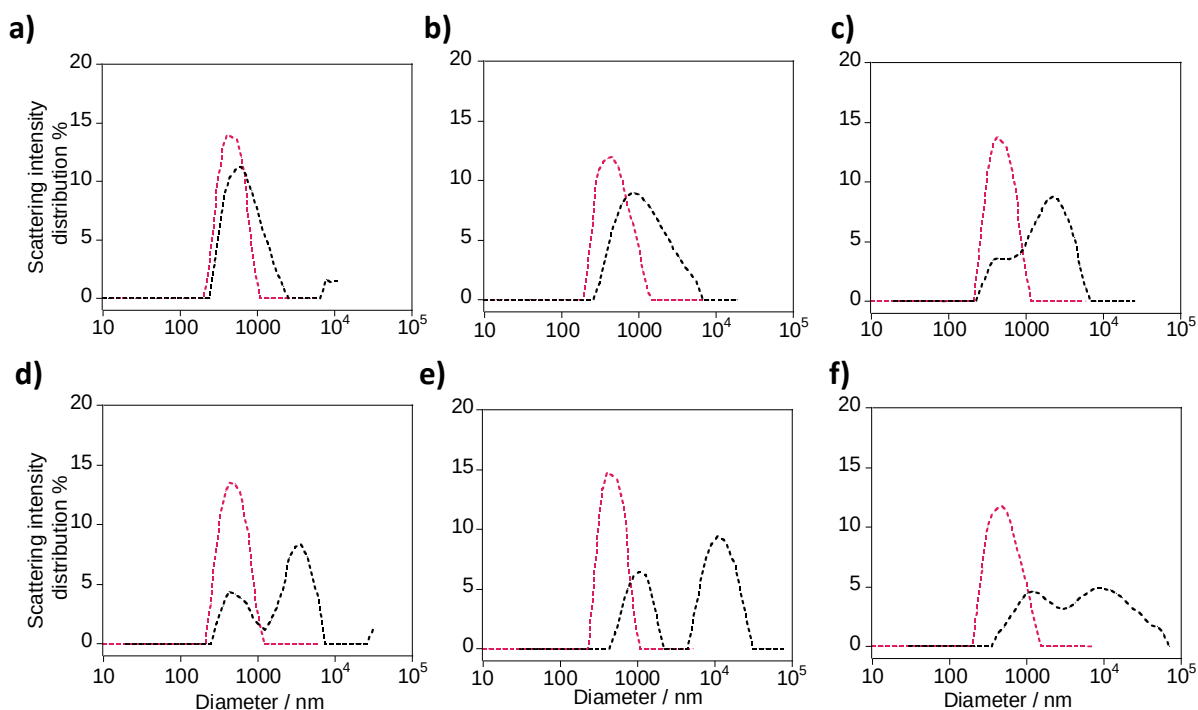


Figure 2-15 Agglomerate size distribution of the spray ink of Vulcan/Pt (black dotted line) and Vulcan/PBI/Pt (red dotted line) at **a)** 5 min, **b)** 30 min, **c)** 1 hr, **d)** 3 hr, **e)** 6 hr and **f)** 1 day after sonication.

Because it took a couple of hours to complete the spraying of one MEA, the low dispersion stability of Vulcan/Pt may adversely affect the quality of the catalyst layer. Indeed, SEM observation revealed that the surface of the Vulcan/Pt catalyst layer possessed larger agglomerates, while Vulcan/PBI/Pt provided smoother catalyst layer as shown in **Figure 2-16**.

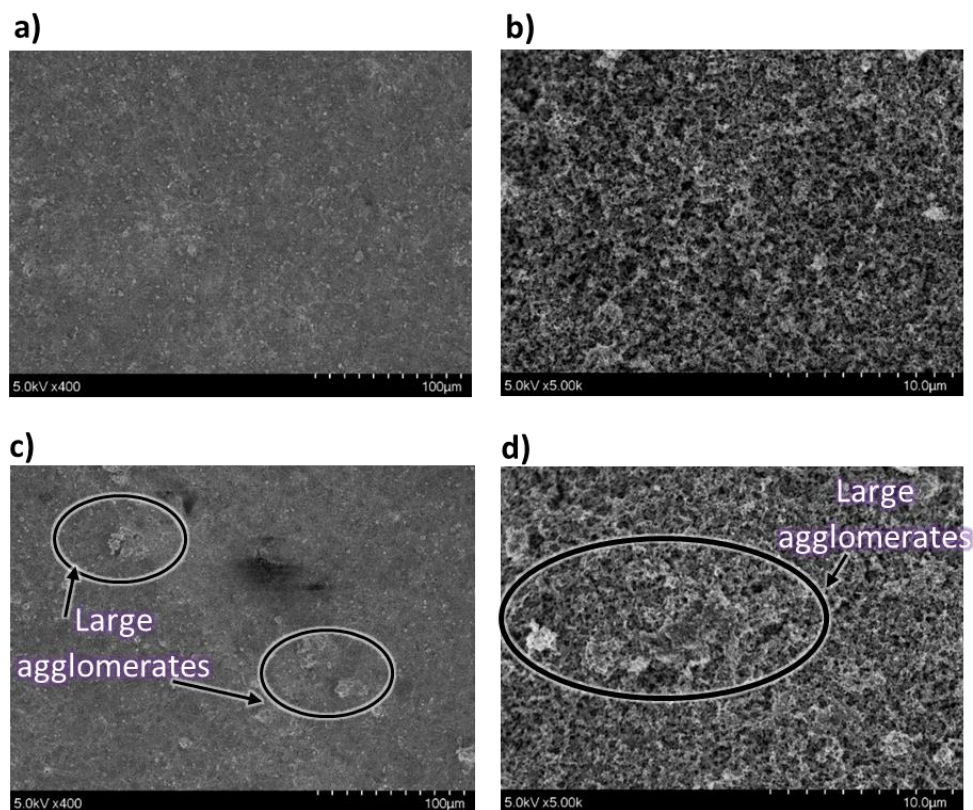


Figure 2-16 SEM images of catalyst layers of **a,b)** Vulcan/PBI/Pt and **c,d)** Vulcan/Pt.

To explore the mechanism behind the difference of the dispersion stability of spray inks, surface analysis of Vulcan and Vulcan/PBI was carried out using zeta potential measurements and XPS analysis. The zeta potentials of Vulcan and Vulcan/PBI in 90% aqueous ethanol were -32.3 and $+8.4$ mV, respectively. It has been reported that Vulcan possesses acidic functional groups, such as $-\text{COOH}$ and $-\text{OH}$, and these groups render the surface of Vulcan negatively charged (**Figure 2-17 a**).⁸⁰ In contrast, PBI contains imidazole groups ($\text{pK}_a = 14.5$) that can be protonated to render Vulcan/PBI being positively charged (**Figure 2-17 b**).

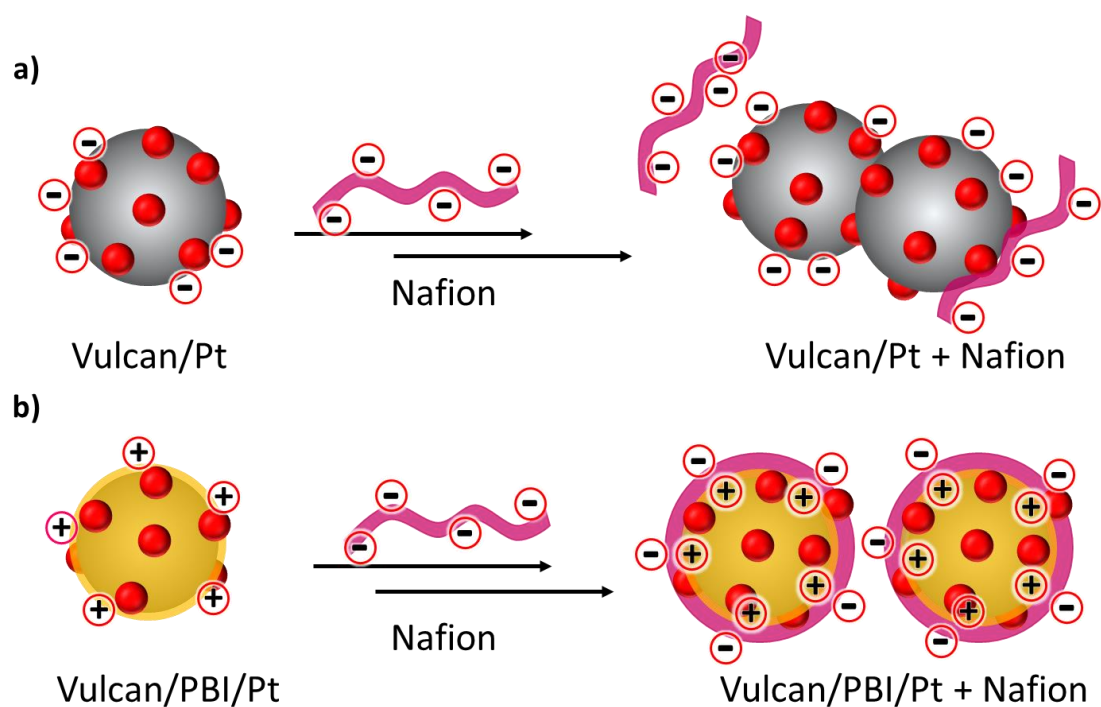


Figure 2-17 Schematic illustration of mechanism of dispersion condition of **a)** Vulcan/Pt and **b)** Vulcan/PBI/Pt.

To examine the interactions of Vulcan and Vulcan/PBI with Nafion, mixtures of either Vulcan or Vulcan/PBI with Nafion were prepared, filtered, and then washed with methanol several times to remove any unbound Nafion. **Figures 2-18 a** and **b** depict the XPS analysis results for Vulcan and Vulcan/PBI coated with Nafion after washing together with those for the original materials. For Vulcan/PBI (**Figure 2-18 b**), together with the N1s peaks of PBI,⁸¹ F1s peak at ~689 eV were observed after washing, clearly indicating that Nafion remained after the washing process. In contrast, the F1s peak of Vulcan was not detected after washing (**Figure 2-18 b**), indicating that Nafion was washed away from Vulcan.

Based on these results, it is concluded that negatively charged Nafion⁸² was stably and homogeneously coated on the surface of positively charged Vulcan/PBI due to electrostatic attraction and as a result, the composite was stably dispersed in the ink (**Figure 2-17 b**). In contrast, it was difficult to uniformly coat Nafion on the Vulcan/Pt surface because of the repulsive forces between negatively charged Vulcan and Nafion (**Figure 2-17 a**). Since Vulcan contains not only negatively charged area but also large hydrophobic graphitic surface,^{80, 83} hydrophobic interaction between graphitic surface may induce aggregation in the ink over time.

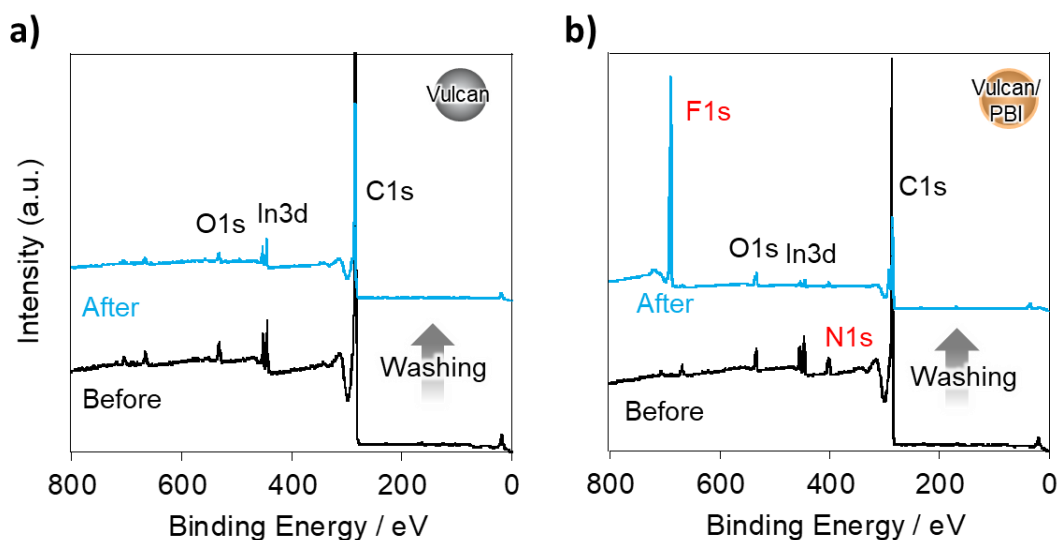


Figure 2-18 XPS survey scans of **a)** Vulcan and **b)** Vulcan/PBI before (black line) and after (blue line) the Nafion coating. Indium was used as the substrate.

The stable ink condition of Vulcan/PBI/Pt with Nafion also resulted better ink casting on GCE compared to Vulcan/Pt with Nafion, resulting better ORR profile as discussed in section 2.3.2 **Figure 2-9 a.** **Figure 2-19** shows digital microscopy images of thin layer of catalyst present on GCE of Vulcan/PBI/Pt and Vulcan/Pt. Having a uniformly casted catalyst layer on GCE may be effective for improved ORR in Vulcan/PBI/Pt and relationship between casting homogeneity and the ORR performance have been discussed by Y. Garsany *et al.*⁸⁴

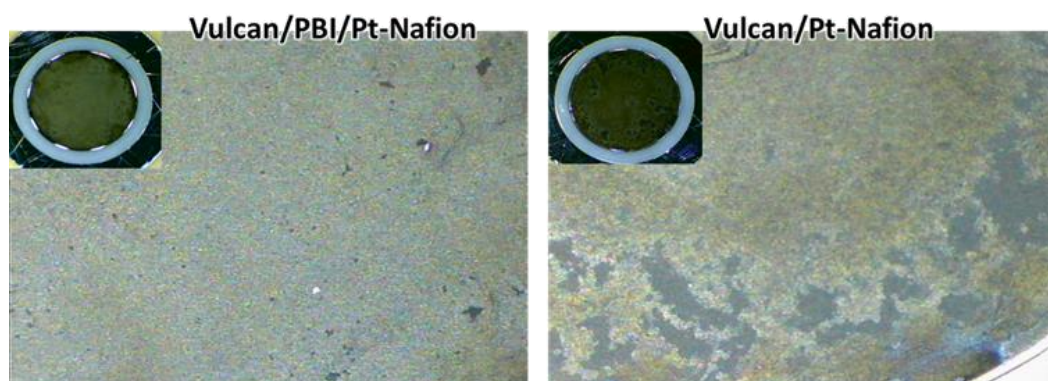


Figure 2-19 Digital microscopy images of thin catalyst layer present on GCE of Vulcan/PBI/Pt (left) and Vulcan/Pt (right).

2.3.5. Fuel cell characterization

Figure 2-20 a shows the polarization curves of the MEAs containing Vulcan/PBI/Pt (red) and Vulcan/Pt (black) operated under H_2 /air (solid line) and H_2 / O_2 (filled circled line). The MEAs have comparable catalyst layer thicknesses because the electrocatalysts have similar Pt loading, which can avoid the dependence of cell performance on catalyst layer thickness.⁸⁵⁻⁸⁷ It is noted that the Tafel slopes of Vulcan/PBI/Pt and Vulcan/Pt were 75 and 76 $mV\ dec^{-1}$ (**Figure 2-20 c**), respectively and thus quite close to their theoretical value of 70 $mV\ dec^{-1}$ at 80 °C, indicating that comparable Pt reactivity in both catalyst layers. It is also clear that the performance of the Vulcan/PBI/Pt MEA was much higher than that of the Vulcan/Pt MEA both at low and high current densities.

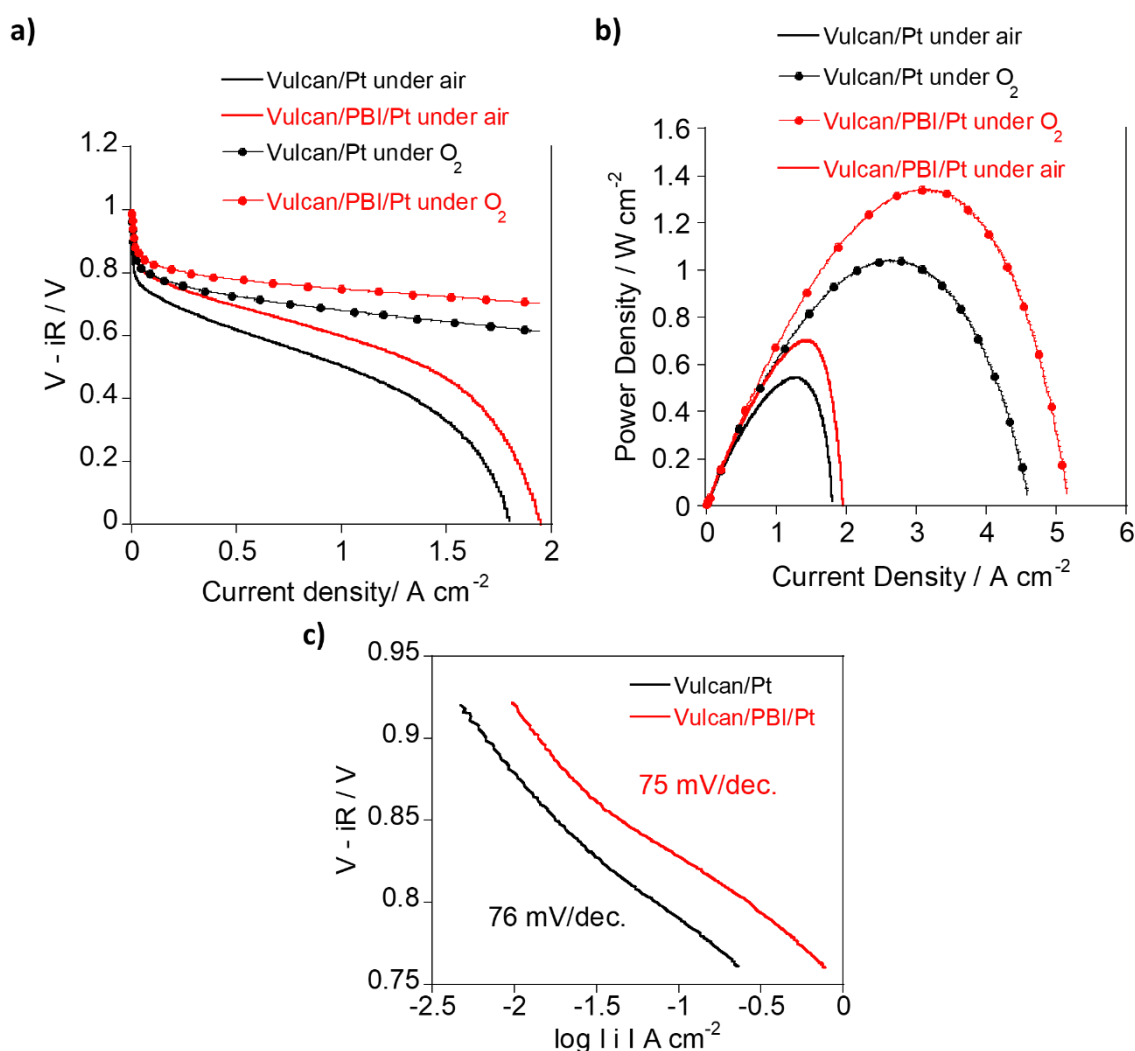


Figure 2-20 a) Polarization $I-V$ and **b)** power density curves of MEAs of Vulcan/Pt under air at cathode (black line), under O_2 at cathode (black filled circled line) and Vulcan/PBI/Pt under air at cathode (red line), under O_2 at cathode (red filled circled line) and **c)** Tafel slopes of Vulcan/Pt and Vulcan/PBI/Pt measured at 80 °C and 100% humidity.

Figure 2-20 b reveals that maximum power density of Vulcan/PBI/Pt (red) under air (solid line) and O₂ (filled circled line) were 0.70 and 1.34 W cm⁻², respectively, while, for Vulcan/Pt (black), maximum power density under air (solid line) and O₂ (filled circled line) were 0.58 and 1.04 W cm⁻², respectively. Therefore, power density of the Vulcan/PBI/Pt MEA at air and O₂ was increased by 21% and 29%, respectively, compared with that of the Vulcan/Pt. On the other hand, it was found that mass activity of Vulcan/PBI/Pt at 0.9 V is 56 A g⁻¹ and it was 1.5 times higher than that of Vulcan/Pt (36 A g⁻¹). The difference was explained by the larger ECSA of Vulcan/PBI/Pt as discussed in section 2.3.3. On the other hand, value of Vulcan/PBI/Pt mass activity at 0.65 V was 3 times higher than of Vulcan/Pt. This significant difference of mass activity at 0.65 V suggested that Vulcan/PBI/Pt has much more efficient ORR activity due to the better mass transport. It is assumed that PBI wrapping approach allows homogeneous Nafion coating and Pt loading at exterior surface as discussed above, thus, resulting effective proton conduction and better O₂ accessibility compared to Vulcan/Pt.

Figure2-21 showed O₂ gain voltage calculated from the potential difference between O₂ and air for a given current density; i.e., a sign of gas diffusivity in the cathode catalyst layer.³¹ The O₂ gain of Vulcan/Pt catalyst increased rapidly with increasing current density at high current region compared with the Vulcan/PBI/Pt catalysts, implying a rapid increase of O₂ diffusion resistance in Vulcan/Pt at high current region. The result further proved the better O₂ accessibility for Vulcan/PBI/Pt since it is well known that the supply of O₂ is rate limiting at high current region.

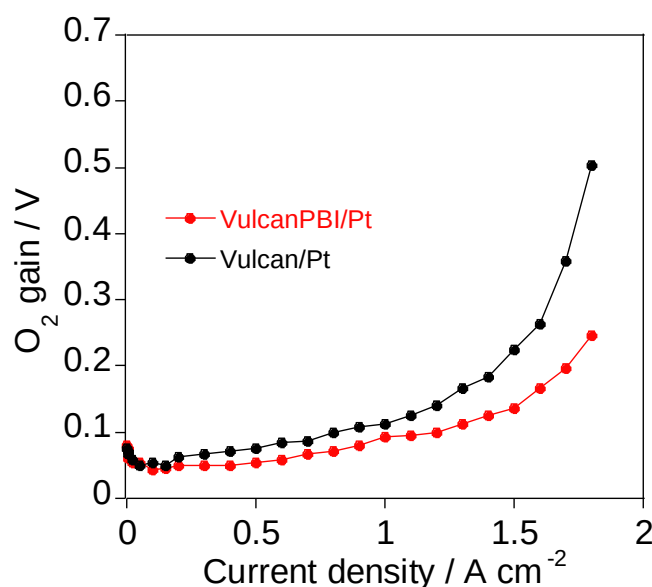


Figure 2-21 O₂ gain results of Vulcan/Pt (filled black circled line) and Vulcan /PBI/Pt (filled red circled line).

Figures 2-22 a and b (dotted lines) displays the polarization curves of MEAs prepared with catalyst inks aged for 1 day before spraying. Of interest, the performance of the Vulcan/Pt MEA was dramatically decreased by 50% compared with that of the MEA prepared with fresh ink, while, the Vulcan/PBI/Pt MEA showed almost identical I - V performance compared with that of fresh ink. Because of the agglomerates formed in the Vulcan/Pt ink, as depicted in **Figure 2-13 a**, the Vulcan/Pt MEA also contained agglomerates in its catalyst layer, as supported by SEM observation (**Figure 2-22 c**). Conversely, because of the Vulcan/PBI/Pt ink remained stable after 1 day, the catalyst layer formed from the aged Vulcan/PBI/Pt ink was as smooth as that of the catalyst layer produced using fresh ink (**Figure 2-22 d**). The results suggested that the dispersion stability of the ink strongly affects the macroscopic aggregation of the catalyst and affects the I - V performance of the MEA.

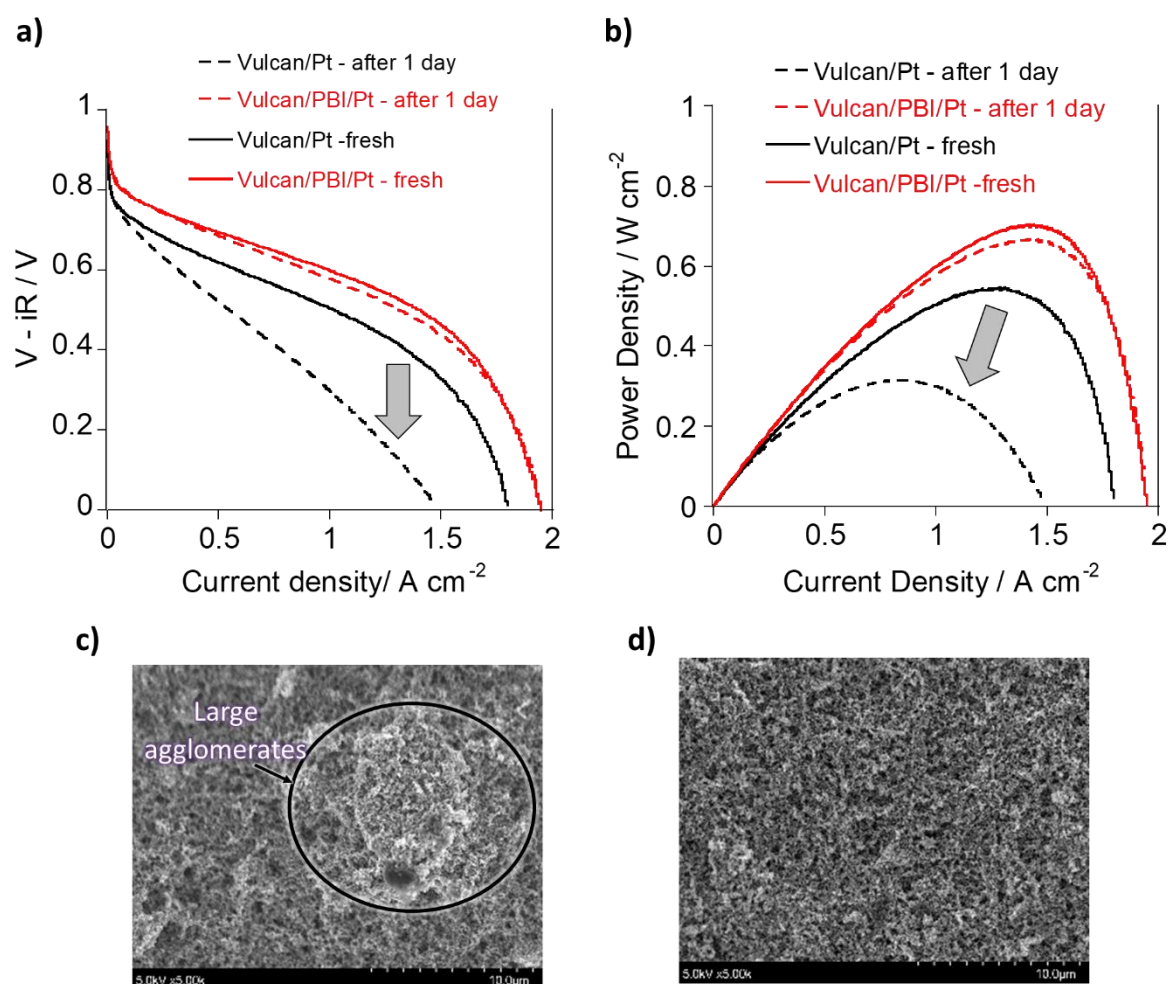


Figure 2-22 a) Polarization I - V and **b)** power density curves of MEAs fabricated from freshly prepared inks of Vulcan/Pt (black solid line) and Vulcan/PBI/Pt (red solid line) and MEAs fabricated from 1-day-old inks of Vulcan/Pt (black dashed line) and Vulcan/PBI/Pt (red dashed line) at 80 °C and 100% humidity. SEM images of catalyst layers prepared with 1 day old inks of **c)** Vulcan/Pt and **d)** Vulcan/PBI/Pt.

To evaluate proton conduction in the catalyst layer, impedance was measured under H₂ (anode)/N₂ (cathode) and the impedance at high frequency (10³–10¹ Hz) are presented in **Figure 2-23**. The protonic resistance of a catalyst layer can be quantified based on the previous reports.^{88, 89} The linear slope of the high-frequency region (10³–10¹ Hz) represents the contributions from protonic resistance and the double-layer charging capacitance of the catalyst layer as expressed by **Eq. (2-4)**,^{89, 90}

$$|Z| = \sqrt{R_p/C_{dl}} * \omega^{-1/2} \longrightarrow K = \sqrt{R_p/C_{dl}} \dots\dots\dots \text{Eq. (2-4)}$$

where $|Z|$ is the magnitude of the impedance, C_{dl} is the double-layer capacitance of the electrode, R_p is the protonic resistance in the catalyst layer, and ω is the frequency of the harmonic signal equal to $2\pi f$ (f = linear frequency). Considering **Eq. 2-4**, plotting $|Z|$ vs. $\omega^{-1/2}$ gives the slope K , which is the ratio of R_p to C_{dl} . By considering C_{dl} from the CV, the calculated R_p of the Vulcan/PBI/Pt and Vulcan/Pt CLs were 0.44 and 1.26 $\Omega \text{ cm}^2$, respectively. The catalyst layer resistance was lowered by 65 %. The lower protonic resistance of the Vulcan/PBI/Pt catalyst layer than that of the Vulcan/Pt strongly supported the formation of homogeneous Nafion layer, serving as the connected proton conduction path in the Vulcan/PBI/Pt.

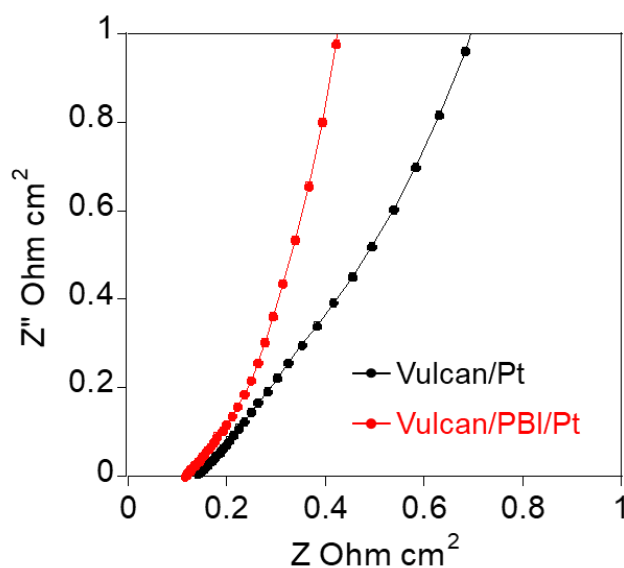


Figure 2-23 Nyquist electrochemical impedance spectroscopy response of Vulcan/Pt (black) and Vulcan/PBI/Pt (red) .measured under H₂/N₂ from 10⁴ Hz to 10³ Hz at 0.45 V

Finally, the Pt utilization efficiency of the MEAs were calculated based on the maximum power density and Pt loading of the electrodes,⁹¹⁻⁹³ and found that Pt utilization of Vulcan/Pt and Vulcan/PBI/Pt MEAs were 0.535 and 0.373 g kW⁻¹, respectively under H₂/O₂ operation. The **Figure 2-24** shows the DOE target (0.125 g kW⁻¹) and obtained Pt utilization value using strategy

1, where prevention of Pt deposition into pores and homogeneous Nafion coating play significantly important role improving Pt utilization efficiency.

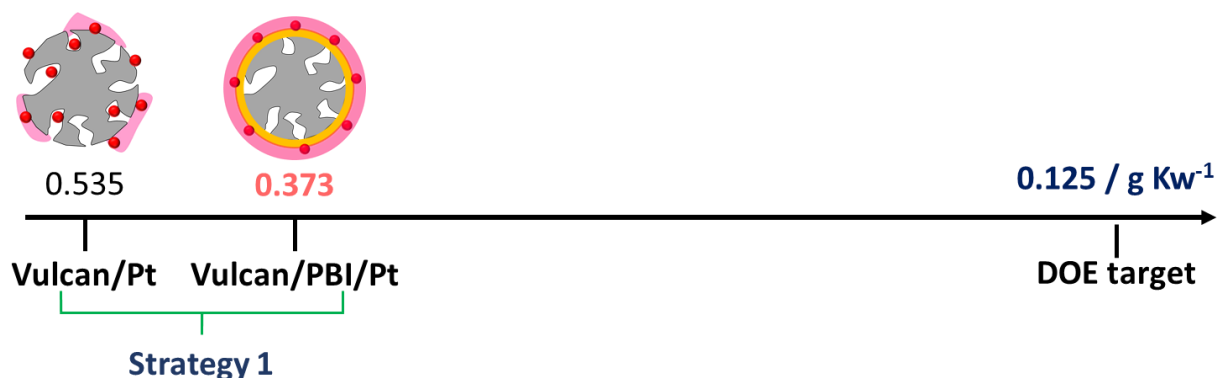


Figure 2-24 Schematic of achieving DOE target after strategy 1.

2.4. Conclusion

This study revealed that coating PBI on Vulcan prior to Pt deposition can improve the Pt utilization efficiency of PEMFCs. PBI wrapping process was easy to apply to Vulcan, resulting 84 % of micropore capping. Micropore capping phenomena suppressed the deposition of Pt nanoparticles into the micropores and resulting in efficacious contact of Pt with Nafion, which could ultimately resulted in 21 % improvement in ECSA. Moreover, micropore capping improved O₂ supply to each reaction sites in Vulcan/PBI/Pt electrocatalyst, resulting higher ORR compared to conventional Vulcan/Pt and power density of Vulcan/PBI/Pt system was improved by 18 %. It was also found that the homogeneous Nafion coating assisted by the acid–base interaction between Nafion and PBI facilitate the higher proton conductivity. Protonic resistance of the catalyst layer was lowered by 65 % due to the long range proton conduction in Vulcan/PBI/Pt catalyst layer. Additionally, establishing highly stable catalyst ink condition made this PBI wrapping approach much more appealing to industries relate to MEA fabrications. Mainly two mechanism; prevention of Pt deposition into pores and homogeneous Nafion coating in the catalyst layer contributed to the improved Pt utilization efficiency of the Vulcan/PBI/Pt compared with that of the Vulcan/Pt one. Therefore, coating with PBI will be helpful to decrease the amount of Pt needed in PEMFC, thus lowering their cost.

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Chapter 3

Effect of PBI wrapping approach to improve Pt utilization and durability in different types of carbon blacks for polymer electrolyte membrane fuel cells

3.1. Introduction

Heavy usage of scarce Pt in the electrodes of polymer electrolyte membrane fuel cell (PEMFC) occupied more than 40% of the cost of the PEMFC¹ as mentioned in the 2nd chapter and has been a barrier towards worldwide commercialization. Therefore, Pt-group metals per fuel cell vehicle is needed to be reduced.² One of the most effective strategies to reduce the amount of Pt in PEMFC is to enhance Pt utilization efficiency by increasing the number of three-phase boundary (TPB) on the Pt surface especially for cathode, where O₂ meets electrons and protons.^{3, 4} To increase the area of TPB, nano-sized Pt with large specific surface area is immobilized on the carbon support together with proton-conductive ionomer to supply proton to TPB.^{5, 6} As carbon support materials, various types of carbon blacks (CBs) having high surface area (HSA) and low surface area (LSA) with different pore size distributions have been studied.^{7, 8} It is widely recognized that ionomer distribution as well as O₂ diffusion greatly depend on the structure of the carbon support, and thus, the Pt utilization efficiency greatly relies on the types of the CBs used in the PEMFC system.⁷⁻¹¹

Among HSA CBs, abundantly having pores smaller than 2 nm (micropores) in diameter such as Ketjen black (KB), Black pearls 2000 and Printex XE2 possess surface area to load nano-sized Pt and their sp³-riched graphitic surface structure is favorable to load nano-sized Pt due to the anchoring effect of sp³ defects.^{7, 12} However, widely known issues of HSA CBs are their poor durability under PEMFC operation due to the presence of sp³ defects¹³⁻¹⁵ and insufficient ionomer/Nafion distribution especially in micropore.¹⁶ Watanabe *et al.* reported that sufficient contact of either liquid electrolyte or Nafion with Pt which is deposited in the interior of HSA CBs is difficult, resulting the decrease of TPB.¹⁷ Furthermore, it was pointed out that the Nafion distribution on the outer surface of HSA CBs is also inhomogeneous¹⁸ due to the lack of attracting electrostatic forces between Nafion and CB surface¹⁹⁻²¹, subsequently reducing TPB in the catalyst layer. In addition, gas transport resistance in the micropore is greater than that of the pore outside, which also decreases the amount of TPB especially at high current density region.^{8, 22, 23}

On the other hand, LSA CBs such as Denka Acetylene black (AB) and Shawinigan AB are advantageous in terms of high durability due to their highly crystalline sp^2 -riched graphitic structure of the surface as well as their good proton and O_2 diffusion to TPB, since Pt are loaded at exterior surface.⁷ However, the high crystallinity of CB surface resulted an inhomogeneous loading of Pt nanoparticles on the surface due to the lack of sp^3 anchoring sites,²⁴ resulting in the decrease of TPB and Pt durability.²⁵ Therefore, both LSA and HSA CBs have advantages and disadvantages and these disadvantages have not been eliminated yet.

It is found that coating of porous Vulcan by polybenzimidazole (PBI) before Pt loading improves Pt utilization efficiency.²¹ In this technique, micropore is capped by PBI wrapping to prevent the loading of Pt inside micropore and also PBI facilitates homogeneous ionomer coating, subsequently improving TPB amount.

In this study, the PBI wrapping method is extended to HSA and LSA CBs to explore the relationship between CB structure and Pt utilization efficiency.

3.2. Experimental

3.2.1. Materials

Hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), *N, N*-dimethylacetamide (DMAc), ethylene glycol (EG) and ethanol (99.5%) were purchased from Wako Pure Chemicals, Ltd. Tokyo. KB and Denka AB were purchased from Cobot Chemical Co., Ltd. Nafion solution (5%) and Nafion[®] 212 membranes were purchased from Sigma-Aldrich. PBI was provided by Sato Light Industrial Co., Ltd.

3.2.2. Material characterization

Thermogravimetric analysis (TGA) was performed using an EXSTAR TG/DTA6300 analyzer (Seiko Instruments, Inc.) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under an air flow of 200 mL min^{-1} . Transmission electron microscopy (TEM) was executed using a JEOL 2010 microscope operating at 30 kV. CHN elemental analysis was performed using a CHN Corder MT-6 (Yanaco). N_2 adsorption isotherm measurement was conducted using a BELSORP-max (BEL Japan, Inc., 77 K and $1 \times 10^{-8} < P/P_0 < 1$). The specific surface area and quantitative analysis of micropore surface area were determined by Bruauer-Emmett-Teller (BET) and t-plot method, respectively.

3.2.3. Electrocatalyst preparation

AB (20.0 mg) was dispersed in a solution of PBI (10 mg) in DMAc (20 mL) by sonication for 30 min in a bath-type sonicator (Brason 5510) followed by 3 hr mechanical shaking (Neo Shaker) to obtain AB/PBI and the obtained composite was filtered, washed with DMAc and then dried overnight under vacuum at 80 °C. After that AB/PBI (100.0 mg) was dispersed in 60% EG aqueous solution (400 mL). $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (4.3 g) dissolved in 60% EG aqueous solution (200 mL) was added and then the mixture was refluxed at 140 °C for 6 hr under nitrogen (N_2) atmosphere. The obtained composite (denoted as AB/PBI/Pt) was collected by filtration after cooling, and then filtered composite was washed several times with Milli-Q water, after that collected composite was dried overnight at 60 °C. Similar experimental procedure was followed to prepare KB/PBI/Pt using 20 mg of PBI and both 15 min and 30 min sonication time were used followed by 3 hr shaking to prepare KB/PBI. Control samples without PBI (AB/Pt and KB/Pt) were prepared in similar manner by skipping the addition of PBI.

3.2.4. Membrane electrode assembly (MEA) preparation

Each composite (AB/Pt, AB/PBI/Pt, KB/Pt, KB/PBI/Pt) dispersed in 90 % aqueous ethanol solution was cast on Nafion[®] 212 membranes using a spray coater (PS-1000, Nordson), separately. Ionomer/carbon (I/C) ratio was 0.8. Each catalyst-coated membrane was laminated with two gas diffusion layers (SIGRACET[®] GDL 25 BC, SGL Group) under 0.6 MPa at 132 °C for 190 s, separately. The Pt loading of each catalyst-coated membrane was 0.3 mg cm⁻² with geometric area of 1.0 cm².

3.2.5. Fuel cell operation

In-situ cyclic voltammogram (CV) was performed by feeding with humidified N_2 at a flow rate of 200 mL min⁻¹ and humidified hydrogen (H_2) at a flow rate of 100 mL min⁻¹ at 40 °C in cathode and anode, respectively.²¹ Polarization (*I-V*) curves of each MEA was tested by feeding with fully humidified H_2 (anode, 100 mL min⁻¹) and air/oxygen (O_2) (cathode, 200 mL min⁻¹) at 80 °C, using an in-house single cell system (Auto PEM-ER01). Impedance of each MEA was measured by feeding N_2 instead of air at the cathode in the frequency range of 0.1 Hz to 10 kHz at working potential of 0.45 V.²¹

3.2.6. Accelerated durability test (ADT)

The ADT was carried out based on the protocol designed by the FCCJ²⁶, using a conventional three electrode configuration at room temperature (25 °C) in N_2 saturated 0.1 M

HClO₄. The potential was changed rectangular from 0.6 V (3s) to 1.0 V (3s). Pt loading on the rotating ring disk electrode was 14.0 $\mu\text{g cm}^{-2}$.

3.3. Results and discussion

3.3.1. PBI wrapping and surface characterization

KB and Denka AB were used as HSA and LSA CBs, respectively in this study. To wrap CBs with PBI, CBs were mixed with PBI in *N,N*-dimethylacetamide (DMAc) by sonication for 15 min or/and 30 min followed by vigorous washing with DMAc to remove unbound PBI to obtain PBI-wrapped CBs (KB/PBI and AB/PBI). PBI interact with both graphitic surfaces and hydrophilic functional groups to form a stable layer on the CB surface.²⁵ PBI wrapping is found to be involved in micropore capping in KB as found in Vulcan.^{25, 27} According to the t plot analysis,²⁸ micropore capping % in KB with 15 min sonication was 46 (**Figure 3-1** and **Table 3-1**) which was much smaller compared to Vulcan (84 %) as indicated in chapter 2. It can be assumed that applied condition for PBI wrapping was not enough for KB as KB has higher micropore density (60 % from total surface) compared to that of Vulcan (38%).

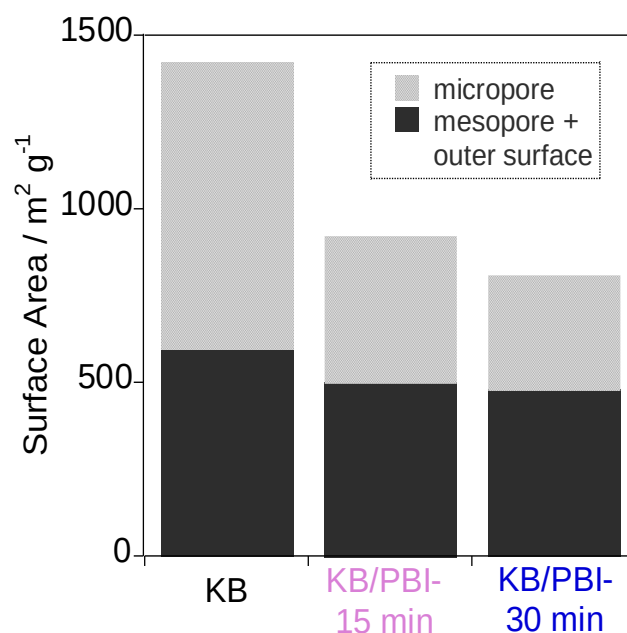


Figure 3-1 Bar graphs displaying outer + mesopore and micropore surface area of KB and KB/PBI with different wrapping conditions.

Table 3-1 Outer + mesopore and micropore surface area of KB and KB/PBI by t-plot analysis.

Composite	Outer + meso surface area / $\text{m}^2 \text{g}^{-1}$	Micropore surface area / $\text{m}^2 \text{g}^{-1}$
KB	599.2	823.8
KB/PBI (15 min sonication)	500.0	421.0
KB/PBI (30 min sonication)	480.0	330.0

Therefore, change of wrapping condition was required. Increasing sonication time to 30 min increased the micropore wrapping % up to 58 (**Figure 3-1**). Increasing sonication time may be helpful in breaking down of KB agglomerates, exposing bare surface for wrapping as shown in **Figure 3-2**. However, further increase of sonication time to 1 hr caused reduction of micropore capping to 23 %.²⁵ This may be due to the degradation of material upon sonication.²⁹ Hence, careful control of PBI wrapping condition is required especially when applying in cost effective large scale production of PBI wrapped CBs.

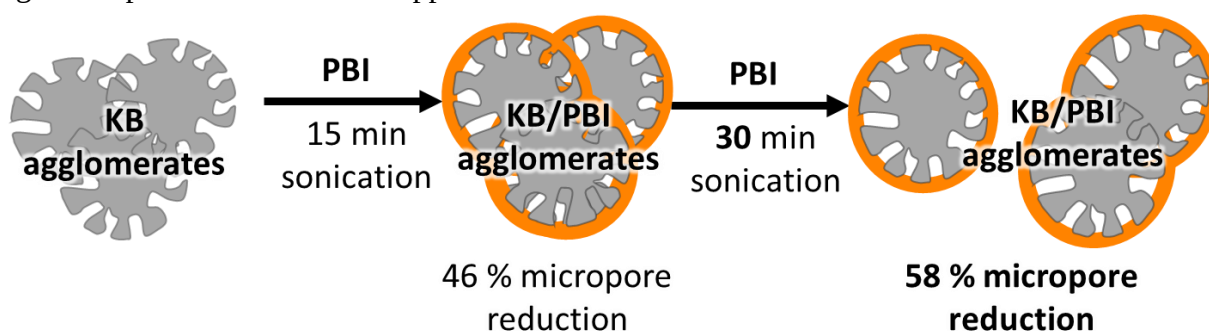


Figure 3-2 Schematic illustration of degree of PBI wrapping depending on the condition applied.

Figure 3-3 shows N_2 adsorption/desorption isotherms of KB and KB/PBI (**Figure 3-3 a**) as well as AB and AB/PBI (**Figure 3-3 b**).

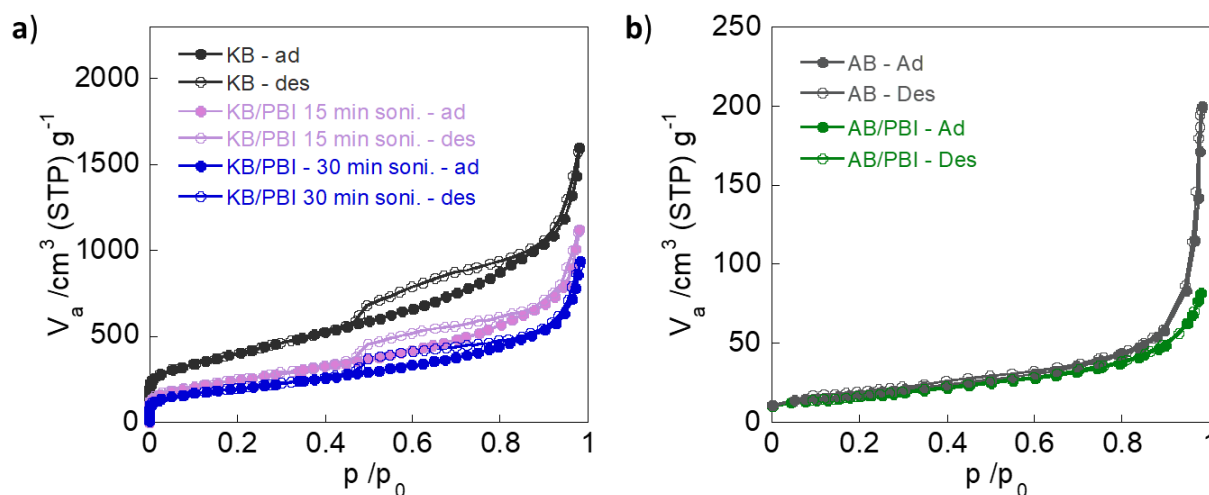


Figure 3-3 N_2 Adsorption-desorption isotherms of a) KB and KB/PBI and b) AB and AB/PBI.

A large adsorption of N₂ at very low gas partial pressures together with a clear hysteresis was observed for KB, indicating the presence of micropore network in KB.¹¹ On the other hand, no such features were observed for AB. After the PBI wrapping, we found that amount of N₂ adsorption decreases in KB/PBI at low gas partial pressures as reported previously²⁵, while N₂ adsorption isotherm of AB/PBI is overlapped with that of AB. According to **Figure 3-3**, isotherms of KB is type II according to IUPAC classification. Type II isotherms are characteristic of systems containing micropores because they exhibit a strong interaction between adsorbate and adsorbent, which is result in a steep rise in the isotherm under low partial pressures. KB shows hysteresis in the adsorption isotherm. This hysteresis is H3 type according to the IUPAC classification, which is characteristic of aggregates of plate-like particles giving rise to slit-shaped pores and common for carbonaceous materials. The hysteresis in the case of KB implies the presence of a more extensively developed pore network wherein the fraction of larger pores trapped within the network of smaller pores is much larger. This is consistent with the fact that KB possesses a larger fraction of micropores.¹¹ On the other hand AB (**Figure 3-3 b**) doesn't show hysteresis and contains mesopores most dominantly.

BET equation³⁰ is the most widely used for the calculation of specific surface area of porous materials. BET surface area (BET SA) was decreased with PBI wrapping especially in KB and Vulcan. BET SA of KB (1423 m² g⁻¹) is drastically decreased to 805.5 m² g⁻¹ when KB is wrapped with PBI under 15 min sonication and further reduced to 698.0 m² g⁻¹ with 30 min sonication. Vulcan showed BET SA reduction from 220 to 113 m² g⁻¹ with PBI wrapping under 15 min sonication as reported in chapter 2. Interestingly, there is no significant surface reduction in AB (60 m² g⁻¹) after wrapping with PBI, making AB/PBI (58 m² g⁻¹). Therefore, there should have relationship between PBI wrapping and surface characteristics. Only CB containing micropores showed surface area reduction, implying that reduction of micropore surface area during the PBI wrapping. Quantitative analysis of micropore area of AB and AB/PBI by t-plot revealed absence of micropore in AB (**Figure 3-4** and **Table 3-2**). Therefore, total surface area of AB was occupied by mesopore and outer surface area.

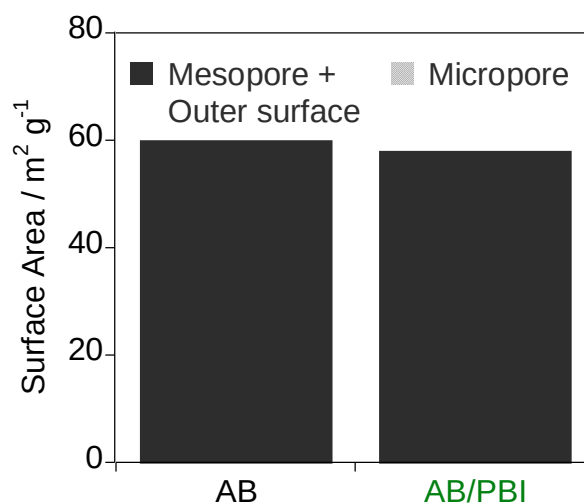


Figure 3-4 Bar graphs displaying outer + mesopore and micropore surface area of AB and AB/PBI.

Table 3-2 Outer + mesopore and micropore surface area of AB and AB/PBI by t-plot analysis.

Composite	Outer + meso surface area / $\text{m}^2 \text{g}^{-1}$	Micropore surface area / $\text{m}^2 \text{g}^{-1}$
AB	60.0	0.0
AB/PBI	58.3	0.0

The phenomena of having micropores and capping of micropore upon PBI wrapping is easily seen in pore size distribution graphs in **Figure 3-5**. Pore distribution was analyzed by HK method.

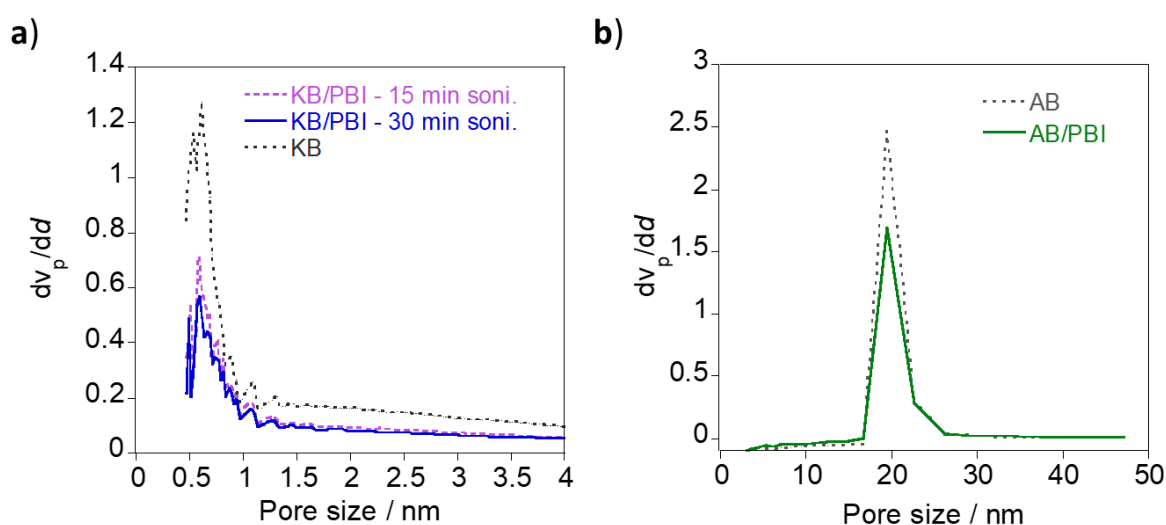


Figure 3-5 Pore diameter distribution evaluated based on HK method for **a)** KB and KB/PBI and **b)** AB and AB/PBI.

This pore size distribution further confirmed that surface area reduction is mainly due to the micropore capping where pore size specially below 1 nm has been reduced with PBI wrapping in KB (**Figure 3-5 a**) and there was no capping phenomena occurred in AB (**Figure 3-5 b**).

However, outer surface of AB would have wrapped with PBI since it showed 2.2 wt. % PBI in the AB/PBI sample according to the elemental analysis data. By considering that nitrogen was only from PBI and carbon was from both PBI and each CB, PBI contents in KB/PBI and AB/PBI can be calculated. PBI content in KB/PBI with 15 min sonication was 21.3 wt. % and value was increased up to 27.3 wt. % with 30 min sonication. Since 30 min of wrapping is required for KB/PBI to achieve highest capping, 30 min of wrapping condition was used for both KB and AB for further experiments, **Table 3-3** shows elemental composition of KB/PBI and AB/PBI. The PBI content in Vulcan/PBI was 7.3 wt. % as mentioned in chapter 2. The difference of PBI contents in each CB can be explained by considering bare surface area of KB ($1423 \text{ m}^2 \text{ g}^{-1}$), Vulcan ($220 \text{ m}^2 \text{ g}^{-1}$) and AB ($60 \text{ m}^2 \text{ g}^{-1}$). The higher the surface area the higher the PBI wrapping amount.

Table 3-3 Elemental analysis of KB/PBI and AB/PBI.

Composite	N %	C %	H %
KB/PBI– 15 min	3.80	88.42	1.85
KB/PBI– 30 min	4.93	80.96	2.5
AB/PBI	0.4	98.51	0.31

3.3.2. Preparation of electrocatalysts and their characteristics

Pt loading on AB/PBI and KB/PBI were carried out using polyol reduction method^{31, 32} to prepare AB/PBI/Pt and KB/PBI/Pt, respectively. As the control, KB/Pt and AB/Pt were also prepared by Pt loading on KB and AB, respectively employing the same method. Pt loading amount in each composite was determined by TGA and found that ca. 45 wt. % of Pt was loaded as shown in **Figure 3-6** and **Table 3-4**.

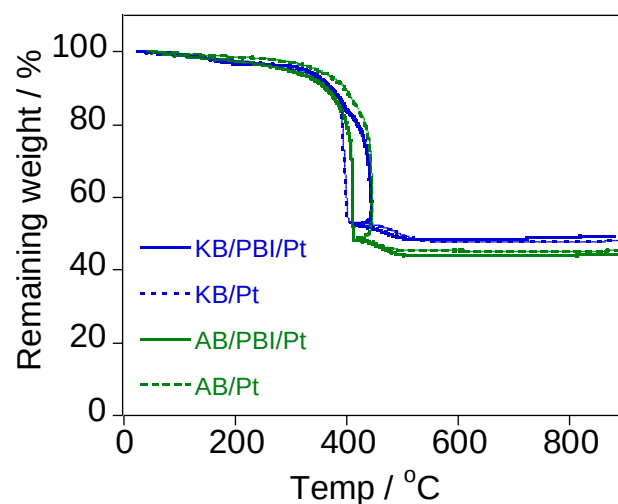


Figure 3-6 TGA curves of AB/Pt, AB/PBI/Pt, KB/Pt and KB/PBI/Pt.

Table 3-4 Pt wt. % and Pt mean particle sizes of CB/Pts and CB/PBI/Pts.

Composite	TGA / Pt wt. %	Pt mean particle size / nm
KB/Pt	45.1	2.3 ± 0.6
KB/PBI/Pt	45.0	2.3 ± 0.5
AB/Pt	44.6	4.4 ± 1.2
AB/PBI/Pt	44.5	3.5 ± 0.5

In the TEM measurement of the composites, Pt nanoparticles, several nanometers in diameter with darker contrast, are dispersed on KB (**Figure 3-7 a**) and KB/PBI (**Figure 3-7 b**) with lighter contrast. The mean particle size of KB/Pt (2.3 ± 0.6 nm) and KB/PBI/Pt (2.3 ± 0.5 nm) were comparable.

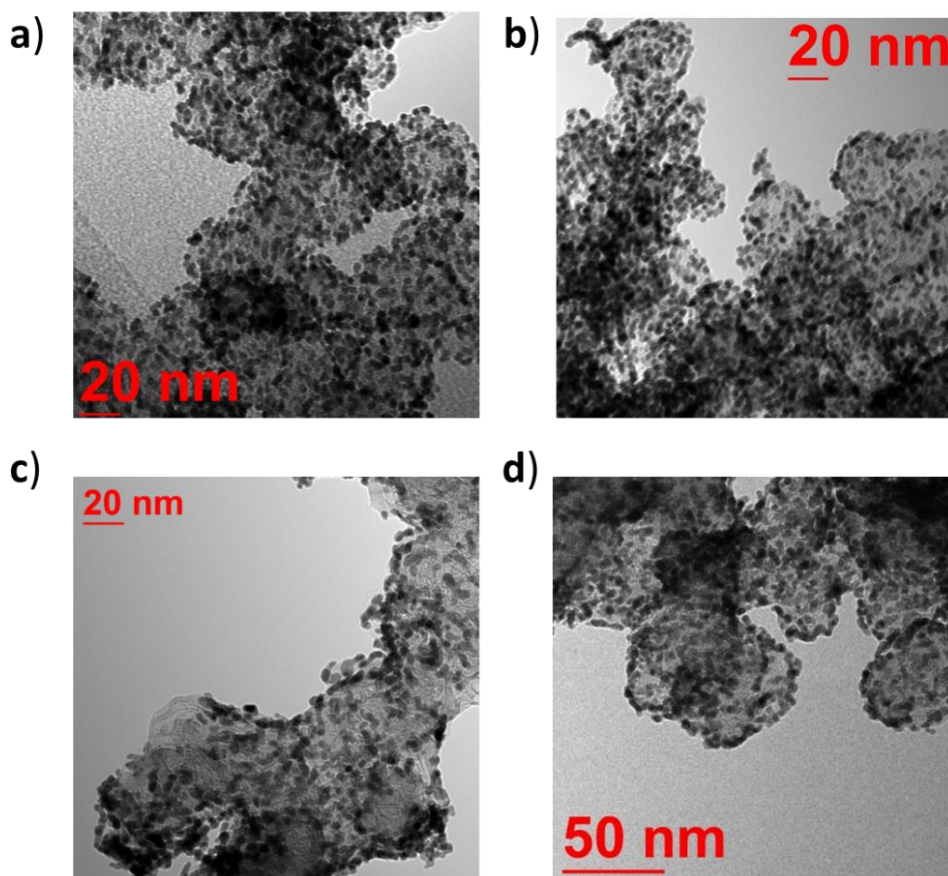


Figure 3-7 TEM images of **a)** KB/Pt (low magnification), **b)** KB/PBI/Pt (low magnification), **c)** AB/Pt (low magnification) and **d)** AB/PBI/Pt (low magnification).

In contrast, AB/Pt (4.4 ± 1.2 nm, **Figure 3-7 c**) is slightly larger than that of AB/PBI/Pt (3.5 ± 0.5 nm, **Figure 3-7 d**). Furthermore, Pt dispersion was uniform in AB/PBI/Pt compared to AB/Pt. It is reported that PBI could enhanced Pt deposition efficiency together with homogeneity due to the Pt ion coordination on the PBI during the Pt loading process.³³ Therefore, inhomogeneity Pt dispersion along with larger size is probably due to weaker Pt anchoring effect on AB compared to KB due to the lack of sp^3 defects such as -COOH and -OH on AB acting as anchoring sites.³⁴ Because AB has high crystallinity³⁴ compared to KB and Vulcan, resulting Pt agglomeration. That's why KB and Vulcan based electrocatalysts have similar Pt mean particle size with respective to their PBI-wrapped and non-wrapped versions. The high magnification TEM images of AB/Pt (**Figure 3-8 a**) and AB/PBI/Pt (**Figure 3-8 b**) were clearly evident that larger size of Pt particles on AB is due to Pt aggregation. On the other hand, since aromatic N in PBI act as the effective anchoring sites^{31, 35}, AB/PBI/Pt showed a good Pt dispersion along with smaller Pt size (**Figure 3-8 b**).

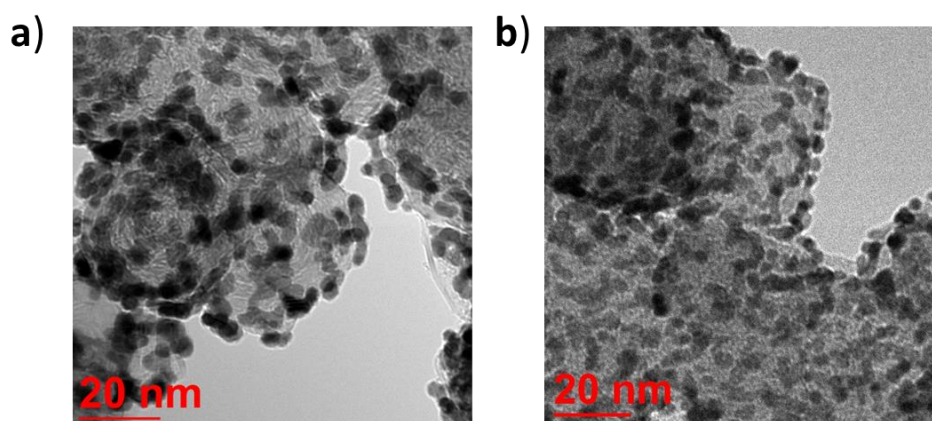


Figure 3-8 TEM images of **a)** AB/Pt (high magnification) and **b)** AB/BI/Pt (high magnification).

Therefore, PBI wrapping on AB is an outstanding method to prepare uniformly dispersed Pt which avoids the complicated Pt depositions methods like nano capsule used by other researches⁷. On the other hand KB based electrocatalysts have smaller Pt size compared to AB based electrocatalysts due the high surface area of KB compared to AB. The higher the surface area the smaller the Pt particle size with same Pt loading.

3.3.3. Evaluation of electrochemically active surface area (ECSA)

ECSA was evaluated by feeding H₂ in anode and N₂ in cathode using MEAs containing Pt loading of 0.3 mg cm⁻² with I/C of 0.8. To access the area of TPB; accessible Pt surface area in the composites in the practical operation condition, ECSA of CB/Pts and CB/PBI/Pts were measured. It is noted that thickness of the catalyst layer in these MEAs are controlled to be comparable by adjusting the Pt loading amount (0.3 g cm⁻²) to avoid the dependence of MEA performance on catalyst layer thickness.^{5, 36, 37} **Figure 3-9** shows the *in-situ* CV of KB/PBI/Pt (**Figure 3-9 a**) and AB/PBI/Pt (**Figure 3-9 b**) recorded at 40 °C, where well-defined hydrogen adsorption/desorption peaks were clearly observed in the range of 0.05–0.4 V (vs. SHE). ECSA values were determined (**Table 3-5**) by extrapolation of the double-layer charging current and integrating the charge for hydrogen desorption using the following **Eq. (3-1)** (introduced in chapter 2 as well),

$$ECSA_H = Q_H / 0.210 \times (\text{Pt loading of the MEA}) \dots\dots\dots \text{Eq. (3-1)}$$

where Q_H is the charge exchanged during the hydrogen desorption on Pt and 0.210 mC cm⁻² is the specific charge for a monolayer of adsorbed hydrogen on Pt.³⁸⁻⁴⁰

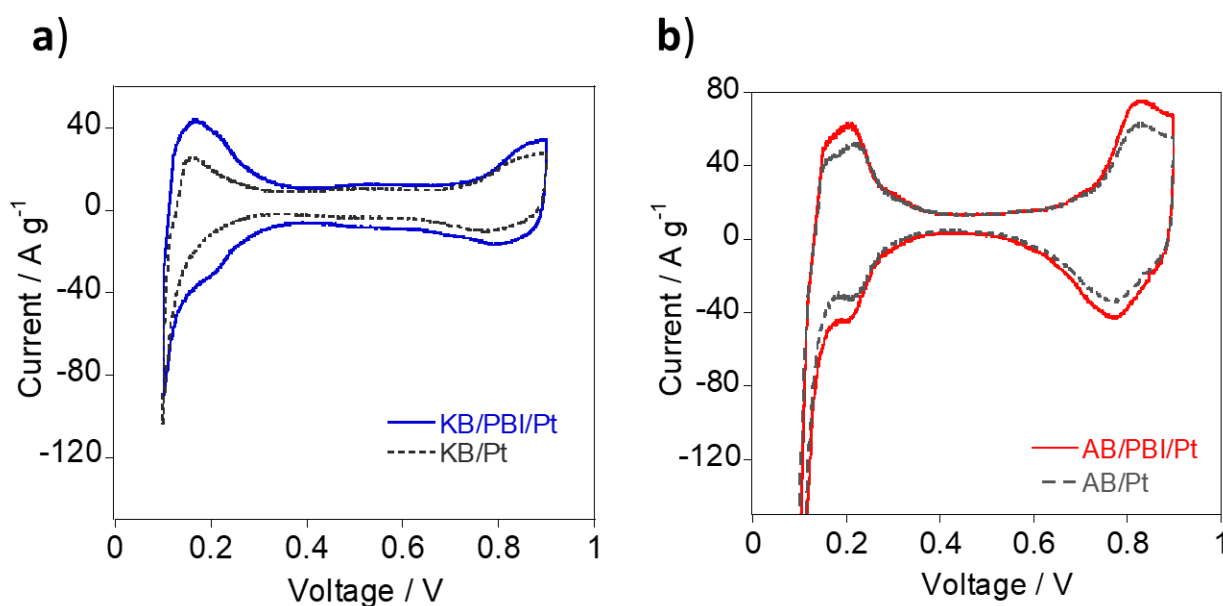


Figure 3-9 *In-situ* CV curves of **a)** KB/Pt (dotted line) and KB/PBI/Pt (solid line) and **b)** AB/Pt (dotted line) AB/PBI/Pt (solid line).

Table 3-5 ECSA of CB/Pts and CB/PBI/Pts.

Composite	ECSA / $\text{m}^2 \text{g}^{-1}_{\text{Pt}}$
KB/Pt	42.1
KB/PBI/Pt	66.6
AB/Pt	73.0
AB/PBI/Pt	87.4

As the result, both KB/PBI/Pt and AB/PBI/Pt showed higher ECSA compared to KB/Pt and AB/Pt by 37% and 16%, respectively. Vulcan/PBI/Pt showed 21% improvement in ECSA compared to Vulcan/Pt as indicated in chapter 2.²¹ One of the possible reasons is the micropore capping phenomena which prevents deposition of Pt nanoparticles into deep pores²⁷ in microporous carbons supports like KB and Vulcan. It is reported that Pt loaded inside CB micropore was poorly contributed for ECSA due to the low accessibility even in the electrolyte solution.^{16, 41} And furthermore, it is reported that Nafion is not penetrated into small pores⁴², limiting the contribution in HAD current due to the inaccessibility of protons to the Pt inside pores.⁴³

The greater ECSA increase for KB suggests that the greater effect of PBI wrapping on HSA CB. The ECSA increment in both KB/PBI/Pt and AB/PBI/Pt contributed to extent TPB in the MEA. Therefore, the increase of TPB by PBI wrapping is originated from the following two mechanisms; namely 1) prevention of Pt nanoparticles loading inside micropore by micropore capping²¹ which increases the number of Pt nanoparticles outside micropore and subsequently increases the contact area of Pt and Nafion by the interaction between PBI and Nafion^{21, 44} and 2) loading of smaller Pt with better uniformity.⁴⁵ Therefore, the greater improvement of TPB for HSA CB is due to micropore capping by PBI wrapping (mechanism 1). On the other hand, mechanism 2; deposition of smaller Pt as observed in TEM measurement contributed to increase the TPB in LSA CB due to high surface area to volume ratio. The **Figure 3-10** summarizes the two mechanisms involved in HSA and LAS CBs.

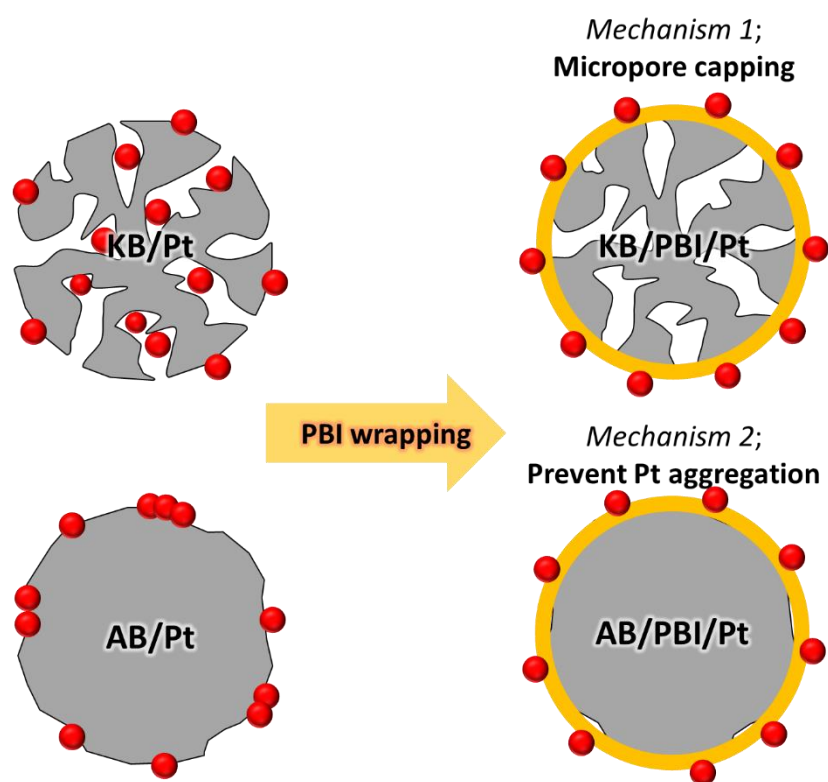


Figure 3-10 Schematics of ECSA increasing mechanisms in KB/PBI/Pt and AB/PBI/Pt.

3.3.4. Fuel cell performance

Figure 3-11 shows the polarization curves of MEAs containing KB/PBI/Pt (**Figure 3-11 a**) and AB/PBI/Pt (**Figure 3-11 b**) operating under H₂ and air in anode and cathode, respectively. Interestingly, both KB/PBI/Pt and AB/PBI/Pt showed higher performance in terms of power density (**Table 3-6**) and limiting current compared to KB/Pt and AB/Pt, respectively. The maximum power density of KB/PBI/Pt and AB/PBI/Pt were improved by 33 % and 9 %, respectively.

respectively (**Figure 3-11 c and d**). The greater increase of MEA performance for KB than AB by PBI wrapping is in the similar trend with *in-situ* ECSA increment and this trend strongly supports the difference of TPB amount found in *in-situ* ECSA is reflected to the single-cell performance and thus, PBI wrapping method is more effective for HSA CBs.

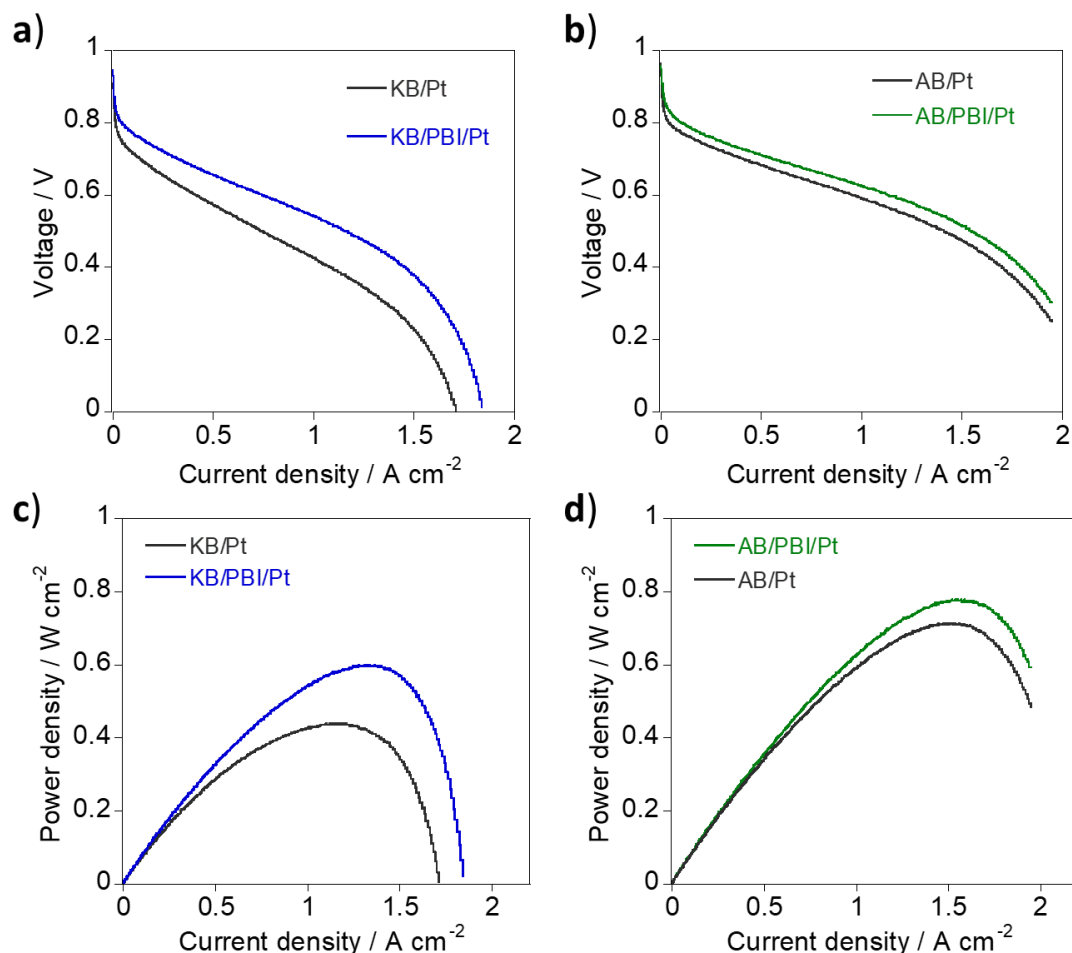


Figure 3-11 Polarization I - V curves of **a)** KB/Pt vs KB/PBI/Pt and **b)** AB/Pt vs AB/PBI/Pt and power density curves of **c)** KB/Pt vs KB/PBI/Pt and **d)** AB/Pt vs AB/PBI/Pt measured at 80 °C with fully humidified H₂ and air.

Table 3-6 Maximum power density and protonic resistance of CB/Pts and CB/PBI/Pts.

Composite	Max. power density with H ₂ /Air / W cm ⁻²	R _p / Ohm cm ²
KB/Pt	0.43	1.42
KB/PBI/Pt	0.64	0.27
AB/Pt	0.71	0.08
AB/PBI/Pt	0.78	0.05

To evaluate proton conduction of cathode catalyst layer, impedance measurements using H₂ (anode) and N₂ (cathode) (**Figure 3-12**)^{21, 46, 47} was carried out. Of interest, calculated proton conduction resistance (R_p) of KB/PBI/Pt MEA (0.27 Ω cm²) is much smaller compared to that of KB/Pt MEA (1.42 Ω cm²) (**Table 3-6**), while improvement of R_p from AB/Pt (0.08 Ω cm²) to AB/PBI/Pt (0.05 Ω cm²) is not much significant.

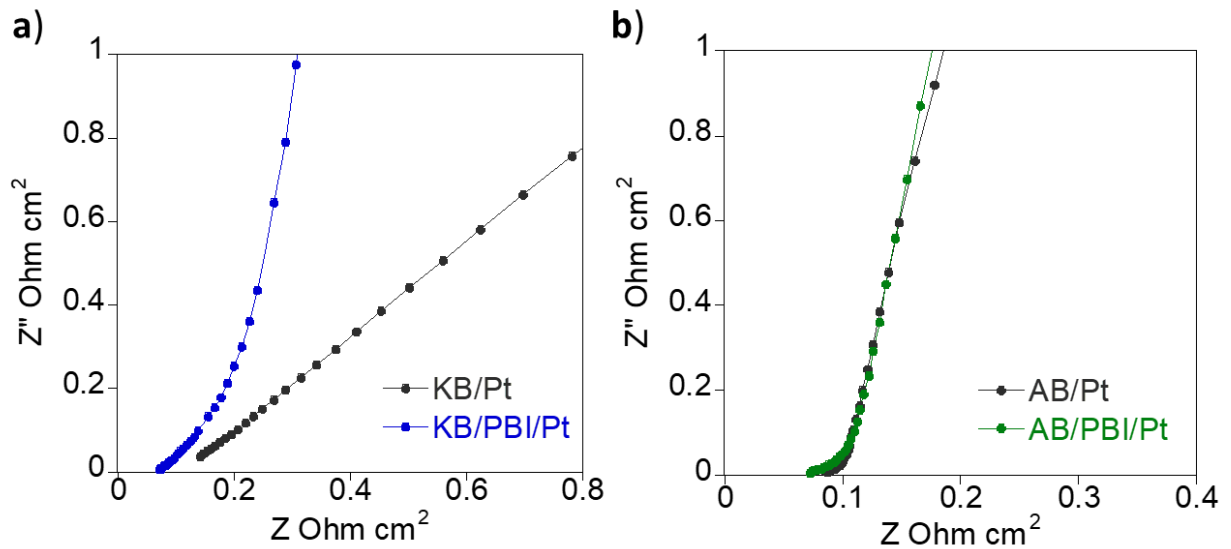


Figure 3-12 Nyquist electrochemical impedance spectroscopy response of **a)** KB/Pt vs KB/PBI/Pt and **b)** AB/Pt vs AB/PBI/Pt measured under H₂/N₂ from 10⁴ Hz to 10³ Hz at 0.45 V.

Since the improvement of proton conductivity is larger for HSA CB compared to LSA CB by PBI wrapping, it is considered that the micropore capping process (mechanism 1) strongly contributed to the improvement of proton conductivity and TPB is also increased accordingly. Not

only capping of micropore area but also coating of CB outer surface with PBI layer²⁵ facilitated the formation of continuous Nafion network in the catalyst layer due to the electrostatic interaction between Nafion and PBI²¹, which offered the greater improvement of proton conductivity, and thereby extending TPB in the catalyst layer. In the case of AB system, due to the absence of micropores and lack of sp^3 rich outer surface, a reasonable Nafion distribution can be expected in AB/Pt, resulting comparable R_p with AB/PBI/Pt.

To evaluate gas diffusion in the catalyst layer, O_2 gain voltage was calculated from the potential difference between O_2 and air for a given current density.⁸ The polarization curves measured for KB system under O_2 and air at cathode are shown in **Figure 3-13**. The significant difference in performance in non-wrapped catalysts is clearly seen.

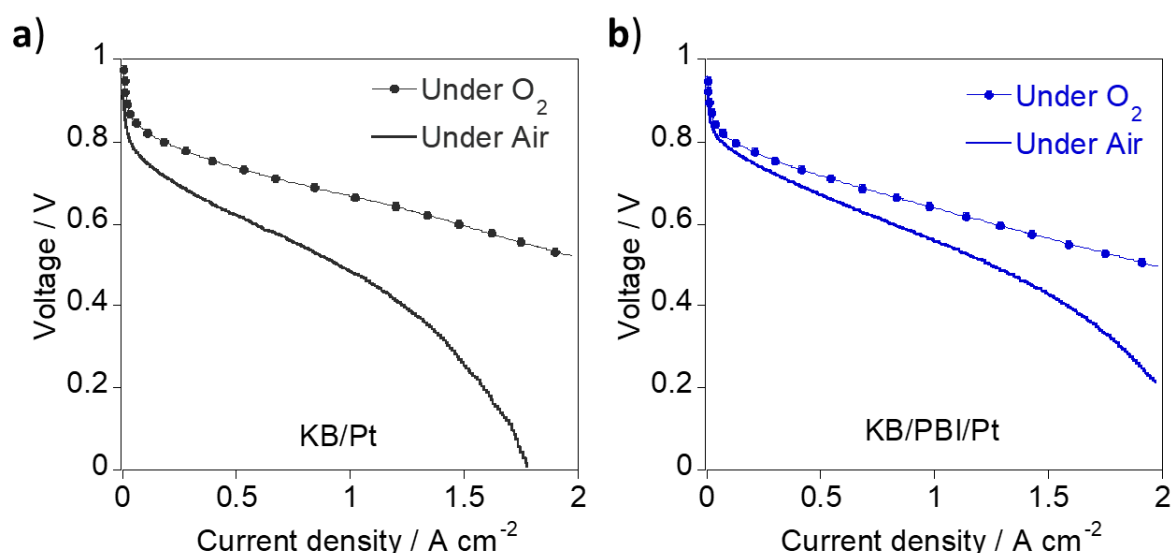


Figure 3-13 Polarization I - V curves of **a)** KB/Pt and **b)** KB/PBI/Pt under air and O_2 at cathode.

On the other hand, the performance improvement upon switching from air to O_2 (**Figure 3-14**) was not significant in AB system compared to KB system. However, AB/PBI/Pt showed the least performance improvement under O_2 , suggesting the highest O_2 diffusion condition among these electrocatalysts.

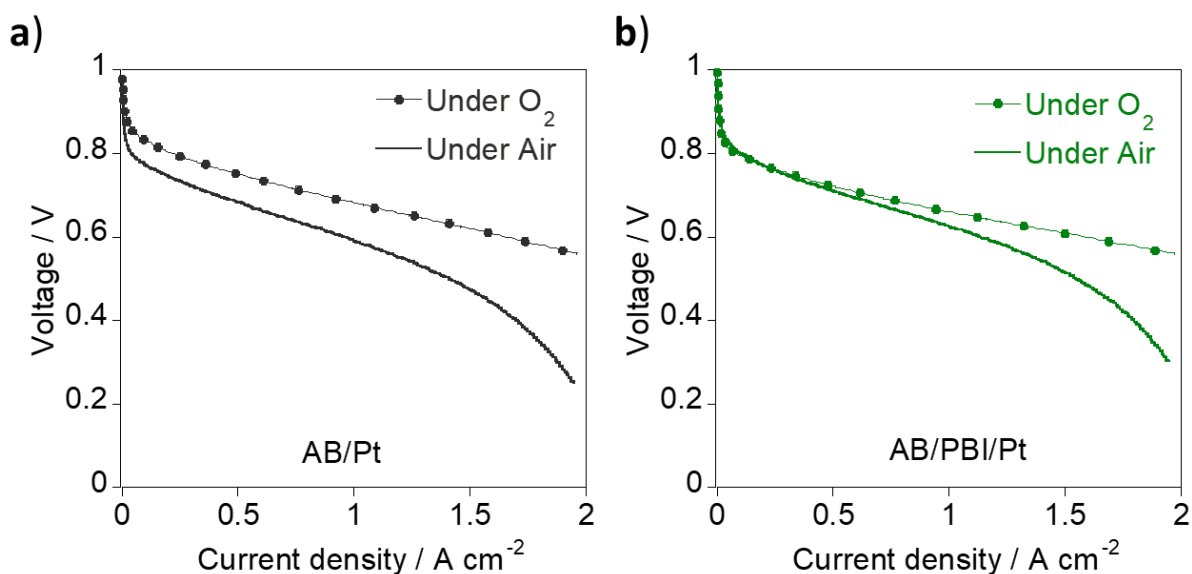


Figure 3-14 Polarization I - V curves **a)** AB/Pt and **b)** AB/PBI/Pt under air and O_2 at cathode.

Considering all the above polarization graphs, O_2 gain graph can be drawn. The lower the O_2 gain the higher the gas diffusion in the catalyst layer. Lowering of O_2 gain for both HSA and LSA CBs after PBI wrapping was observed (**Figure 3-15 a**). **Figure 3-15 b** shows the O_2 gain at $1.6\ A\ cm^{-2}$ (high current density region).

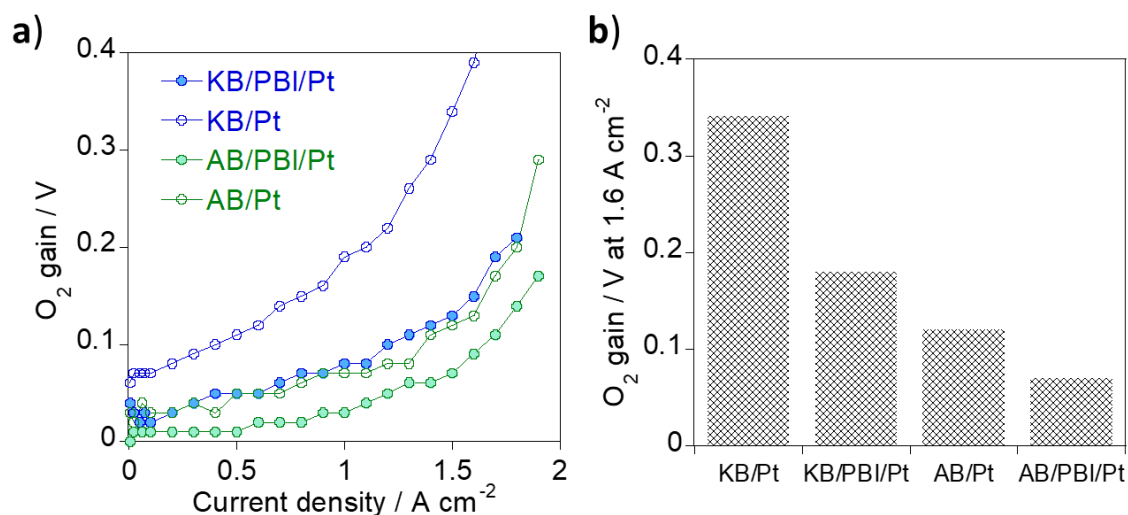


Figure 3-15 a) O_2 gain variation of CB/Pts and CB/PBI/Pts and **b)** O_2 gain at $1.6\ A\ cm^{-2}$.

The O_2 gain of KB/PBI/Pt is significantly reduced compared to KB/Pt, while the reduction of O_2 gain is not that much significant between AB/PBI/Pt and AB/Pt. The O_2 diffusion in HSA CB is greatly improved by the pore capping mechanism, which provides the larger improvement

of performance at high current density. Because, Pt nanoparticles inside micropores are inactive toward oxygen reduction reaction due to the limitation of O₂ diffusion²³ and similar phenomena was observed by Watanabe *et al* for KB/Pt catalyst layer.⁸ On the other hand for LSA CB, having a good dispersion of Pt became beneficial for AB/PBI/Pt due to the reduced number of overlapped O₂ diffusion paths for the individual Pt particles, leading to an effective O₂ transport to these particles.

Not only the Pt dispersion quality but also quality of catalyst layer contributed to the improved performance in CB/PBI/Pts. Because, PBI wrapping has great influence on formation of stable ink condition, resulting smoother catalyst layer²⁷ as explained in the chapter 2. **Figure 3-16** shows SEM images of catalyst layer of KB/Pt and KB/PBI/Pt. Formation of catalyst particle agglomeration was quite prominent in KB/Pt catalyst layer. However, there were few agglomerations in KB/PBI/Pt as well, resulting limitations for gas permeation. That can be one of the reasons for the reduced performance of KB/PBI/Pt when compared to AB/PBI/Pt.

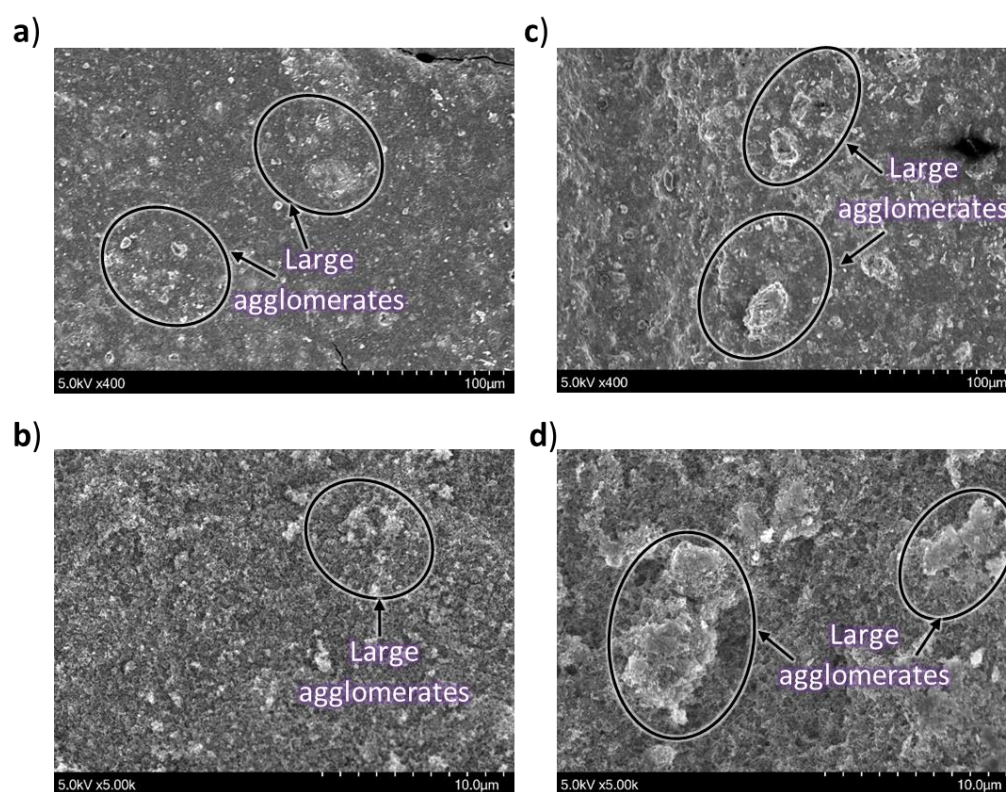


Figure 3-16 SEM images of catalyst layers of **a,b)** KB/PBI/Pt and **c,d)** KB/Pt.

Figure 3-17 shows the SEM images of AB/Pt and AB/PBI/Pt catalyst layers. Formation of large agglomerations were not significant on both of the catalyst layers. Therefore, LSA CB has high potential of having homogeneous Nafion dispersion with higher I/C value like 0.8. However, distribution of Nafion was inhomogeneous in HSA CB despite of having higher I/C of 0.8. Considering all these facts, having a PBI layer improved the Nafion dispersion in both of the catalyst layers in different degrees.

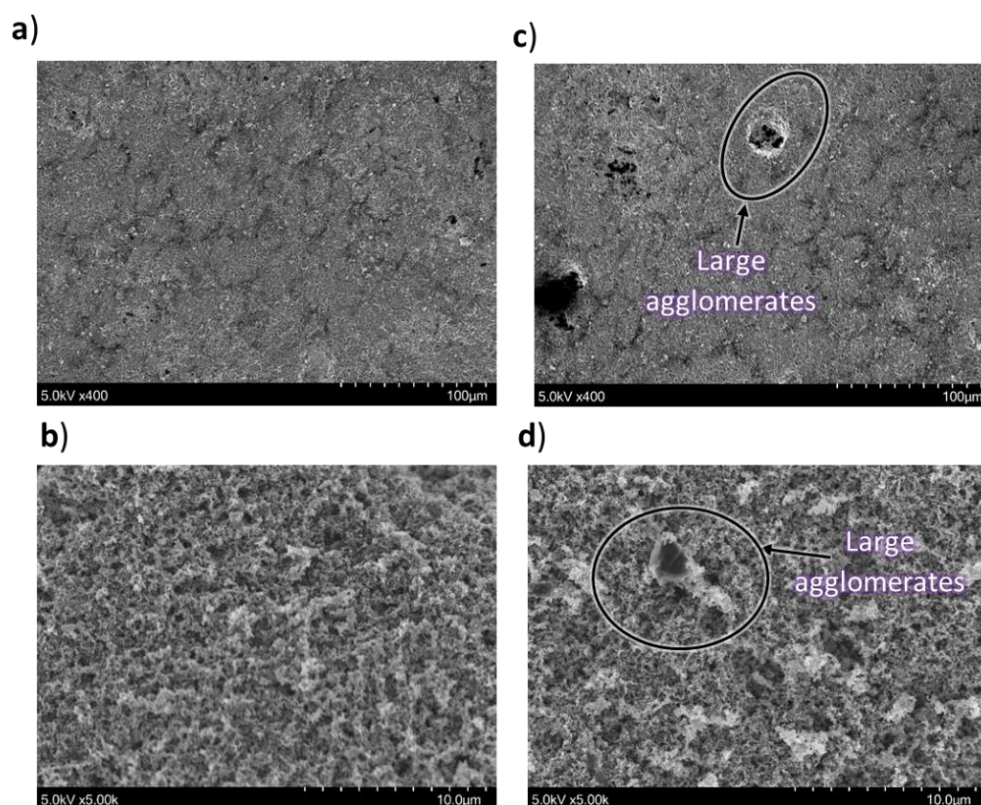


Figure 3-17 SEM images of catalyst layers of **a,b)** AB/PBI/Pt and **c,d)** AB/Pt.

Considering all the mass transfers (protons; H^+ and O_2) in the catalyst layer, **Figure 3-18** summarizes the mass transport conditions in CB/Pts and CB/PBI/Pts.

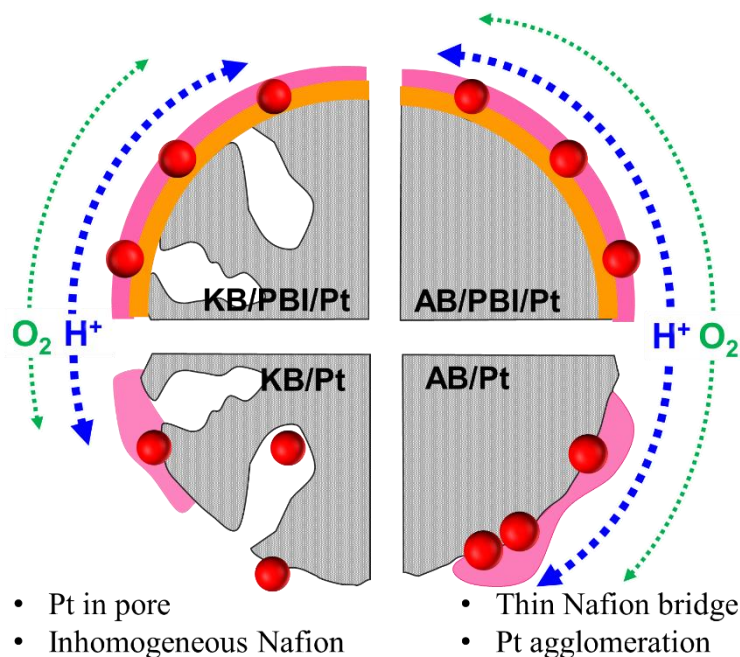


Figure 3-18 Schematic of mass transport condition in each catalyst.

Pt utilization was calculated considering maximum power density measured under H_2/O_2 condition and total Pt loading of the MEA (0.5 mg cm^{-2}). The **Figure 3-19** shows power density curves of KB/Pt vs AB/PBI/Pt (**Figure 3-19 a**) and AB/Pt vs AB/PBI/Pt (**Figure 3-19 b**) measured under H_2/O_2 condition. The found maximum power density and calculated Pt utilization values of each composite were summarized in the **Table 3-7**.

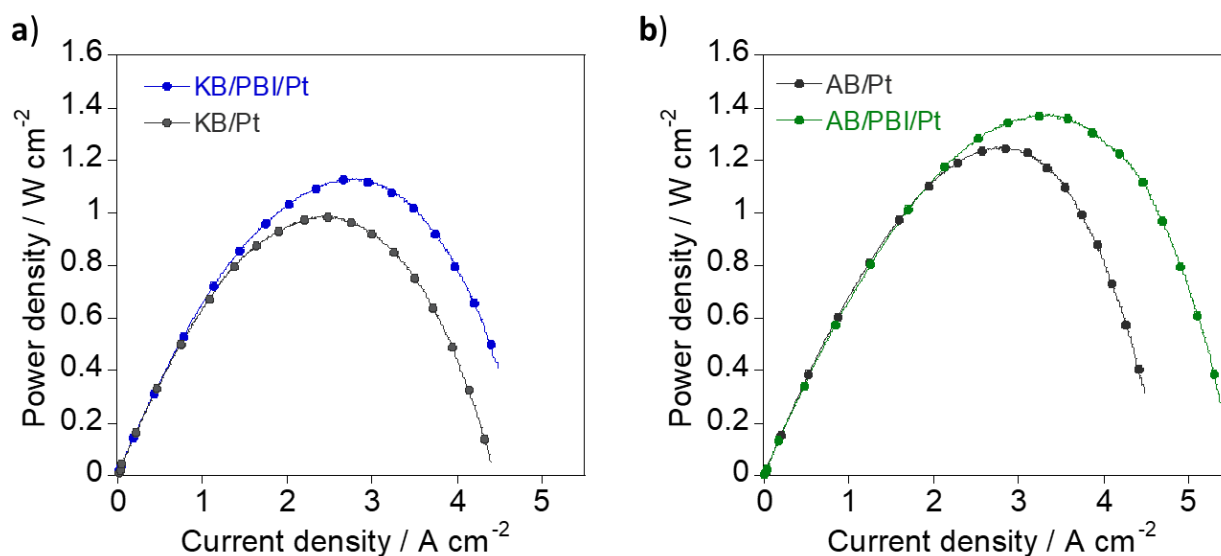


Figure 3-19 Power density curves of **a)** KB/Pt vs KB/PBI/Pt and **b)** AB/Pt vs AB/PBI/Pt measured under H_2/O_2 condition.

Table 3-7 Maximum power density and Pt utilization of CB/Pts and CB/PBI/Pts.

Composite	Max. power density with H_2/O_2 / $W\ cm^{-2}$	Pt utilization / $g\ kW^{-1}$
KB/Pt	0.98	0.510
KB/PBI/Pt	1.12	0.446
AB/Pt	1.24	0.403
AB/PBI/Pt	1.37	0.364

According to the above table AB/PBI/Pt gave the highest Pt utilization of $0.364\ g\ kW^{-1}$ through the application of strategy 2. **Figure 3-20** shows Pt utilization values obtained from strategy 1 and 2. The effect PBI wrapping on HSA CB and LSA CB was very interesting to investigate, where it helped to identify factors influencing fuel cell performance depending on the CB type.

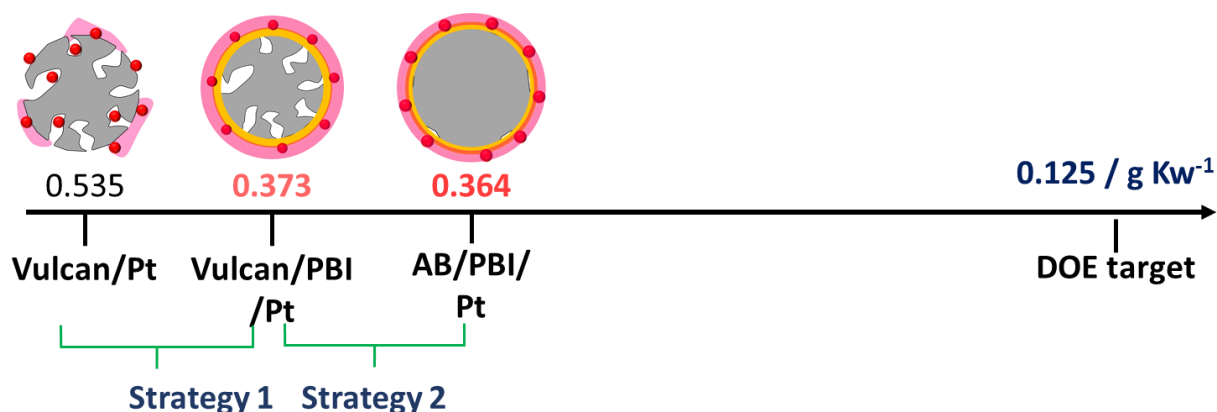


Figure 3-20 Schematic of achieving DOE target after strategy 2.

Since AB system gave the highest performance compared to KB system, doing further investigations such as durability of Pt nanoparticle is worthwhile.

3.3.5. Durability study of AB/Pt and AB/PBI/Pt

The potential rectangular wave was stepped from 0.6 to 1.0 V vs. RHE (6 s cycle⁻¹) using 3 electrode system. In between certain number of potential cycles, CV was measured for the ECSA assessment. It is reported that this load cycle protocol (FCCJ) effectively differentiates degradation of Pt catalyst from that of carbon support²⁶ and hence would be helpful in studying degradation of Pt nanoparticles in AB system. Pt particle durability until 15,000 load cycles were conducted during this experiment. **Figure 3-21** shows the CV taken before and after 15,000 potential cycles of AB/Pt. The initial ECSA of AB/Pt was 25.4 m² g⁻¹_{Pt} and after 15,000 load cycles it dropped to 13.5 m² g⁻¹_{Pt} showing 47% Pt degradation.

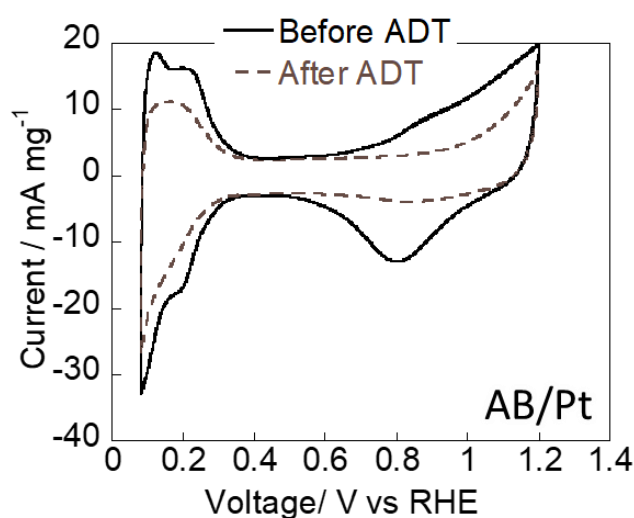


Figure 3-21 *Ex-situ* cyclic voltammograms of AB/Pt before and after 15,000 load cycles.

Figure 3-22 shows CV recorded for AB/PBI/Pt before and after 15,000 load cycles. AB/PBI/Pt showed only 15% Pt degradation after ADT test where ECSA was dropped from 53.7 to 47.1 m² g⁻¹_{Pt}.

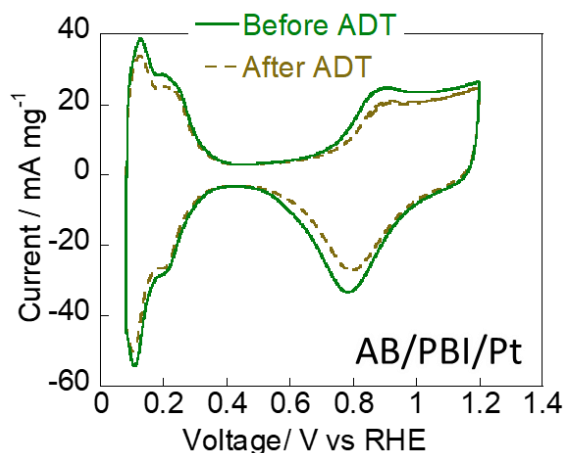


Figure 3-22 *Ex-situ* cyclic voltammograms of AB/PBI/Pt before and after 15,000 load cycles.

According to the above ADT, having a PBI layer is advantageous in terms of Pt durability. It is reported that having N as Pt anchoring sites is helpful in improving Pt durability. It is believed that the strong interaction between the nitrogen sites and Pt nanoparticles plays a significant role in confining Pt nanoparticles from Pt migration and/or dissolution^{48, 49} as shown in following schematics (**Figure 3-23**).

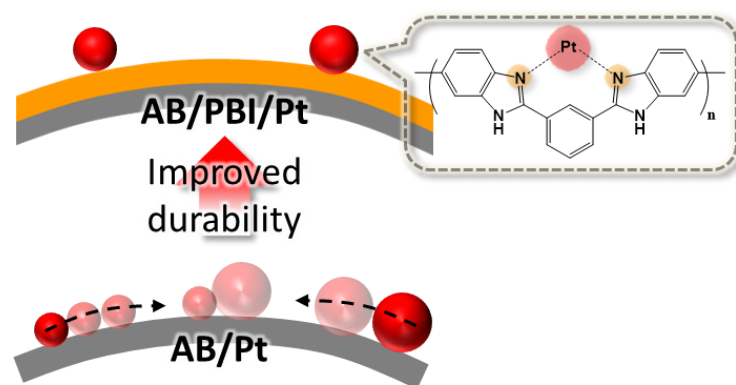


Figure 3-23 Schematic of effect of PBI wrapping on durability.

3.4. Conclusion

A simple method like PBI wrapping onto CBs is a promising approach which could solve some of the issues found in fuel cell applications. PBI wrapping significantly enhances the performance of HSA CB based electro catalyst compared to that of LSA CB based electro catalyst. Prevention of Pt deposition into restricted pores is the key, when considering highly porous HSA carbon supports in fuel cell applications, where they have abundant amount of Pt particles anchoring sites, resulting a uniform Pt particle dispersion on the carbon support. Pt deposition into micropore was prevented by micropore capping which resulted in increased ECSA, proton conductivity and O₂ diffusion in the MEA. On the other hand, uniform Pt particle size distribution on the carbon support is the crucial factor to consider in choosing highly graphitized LSA carbon supports which tend to improve ECSA and O₂ diffusion efficiency. Meanwhile PBI wrapping provides a continuous Nafion network in the catalyst layer. Therefore, surface modification to all the types of CBs is an essential step to fabricate highly efficient MEA by improving mass diffusion.

The highest Pt utilization obtained in this study was 0.364 g kW⁻¹ with AB/PBI/Pt. Furthermore, it was found that AB/PBI/Pt has higher durability compared to AB/Pt make it more appealing in real word application of fuel cell. Having N in PBI found to be effective for Pt nanoparticle durability due to prevention of Pt nanoparticle aggregation.

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Chapter 4

Design of highly efficient fuel cell catalyst layer by triggering favorable interaction between carbon support and ionomer

4.1. Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are promising power source since PEMFC provides on demand electrical power with zero local carbon emissions. In order to lower the cost of PEMFC, improvement of the efficiency of the catalyst is highly required since the catalyst mostly dominate the cost as well as the performance of the PEMFC.¹⁻² Catalyst composite in the catalyst layer consist of the 1-7 nm Pt nanoparticles loaded on carbon particles (15-45 nm in diameter), in which the proton conductive polymer (ionomer) is blended with the catalyst composite.³ The catalyst composites assembled there-dimensionally in the catalyst layer forming hierarchal pore network structure from micro scale to nano scale.⁴⁻⁵ In micro scale, 3D pore network facilitates the diffusion of both gas to the reaction site and water from the reaction sites, while ionomer network facilitates the proton transport from/to the reaction site. On the other hand, in nano scale, triple-phase boundary (TPB) on the surface of Pt nanoparticles act as the reaction site.

It is widely recognized that the number of the ‘active’ TPB determine the efficiency of the catalyst (i.e. Pt utilization efficiency) and it is determined by how effectively 3D network structure is connected. And the connectivity of the network structure is largely depended on the structure of the catalyst agglomerations as well as the homogeneity of the ionomer on the carbon supporting materials. On the other hand ‘inactive’ TPB due to the disconnection of the network resulted in decreasing Pt utilization efficiency.^{6,7}

The amount of ionomer in the catalyst layer (i.e. carbon to ionomer ratio; I/C) are highly important to ensure the connectivity of the ionomer network to improve the efficiency.⁸ However, it is pointed out that too much ionomer amount resulted in the increase of the O₂ permeation resistance at the TPB, which is more than 10 times higher than the O₂ diffusion resistance at the bulk pore network, and make the reaction site ‘less active’ especially at high current region.⁹ Therefore, optimization of the I/C have been extensively studied to realize both the sufficient proton conductivity together with the lower O₂ permeation resistance.¹⁰⁻¹³ It is also recognized that the I/C strongly affect not only for the TPB but also for the micro-scale 3D pore network especially at higher I/C since the too much ionomer clog the pore network, resulting in the increase of the O₂ diffusion resistance and water flooding at the high current density.^{9,14}

However, maximizing the efficiency with minimum I/C is challenging. Recently, inhomogeneous ionomer distribution at relatively higher I/C caused by the insufficient interaction between ionomer and carbon surface was pointed out.¹⁵ To solve such a crucial issue, modification of the carbon support was reported by A. Orfanidi *et al.* They successfully reduced effective I/C ratio from 0.65 to 0.4 by chemical modification of the carbon (Vulcan XC72) surface with amide/imide/lactam groups (-NH_x) to improve the interaction with Nafion.¹⁶ K. Kakinuma and coworkers also realized the improvement of the efficiency at low I/C (0.24) by designing the favorable interaction between ionomer and non-carbon support (Nb-SnO₂).¹⁷

In this study, investigation of the lowering of I/C by modifying the carbon surface with the polymer to realize the preferential interaction between ionomer and the carbon support is considered. Here, polybenzimidazole (PBI) was used as a modifying polymer since PBI have strong interaction for both carbon surface and Nafion. The *I-V* performance of the membrane electrode assembly (MEA) depending on the I/C was carefully studied using the non-wrapped counterpart as a comparison and it is found that the lower I/C at around 0.2 showed highest efficiency and importantly, the efficiency is 23 % higher than the highest efficiency of the counterpart at the optimized I/C (0.6). Therefore, this highly efficient MEA offers the possibility of increasing the current density, which in turn allows a reduction in cell areas, enabling cost reduction. Moreover, reduction of Pt loadings in both anode and cathode is expected with such a low I/C, enabling efficient water management. Because, in low loaded Pt catalyst layers water management is quite challenging.^{18, 19}

4.2. Experimental

4.2.1. Materials

Hydrogen hexachloroplatinate hexahydrate (H₂PtCl₆·6H₂O), *N, N*-dimethylacetamide (DMAc), ethylene glycol (EG) and ethanol (99.5%) were purchased from Wako Pure Chemicals, Ltd. Tokyo. Vulcan XC72 and acetylene black (AB) was purchased from Cobot Chemical Co., Ltd. Nafion solution (5%) and Nafion[®] 212 membranes were purchased from Sigma-Aldrich. PBI was provided by Sato Light Industrial Co., Ltd.

4.2.2. Material characterization

Thermogravimetric analysis (TGA) was performed using an EXSTAR TG/DTA6300 analyzer (Seiko Instruments, Inc.) at a heating rate of 10 °C min⁻¹ under an air flow of 200 mL min⁻¹. Transmission electron microscopy (TEM) was executed using a JEOL 2010 microscope operating at 30 kV. The three-dimensional structure of the catalyst layer was examined

by focused ion beam-scanning electron microscopy (FIB-SEM) using triple beam^R FIB-SEM-Ar MI4000L (Hitachi High Technologies) at 1.0 kV. Catalyst layers were subjected to continuous cross-sectional imaging via FIB-SEM and reconstruction was performed by the image composition method using both secondary-electron and reflected-electron images.⁹

4.2.3. Electrocatalyst preparation

Vulcan (20.0 mg) was dispersed in a solution of PBI (13.0 mg) in DMAc (20 mL) by sonication for 15 min using a bath-type sonicator (Branson 5510) followed by 3 hr mechanical shaking (Neo Shaker) to obtain Vulcan/PBI. Then resulted Vulcan/PBI composite was filtered, washed with DMAc, and then dried overnight under vacuum at 80 °C. Vulcan/PBI (100.0 mg) was dispersed in 60% EG aqueous solution (400 mL). H₂PtCl₆.6H₂O (4.3 g) dissolved in 60% EG aqueous solution (200 mL) was added and then the mixture was refluxed at 140 °C for 6 hr under nitrogen (N₂) atmosphere. After cooling, the obtained composite (denoted as Vulcan/PBI/Pt) was collected by filtration, washed several times with Milli-Q water, and then obtained black color product dried overnight at 60 °C to get well dried Vulcan/PBI/Pt. Vulcan/Pt was prepared in similar manner omitting PBI wrapping part. Finally, a sample of AB/PBI/Pt was prepared following the same procedure for the comparison.

4.2.4. MEA fabrication

All 1 cm² MEA were fabricated using spray coating method. Catalyst inks were prepared by dispersing each composite (Vulcan/PBI/Pt and Vulcan/Pt) and Nafion in 90 % aqueous ethanol solution, separately. The I/C was adjusted at 0.2, 0.4, 0.6 and 1.0. Then dispersed inks were casted onto on Nafion[®] 212 membranes using a spray coater (PS-1000, Nordson), separately. Each catalyst-coated membrane was laminated with two gas diffusion layers (SIGRACET[®] GDL 25 BC, SGL Group) under 0.6 MPa at 132 °C for 190 s, separately. The Pt loading of each catalyst-coated membrane was 0.3 mg cm⁻². Then MEA of AB/PBI/Pt with I/C = 0.2 was prepared for the comparison. After finding optimum I/C, low Pt loaded catalyst layers were sprayed using two times diluted Vulcan/PBI/Pt spray ink with optimum I/C. Pt loadings of anode/cathode at 0.3/0.1, 0.1/0.1 and 0.1/0.05 mg cm⁻² were set.

4.2.5. Fuel cell operation

In-situ cyclic voltammogram (CV) was performed by feeding with humidified N₂ at a flow rate of 200 mL min⁻¹ and humidified hydrogen (H₂) at a flow rate of 100 mL min⁻¹ at 40 °C in cathode and anode, respectively as reported in elsewhere.¹⁵ Polarization *I-V* curves of each MEA was tested by feeding with fully humidified H₂ (anode, 100 mL min⁻¹) and air/Oxygen (O₂)

(cathode, 200 mL min⁻¹) at 80 °C, using an in-house single cell system (Auto PEM-ER01). Impedance of each MEA was measured by feeding N₂ instead of air at the cathode in the frequency range of 10 kHz to 0.1 Hz at working potential of 0.45.¹⁵

4.3. Results and discussion

4.3.1. Characterization of catalyst

Vulcan-XC72 (Vulcan) and Nafion were chosen as carbon support and ionomer since both of them are commonly used and extensively studied. **Figure 4-1** shows TEM images of the Vulcan/Pt (**Figure 4-1 a**) and Vulcan/PBI/Pt (**Figure 4-1 b**), in which Pt nanoparticles with similar diameter of 3.2 ± 0.7 and 3.1 ± 0.3 nm was observed for Vulcan/Pt and Vulcan/PBI/Pt, respectively. The Pt content determined by TGA for Vulcan/Pt and Vulcan/PBI/Pt were 43.5 and 42.0 wt%, respectively.

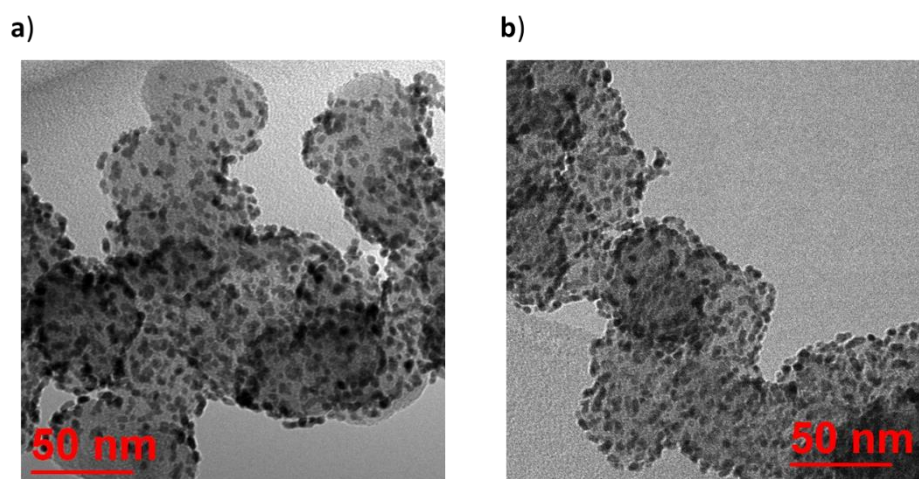


Figure 4-1 TEM images of a) Vulcan/Pt and b) Vulcan/PBI/Pt.

4.3.2. Effect of Nafion content on MEA performance

The polarization curves of the MEA containing Vulcan/Pt and Vulcan/PBI/Pt with varying I/C ratios are shown in **Figure 4-2**. Vulcan/Pt MEA (**Figure 4-2 a**) shows strong I/C dependency over the entire polarization range around kinetic, ohmic and mass-transport losses at low, middle and high current density region, respectively. Interestingly, there is no such significant difference in performance of Vulcan/PBI/Pt MEA (**Figure 4-2 b**) depending on the Nafion amount in the catalyst layer except for the mass-transfer region (> 1.5 A cm⁻²) with I/C = 1.0. Beginning with low Nafion content, Vulcan/PBI/Pt MEA showed highest performance in the means of

limiting current density at $I/C = 0.2$ and for Vulcan/Pt it was at $I/C = 0.6$. Further increment in Nafion content resulted in reduced performance, particularly in the mass transport region probably due to the limited O_2 diffusion.

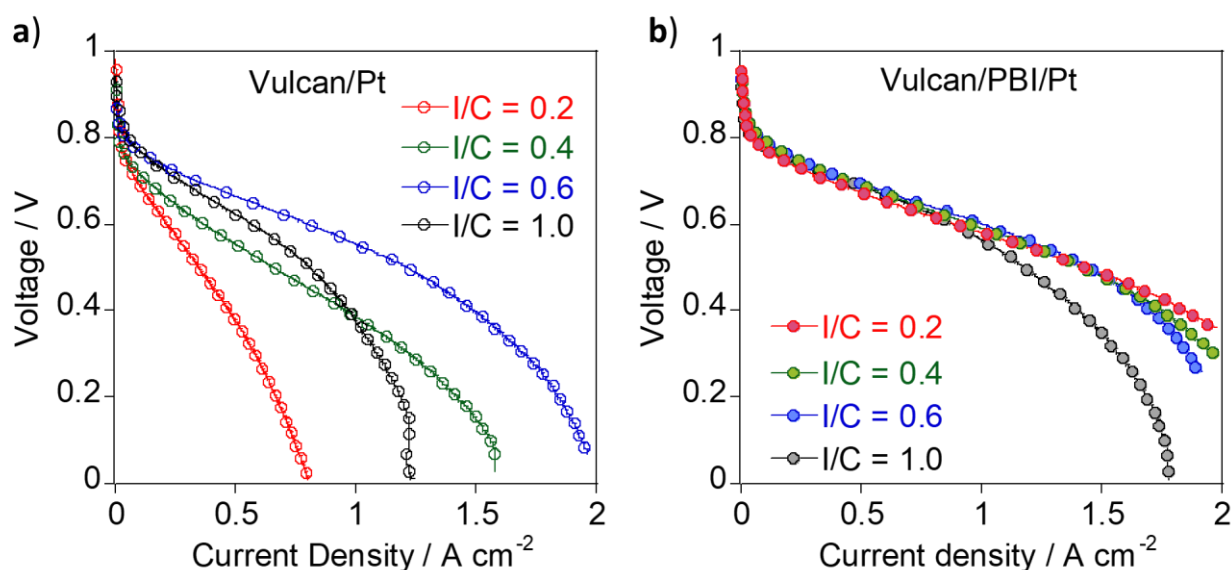


Figure 4-2 Polarization I - V curves of a) Vulcan/Pt and b) Vulcan/PBI/Pt with changing $I/C = 0.2$ - 1.0 .

The power density curves of the MEA containing Vulcan/Pt and Vulcan/PBI/Pt with varying I/C ratios are shown in **Figure 4-3**. The obtained power density values are shown in **Table 4-1**. The maximum power densities were $0.61\ W\ cm^{-2}$ ($I/C = 0.6$; **Figure 4-3 a**) for Vulcan/Pt and $0.75\ W\ cm^{-2}$ ($I/C = 0.2$; **Figure 4-3 b**) for Vulcan/PBI/Pt. The power density variation with changing I/C was insignificant in Vulcan/PBI/Pt system as it only changes from 0.75 to $0.72\ W\ cm^{-2}$ when increasing I/C from 0.2 to 0.6 . However, noticeable reduction of power density was observed with $I/C = 1.0$. On the other hand the power density variation with changing I/C was very significant in Vulcan/Pt system as it highly changes from 0.19 to $0.61\ W\ cm^{-2}$ when increasing I/C from 0.2 to 0.6 and power density decreases to 0.41 as increasing I/C up to 1.0 . This means effective utilization of Nafion was occurred in Vulcan/PBI/Pt compared to Vulcan/Pt due to homogeneous Nafion distribution.

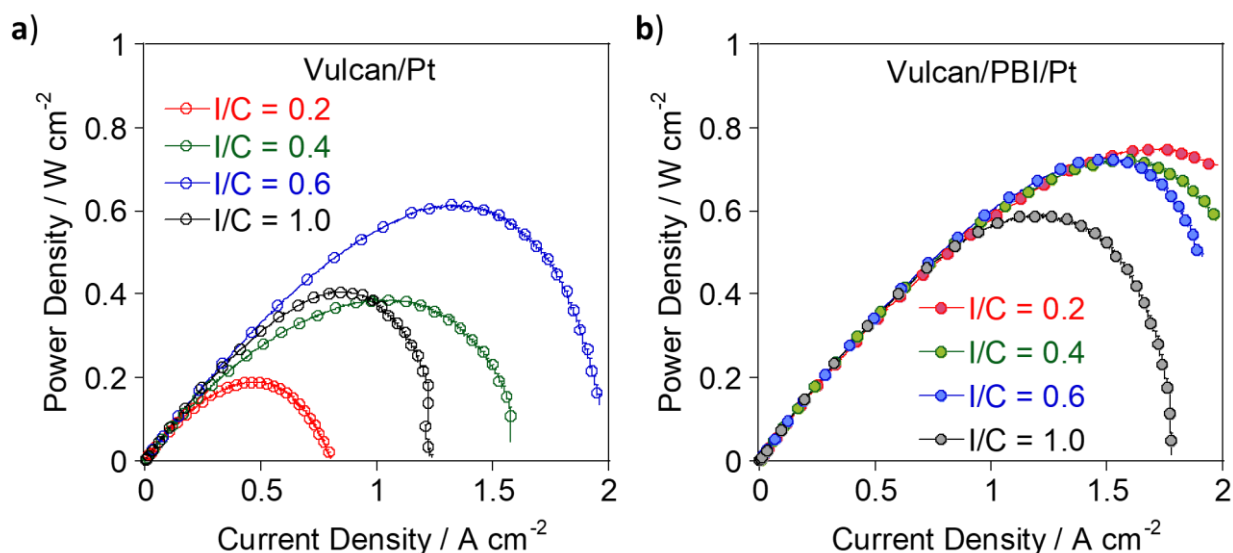


Figure 4-3 Power density curves of **a)** Vulcan/Pt and **b)** Vulcan/PBI/Pt with changing I/C = 0.2-1.0.

Table 4-1 Power density values of Vulcan/Pt and Vulcan/PBI/Pt with I/C = 0.2-1.0.

I/C		0.2	0.4	0.6	1.0
Power density / W cm ⁻²	Vulcan/Pt	0.19	0.39	0.61	0.41
	Vulcan/PBI/Pt	0.75	0.73	0.72	0.59

Another important observation is that all the Vulcan/PBI/Pt with I/C ranging from 0.2 to 1.0 gave always higher performance compared that of respective Vulcan/Pts as shown in **Table 4-1**. Preventing deposition of Pt nanoparticles into small pores of Vulcan due the micropore capping phenomena imposed by PBI wrapping and connected network path for protons due to the homogeneous Nafion dispersion aided by acid base interaction between Nafion and PBI are the reasonable mechanisms for the enhanced performance in Vulcan/PBI/Pt.¹⁵ It is reported that ionomer dispersion in actual catalyst layer is rather inhomogeneous.²⁰ Therefore PBI wrapping which aided the homogeneous Nafion dispersion is promising. Because, achieving such a small optimized I/C value like 0.2 for Vulcan/PBI/Pt compared to that of Vulcan/Pt (I/C = 0.6) made the importance of PBI wrapping approach more significant. The reduction of Nafion volume used was 66 % compared to Vulcan/Pt, leading to cost reduction coming from ionomer usage.

Since, $I/C = 0.2$ was the optimized value which is the lowest in the I/C values tested in this study, further lowering of I/C ($I/C = 0.175$) was carried out and found that maximum power density is only 0.67 W cm^{-2} , which is lower than $I/C = 0.2$ (**Figure 4 -4**).

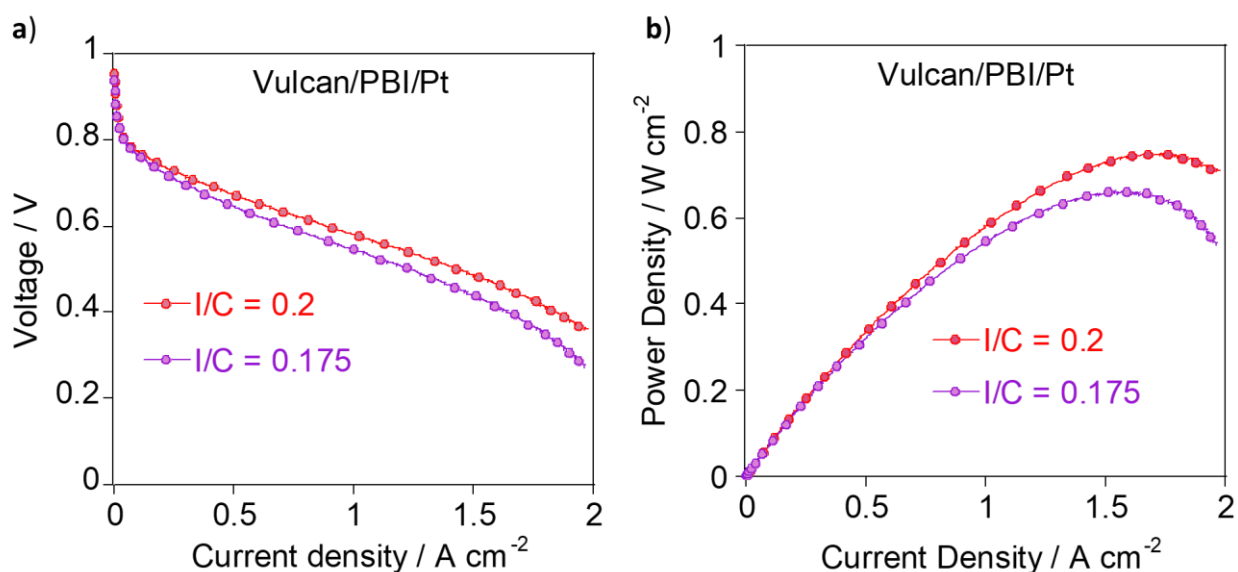


Figure 4-4 a) Polarization and b) Power density curves of Vulcan/PBI/Pt with $I/C = 0.2$ and 0.175.

Maximum power density of Vulcan/Pt and Vulcan/PBI/Pt MEAs as a function of I/C was plotted in **Figure 4-5**. Quite interestingly, all the Vulcan/PBI/Pt with I/C ranging from 0.2 to 1.0 gave always higher performance compared that of respective Vulcan/Pts as explained before.

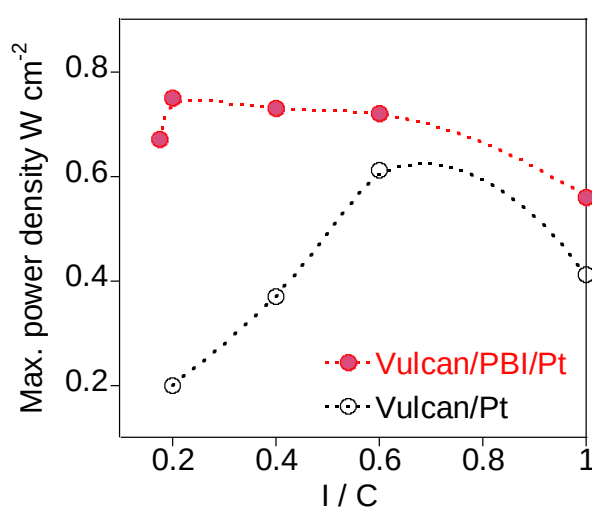


Figure 4-5 Variation of maximum power density vs I/C for Vulcan/Pt and Vulcan/PBI/Pt.

Furthermore, it is clear that Vulcan/PBI/Pt MEA showed the highest maximum power density at very low I/C ($I/C = 0.2$), while that of Vulcan/Pt was at $I/C = 0.6$. It was found that the maximum power density at $I/C = 0.2$ of Vulcan/PBI/Pt MEA (0.75 W cm^{-2}) is 23 % higher than that of Vulcan/Pt MEA at $I/C = 0.6$ (0.61 W cm^{-2}).

It is known that changing porous carbon support to nonporous carbon support like AB can improve fuel cell performance due to the better mass transfer, due to presence of Pt at outer surface which could easily accessible by protons and O_2 .²¹ **Figure 4-6** show polarization and power density curves of AB/PBI/Pt MEA with $I/C = 0.2$. It is interesting to identify that fuel cell performance of Vulcan/PBI/Pt with $I/C = 0.2$ gave very close performance to AB/PBI/Pt which has highest power density of 0.79 W cm^{-2} . It means that better mass transfer condition could be achieved even with porous carbon supports like Vulcan, if there is potential to operate under very low I/C value like 0.2. Because, it could provide well balanced O_2 and proton supply to the reaction sites. Especially clogging of secondary pores of the catalyst layer due to Nafion will be minimized with lower I/C.

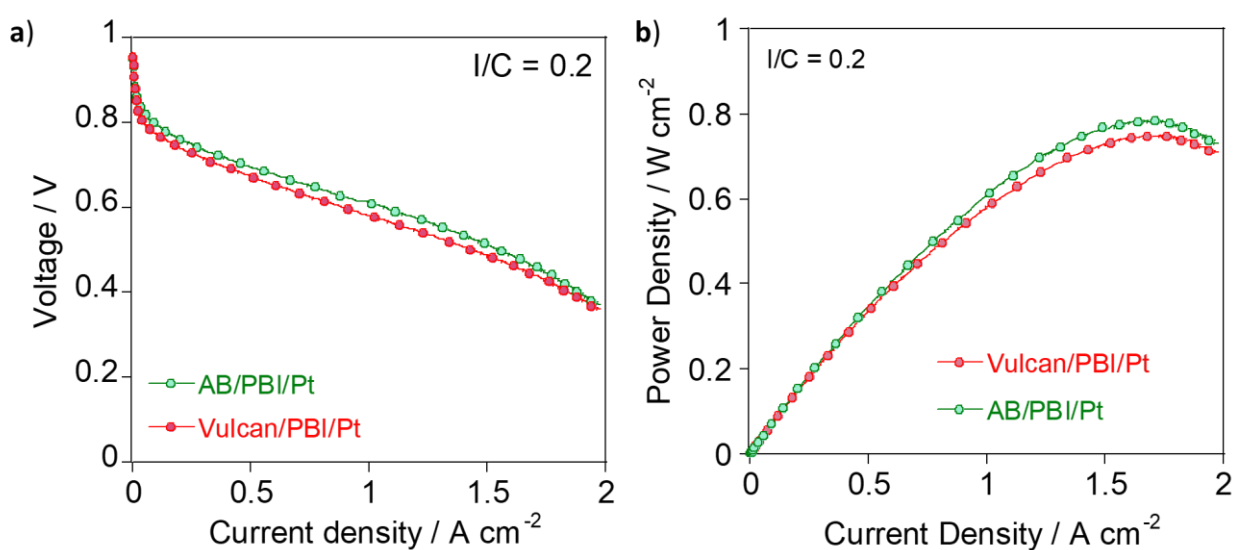


Figure 4-6 a) Polarization I - V and b) Power density curves of Vulcan/PBI/Pt and AB/PBI/Pt with $I/C = 0.2$.

Further understanding of unique behavior of polarization performance of Vulcan/PBI/Pt especially at lower I/C range, electrochemical surface area (ECSA), protonic resistance in the catalyst layer (ohmic over-potential) and limited transport rate of reactants to Pt nanoparticles (mass transfer over-potential) at various I/C were studied.²²

4.3.3. Activation over-potential under various Nafion contents

Figure 4-7 shows the cell voltages at 0.1 A cm^{-2} (low current density), where the single cell performance is mostly determined by the activation over-potential of oxygen reduction reaction (ORR) at the cathode.²² Similar to the trend in the power density, as the Nafion content increased from $I/C = 0.2$ to 1.0 , the single cell voltage at 0.1 A cm^{-2} is gradually increased in Vulcan/Pt MEAs. It means that utilization of Pt catalyst is increased with increasing I/C . On the other hand, the trend is quite different for Vulcan/PBI/Pt MEAs, where change of cell voltage was insignificant, ensuring homogenous Nafion coverage even with lower I/C . When $I/C = 0.72$ (chapter 2) it is found that PBI wrapping of Vulcan facilitated the development of connected proton network path due to the homogeneous Nafion distribution aided by acid base interaction between Nafion and PBI layer and enhanced the performance of Vulcan/PBI/Pt.¹⁵ It is considered that similar homogeneous distribution of Nafion works below $I/C = 0.72$ since the homogenous distribution can efficiently utilize Nafion in the catalyst layer even with lower I/C .

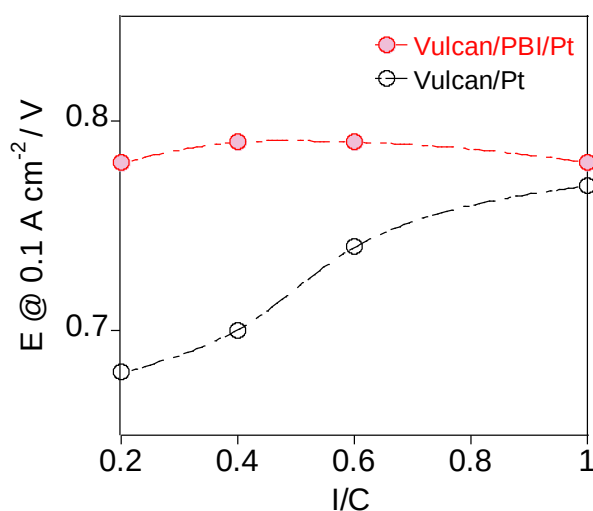


Figure 4-7 Activation cell voltages at 0.1 A cm^{-2} for Vulcan/Pt and Vulcan/PBI/Pt as a function of I/C values.

To investigate the catalyst/ionomer interfacial area in the cathode catalyst layer, *in-situ* CV was carried out. Hydrogen adsorption/desorption on the Pt surface measured potential lower than 0.4 V was monitored and electrochemical active surface area (ECSA) was calculated by integrating charges proportional to the amount of desorbed hydrogen, which is in turn dependent on the Pt/Nafion interfacial area.²² Hence, ECSA of the Pt catalyst can be calculated using coulombic charge for hydrogen desorption on the Pt catalyst surface ($220 \mu\text{C cm}^{-2}$).²³⁻²⁵

The ECSA values increased with increasing Nafion amount from I/C to = 0.2 to 1.0 in Vulcan/Pt MEA as shown in **Figure 4-8 a** and **Table 4-2**. This is probably due to the increasing number of Pt/Nafion interfaces with increasing I/C. However, for Vulcan/PBI/Pt MEA, this phenomena is quite different and it shows insignificant variation of ECSA depending on the varying I/C (**Figure 4-8 b** and **Table 4-2**). This is probably due to the homogeneous Nafion dispersion in both low and high I/C values as explained before. The maximum number of Pt/Nafion interfaces have been achieved even with lower I/C like 0.2. Furthermore, ECSA values of Vulcan/PBI/Pt MEAs are always higher than that of Vulcan/Pt MEAs as shown in **Figure 4-8 c**. All the Pt catalyst particle are located on the Nafion accessible regions of Vulcan/PBI/Pt due to the micropore capping phenomena is the key factor. Therefore, both homogeneous Nafion distribution and limited deposition of Pt nanoparticles into micropores gave enhanced ECSA in Vulcan/PBI/Pt compared to that of Vulcan/Pt.

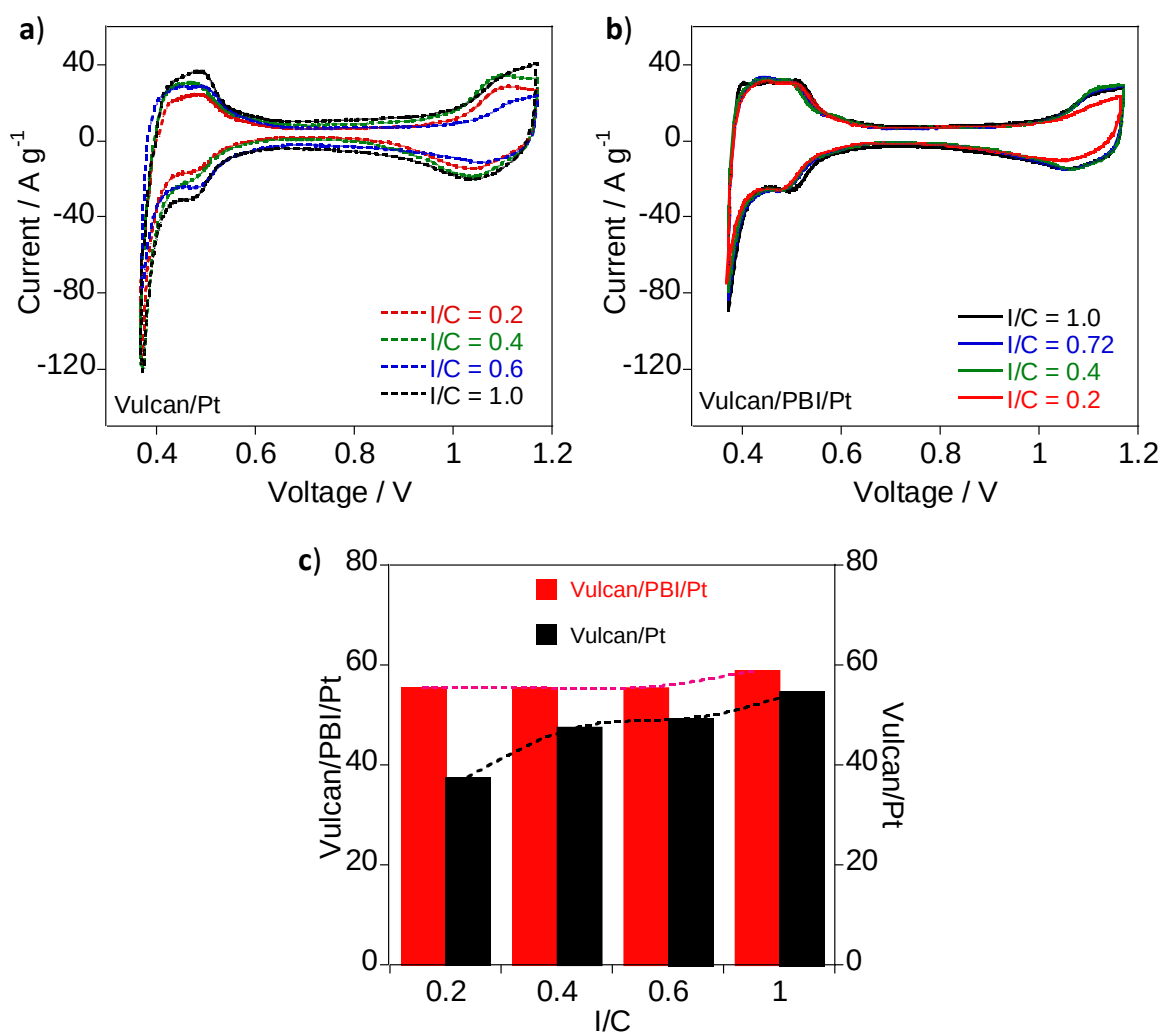


Figure 4-8 In-situ CV of a) Vulcan/Pt and b) Vulcan/PBI/Pt under N_2 atmosphere and c) ECSA with varying I/C.

Table 4-2 Calculated ECSA of Vulcan/Pt and Vulcan/PBI/Pt with I/C = 0.2-1.0.

I/C		0.2	0.4	0.6	1.0
ECSA / $\text{m}^2 \text{g}^{-1}_{\text{Pt}}$	Vulcan/Pt	37.54	47.59	49.37	54.90
	Vulcan/PBI/Pt	55.45	55.50	55.62	58.95

Generally, MEA performance will be directly proportional to the ECSA only when the ionic resistance through the Nafion network is low enough for protons to access the entire catalyst/ionomer interfacial area. Therefore, optimizing Nafion amount which allows effective proton conduction in the catalyst layer is practically important in lowering ohmic over-potential which is discussing in the next section.

4.3.4. Ohmic over-potential under various Nafion contents

The fabrication of both types of MEAs (Vulcan/Pt and Vulcan/PBI/Pt) involved same type of Nafion membrane contributing to the same amount of ohmic resistance in the system. Therefore, any difference in ohmic resistance in the system resembles the protonic resistance (R_p) in the catalyst layer. To evaluate proton conduction in the catalyst layer, impedance of Vulcan/Pt and Vulcan/PBI/Pt MEAs with different I/C values was measured under H_2 (anode) / N_2 (cathode) as shown **Figure 4-9** and calculated R_p values are shown in **Table 4-3**. The R_p of a catalyst layer can be quantified based on the high frequency region of the impedance spectra.^{26, 27}

Interestingly, Vulcan/PBI/Pt MEAs always showed much lower R_p compared to that of corresponding Vulcan/Pt MEAs at the selected I/C range, implying that Nafion was more effectively utilized in Vulcan/PBI/Pt even with lower I/C. Vulcan/PBI/Pt could achieve effective coverage of Nafion around catalyst particles with lower I/C like 0.2 compared to that of Vulcan/Pt. Because, Vulcan/PBI/Pt MEA with I/C = 0.2 (max. power density; 0.75 W cm^{-2}) gave much higher performance compared to that of Vulcan/Pt MEA with I/C = 0.2 (max. power density; 0.19 W cm^{-2}). This phenomena was observed may be due to the homogeneous Nafion dispersion owing to the preferential interaction between Nafion and PBI. The higher the I/C value the lower the R_p in both types of MEAs, suggesting the increasing of the thickness of Nafion layer around catalyst particles with increasing I/C, and thus reducing the R_p in the catalyst layer as shown in the **Table 4-3**.

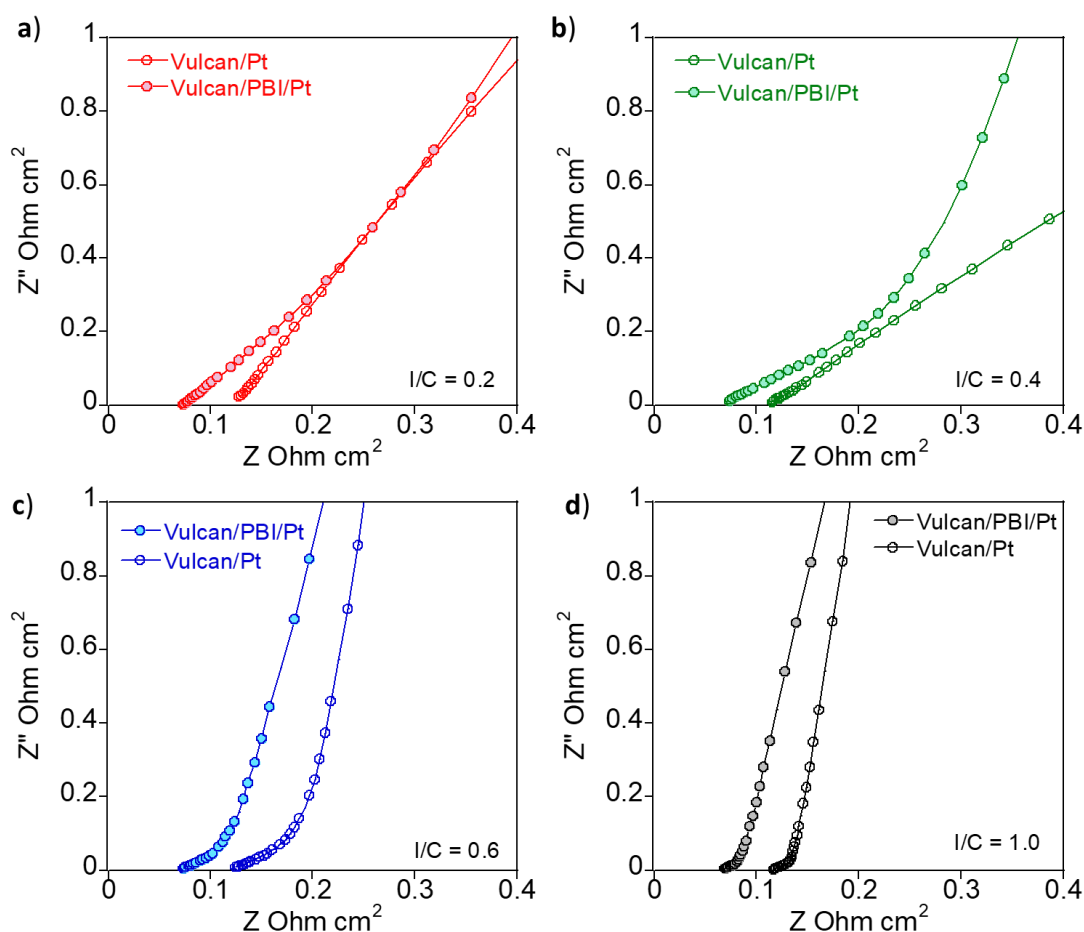


Figure 4-9 Nyquist electrochemical impedance spectroscopy response of Vulcan/Pt and Vulcan/PBI/Pt at $I/C =$ **a)** 0.2, **b)** 0.4, **c)** 0.6 and **d)** 1.0 measured from 10^4 Hz to 10^3 Hz at 0.45 V under H_2/N_2 .

Table 4-3 Proton conduction resistance of Vulcan/Pt and Vulcan/PBI/Pt with $I/C = 0.2-1.0$.

I/C		0.2	0.4	0.6	1.0
H^+ resistance/ Ohm cm^2	Vulcan/Pt	0.395	0.330	0.151	0.076
	Vulcan/PBI/Pt	0.305	0.223	0.069	0.043

4.3.5. Concentration over-potential under various Nafion contents

The concentration over-potential, which is basically related to the mass transport of reactant gases through the porous catalyst layer. Catalyst-layer porosity and ionomer surface coverage of supported catalyst particles affect the gas phase O_2 participation in the ORR at the TPB. As shown in **Figure 4-2**, fuel cell performance at high current density is varied depending on the I/C. The maximum limiting current of Vulcan/PBI/Pt at $I/C = 0.2$ was much higher than that of Vulcan/Pt at $I/C = 0.6$. The higher the I/C the thicker the Nafion coverage. Moreover, increasing I/C from 0.2 to 1.0 in Vulcan/PBI/Pt gradually decreased the maximum limiting current may be due to the local O_2 diffusion resistance by increasing Nafion thickness. The **Figure 4-10** shows the schematics of expected change of Nafion thickness depending on the I/C of Vulcan/PBI/Pt.

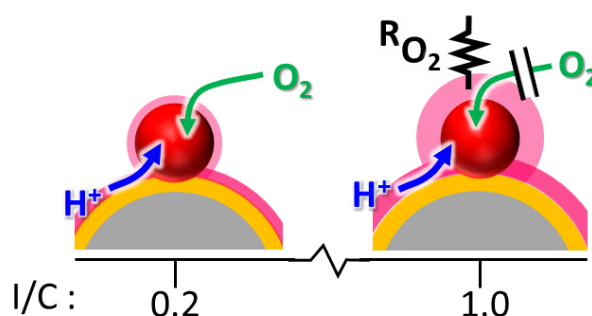


Figure 4-10 Schematics of O_2 diffusion depending on the Nafion thickness.

The presence of thicker Nafion film covering active catalyst sites would result in higher resistance for O_2 molecules to diffuse through the film, in which liquid water is also encased. This diffusion process is greatly affected by the local film thickness around a given catalyst particle, which is then associated with the overall ionomer content of the bulk catalyst layer.²⁸ The thicker ionomer coating significantly reduce O_2 diffusion on the coated Pt surface, because O_2 diffusion coefficient in the ionomer is more than 100 fold lower than in pores.²

The O_2 diffusion in the catalyst layer was determined by the O_2 gain results, which were calculated from the difference in the potentials measured under air and O_2 at cathode for a given current density. The obtained polarization curves under O_2 and air are shown in **Figure 4-11**. The significant difference in performance between O_2 and air in Vulcan/Pt with changing I/C from 0.2 – 1.0 was clearly seen. Especially when $I/C = 0.2$, both performances under O_2 and air were significantly lowered due to higher R_p in the catalyst layer as found from the impedance measurement.

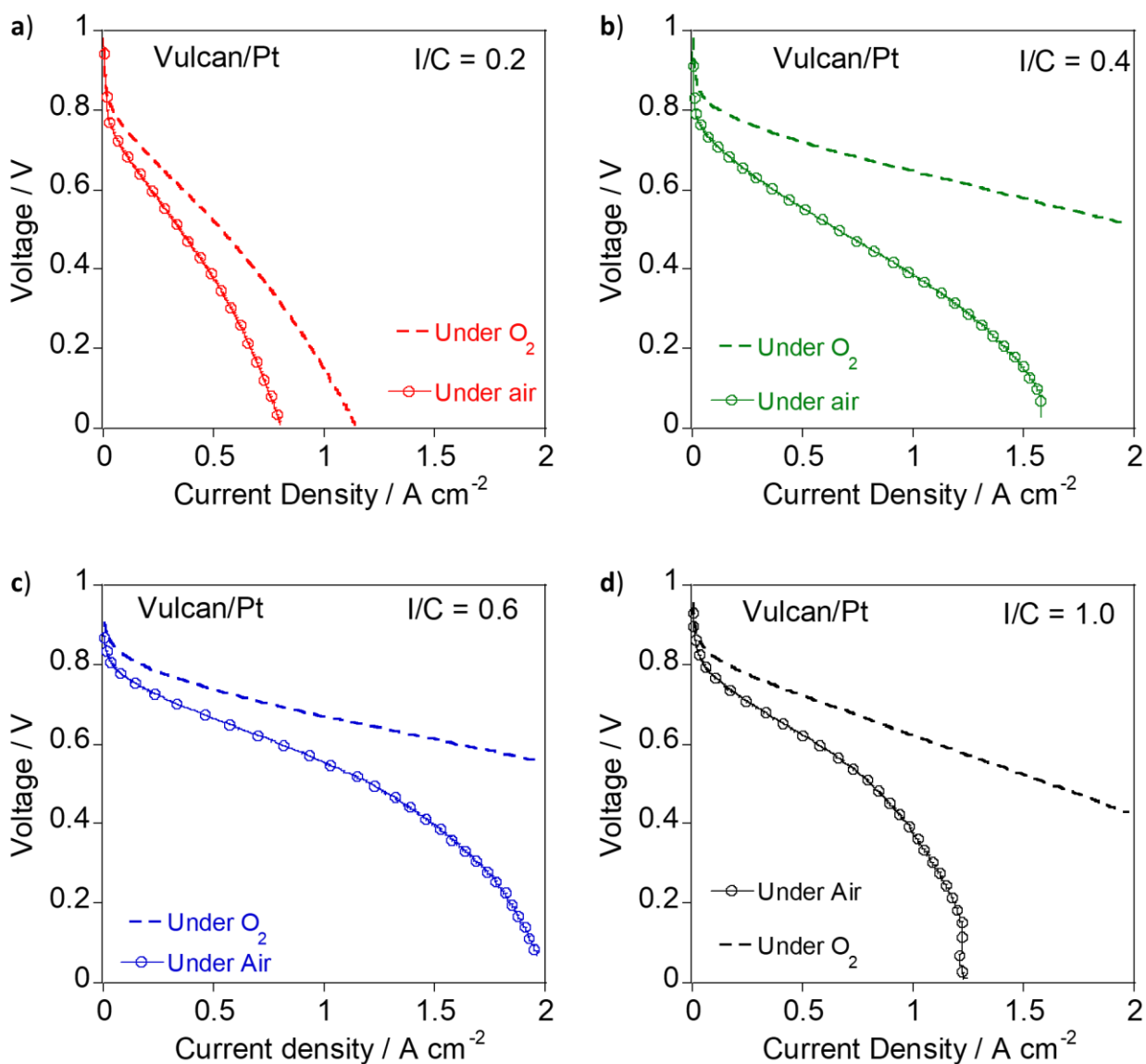


Figure 4-11 Polarization I - V curves of Vulcan/Pt measured under air and O_2 at cathode of $I/C =$ **a)** 0.2, **b)** 0.4, **c)** 0.6 and **d)** 1.0.

On the other hand, the performance improvement upon switching from air to O_2 (**Figure 4-12**) was not significant in Vulcan/PBI/Pt when changing I/C from 0.2 – 0.6, implying better O_2 diffusion even with air. However, at $I/C = 1.0$ gave significant performance difference compared to other I/C values, implying that $I/C = 1.0$ has the highest O_2 diffusion resistance as shown in schematic illustration (**Figure 4-10**).

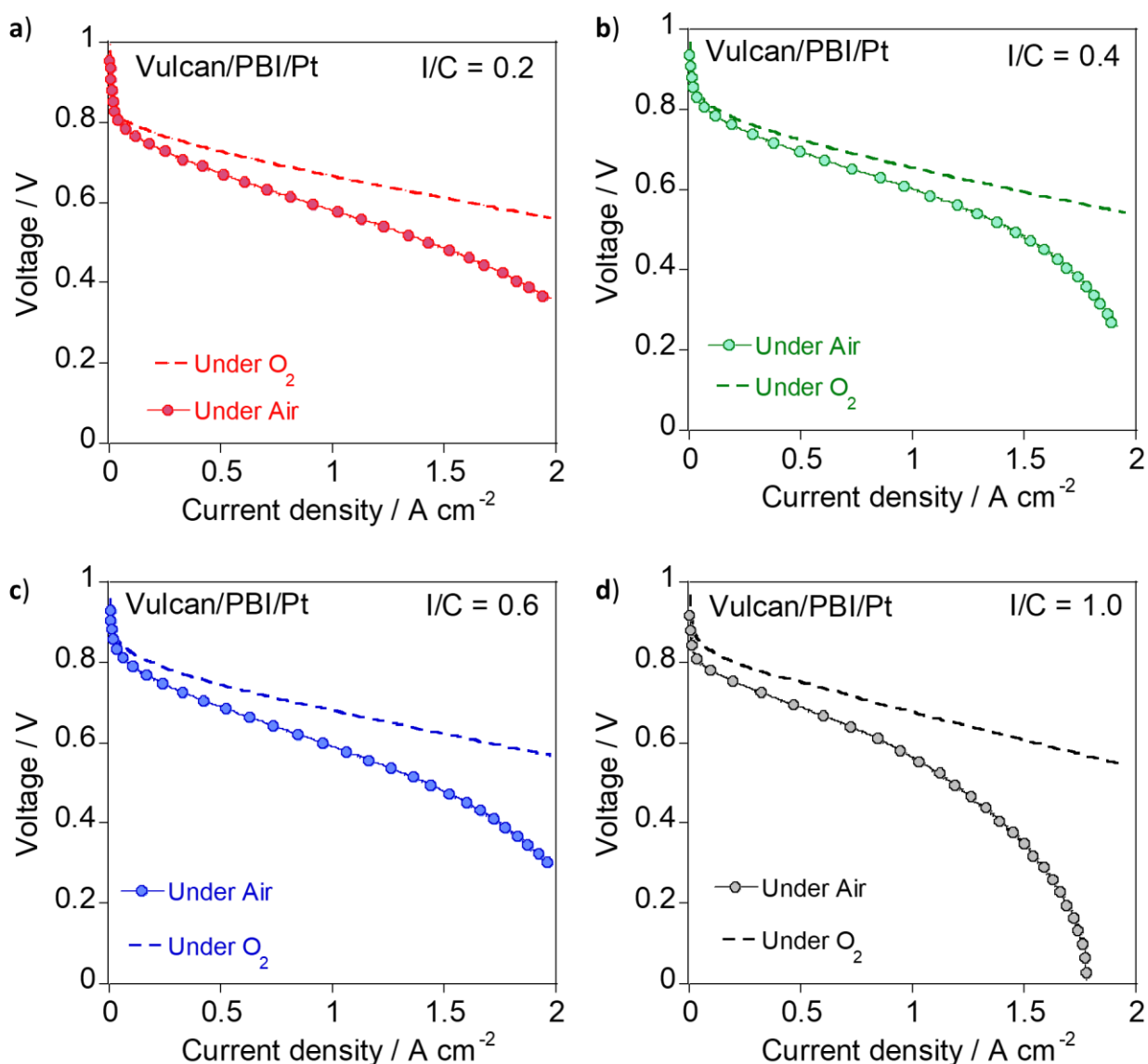


Figure 4-12 Polarization I - V curves of Vulcan/PBI/Pt measured under air and O_2 at cathode of $I/C =$ **a)** 0.2, **b)** 0.4, **c)** 0.6 and **d)** 1.0.

The **Figure 4-13 a** and **b** show the O_2 gain result of Vulcan/Pt and Vulcan/PBI/Pt with different I/C values, respectively. The lowest O_2 gain was observed with optimized I/C of Vulcan/Pt and Vulcan/PBI/Pt where best polarization performances were obtained for both of the systems. However, trend in O_2 gain is quite different in each system. For Vulcan/PBI/Pt, the higher the I/C values the higher the O_2 gain (**Figure 4-13 b**), implying greater barrier for O_2 diffusion with increasing I/C . On the other hand, there is no linear relationship between O_2 again and I/C for Vulcan/Pt system. The O_2 gain voltages were increased at both low and high I/C values as shown in **Figure 4-13 a** for Vulcan/Pt. At higher I/C values, not having enough O_2 supply confines the performance, while at lower I/C values, insufficient proton supply limits the performance as

observed by R_p measured via impedance. Therefore, well-balanced proton and O_2 supply was realized with different I/C values for Vulcan/Pt and Vulcan/PBI/Pt.

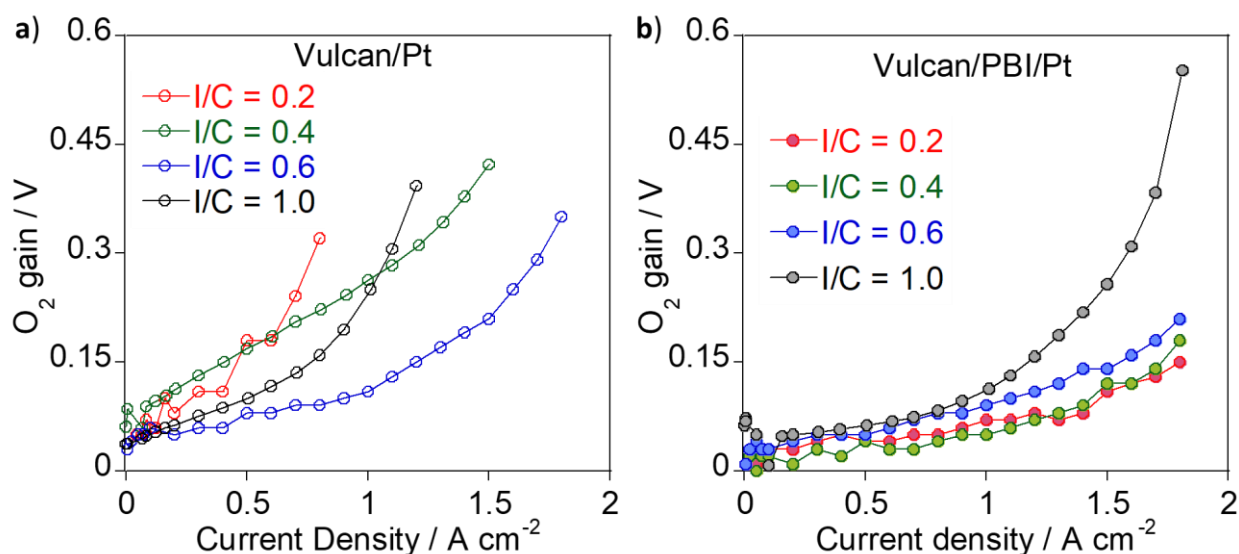


Figure 4-13 O_2 gain of **a)** Vulcan/Pt and **b)** Vulcan/PBI/Pt.

Preferential interaction between Nafion and PBI in Vulcan/PBI/Pt shifted effective I/C to a lower value of 0.2. The presence of a thicker Nafion film covering active catalyst sites would result in high resistance for O_2 molecules to diffuse through the film²⁸ as explained before. Furthermore, an increase of ionomer amount in the catalyst layer causes pore isolation and loss of pore connectivity², resulting reduced O_2 diffusion in the secondary pores of the catalyst layer. In addition, the thicker Nafion film will hamper the diffusion of product water away from reaction sites, likely inducing flooding at higher current density. Therefore, porous morphology of the catalyst layer was studied further to understand the gas transport behavior of Vulcan/PBI/Pt catalyst as an effective electrode material.

4.3.6. Gas diffusion characteristics of catalyst layer

Heterogeneous porous structure of the catalyst layer is a significantly important parameter to consider, because it strongly determines the gas diffusion properties of the catalyst layer. FIB-SEM is a great tool to investigate catalyst layer characteristics towards gas diffusion in secondary pores. In FIB-SEM both secondary-electron images and reflected electron images were captured at the time when the cross section image was taken to reconstruct the 3D structure. The **Figure 4-14** shows the FIB-SEM images (**Figure 4-14 a & b**) and 3D reconstructed images (**Figure 4-14 c & d**) of Vulcan/Pt catalyst layer with I/C = 0.6 and Vulcan/PBI/Pt catalyst layer with I/C = 0.2,

respectively. **Table 4-4** symmetrizes porosity and relative conductivity of each catalyst layer with considered I/C values.

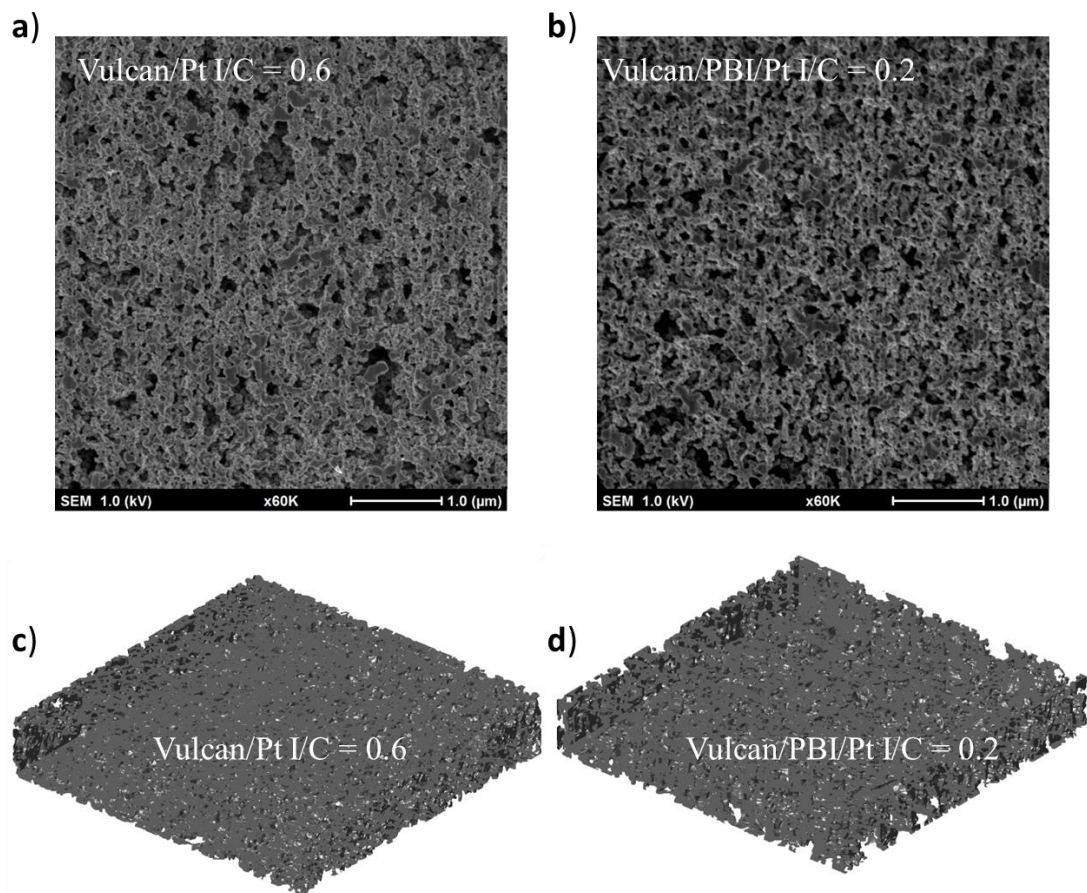


Figure 4-14 FIB-SEM images of **a)** Vulcan/Pt ($I/C = 0.6$) and **b)** Vulcan/PBI/Pt ($I/C = 0.2$) and 3D reconstructed images of **c)** Vulcan/Pt ($I/C = 0.6$) and **d)** Vulcan/PBI/Pt ($I/C = 0.2$).

Table 4-4 Porosity and relative conductivity of Vulcan/Pt and Vulcan/PBI/Pt.

Composite composition	Porosity ϵ	Relative conductivity σ
Vulcan/Pt – $I/C = 0.6$	0.698	0.178
Vulcan/PBI/Pt – $I/C = 0.2$	0.699	0.269
Vulcan/Pt – $I/C = 1.0$	0.607	0.163
Vulcan/PBI/Pt – $I/C = 1.0$	0.640	0.175

Vulcan/Pt with $I/C = 0.6$ and Vulcan/PBI/Pt with $I/C = 0.2$ has almost same porosity of ca.0.7. Not only porosity, but also relative conductivity (ϵ/τ) matters for the effective gas transport condition within the catalyst layer. The relative diffusion coefficient of porous medium (D^R) can be simply expressed according to the **Eq. (4-1)**.

$$D^R = D^{\text{eff}} / D^{\text{bulk}} = \varepsilon / \tau = \varepsilon^\gamma \dots \text{Eq. (4-1)}$$

Where D^{eff} is effective diffusion coefficient, D^{bulk} is bulk molecular diffusion coefficient, ε is porosity and τ is tortuosity. Relative conductivity (σ) is the ratio of porosity and tortuosity. Therefore, lower value of tortuosity of the porous medium is important for the effective gas diffusion. It is reported that difference in γ leads to a different diffusion coefficient in spite of the porosity being same.⁹ Therefore, despite of having similar porosity for Vulcan/Pt with I/C = 0.6 and Vulcan/PBI/Pt with I/C = 0.2, Vulcan/PBI/Pt with I/C = 0.2 has better gas diffusion property due to the higher value of relative conductivity ($\sigma = 0.269$), in other words having a smaller tortuosity. Vulcan/Pt with I/C = 0.6 may have higher tortuosity ($\sigma = 0.178$) which signifies gas transport with twisty and winding curves. The **Figure 4-15** shows the schematic illustration of O_2 diffusion in Vulcan/Pt and Vulcan/PBI/Pt.

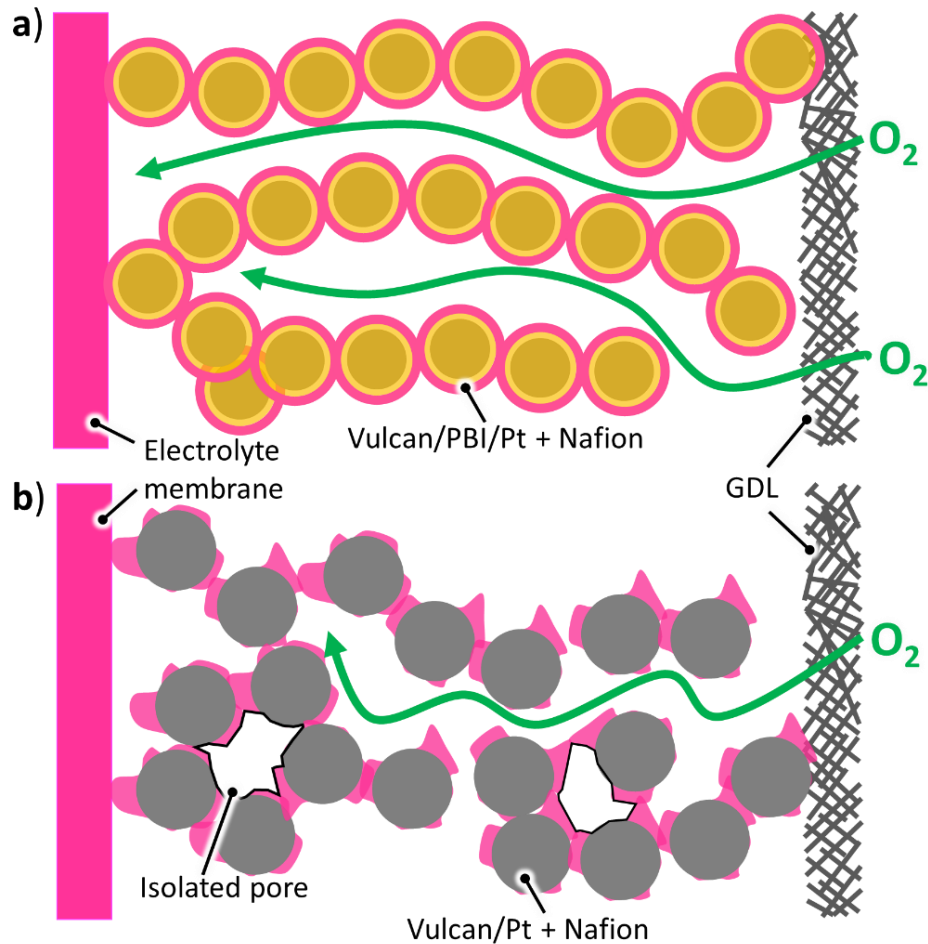


Figure 4-15 Schematics of O_2 diffusion properties of **a)** Vulcan/PBI/Pt (I/C = 0.2) and **b)** Vulcan/Pt (I/C = 0.6).

It is reported that increasing I/C from 0.5-1.5, pore connectivity decreased significantly and large pores became isolated due to Nafion adhesion. Thus, tortuosity increased and then relative diffusion coefficient decreased.² It is also reported that the presence of isolated pores

increased the O₂ transport resistance in the catalyst layer^{1,9,14}, resulting lower fuel cell performance especially at high current density as observed for Vulcan/Pt in **Figure 4-2 a**.

Figure 4-16 shows the FIB-SEM images (**Figure 4-16 a & b**) and 3D reconstructed images (**Figure 4-16 c & d**) of Vulcan/Pt and Vulcan/PBI/Pt catalyst layer with I/C = 1.0 respectively. In both of the catalyst layers, porous structure is decreased compared to that of respective lower I/C values. Nevertheless, Vulcan/PBI/Pt catalyst layer still showed better porous structure with the porosity of 0.640 compared to that of Vulcan/Pt catalyst layer (porosity; 0.607). Interestingly relative conductivity of Vulcan/PBI/Pt with I/C = 1.0 (0.175) still higher than that of respective Vulcan/Pt (0.163), confirming the obtained higher fuel cell performance of Vulcan/PBI/Pt compared to that of Vulcan/Pt with I/C = 1.0, due to better O₂ diffusion characteristics of Vulcan/PBI/Pt catalyst layers.

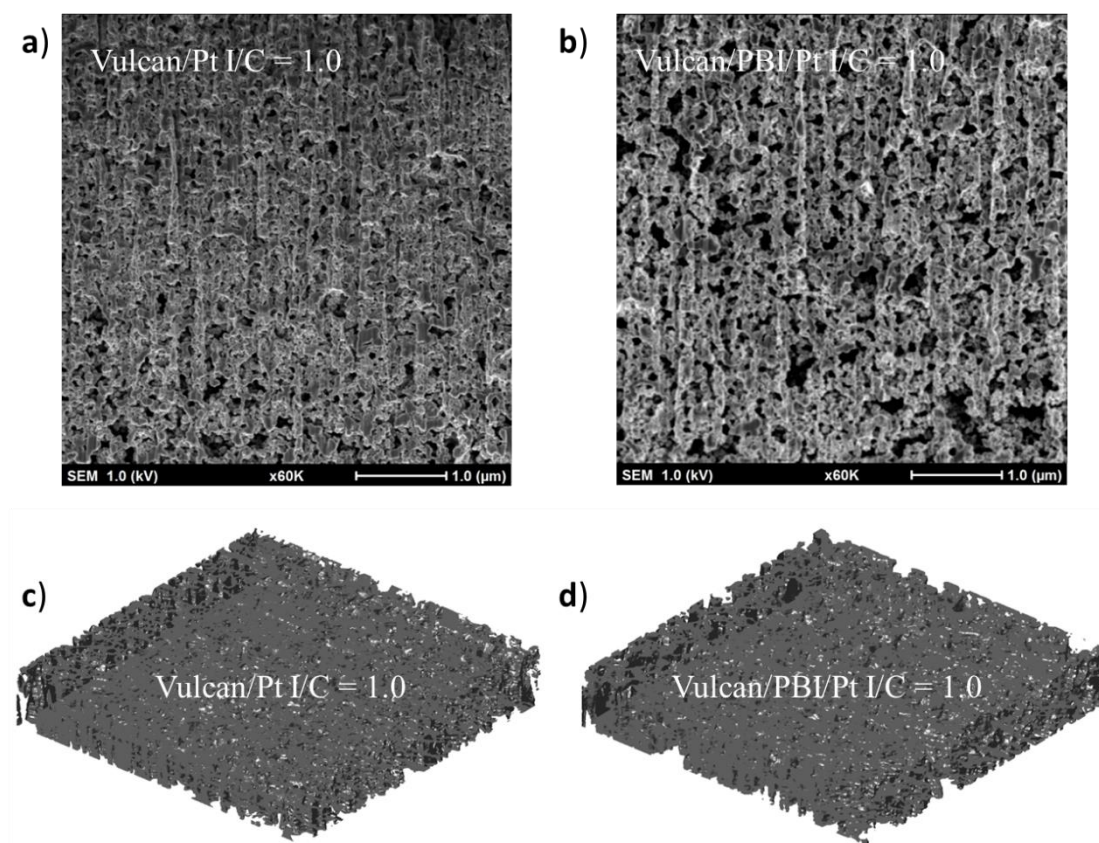


Figure 4-16 FIB-SEM images of **a)** Vulcan/Pt (I/C = 1.0) and **b)** Vulcan/PBI/Pt (I/C = 1.0) and 3D reconstructed images of respective **c)** Vulcan/Pt and **d)** Vulcan/PBI/Pt.

It is reported that Nafion tends to pile up with increasing I/C ratio,²⁹ which further promotes the generation of dead-end macro pores in catalyst layer, resulting resistance for O₂ diffusion due to generated invalid spaces.^{1, 30} **Figure 4-17** shows the relationship between porosity

vs relative conductivity and pore size distribution of the catalyst layer. Vulcan/PBI/Pt with I/C = 0.2 has the best condition while Vulcan/Pt with I/C = 1.0 has the least favorable condition for mass diffusion according to the **Figure 4-17 a**. Furthermore, both of Vulcan/PBI/Pt with I/C = 0.2 and 1.0 showed higher pore size compared to Vulcan/Pt (**Figure 17 b**), agreeing well with the improved fuel cell performance of Vulcan/PBI/Pt compared to Vulcan/Pt at I/C = 0.2 and 1.0. Having larger pores may be facilitated O₂ diffusion and encouraged to remove product water from the catalyst layer of Vulcan/PBI/Pt effectively.

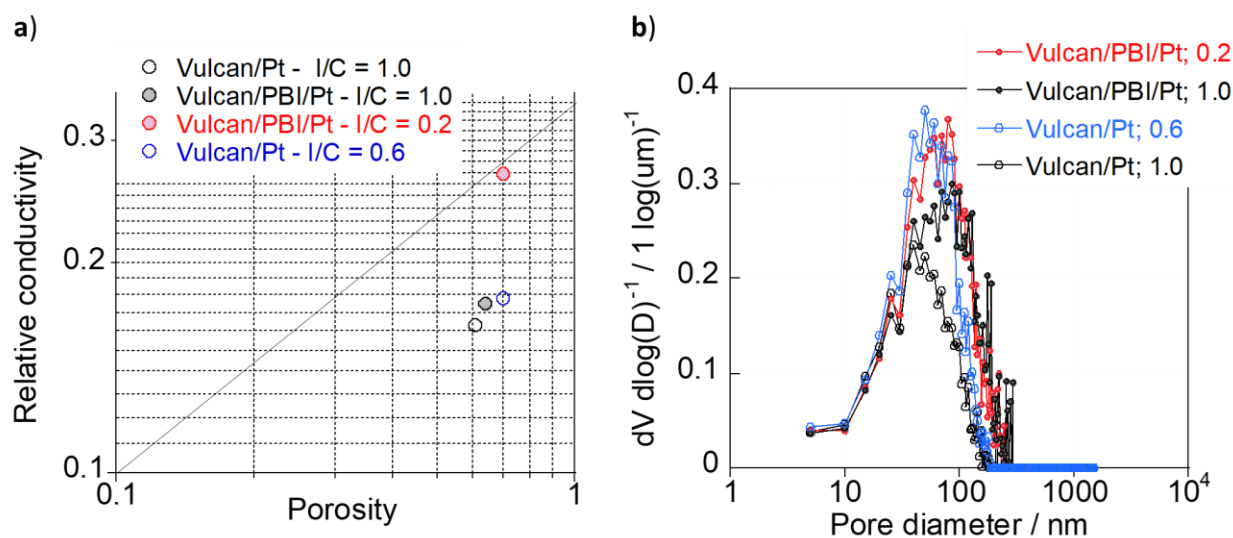


Figure 4-17 a) Relationship between relative conductivity vs porosity and **b)** pore size distribution of Vulcan/Pt (I/C = 0.6 & 1.0) and Vulcan/PBI/Pt (I/C = 0.2 & 1.0).

Finally, **Figure 4-18** shows power density curves obtained with H₂/O₂ condition. The maximum power density of Vulcan/Pt with I/C = 0.6 and Vulcan/PBI/Pt with I/C = 0.2 were 1.15 and 1.38 W cm⁻², respectively. Considering total Pt loading of 0.5 mg cm⁻², calculated Pt utilization of Vulcan/Pt with I/C = 0.6 and Vulcan/PBI/Pt with I/C = 0.2 were 0.435 and 0.362 g kW⁻¹, respectively (**Table 4-5**). Operating a fuel cell with lower I/C by triggering the favorable interaction between carbon support and Nafion is promising which ultimately resulted in improved Pt utilization.

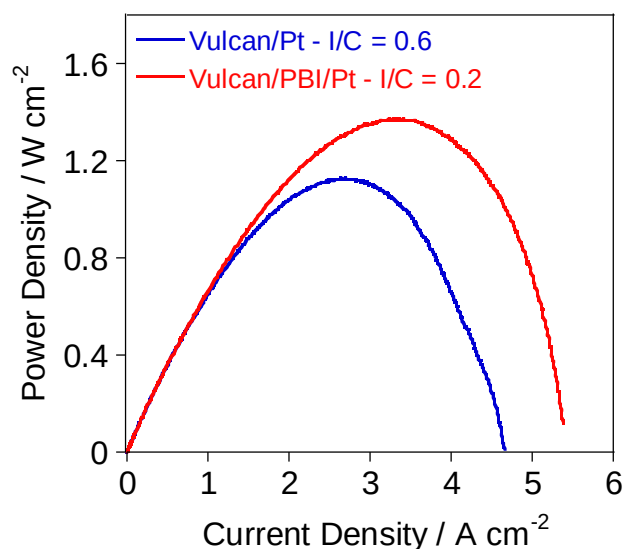


Figure 4-18 Power density curve of Vulcan/Pt with I/C = 0.6 and Vulcan/PBI/Pt with I/C = 0.2 measured under H₂/O₂.

Table 4-5 Pt utilization of Vulcan/Pt and Vulcan/PBI/Pt with optimized I/C.

Composite	Max. power density/ W cm ⁻²	Pt utilization / g kW ⁻¹
Vulcan/Pt – I/C = 0.6	1.15	0.435
Vulcan/PBI/Pt – I/C = 0.2	1.38	0.362

Since Vulcan/PBI/Pt system can be operated with lower I/C value of 0.2, it is worthwhile to investigate possibility of application of Vulcan/PBI/Pt with lower I/C in low Pt loaded catalyst layer in fuel cells. Because it is known that obstacles for lowering Pt loading in the catalyst layer are reduced O₂ diffusion through the Nafion coverage and poor water management.¹⁸

4.3.7. Fuel cell performance of low Pt loaded catalyst layers

So far Pt loadings in both anode and cathode were 0.3 mg cm⁻². First, cathode Pt loading was decreased from 0.3 – 0.1 mg cm⁻², keeping a higher I/C = 0.7 (MEA 1: 0.3, 0.1 @ 0.7). Then Pt loading of anode was declined from 0.3 to 0.1 mg cm⁻² with I/C = 0.2 (MEA 2: 0.1, 0.1 @ 0.2). Preparation of low Pt loaded catalyst layers involved dilution of spray ink and factor of dilution used was 2 times. **Figure 4-19** shows the polarization curves and power density curves of MEA 1 and 2 measured under H₂/air.

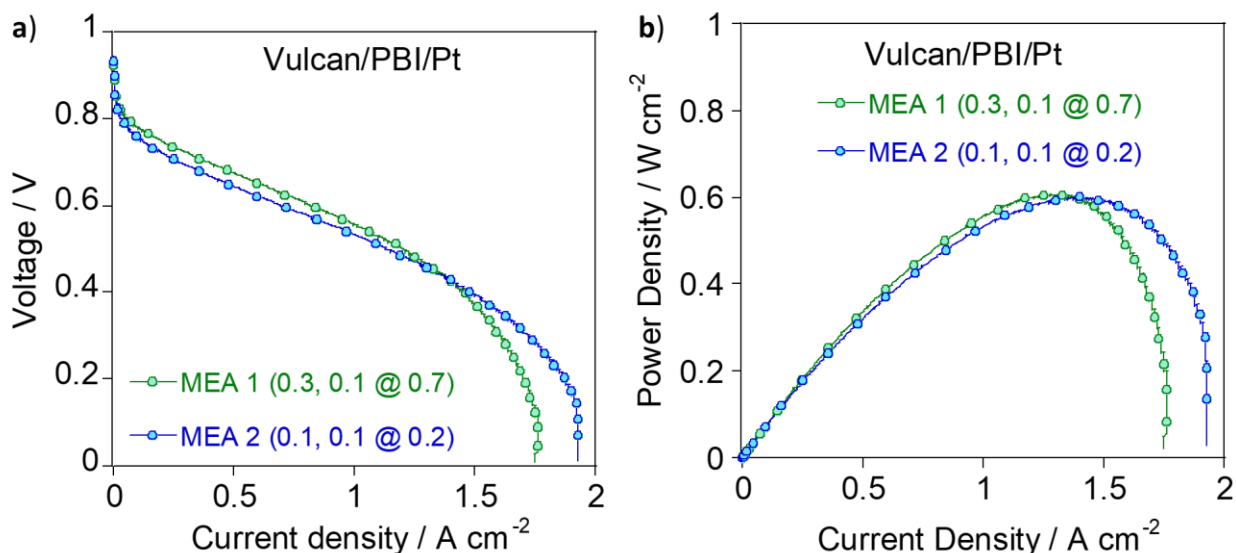


Figure 4-19 a) Polarization and b) power density curves of Vulcan/PBI/Pt with different Pt loadings.

According to the **Figure 4-19 a**, there is no significant difference in performance except for high current density region. As expected performance at high current density improved because of lower I/C in MEA 2. Furthermore, polarization losses coming from anode was insignificant, since there is no change of power density was observed when anode Pt loading was reduced from 0.3 to 0.1 mg cm⁻². Both of the MEAs have similar power density of 0.60 W cm⁻² (**Figure 4-19 b**).

Finally, Pt loading of cathode side was further reduced to 0.05 mg cm⁻² (MEA 3: 0.1, 0.05 @ 0.2), keeping I/C = 0.2. The obtained polarization curves under H₂/air and power density curves under H₂/air and H₂/O₂ are shown in **Figure 4-20**. According to the **Figure 4-20 a**, there is no significant difference in performance except for high current density region. As expected performance at high current density reduced in MEA 3 most probably due to flooding happened with ultra-low Pt loading. Power density was reduced from 0.60 to 0.55 W cm⁻² when decreasing the cathode Pt loading from 0.1 to 0.05 mg cm⁻² (**Figure 4-20 b**). Pt utilization was calculated using maximum power density obtained under H₂/O₂ condition. **Figure 4-20 c** shows the power density curves obtained. The maximum power density obtained for MEA 2 and MEA 3 were 1.13 and 0.90 W cm⁻², respectively. The calculated Pt utilization values are showing in **Table 4-6**. Pt utilization values for MEA 2 and MEA 3 were 0.177 and 0.166 g kW⁻¹, respectively.

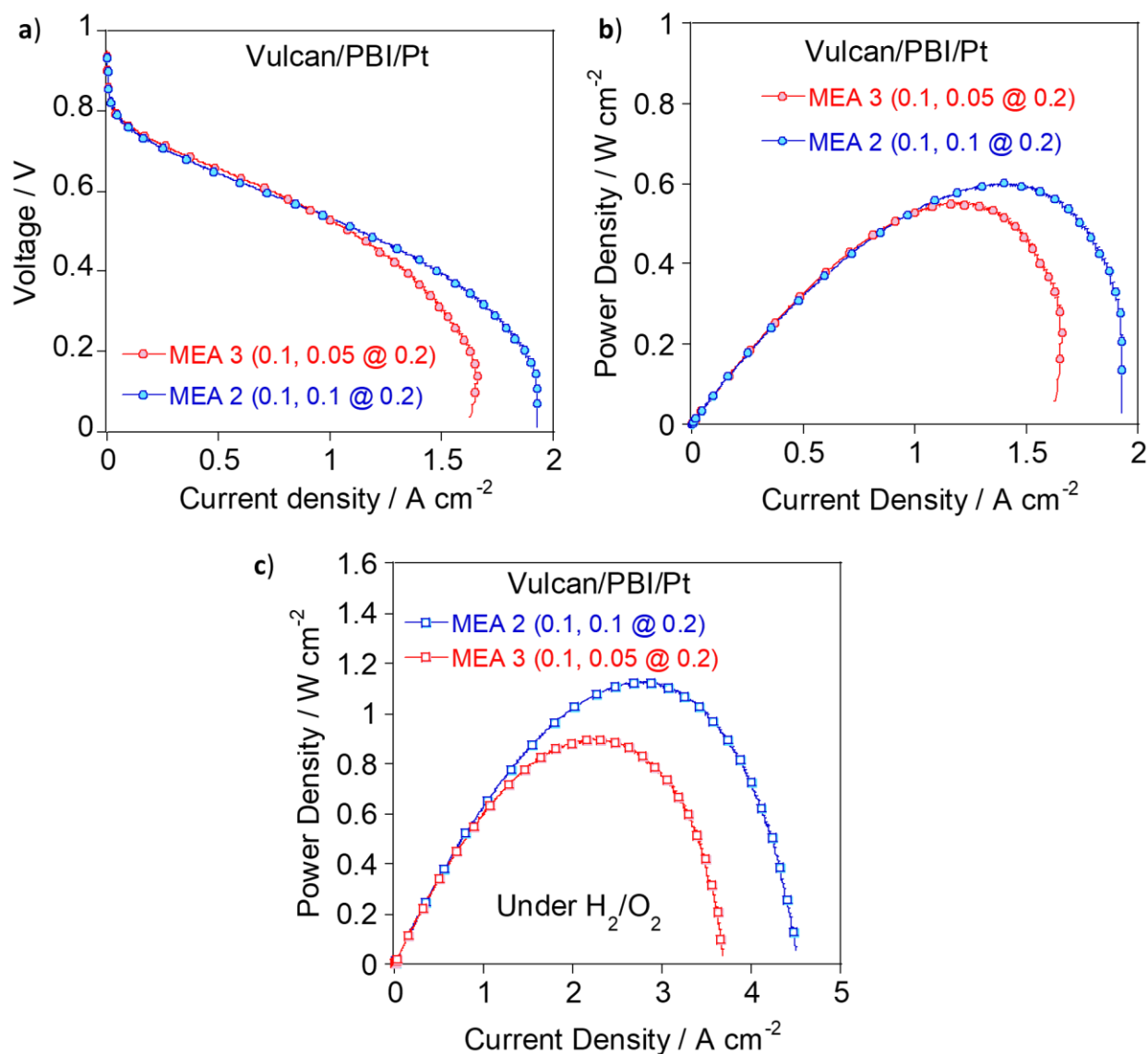


Figure 4-20 a) Polarization $I-V$ and b) power density curves under H_2 /air and c) power density curves under H_2/O_2 of Vulcan/PBI/Pt with different Pt loadings.

Table 4-6 Pt utilization efficiency of Vulcan/PBI/Pt with different Pt loadings.

MEA	Total Pt loading / $mg\ cm^{-2}$	Max. power density / $W\ cm^{-2}$	Pt utilization / $g\ kW^{-1}$
MEA2 (0.1, 0.1 @ 0.2)	0.12	1.13	0.177
MEA 3 (0.1, 0.05 @ 0.2)	0.15	0.90	0.166

The highest Pt utilization obtained in this study was $0.166\ g\ kW^{-1}$ and it was achieved by optimizing ionomer amount in the catalyst layer and ultimately fabricating low Pt loaded MEAs (Strategy 3). **Figure 4-21** shows Pt utilization values obtained via strategy 3 along with strategy 1 and 2.

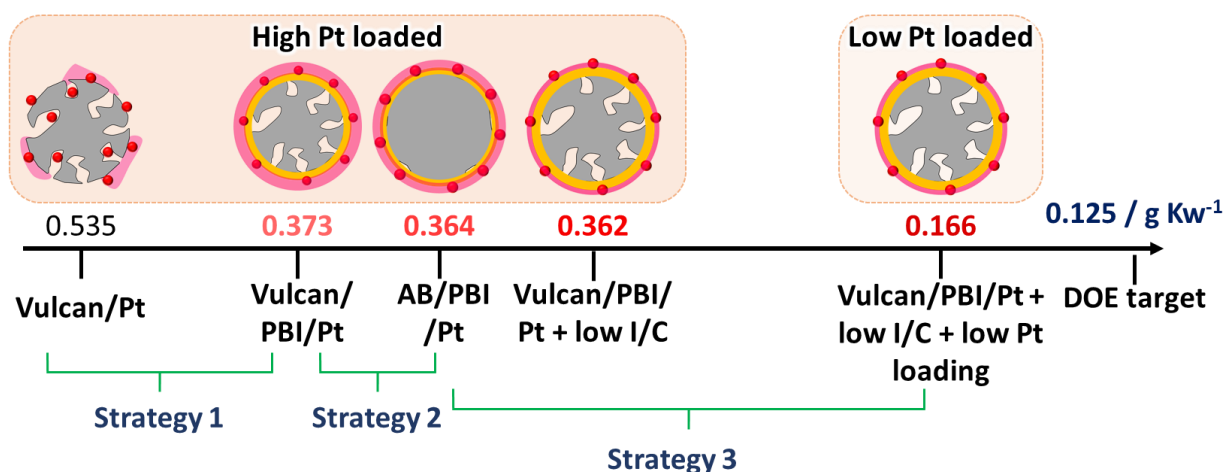


Figure 4-21 Schematic of achieving DOE target after strategy 3.

After exploiting strategy 3, achieved Pt utilization is very close to the department of energy U.S. (DOE) target of 0.125 g Kw^{-1} . The gap between obtained Pt utilization from this study and DOE target could be easily filled by incorporating Pt core shell method with this lower I/C (0.2) found in this study. It is reported that applying core shell in catalyst system could improve Pt mass activity (Pt decorated Pd/C³¹, Pt@Ni/C³²) due to less oxophilicity. Finally, incorporating Pt core shell method into PBI wrapping could improve Pt utilization at least by 4 time due to the improved mass activity³³, ultimately achieving DOE target.

4.4. Conclusion

Fabrication of highly efficient catalyst layer by triggering favorable interaction between Nafion and carbon support is a promising approach. Formation of well-connected network of proton was achieved with very low I/C ratio of 0.2 due to easily applicable PBI wrapping method. The *I-V* performance of Vulcan/PBI/Pt MEA with I/C = 0.2 showed highest efficiency and importantly, the efficiency was 23 % higher than the highest efficiency of the counterpart (Vulcan/Pt) at the optimized I/C (0.6). Furthermore, it was found that relative conductivity of Vulcan/PBI/Pt with I/C = 0.2 was considerably higher compared to Vulcan/Pt with I/C = 0.6, resulting favorable condition for O₂ diffusion. Moreover, increasing I/C from 0.2 to 1.0 preserved higher relative conductivity in Vulcan/PBI/Pt compared to Vulcan/Pt, even though the porosity of both the systems were lowered. Therefore, it is concluded that interaction between Nafion and PBI encouraged to form well balanced mass diffusion between protons and O₂ within the catalyst layer. Finally application of such a low Nafion amount in the catalyst layer is widen up the way to

fabricate low Pt loaded MEA by decreasing Pt loading of cathode from 0.3 to 0.05 mg cm⁻², resulting highest Pt utilization of 0.166 g kW⁻¹ which is very close to DOE target. Ultimately, incorporation of Pt core shell into this PBI wrapping method will allow to achieve DOE target of 0.125 g kW⁻¹ without any doubt.

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Chapter 5

Conclusions and perspectives

5.1. Summary of the dissertation

In this dissertation brief overview about importance of application of fuel cell technology into our day to day life and advantages of fuel cells were discussed. However, high cost of fuel cell due to usage of precious metal Pt as the catalyst hinders the worldwide commercialization. Therefore, improving Pt utilization efficiency is highly required. To achieve this, 3 strategies were considered via polybenzimidazole (PBI) wrapping method. Strategy 1; improving Pt utilization efficiency of Pt supported Vulcan (chapter 2), strategy 2; application of PBI wrapping method to other types of carbon blacks (CBs) (chapter 3) and strategy 3; optimization of Nafion in the catalyst layer by triggering interaction between Nafion and carbon support (chapter 3) were discussed. Conclusions obtained in each chapter are summarized as follows.

Chapter 2¹

In chapter 2, it was revealed that coating of PBI on Vulcan prior to Pt deposition can improve Pt utilization efficiency of polymer electrolyte membrane fuel cells (PEMFCs). PBI wrapping process was easy to apply to Vulcan, resulting 84 % of micropore capping. Micropore capping phenomena suppressed the deposition of Pt into the micropores and resulting in efficacious contact of Pt with Nafion, which could ultimately resulted in 21 % improvement in electrochemical active surface area (ECSA). Moreover, micropore capping improved O₂ supply to each of the reaction sites in PBI wrapped Vulcan supported Pt (Vulcan/PBI/Pt) electrocatalyst, resulting higher oxygen reduction reaction compared to conventional Vulcan supported Pt (Vulcan/Pt) and power density of Vulcan/PBI/Pt system was improved by 18 %. It was also found that the homogeneous Nafion coating assisted by the acid–base interaction between Nafion and PBI facilitated the higher proton conductivity in the catalyst layer. Protonic resistance of the catalyst layer was lowered by 65 % due to the long range proton conduction in Vulcan/PBI/Pt catalyst layer. Additionally, establishing highly stable catalyst ink condition made this PBI wrapping approach much more appealing to industries relate to membrane electrode assembly (MEA) fabrications. Mainly two mechanisms; prevention of Pt deposition into pores and homogeneous Nafion coating in the catalyst layer contributed to the improved Pt utilization efficiency of the Vulcan/PBI/Pt compared with that of the Vulcan/Pt one. Therefore, coating with PBI will be helpful to decrease the amount of Pt needed in PEMFCs, thus lowering their cost.

Chapter 3²

In chapter 3, it was further confirmed that simple method like PBI wrapping on CBs is a promising approach which could solve some of the issues found in fuel cell applications. PBI wrapping significantly enhances the performance of high surface area CB (HSA CB; Ketjen black) based electrocatalyst compared to that of low surface area CB (LSA CB; Acetylene black) based electrocatalyst. Prevention of Pt deposition into restricted pores is the key, when considering highly porous HSA carbon supports in fuel cell applications, where they have abundant amount of Pt particles binding sites, resulting a uniform Pt particle dispersion on the carbon support. Pt nanoparticle deposition into micropore was prevented by micropore capping which resulted in increased ECSA, proton conductivity and O₂ diffusion in the MEA. On the other hand, uniform Pt particle size distribution on the carbon support is the crucial factor to consider in choosing highly graphitized LSA carbon supports which tend to improve ECSA and O₂ diffusion efficiency. Meanwhile PBI wrapping provided a continuous Nafion network in the catalyst layer. Therefore, surface modification to all the types of CBs is an essential step to fabricate highly efficient MEA by improving mass diffusion.

The highest Pt utilization obtained in this part of study was 0.364 g kW⁻¹ with PBI wrapped acetylene black supported Pt (AB/PBI/Pt). Furthermore, it was found that AB/PBI/Pt has higher durability compared to acetylene black supported Pt (AB/Pt) makes it more appealing in real word application of fuel cell. Having N in PBI found to be effective for Pt nanoparticle durability due to prevention of Pt dissolution and migration

Chapter 4³

In chapter 4, it was found that fabrication of highly efficient catalyst layer by triggering favorable interaction between Nafion and carbon support is a promising approach. Formation of well-connected network of proton was achieved with very lower ionomer/carbon (I/C) ratio of 0.2 due to easily applicable PBI wrapping method. The polarization performance of Vulcan/PBI/Pt MEA with I/C = 0.2 showed highest efficiency and importantly, the efficiency was 23 % higher than the highest efficiency of the counterpart (Vulcan/Pt) at the optimized I/C (0.6). Furthermore, it was found that relative conductivity of Vulcan/PBI/Pt with I/C = 0.2 was relatively higher compared to Vulcan/Pt with I/C = 0.6, resulting favorable condition for O₂ diffusion. Moreover, increasing I/C from 0.2 to 1.0 preserved higher relative conductivity in Vulcan/PBI/Pt compared to Vulcan/Pt, even though the porosity of both the systems were lowered. Therefore, it is concluded that interaction between Nafion and PBI encouraged to form well balanced mass diffusion between proton and O₂ within the catalyst layer. Finally, application of such a low Nafion amount in the

catalyst layer is widen up the way to fabricate low Pt loaded MEA by decreasing Pt loading of cathode from 0.3 to 0.05 mg cm⁻², resulting highest Pt utilization of 0.166 g kW⁻¹ which is very close to department of energy U.S. (DOE) target. Ultimately, incorporation of Pt core shell into this PBI wrapping method under optimized condition will allow to achieve DOE target of 0.125 g kW⁻¹ without any doubt.

5.2. Perspective

In this dissertation, it has recognized the importance of applying PBI wrapping onto CBs in order to enhance Pt utilization efficiency. Because structure of PBI has different active sites to interact with carbon surface, Pt nanoparticles and Nafion. Therefore, problems relates to Pt aggregation due to lack of Pt anchoring sites and inhomogeneous Nafion distribution in the catalyst layer can be easily solved by this approach. Since PBI easily interacts with graphitized surfaces and hydrophilic groups like –COOH and –OH, PBI wrapping can be applied to different types of CBs and thereby able to solve problem associated with each type of CBs. Most importantly it was found that PBI wrapping worked as micropore blocking agent, preventing Pt nanoparticle deposition into small pores of porous CBs like Vulcan and ketjen black. On the other hand PBI wrapping is advantageous on highly graphitized CB like acetylene black by providing Pt binding sites. Therefore, PBI wrapping is helpful in extending Nafion/Pt interface in the catalyst layer. Furthermore, it is found that PBI wrapping provided well stable catalyst ink condition due to favorable interaction between Nafion and PBI as well.

In addition, the porous structure of the catalyst layer is highly import to facilitate effective O₂ diffusion and proper water management within the catalyst layer. Nafion amount present in the catalyst layer determines the porosity and relative conductivity. The higher the amount of Nafion the lower the relative conductivity and porosity. Therefore, MEA operating with lower amount of Nafion is highly recommended. It is realized that smaller amount of Nafion is sufficiently enough for the proton conduction in the catalyst layer due to the interaction between Nafion and PBI. Therefore, porosity and relative conductivity of catalyst layer are extremely encouraging for mass diffusion due to this PBI wrapping method. All together PBI wrapping method is really useful in well balanced O₂ diffusion and proton conduction and as well as proper water management in the catalyst layer. Therefore, feasibility of fabrication of thinner catalyst layers with low Pt loading is high. Finally, incorporation of Pt core-shell method is highly recommended under optimized conditions in this study to achieve Pt utilization with DOE targets. Altogether PBI wrapping enables fabrication of highly efficient, durable and cost effect fuel cell catalyst layers.

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Chapter 6

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