

Catalyst Interface Control for Reducing Cathode Overpotential in Proton Exchange Membrane Fuel Cell

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Catalyst Interface Control for Reducing Cathode Overpotential in Proton Exchange Membrane Fuel Cell

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Table of Contents

Chapter 1	6
Background of the study	6
1.1 Environmental issues with energy sources.....	6
1.1.1 Introduction of fuel cell.....	8
1.1.2 Types of fuel cells and their applications.....	9
1.2 Proton exchange membrane fuel cell (PEMFC)	10
1.2.1 Principles and mechanisms	10
1.2.2 Main components in PEMFC	12
1.2.2.1 Gas diffusion layer (GDL)	12
1.2.2.2 Polymer exchange membrane (PEM).....	13
1.2.2.3 Catalyst layer (CL)	14
1.2.2.4 Electrode catalyst	14
1.2.2.5 Ionomer (binder)	17
1.3 Main problems in the catalyst layer of PEMFC	19
1.3.1 Durability of electrode catalyst	19
1.3.2 Pt utilization and overpotential in cathode	21
1.3.3 Catalyst layer structure	23
1.4 Polybenzimidazole (PBI) wrapping technology in PEMFC	24
1.5 Carbon surface modification	26
1.6 Objectives of this study	28
1.6.1 Strategy 1: PBI wrapping acetylene black (AB)	28
1.6.2 Strategy 2: Electroactive polymer of S-PEDOT	30
1.6.3 Strategy 3: Ionomer-free catalyst	31
1.6.4 Strategy 4: ionomer adsorption behavior on catalyst surface.....	34
1.7. Overview of this dissertation.....	35
References	38
Chapter 2	49
Effect of polymer-coating on acetylene black for durability of polymer electrolyte membrane fuel cell	49
2.1. Introduction	49
2.2. Experimental	52
2.2.1. Materials.....	52

2.2.2. Material characterization.....	53
2.2.3. Fabrication of MEA and fuel cell measurements.....	53
2.2.4. Durability test in half-cell condition	54
2.3. Results and discussion.....	56
2.3.1. Preparation of the catalysts.....	56
2.3.2. Durability test.....	59
2.3.3. Analysis of the catalyst after ADT	65
2.4. Conclusion.....	69
References	70
Chapter 3	76
Creating Electron Conductive Polymer-Coated Carbon Catalysts to Reduce Overpotential in Polymer Electrolyte Membrane Fuel Cell.....	76
3.1. Introduction	76
3.2. Experimental	77
3.2.1. Materials.....	77
3.2.2. Material characterization.....	78
3.2.3. Preparation of CB/S-PEDOT composite and CB/S-PEDOT/Pt catalyst.....	79
3.2.4. Fabrication of MEA	80
3.2.5. Fuel cell measurements	81
3.3. Results and discussion.....	83
3.3.1. Material properties analysis.....	83
3.3.2. Electrical resistivity of the composites.....	85
3.3.3. Single Cell Measurements.....	86
3.4. Conclusion.....	92
References	94
Chapter 4	97
Development of Proton-conductive Carbon Support via Polymer Coating Method for Fuel Cell Electrocatalyst	97
4.1. Introduction	97
4.2 Experimental	99
4.2.1. Materials.....	99
4.2.2. Material Characterization.....	100
4.2.3. Preparation of CB/PBI-PS/Pt catalysts.....	101

4.2.4. Fabrication of MEA and Fuel Cell Measurements.....	101
4.2.5. Single-cell measurements.....	102
4.3. Results and Discussion.....	103
4.3.1 Material properties analysis.....	103
4.3.2 Electrical resistivity of the composites.....	107
4.3.3 Single Cell Measurements.....	108
4.4. Conclusion.....	114
References	115
Chapter 5	116
Effect of alcohol content on the ionomer adsorption of polymer electrolyte membrane fuel cell catalysts	116
5.1. Introduction	116
5.2. Experimental	120
5.2.1. Materials.....	120
5.2.2. Material characterization.....	121
5.2.3. Preparation of CB/PBI/Pt	122
5.2.4. Adsorption isotherm.....	123
5.2.5. Preparation of inks	124
5.2.6. Membrane electrode assembly (MEA) preparation	124
5.2.7. Fuel cell operation.....	124
5.3. Results and discussion.....	125
5.3.1. Ionomer adsorption on CB and CB/Pt.....	125
5.3.2. Ionomer adsorption on the CB/PBI and CB/PBI/Pt.....	135
5.3.3. Ink coating.....	141
5.3.4. Fuel cell study using CB/Pt as the catalyst	143
5.3.5. Fuel cell study using CB/PBI/Pt as the catalyst	147
5.4. Conclusion.....	152
References	153
Chapter 6	160
Conclusions and perspectives.....	160
6.1. Summary of the dissertation.....	160
6.2. Perspective	164
6.3. Future work	165

6.3.1 Future work 1	165
6.3.2 Future work 2	166
Chapter 7	167
Acknowledgements	167

Chapter 1

Background of the study

1.1 Environmental issues with energy sources

The growing global demand for energy has led to significant environmental challenges, primarily driven by the heavy reliance on fossil fuels such as coal, oil, and natural gas. The combustion of these fuels releases large amounts of greenhouse gases (GHGs), particularly carbon dioxide (CO₂) (**Figure 1-1**), contributing to climate change, air pollution, and adverse health effects ¹. Furthermore, the extraction, transportation, and processing of fossil fuels can lead to

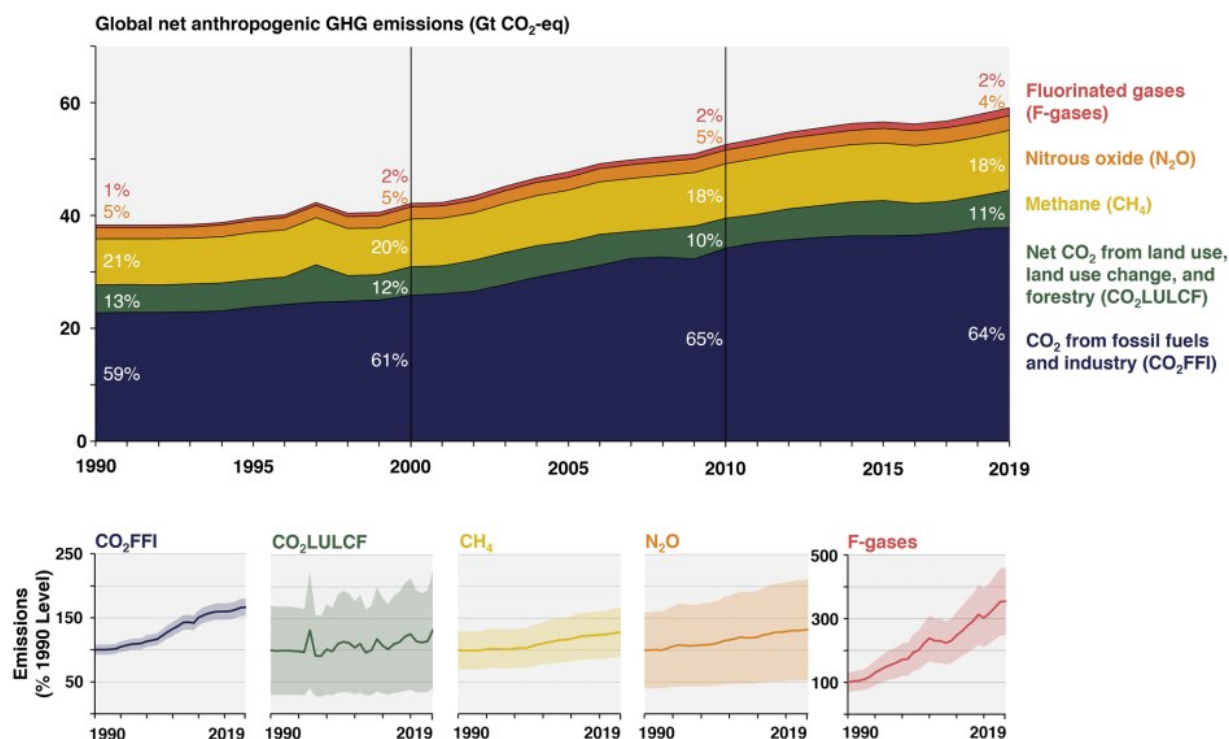


Figure 1-1 Global greenhouse gas overview. Source: Data taken from IPCC (2022)

habitat destruction, water pollution, and other environmental hazards ^{2,3}. To mitigate these issues, the shift toward sustainable energy technologies, including renewable sources and clean energy systems like fuel cells, has become imperative ⁴.

Fuel cells represent a promising solution to address these challenges, offering high energy efficiency, zero or low emissions, and versatility in various applications^{5,6}. Their ability to operate on hydrogen (H₂), which can be produced from renewable resources, positions them as a key technology for a sustainable energy future.

1.1.1 Introduction of fuel cell

Over the past two centuries, numerous battery types have been developed and commercialized. The Leclanché cell and lead-acid accumulator, initially introduced, are still in use today. D. Ilic et al. have provided a comprehensive summary of the evolution of commercially available batteries over the last fifty years, with a brief history of batteries presented in **Table 1-1**⁷. In these years, the concept of the fuel cell dates back to 1839 when Sir William Grove demonstrated its principles⁷. Despite this early discovery, practical development was delayed until the mid-20th century, when NASA utilized fuel cells in space missions for electricity and water production.

Table 1-1. History of battery. Taken from ref. 7.

Time	Inventor	System	Remark
1800	Volta	Volta column	First battery. Unit 'Volt' named after A. Volta
1839	Grove	Fuel cell (H_2/O_2)	First fuel cell
1868	Leclanché	Manganic	Primary
1902	Jungner	Nickel–cadmium	Rechargeable
1912		Alkalimanganic	Primary
1960s		Lithium	Primary
1980s	Goodenough (AEA technology)	$LiMeO_2$ (rocking chair principle)	Lithiated metal oxide
1989	SONY	Lithium ion	First lithium ion battery
1991		Nickel-metal hydride	Series production
1991		Lithium ion	Series production
1994	Bellcore	Polymer lithium ion	Main patent. latest battery technology.

Fuel cells are electrochemical devices that convert chemical energy into electrical energy through a controlled oxidation-reduction process⁸. Unlike conventional power generation methods, fuel cells emit only water as byproduct, so there are no carbon dioxide emissions and no air pollutants that create smog and cause health problems at the point of operation, making them an environmentally friendly alternative.

1.1.2 Types of fuel cells and their applications

In contrast to batteries, which store energy internally, fuel cells require a continuous supply of fuel and an oxidant (usually oxygen) to function. Fuel cells are classified into several types based on the electrolyte used, including Alkaline Fuel Cells (AFC), Proton Exchange Membrane Fuel Cells (PEMFC), Direct Methanol Fuel Cells (DMFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), and Solid Oxide Fuel Cells (SOFC). The most used fuels

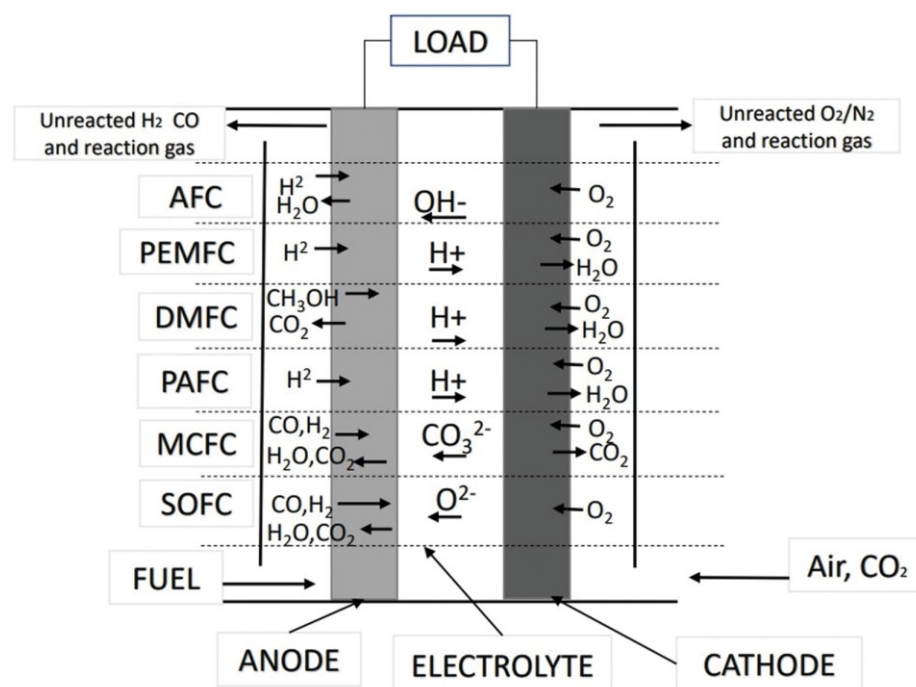


Figure 1-2 Components and reactions in fuel cells. Taken from ref 8.

in fuel cells are H_2 , methanol, and ethanol. H_2 and other hydrocarbon fuels are known to store significantly more chemical energy than conventional battery materials. **Figure 1-2** illustrates the various reactions and processes occurring in different types of fuel cells ^{8,9}.

Due to their high energy conversion efficiency and versatility in various applications, including transportation, material handling, stationary systems, portable devices, and emergency backup power, fuel cells are positioned at the forefront of clean energy innovations ¹⁰⁻¹². Among these, PEMFC stand out for their role in advancing sustainable transportation and portable power, addressing key environmental challenges associated with traditional energy sources ¹³.

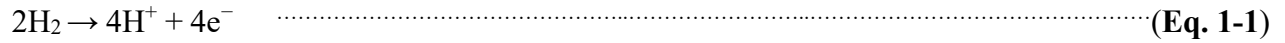
1.2 Proton exchange membrane fuel cell (PEMFC)

H_2 is the most abundant chemical substance in the universe, making it available for various applications. Hence, Proton Exchange Membrane Fuel Cell (PEMFC) is the most promising fuel cell candidate because H_2 as a fuel.

1.2.1 Principles and mechanisms

In PEMFC, electricity is generated through an electrochemical reaction that occurs when H_2 reacts with oxygen (O_2). As shown in **Figure 1-3**, H_2 is delivered to the anode side of the fuel cell, where it undergoes catalytic splitting into protons (H^+) and electrons (e^-). This hydrogen oxidation reaction (HOR) is represented by:

At the anode:



The H^+ generated at the anode permeate through the proton-conducting membrane to the cathode side, while the electrons travel through an external circuit to the cathode side, thus generating the fuel cell's current output. Simultaneously, O_2 is supplied to the cathode side, where it reacts with the H^+ that have permeated through the polymer electrolyte membrane and the electrons that have traveled through the external circuit, resulting in the formation of water molecules. This oxygen reduction reaction (ORR) is represented by:

At the cathode:

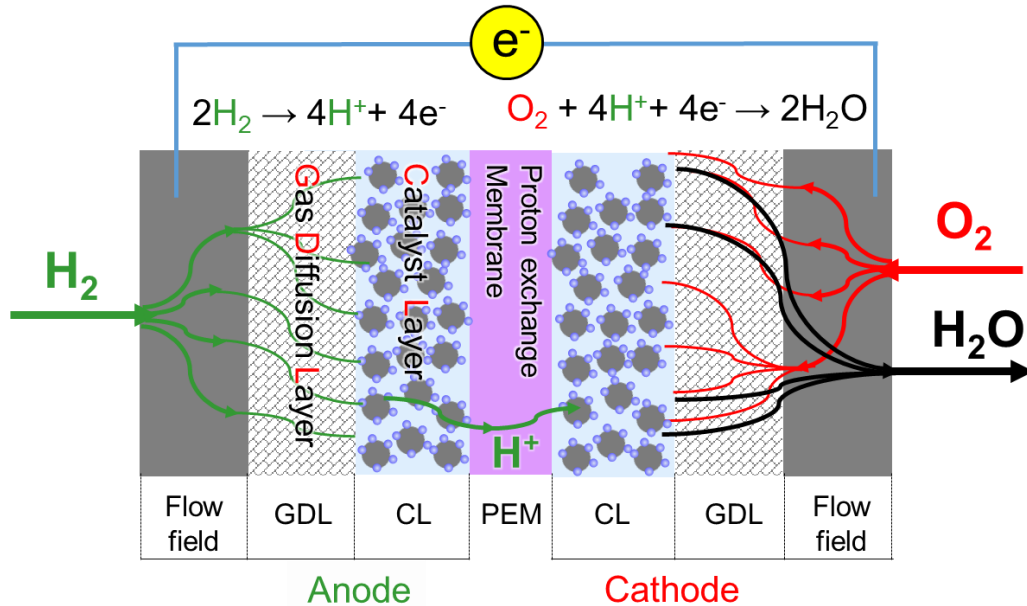
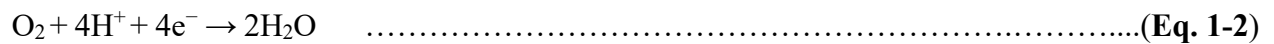


Figure 1-3 Working principle and structure of PEMFC.

The overall reaction of the PEMFC is the combination of these two half-reactions, where H_2 and O_2 react to produce water, releasing electrical energy in the process ^{14 15}.

1.2.2 Main components in PEMFC

PEMFC consist of several key components that work together to convert chemical energy into electrical energy. These components include:

1.2.2.1 Gas diffusion layer (GDL)

The Gas Diffusion Layer (GDL) serves several essential roles in the operation of a PEMFC.

Figure 1-4 showcasing the main components of a PEMFC ¹⁶, including the GDL. GDL facilitates the uniform supply of reactant gases (H_2 to the anode and O_2 to the cathode) to the catalyst layers

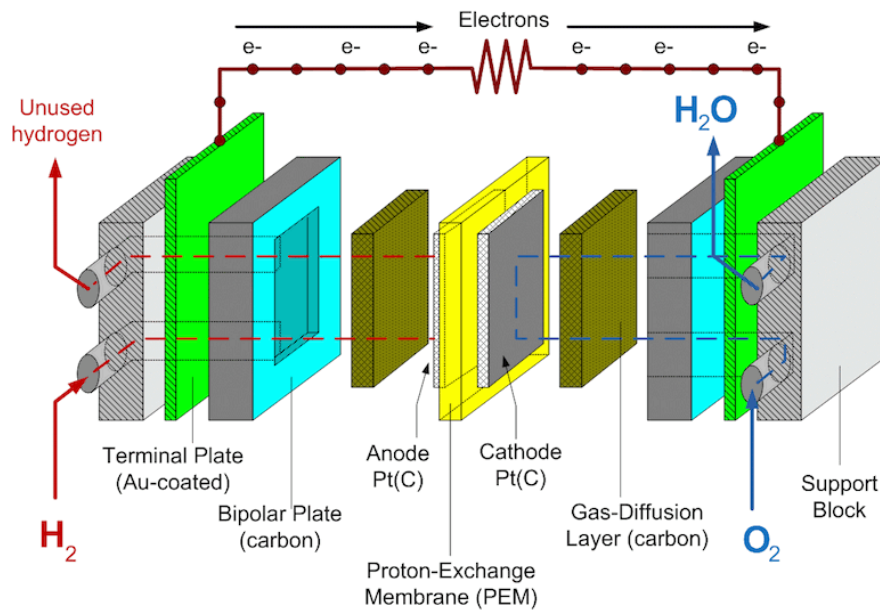


Figure 1-4 The main components of a PEMFC. Taken from ref. 16.

and efficiently evacuates liquid water generated during the electrochemical reactions on the cathode side. Additionally, the GDL collects the produced current, provides thermal conductivity, and offers mechanical support to the catalyst layer. The GDL is typically made of carbon-based materials ¹⁷, such as carbon paper or carbon cloth, and is treated to improve its hydrophobicity to prevent flooding in the fuel cell ¹⁸.

1.2.2.2 Polymer exchange membrane (PEM)

The Polymer Electrolyte Membrane (PEM) is the central component of the PEMFC, separating the anode and cathode while allowing H^+ to pass through from the anode to the cathode (**Figure 1-3**). The PEM is typically made from a proton-conductive polymer, such as Nafion¹⁹, with perfluorinated backbones and sulfonated side-chains, which maintains high proton conductivity at low temperatures (below 100°C) and under operating conditions²⁰. The chemical structure of Nafion is shown in **Figure 1-5** (a). The membrane's primary function is to provide a conductive medium for H^+ while preventing the direct mixing of H_2 and O_2 . However, Nafion membranes exhibit limitations, such as reduced ionic conductivity under low humidity and high-

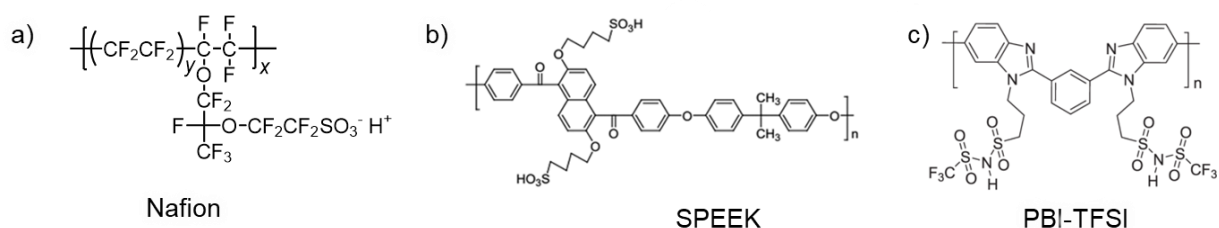


Figure 1-5 Chemical structure of (a) Nafion, (b) SPEEK and (c) PBI-TFSI.

temperature conditions, which hinder their widespread commercialization. To overcome these challenges, alternative proton-conducting membranes have been developed, such as the PEM of sulfonated poly(ether ether ketone) (SPEEK) (**Figure 1-5 (b)**)²¹ and Trifluoromethanesulfonylimide-grafted polybenzimidazole (PBI-TFSI)²² (**Figure 1-5 (c)**) to improve the proton conductivity.

1.2.2.3 Catalyst layer (CL)

The Catalyst Layer (CL) is one of the most critical components in a PEMFC, as it is the site where key electrochemical reactions take place²³. It comprises fine particles of catalyst (typically platinum or platinum alloys) dispersed on a carbon support^{24, 25}. The catalyst accelerates the oxidation of H₂ at the anode and the reduction of O₂ at the cathode. By incorporating a proton exchange membrane (PEM) sandwiched between two CLs, a membrane electrode assembly (MEA) is formed, enabling the efficient electrochemical conversion of chemical energy into electrical energy (**Figure 1-3**).

1.2.2.4 Electrode catalyst

The performance of the PEMFC is strongly influenced by the quality and quantity of the electrode catalyst, as it determines the efficiency and longevity of the fuel cell. Platinum (Pt) is widely regarded as the most effective electrode catalyst for both the anode and cathode in PEMFC

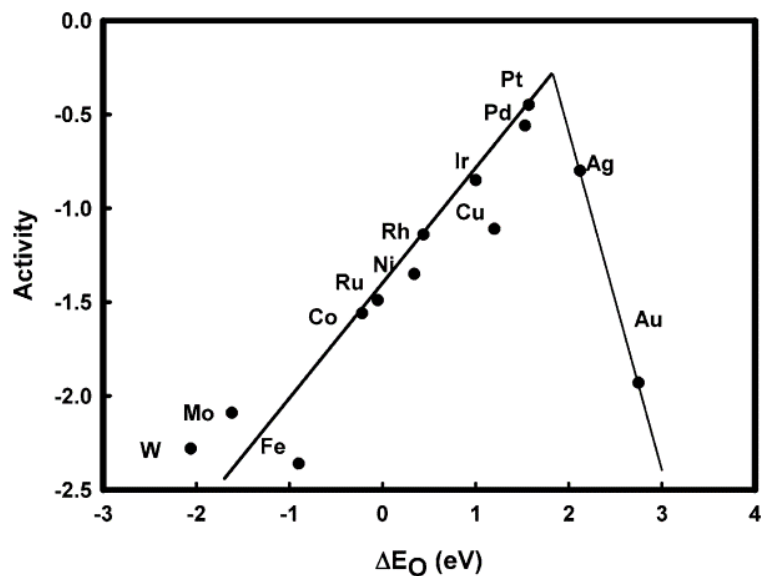


Figure 1-6 Oxygen reduction activity trends of different metals plotted as a function of the oxygen binding energy as a catalyst. Taken from ref. 27.

²⁶. The volcano plot shown in **Figure 1-6**, demonstrates that Pt outperforms other metals as a catalyst ²⁷. For the ORR, despite extensive research aimed at developing alternative catalyst materials, such as Pt alloys, several issues persist that limit their performance and widespread application in PEMFC. These problems include:

(1) Reduced stability:

Pt alloys often suffer from reduced long-term stability compared to pure Pt. The alloying elements can lead to catalyst degradation over time due to leaching, sintering, or corrosion, especially under the harsh operating conditions of PEMFCs, such as high temperature and acidic environments ²⁸.

(2) Lower activity for oxygen reduction reaction (ORR):

While Pt alloys can enhance some properties (e.g., cost reduction), they often exhibit lower catalytic activity for the oxygen reduction reaction (ORR) compared to pure Pt as shown in **Figure 1-6**. The electronic properties and bond strength of the active sites in the alloys may not be as optimal as those of Pt, leading to slower reaction kinetics and reduced.

(3) Surface structure changes:

Pt alloys can undergo changes in their surface structure during operation, which can affect the catalytic sites and their efficiency ²⁹. For example, surface segregation of the alloying metals may occur under fuel cell operating conditions, leading to a loss of active sites or reduced catalytic activity ^{30 31}.

Overall, Pt remains the best choice as an ORR catalyst to date. However, its scarcity and high cost limit its widespread application. Toyota's Mirai, officially launched in Japan on December 15, 2014, is the first mass-produced fuel cell vehicle (FCV). Due to the high cost of the Pt-based catalyst, global sales have only surpassed 9,000 units after more than five years. One of the main reasons for the high price of the Mirai is the high loading of Pt-based electrocatalysts in the fuel cell stack ^{32 33}. Therefore, achieving high cell performance while enhancing Pt utilization to reduce costs is essential.

In addition, the CL must have a high surface area to provide sufficient reaction sites for these processes. The commonly used carbon supports in PEMFC are carbon black (CB)³⁴, such as medium surface area carbons like Vulcan XC-72R and Acetylene black (AB), porous carbons like Ketjen black (KB), and mesoporous carbons like CNovel, which offer high surface areas. An ideal catalyst should consist of Pt metal that is homogeneously distributed with consistent particle size on the carbon support surface to achieve maximum reaction efficiency^{35, 36}.

1.2.2.5 Ionomer (binder)

In the CL, in addition to the electro catalyst, another essential material is the ionomer (binder), which plays a crucial role as the proton-conducting material and helps to bind the catalyst particles together in the CL. Nafion or similar ion-conducting materials are often used. To achieve high performance, the ionomer amount in the triple-phase boundary (TPB) significantly affects the electrode kinetics as shown in **Figure 1-7** (a). Because the ionomer needs to have (1) the maximum interface of ionomer to carbon ratio (I/C) for both anode and cathode gas reactions, (2) the appropriate pore structure to allow gas diffusion and water dissipation, and (3) optimized ionomer networks that bind the carbon aggregates together, providing structural integrity for the CL, and proton conduction path. As shown in **Figure 1-7** (b) at a low ionomer content, the carbon-supported Pt (CB/Pt) is partially covered by ionomer; thus, only a small fraction of Pt will be in contact with the ionomer, providing poor connectivity and therefore inducing a higher resistance

to the proton flow in the catalyst layer. When there is too much ionomer, the ionomer tends to form an agglomerated particle in contact with CB/Pt, which then becomes a significant O_2 diffusion barrier decreasing the cell performance (**Figure 1-7 c**). At the optimal ionomer content, nearly all CB/Pt are covered by ionomer, thus leading to a larger electrochemically active area (**Figure 1-7 d**). Therefore, it is important to control the catalyst surface to optimize the CL, thereby achieving high cell performance in PEMFC.

It is believed that the optimized combination of all these components enables PEMFC to operate efficiently and effectively, making them a promising technology for clean energy applications.

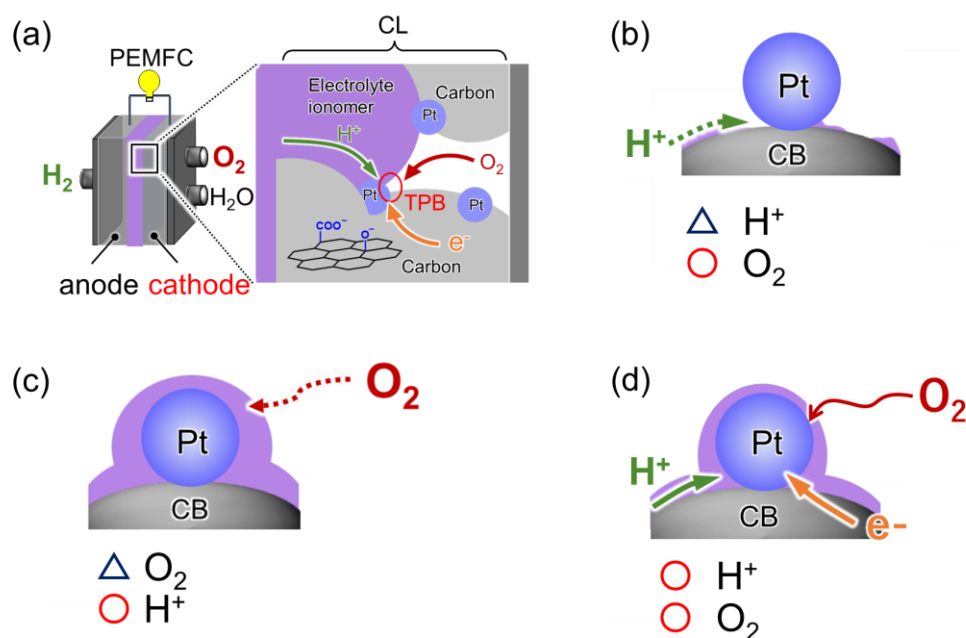


Figure 1-7 The schematic diagram of (a) triple-phase boundary (TPB) in CL, marked in a red circle at CL part illustrate, and the predicated nanostructure models with different ionomer content of (b) low ionomer content, (c) high ionomer content, (d) optimal ionomer content. (purple– ionomer, blue circle – Pt particle, gray – carbon black (CB))

1.3 Main problems in the catalyst layer of PEMFC

1.3.1 Durability of electrode catalyst

Notably, CL composed of CB/Pt and ionomer, plays a crucial role in defining both the durability and activity of PEMFC ³⁷. Improving durability while enhancing activity has been a central focus of research and development in PEMFC technology. Efforts have primarily concentrated on optimizing the interfacial structures within the CL, such as carbon–Pt, Pt–ionomer, and Pt–gas phase interfaces ³⁸.

A major challenge in maintaining the Pt interfacial structure during PEMFC operation arises from the high reactivity and significant surface energy of Pt nanoparticle ³⁹. These properties promote four key degradation mechanisms: (1) nanoparticle agglomeration caused by Pt migration (2) Ostwald ripening, where Pt nanoparticles grow in size through a dissolution-redeposition process during redox cycling, (3) detachment from carbon support, and (4) dissolution and precipitation ($\text{H}_2 + \text{Pt}^{2+} \rightarrow \text{Pt} + 2\text{H}^+ + 2\text{e}^-$) (**Figure 1-8**) ^{40, 41}. These phenomena lead to the loss of Pt interfacial area and deteriorate the PEMFC performance. Furthermore, the stability of carbon

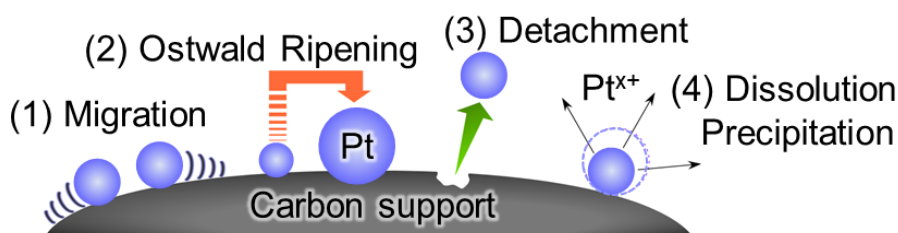


Figure 1-8 Degradation of Pt catalyst in PEMFC (blue circle – Pt particle, gray – carbon support).

supports is critical for enhancing Pt stability since carbon corrosion catalyzed by Pt also takes place at a high potential (typically above 1.0 V). This corrosion can lead to Pt detachment and subsequent nanoparticle agglomeration ^{42, 43}.

Therefore, the use of durable carbon supports resistant to oxidation is essential for enhancing PEMFC durability ⁴⁴. Since sp^2 carbons are more thermodynamically stable than sp^3 carbons during oxidation ⁴⁵, the use of highly graphitized carbons such as carbon nanotube (CNT) have been investigated to employ and it is proved that the use of such carbons mitigates the Pt agglomeration and thus enhance the PEMFC durability ⁴⁶. However, the lack of anchoring sites for Pt deposition on graphitized carbon surfaces, such as -OH and -COOH connected on sp^3 carbons make the uniform deposition of Pt nanoparticles rather difficult ⁴⁷, and inferior to the effective utilization of Pt. Additionally, the weak interaction between graphitized carbon surfaces and Pt nanoparticles often leads to Pt sintering ^{47, 48}, thus highlighting the need to strengthen the Pt-carbon interfacial bond to enhance Pt stability. While a common strategy to introduce anchoring sites on highly graphitized carbons is to oxidize the surface through harsh chemical or physical treatments, such oxidation tends to introduce sp^3 sites ⁴⁹, such oxidation resulted in the decrease of the durability of carbon supports.

1.3.2 Pt utilization and overpotential in cathode

As PEMFC employ expensive Pt catalysts, high costs remain a barrier for PEMFC commercialization⁵⁰. To reduce the cost of PEMFCs, it is essential to improve Pt utilization efficiency, thus minimizing the amount of Pt required^{51 52}. A key factor influencing Pt utilization efficiency is the structure of the Pt interface, especially at the cathode, where protons and electrons are delivered through an ionomer and an electron-conductive carbon support, respectively, whereas O₂ is delivered through the porous network as explained in **section 1.2.1.5**.

In addition, the overpotential problem at the cathode arises due to the complex interactions at these interfaces, where both the Pt surface and the porous network structure within the CL play crucial roles in determining overall cell performance. **Figure 1-9** (a) shows a polarization curve of a PEMFC illustrates various losses, representing different sources of overpotentials, it's knowing that the theoretical voltage of a single cell is 1.23 V, but the equilibrium voltage drops to 1.17 V due to the effects of temperature, pressure, and operating conditions. During the electrochemical

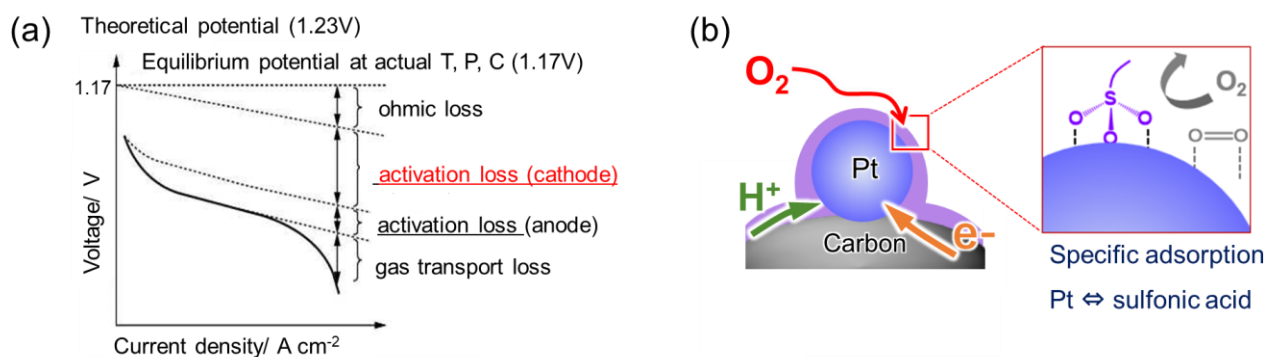


Figure 1-9 (a) The polarization curve of a PEMFC illustrates various losses, representing different sources of overpotentials (b) Specific adsorption between Pt and sulfonic acid group of the ionomer.

reaction, various losses arise, including ohmic loss, which results from issues with proton conduction (**Figure 1-7 (b)**), gas transport loss, mainly caused by the high surface resistance of oxygen reaching the catalyst surface (**Figure 1-7 (c)**). However, the most significant contributor to overpotential is cathode activation loss. This occurs because the reaction at the TPB in the cathode catalyst layer is the rate-limiting step, which greatly affects the reaction rate and the overall performance of the PEMFC.

Furthermore, as shown in **Figure 1-9 (b)**, sulfate anions⁵³ or sulfonic acid groups in ionomers^{54, 55} strongly adsorb on the Pt surface and acts as barriers for O₂ permeation, resulting in increased overpotentials at the cathode^{56, 57}. Therefore, even if the ionomer content is optimized, the presence of ionomers on Pt catalysts inevitably causes overpotentials. Therefore, both the interfacial structure at Pt and the porous network structure in the CL play significant roles in the efficiency. At high current densities, large fluxes of protons and O₂ are indispensable for reactions; therefore, a combination of long-range proton conduction paths with a porous network for O₂ diffusion is highly important⁵⁸⁻⁶⁰.

1.3.3 Catalyst layer structure

To control the structure of the CL, including the distribution of its ionomers and pores, is critically influenced by the composition of the Pt/C, dispersion with ionomer, commonly referred to as “ink,” as well as the casting conditions employed during CL fabrication⁶¹. In addition to the I/C parameter mentioned earlier, the type of solvents used in the ink significantly influences PEMFC performance⁶²⁻⁷⁰. Specifically, binary mixtures of water and alcohols, such as methanol, ethanol, isopropyl alcohol, and 1-propanol, have been widely investigated to optimize the properties of the ink.^{64, 69, 71-74}. Moreover, the amount of ionomer adsorbed onto Pt/C, and its adsorption morphology depend on the solvent system, which in turn influences the distribution of the ionomer⁶⁴, 3D porous structure⁶⁸, microscale voids⁶⁹, and millimeter-scale cracks⁶² in the CL, which affect the PEMFC power density. Therefore, the ionomer morphology in the bulk solution plays a crucial role in determining the morphology of Pt/C, and the distribution of ionomer within the CL⁶⁴. As depicted in **Figure 1-10** (a), an uneven ionomer distribution within the CL

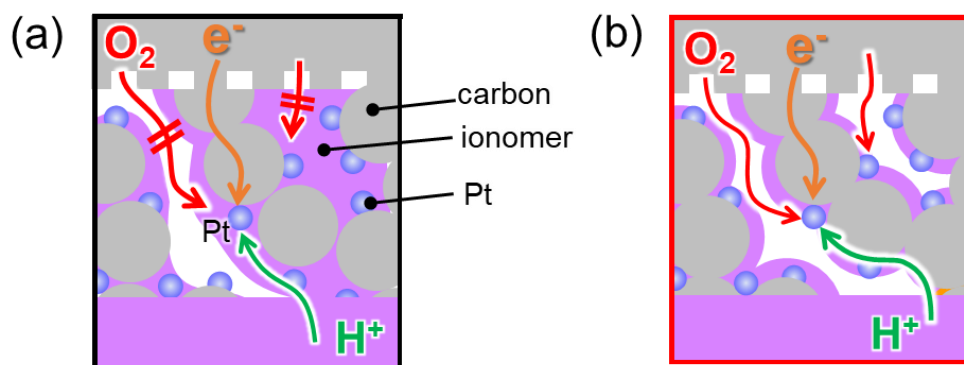


Figure 1-10 (a) Inhomogeneous ionomer distribution in the CL, (b) an ideal CL structure with uniform ionomer distribution. (purple– ionomer, blue circle – Pt particle, gray – carbon black (CB))

hinders the simultaneous access of hydrogen and oxygen to the reaction sites, leading to a significant reduction in Pt utilization. In contrast, an ideal CL structure, shown in **Figure 1-10 (b)**, exhibits a uniform ionomer coating, allowing nearly all Pt reaction sites to be utilized efficiently.

Several studies have highlighted that ionomer (Nafion) adsorption is influenced by the alcohol content in the inks. In water or water-rich solvents, Nafion's backbone tends to adsorb onto the carbon surface of carbons or Pt/C due to hydrophobic interactions, causing the $-\text{SO}_3\text{H}$ groups to orient outward^{75, 76}. This behavior has been demonstrated in multiple studies that systematically explore the relationship between Nafion morphology in the ink, its adsorption morphology on Pt/C, and the resulting CL performance as a function of alcohol content^{64, 69, 72-74}. However, a comprehensive and quantitative analysis of Nafion adsorption onto carbons or Pt/C based on solvent composition remains to be conducted.

In conclusion, the challenges related to catalyst durability, overpotential issues, and CL structure have contributed to suboptimal PEMFC performance. Consequently, there is a critical need to develop new catalysts and design innovative CL structures to improve cell performance.

1.4 Polybenzimidazole (PBI) wrapping technology in PEMFC

To address the issues in the CL of PEMFCs discussed above, the application of polybenzimidazole (PBI) wrapping onto carbon black (CB) is being considered. The structure of PBI is showing in **Figure 1-11 (a)**. PBI offers advantages, including favorable interactions with

the graphitic surface and functional groups (-COOH, -OH) of CB ⁷⁷ which facilitate the formation of a stable coating layer on the CB surface. This coating also promotes strong interaction with Pt nanoparticles through coordination bonding, enhancing the overall catalyst performance. (**Figure 1-11 b**)^{78, 79}. Additionally, PBI is stable under strong acidic conditions, making it suitable for use in PEMFC systems, where such conditions are typically present ⁸⁰.

According to previous reports, it was observed that PBI preferentially coated the outer surface and the interior of the mesopores of CB. This resulted in a significant reduction in the micropore surface area after PBI wrapping. This reduction suggests that, following the PBI coating, the micropore surface either became capped or filled by PBI, making it unavailable for further interactions. A key phenomenon noted in this process is the reduction of the microporous surface area due to the PBI wrapping ⁷⁷. Additionally, PBI is coated on the pristine (non-oxidized) surface of highly graphitized CNTs without causing oxidation of the CNTs ⁸¹. In fact, it was reported that PEMFCs using PBI-coated CNTs as a carbon support demonstrated excellent durability during accelerated durability tests (ADT) between 1.0 and 1.5 V ⁸².

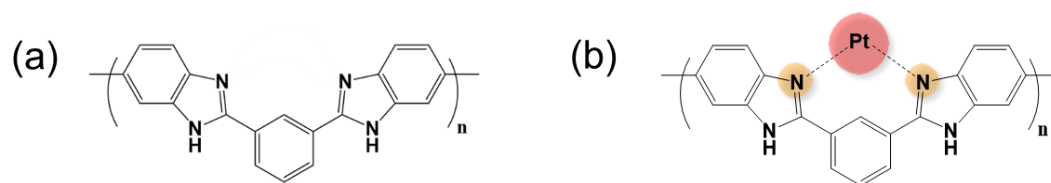


Figure 1-11 (a) Chemical structure of PBI and (b) binding sites for Pt.

Furthermore, the PBI wrapping on CB (Vulcan) allowed for a reduction in the optimal I/C ratio to 0.2 during MEA single-cell tests. We observed that a well-connected proton conduction network was formed even with such a low I/C ratio, due to the interaction between the ionomer and the carbon surface facilitated by the PBI wrapping method. Notably, the maximum power density of the Vulcan/PBI/Pt MEA at an I/C ratio of 0.2 was 23% higher than that of the Vulcan/Pt MEA at its optimized I/C ratio of 0.6 ⁸³.

1.5 Carbon surface modification

As discussed in the main problems in the catalyst layer of PEMFC (**section 1.3**), even if the ionomer content is optimized, the presence of ionomers on Pt catalysts inevitably causes specific adsorption with sulfate anions or sulfonate groups. To avoid these issues, in our previous study, we prepared proton-conductive carbon support, in which acid groups were grafted on the surface of carbon black (SCB) to afford surface proton conduction as shown in **Figure 1-12**. Then, these carbon support with Pt loaded on the surface (SCB/Pt) were tested as ionomer-free electrocatalysts

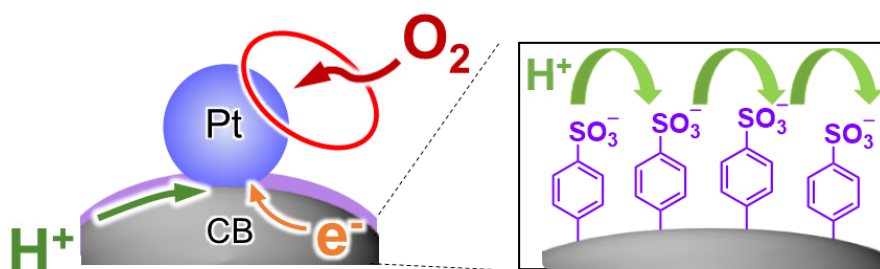


Figure 1-12 Schematic diagram of a proton-conductive carbon support with acid groups grafted onto the surface of CB.

for PEMFC⁸⁴. In this design, proton conduction paths are established on the carbon surface, eliminating the need for ionomers, which can help prevent Pt poisoning while also facilitating the formation of pore channels for efficient O₂ diffusion. However, the covalent modification of acid groups on the carbon surface disrupts the sp² carbon structure (**Figure 1-13**), which significantly reduces the thermal stability of the carbon black. Since thermal stability is closely linked to the electrochemical stability of PEMFCs, this modification poses a risk of compromising PEMFC durability. Additionally, the low proton conductivity of SCB increases activation overpotential, making the benefits of the ionomer-free structure at the Pt interface uncertain. Hence, additional improvements to the proton conductivity of the ionomer-free catalyst could potentially further

Chemical modification: radical addition reaction

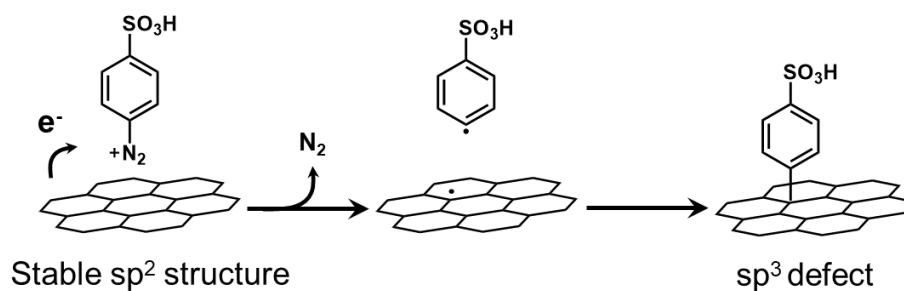


Figure 1-13 Chemical modification method of radical addition reaction.

increase the PEMFC performance but further investigation is needed.

1.6 Objectives of this study

The primary objective of this study is to reduce cathode overpotential in PEMFC by controlling the catalyst interface, hereby improving durability and enhancing the overall performance of the PEMFC system. The total context of this study can be separated into four main parts under four different strategies; (1) utilizing polybenzimidazole (PBI) coating to improve the stability and durability of the catalyst, (2) employing an electron-conductive polymer to reduce charge transfer resistance, (3) designing non-covalent acid-modified carbon to enhance proton conductivity, mitigate O₂ diffusion impedance, and prevent poisoning of the Pt surface by SO₃⁻ groups, thereby reducing overpotential and (4) evaluating the adsorption isotherms of ionomer onto CB and Pt composites in water-rich and alcohol-rich binary mixtures aims to gain insights into how ionomer adsorption behavior varies under different solvent conditions. This helps understand how the solvent composition affects the distribution and interaction of ionomers with the catalyst surface, which in turn influences the performance of PEMFC.

1.6.1 Strategy 1: PBI wrapping acetylene black (AB)

In previous study ⁸², oxidized-CNT was used as a comparison since direct Pt deposition onto the pristine CNT was rather difficult ⁸⁵. Additionally, the ADT protocol, designed to accelerate carbon degradation (1.0 – 1.5 V), was employed. Thus, we successfully demonstrated the advantage of the PBI wrapping to preserve inherent carbon durability but the effect of the PBI

wrapping for the Pt stability was not investigated. We also demonstrated that the PBI wrapping on Vulcan could enhance the durability of Vulcan-based PEMFC ⁸⁶ . However, in that research, PBI coating improved Vulcan stability mainly because the coverage of micropore of Vulcan decelerated the oxidation of the carbon surface during the ADT between 1.0 and 1.5 V. Therefore, the effect of PBI coating for the stability of Pt particles was not observed.

To clarify the effect of PBI wrapping for Pt stability and PEMFC durability, ADT between 0.6 and 1.0 V designed to study Pt stability was applied for the PEMFC having PBI wrapped carbons as a carbon support. Here, acetylene black (AB) was chosen as the carbon support since (1) AB shows high electrochemical stability due to their high crystallinity ⁵⁸ and Pt sintering triggered by the carbon corrosion during the ADT can be minimized and (2) direct Pt deposition

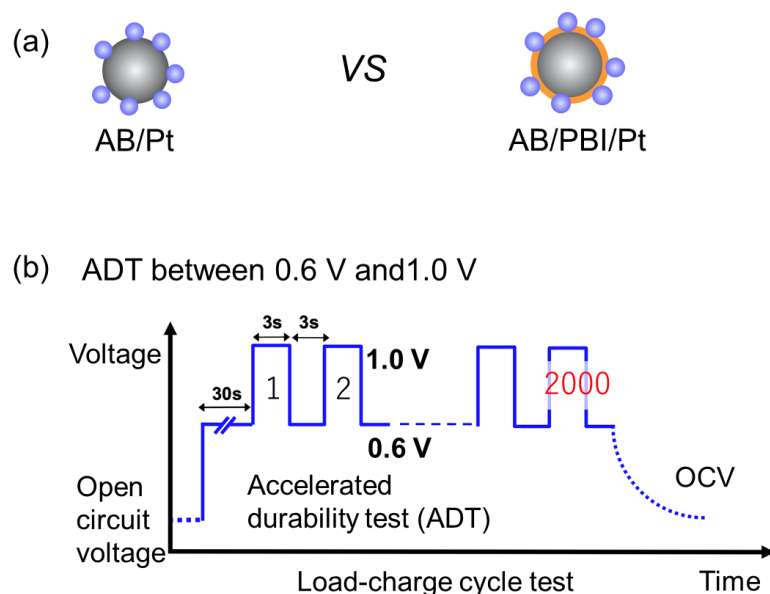


Figure 1-14 Schematics of (a) structure of conventional catalyst AB/Pt and PBI wrapped AB catalyst AB/PBI/Pt (b) ADT measurement condition.

on AB was possible ⁵⁸ and no oxidation pretreatment is necessary for the reference samples. The Pt catalysts deposited on PBI wrapped AB (AB/PBI/Pt) and AB (AB/Pt) were employed in MEA and subjected to ADT (**Figure 1-14 a**), and the loss of the MEA performance together with the changes of the catalyst structure were evaluated. As the ADT condition, the load-cycle protocol ⁸⁷ consists of rectangular potential cycles between 0.6 V– 1.0 V (**Figure 1-14 b**) was conducted to evaluate the stability of Pt with avoiding the degradation of carbon supports ⁸⁸. By comparing AB/Pt and AB/PBI/Pt under the ADT between 0.6 V and 1.0 V, judicial comparisons to clarify the role of PBI layer for Pt stability and PEMFC durability becomes possible.

1.6.2 Strategy 2: Electroactive polymer of S-PEDOT

Though the PBI wrapping on carbon surface generating a well-connected proton path and porous network for O₂ diffusion to the catalyst surface ^{83, 89}. However, one of the drawbacks of the PBI wrapping is slightly larger charge transfer resistance (R_c) due to the insulating PBI layer. Therefore, in this strategy (**Figure 1-15**), we employed electron conductive polymer to replace PBI. As the electron conductive polymer with ionomer interaction, we focused on the use of polythiophene grafted with sulfonic acid group (S-PEDOT). This polymer was developed by Okuzaki et al. ⁹⁰ as the advanced model of the conventional electron conductive polymer such as poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT: PSS) ⁹¹. For PEDOT:PSS, excess amount of PSS as the dopant of PEDOT often act as the insulator depending on their domain

structure⁹². Sulfonic acid in S-PEDOT was covalently grafted in PEDOT main-chain and act as the dopant. Therefore, higher conductivity can be expected independent on the nano phase structure. Because sulfonic acid group interact with PEDOT main-chain via charge transfer, similar interaction can be expected with sulfonic acid in Nafion ionomer. Thereby, homogeneous ionomer distribution can be expected for S-PEDOT similar with PBI.

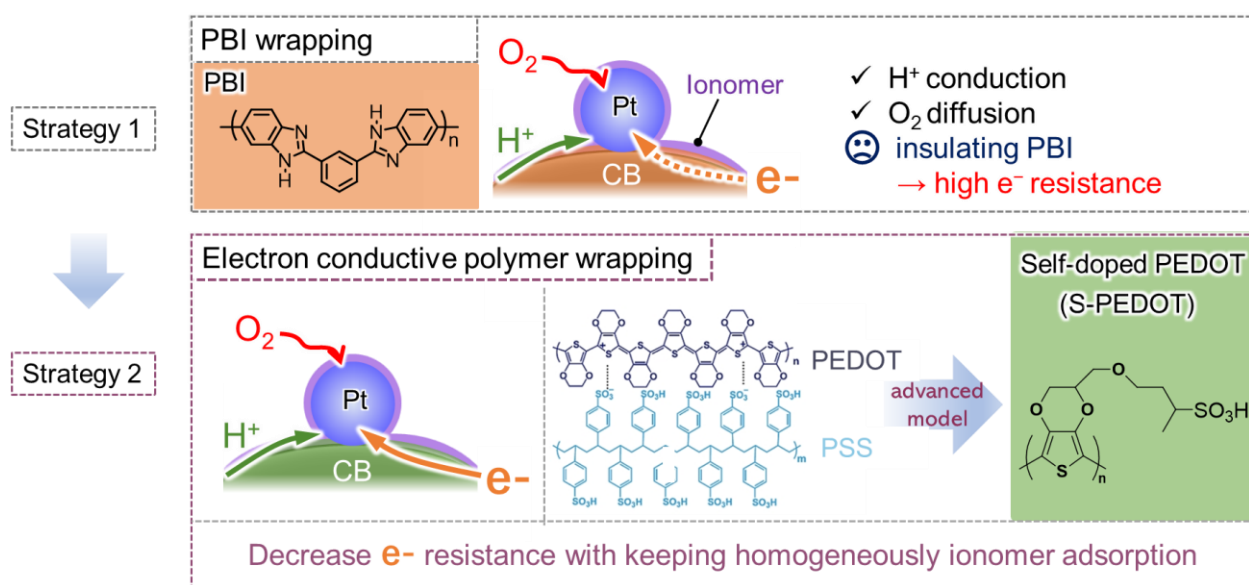


Figure 1-15 Problem of strategy 1 and overview of strategy 2

1.6.3 Strategy 3: Ionomer-free catalyst

Previously, we proposed an ionomer-free catalyst structure in which no ionomer is added to the CL. To achieve this, the carbon support surface was covalently modified with sulfonic acid groups to facilitate proton conduction in the cathode CL, and Pt was loaded onto this acid-modified

carbon black (SCB). Single-cell I-V measurements revealed that the absence of ionomer reduced O_2 diffusion overvoltage at high current densities, primarily due to decreased Knudsen diffusion resistance. However, the low proton conductivity of SCB increased activation overvoltage, rendering the ionomer-free structure's impact at the Pt interface unclear. Moreover, the covalent modification of acid groups on the carbon surface disrupted the sp^2 carbon structure, significantly reducing the thermal stability of the carbon black. Since thermal stability correlates with the electrochemical stability of PEMFCs, this approach risks compromising PEMFC durability. Therefore, developing a novel modification method to enhance the proton conductivity of acid-modified carbons without compromising the sp^2 structure is critical.

In strategy 3, we developed a non-covalent acid modification method. This approach employs polybenzimidazole (PBI) with acid functional groups as side chains, which are used to coat the carbon surface and introduce acid groups. PBI was chosen for its strong adsorption onto carbon

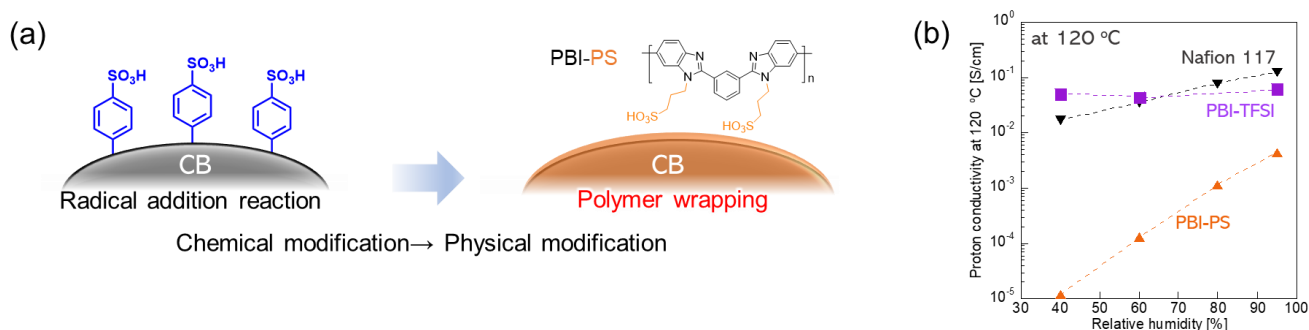


Figure 1-16 Schematics of (a) change the modification method from radical addition reaction to polymer wrapping (b) proton conductivity of Nafion, PBI-TFSI and PBI-PS depended on relative humidity, data taken from ref.22.

materials via non-covalent interactions and its exceptional thermal stability due to its rigid main-chain structure (**Figure 1-16 a**). Our recent research demonstrated that PBI grafted with trifluorosulfonimide (PBI-TFSI) exhibited excellent proton conductivity, especially at low humidity and high temperatures, attributed to the strong acidity of the TFSI group. However, we employed PBI grafted with sulfonic acid (PBI-PS) for its higher potential for hydrogen bonding with water molecules (**Figure 1-16 b**) ²². Although our previous study showed that PBI-PS membranes exhibited lower proton conductivity due to neutralization of the acid by the basic imidazole in the PBI main chain, they displayed greater water uptake compared to PBI-TFSI membranes. Consequently, we employed PBI grafted with sulfonic acid (PBI-PS) for its higher potential for hydrogen bonding with water molecules.

1.6.4 Strategy 4: ionomer adsorption behavior on catalyst surface

In strategy 4, we evaluated the adsorption isotherm of ionomer onto CB and their Pt composites in water-rich (80 wt% water) and alcohol-rich (13 wt% water) binary mixtures (**Figure 1-17 a**). As an alcohol, ethanol was chosen because of the easy evaporation at the practical fabrication process of MEA compared to the other alcohols having higher boiling point such as ethylene glycol. As the catalyst composites, Pt-loaded CB (CB/Pt) and Pt-loaded PBI wrapped CB (CB/PBI/Pt) were compared to study the effects of the alcohol contents on the interaction between ionomer and the surface of the carbon supports. The quantitative analysis of ionomer adsorption onto carbons or Pt/C in water evaluate by adsorption isotherm measurements ⁷⁵ (**Figure 1-17 b**).

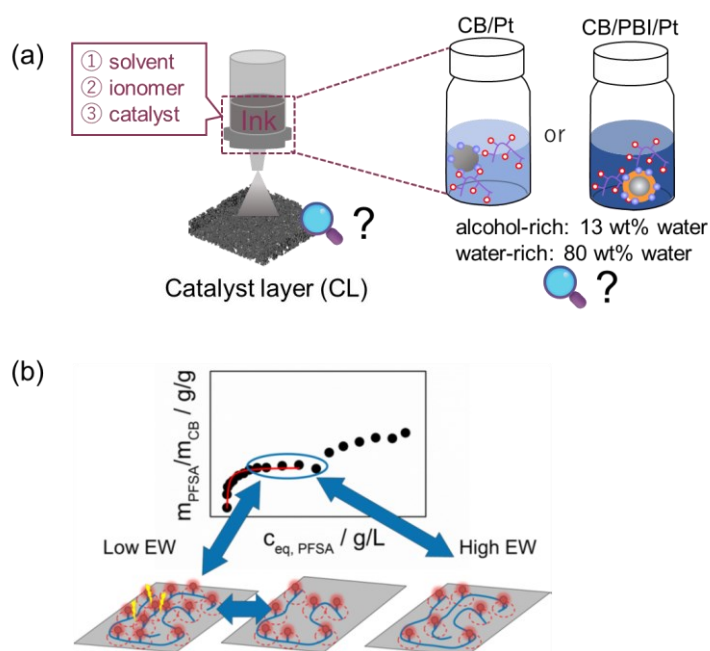


Figure 1-17 (a) overview of strategy 4, (b) quantitative analysis of ionomer adsorption onto carbons by adsorption isotherm measurements. Taken from ref.75.

The control of the interaction between the ionomers and catalyst composites is crucial in controlling the PEMFC performance.

1.7. Overview of this dissertation

This dissertation describes the methods of reduce cathode overpotential in PEMFC.

Chapter 1 outlines a brief introduction on importance, applications and working principle of fuel cells. This chapter highlights the main challenges in PEMFC systems, which primarily arise from the catalyst and catalyst layer. It further explores the primary causes of high overpotential in typical fuel cell cathodes. Finally, the chapter outlines four strategies aimed at reducing overpotential in the cathode by controlling the catalyst interface within the catalyst layer.

Chapter 2 outlines strategy 1. Comparison study PBI effect on durability by comparing the cell performance between PBI wrapped acetylene black (AB/PBI/Pt) and conventional catalyst AB/Pt. Characterizations of AB/PBI/Pt and AB/Pt using transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and X-ray diffraction spectroscopy (XPS) is discussed with procedures. The durability of AB/PBI/Pt and AB/Pt MEAs is investigated through fuel cell testing. Power density and Pt utilization values of AB/PBI/Pt are calculated and compared with AB/Pt to elucidate the mechanism of the PBI-wrapping method in enhancing catalyst durability.

Furthermore, XPS analysis is employed to detect ionomer loss after accelerated durability tests (ADT) for the AB/PBI/Pt and AB/Pt catalyst layers.

Chapter 3 outlines strategy 2. Preparation of electroactive polymer, polythiophene grafted with sulfonic acid groups (S-PEDOT), and its application as a wrapping material for carbon-supported Pt (CB/S-PEDOT/Pt) are discussed. The role of S-PEDOT wrapping in reducing charge transfer resistance is analyzed by comparing the performance of CB/S-PEDOT/Pt with conventional CB/Pt. The electrochemical resistance of CB/S-PEDOT/Pt is evaluated in both powder form and MEA in a single cell. Electrochemical surface area (ECSA) and power density values of CB/S-PEDOT/Pt are measured and compared with CB/Pt to understand the mechanism by which S-PEDOT wrapping improves charge transfer and lowers overpotential in PEMFC systems.

Chapter 4 outlines strategy 3. Development of ionomer-free catalyst with proton conductivity. Introduced acid group on carbon surface by using physical modification method which its exceptional thermal stability and evidenced by TGA. The cell performance of the ionomer-free catalyst is investigated and compared with conventional CB/Pt catalysts containing ionomer.

Chapter 5 outlines the strategy 4. Investigation on the effects of alcohol content in dispersion solvents are investigated using two binary mixtures composed of water and ethanol. Pt-loaded carbon black (CB) and Pt-loaded polymer-wrapped CB are used as catalyst composites to study the impact of alcohol content on the interaction between ionomer and the carbon support surface.

The amount of adsorbed ionomer is evaluated based on ^{19}F -NMR spectra, providing insights into solvent composition effects on ionomer adsorption behavior on catalyst surface and, ultimately, cell performance.

Chapter 6 explains the general summary of the thesis with perspectives on future works.

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Chapter 2

Effect of polymer-coating on acetylene black for durability of polymer electrolyte membrane fuel cell

2.1. Introduction

As discussed in **Chapter 1**, carbon-supported platinum nanoparticles (Pt/C) are commonly employed as electrocatalysts to promote hydrogen oxidation ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$) in anode and oxygen reduction ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$) in cathode. Catalyst layer (CL) composed of Pt/C and ionomer is a key component that determine the durability as well as the activity of the PEMFC ¹. Enhancing durability while boosting activity has driven research and development efforts in PEMFC, with a primary focus on optimizing the interfacial structures of Pt within the CL, including carbon–Pt, Pt–ionomer, and Pt–gas phase interfaces ².

One of the difficulty to retain Pt interfacial structure during PEMFC operation is arose from the high activity and large surface energy of the Pt nanoparticle ³, These properties promote four key degradation mechanisms: (1) nanoparticle agglomeration caused by Pt migration (2) Ostwald ripening, where Pt nanoparticles grow in size through a dissolution-redeposition process during redox cycling^{4,5}, (3) detachment from carbon support, and (4) dissolution and precipitation ($\text{H}_2 + \text{Pt}^{2+} \rightarrow \text{Pt} + 2\text{H}^+ + 2\text{e}^-$). These phenomena lead to the loss of Pt interfacial area and deteriorate the PEMFC performance. Furthermore, stability of carbon supports is also essential to improve Pt stability since carbon corrosion catalyzed by Pt also takes place at a high potential (mainly over

1.0 V), which triggers the detachment of Pt and subsequent agglomeration ^{6, 7}. Thus, the use of durable carbon supports against the oxidation is crucial to increase the PEMFC durability ⁸. Since it is known that sp^2 carbons are more thermodynamically stable than sp^3 carbons upon oxidation ⁹, the use of highly graphitized carbons such as carbon nanotubes (CNTs) have been investigated to employ and it is proved that the use of such carbons mitigates the Pt agglomeration and thus enhance the PEMFC durability ¹⁰. However, an absence of the anchoring sites for Pt deposition on such graphitized carbon surface such as -OH and -COOH connected on sp^3 carbons make the uniform deposition of Pt nanoparticles rather difficult ¹¹, and inferior to the effective utilization of Pt. And it is pointed out that the weak interaction between the graphitized carbon surface and Pt nanoparticles often induces the sintering of Pt particles ^{11, 12} and, therefore the improvement of the Pt-carbon interfacial strength will further improve the Pt stability. Although, general strategy to introduce anchoring sites for the highly graphitized carbons is to oxidize the surface by harsh chemical or physical treatments ¹³, such oxidation always involved the introduction of the sp^3 sites and resulted in the decrease of the durability of carbon supports.

We have developed smart method to introduce anchoring sites without creating sp^3 carbons on the highly graphitized carbon surface, where the carbons are coated by polymer having anchoring sites for metal ions ¹⁴⁻¹⁶. In this method, polymer such as polybenzimidazole (PBI) is coated on the pristine (non-oxidized) carbons and can act as the anchoring site for the Pt deposition. Therefore, Pt can be deposited onto the surface of highly graphitized carbon such as CNTs without

oxidizing the CNTs ¹⁷. Indeed, we reported that PEMFC having PBI-coated CNT as a carbon support showed excellent durability upon fuel cell accelerated durability test (ADT) between 1.0-1.5 V ¹⁸. In that research, oxidized-CNT was used as a comparison since direct Pt deposition onto the pristine CNT was rather difficult ¹⁹ and, in addition, we used the ADT protocol designed to deteriorate the carbon (1.0 – 1.5 V). Thus, we successfully demonstrated the advantage of the PBI coating to preserve inherent carbon durability but the effect of the PBI coating for the Pt stability was not investigated. We also demonstrated that the PBI-coating on Vulcan could enhance the durability of Vulcan-based PEMFC ²⁰. However, in that research, PBI coating improved Vulcan stability mainly because the coverage of micropore of Vulcan decelerated the oxidation of the carbon surface during the ADT between 1.0 and 1.5 V. Therefore, the effect of PBI coating for the stability of Pt particles was not observed.

In this chapter, to clarify the effect of PBI coating for Pt stability and PEMFC durability, ADT between 0.6 and 1.0 V designed to study Pt stability was applied for the PEMFC having PBI-coated carbons as a carbon support. Here, Acetylene Black (AB) was chosen as the carbon support since (1) AB shows high electrochemical stability due to their high crystallinity ²¹ and Pt sintering triggered by the carbon corrosion during the ADT can be minimized and (2) direct Pt deposition on AB was possible ²¹ and no oxidation pretreatment is necessary for the reference samples. The Pt catalysts deposited on PBI-coated AB (AB/PBI/Pt) and AB (AB/Pt) were employed in MEA and subjected to ADT, and the loss of the MEA performance together with the changes of the

catalyst structure were evaluated. As the ADT condition, the load-cycle protocol ²² consists of rectangular potential cycles between 0.6 V– 1.0 V was conducted to evaluate the stability of Pt with avoiding the degradation of carbon supports ²³. By comparing AB/Pt and AB/PBI/Pt under the ADT between 0.6 V and 1.0 V, judicial comparisons to clarify the role of PBI layer for Pt stability and PEMFC durability becomes possible.

2.2. Experimental

2.2.1. Materials

Hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), *N,N*-dimethylacetamide (DMAc), ethylene glycol (EG), and ethanol (99.5%) were purchased from the Wako Pure Chemicals Corp. (Tokyo, Japan). AB (Denka Black; Li-250) was purchased from the Denka (Tokyo, Japan). Nafion solution (5%) and Nafion[®] 212 membranes were purchased from MilliporeSigma (St. Louis, USA). PBI was purchased from the Sato Light Industrial Co. (Kameyama, Japan). The AB/PBI was prepared by dispersing AB into PBI solution, followed by the filtration ²⁴. Deposition of Pt on AB/PBI and AB was conducted using polyol reduction method and detailed procedure can be found in elsewhere ²⁴.

2.2.2. Material characterization

Thermogravimetric analysis (TGA) was performed using an EXSTAR TG/DTA6300 analyzer (Seiko Instruments, Tokyo) at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under air flow of 200 mL min^{-1} . Transmission electron microscopy (TEM) was executed using a JEOL 2010 microscope (JEOL, Tokyo) operating at 30 kV. X-ray photoelectron spectroscopy (XPS) was conducted using an AXIS-ULTRA^{DLD} spectrometer (Shimadzu, Tokyo).

2.2.3. Fabrication of MEA and fuel cell measurements

Catalyst inks were prepared by mixing a given amount of the catalyst powder (AB/Pt or AB/PBI/Pt) and Nafion in ethanol/water mixture (90/10 in volume) followed by sonication for 10 min. Catalyst layer (CL) was fabricated by spraying the catalyst inks onto the Nafion membrane by pulse spray coater (PS-1000, Nordson). Ionomer/carbon ratio (I/C) in the mixture was controlled to $I/C = 0.6$ and the Pt amount in the CL were adjusted to 0.2 mg cm^{-2} . The catalyst-coated membranes were laminated with gas diffusion layers (SIGRACET GDL 25BC, SGL Group) under 0.6 MPa at $132\text{ }^{\circ}\text{C}$ for 20 s to fabricate membrane electrode assembly (MEA). The catalyst areas in MEAs were $1.0 \times 1.0\text{ cm}^2$.

The MEAs were activated by maintaining the cell potential at 0.6 V (vs. RHE) for 3 hours using H_2 (100 mL min^{-1}) and air (200 mL min^{-1}) for anode and cathode, respectively, under 100% relative humidity (RH) at $80\text{ }^{\circ}\text{C}$ using ModuLab XM CHAS 08 potentiometer (Solartron Analytical, UK). The ADT protocol proposed by Fuel Cell Commercialization Conference of

Japan (FCCJ) was used ²³, in which square-wave cycles between 0.6 for 3 s and 1.0 V for 3 s (vs. RHE) were applied at each potential using H₂ (100 mL min⁻¹) and N₂ (1000 mL min⁻¹) for anode and cathode, respectively, at 80 °C (100%RH). ADT were conducted for 10,000 cycles and the polarization curves were measured every after 2,000 ADT cycles using H₂ (100 mL min⁻¹) and air (200 mL min⁻¹) for anode and cathode, respectively, at 80 °C (100%RH) using an in-house single cell system (Auto PEM-ER01, TOYO Corp., Tokyo, Japan). The cyclic voltammetry (CV) was conducted before and after 10,000 ADT cycles between 0.1 and 0.9 V at the rate of 50 mV s⁻¹ using H₂ (200 mL min⁻¹) and N₂ (1000 mL min⁻¹) for anode and cathode, respectively, at 40 °C (16%RH). Electrochemical impedance spectroscopy (EIS) spectra were recorded in the frequency range of 0.1 Hz – 10 kHz at the working potential of 0.45 V using H₂ (200 mL min⁻¹) and N₂ (1000 mL min⁻¹) for anode and cathode, respectively, at 40 °C (16%RH)

2.2.4. Durability test in half-cell condition

Catalyst inks were prepared by mixing a given amount of the catalyst powder (AB/Pt or AB/PBI/Pt) with a mixture of 80% isopropanol and 5% Nafion solution followed by sonication for 10 min. Catalyst inks deposited on glassy carbon (GC) electrodes (0.1275 cm²) cleaned using alumina abrasive (BAS, Japan) before casting with controlling the catalyst amount on the electrode at 14 µgPt cm⁻². The prepared GC electrodes were air dried at room temperature. 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 wires as the counter and reference electrodes, respectively. All RDE measurements were conducted in 0.1 M HClO₄ solution (ACS Reagent, USA). Before starting the measurements, electrolyte was bubbled with N₂ for 1 h to remove dissolved oxygen in 0.1 M HClO₄ solution. Then prepared electrodes were cleaned/conditioned by 50 cycles between 0.05 and 1.2 V (vs. RHE) at a sweep rate of 50 mV s⁻¹. CV measurements were taken before and after 10000 square-wave cycles in the potential range of 0.6–1.0 V_{RHE} with holding of 3 s at each voltage. The ECSA was calculated using the following formula **Eq. (2-1)**,

$$ECSA_H = Q_H / 0.210 \times (\text{Pt loading of the MEA}) \dots\dots\dots \text{Eq. (2-1)}$$

where Q_H is the charge exchanged during the electro-adsorption of H₂ on Pt.

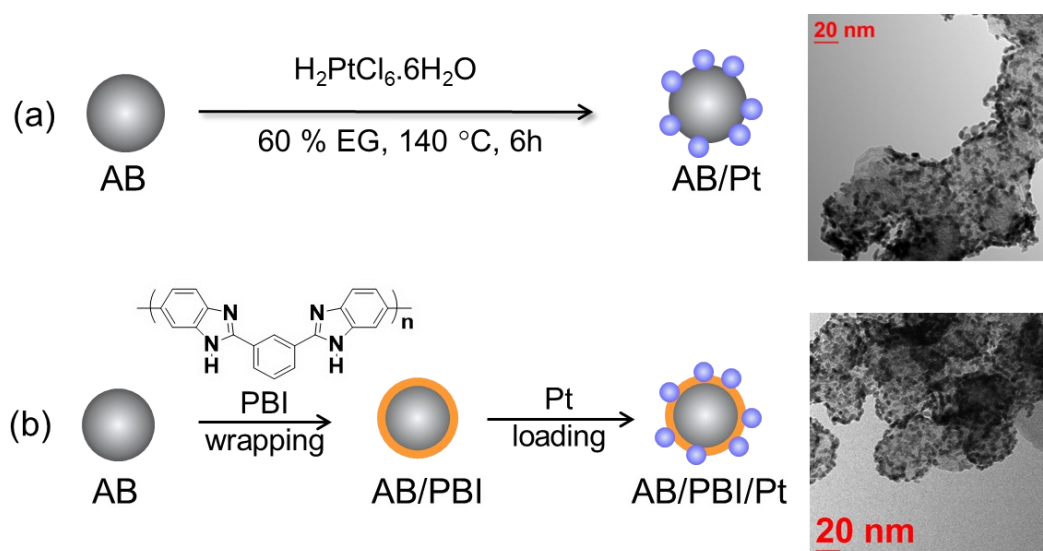
2.3. Results and discussion

2.3.1. Preparation of the catalysts

Table 2-1 Atomic content (%) in AB/PBI.

C	H	O	N
98.00	0.18	1.35	0.47

PBI coating of AB was conducted by dispersing AB into DMAc solution of PBI, followed by the filtration of the solution ²⁴. From the elemental analysis, atomic content of nitrogen in PBI-coated AB (AB/PBI) was 0.47%, corresponding to the PBI content of 2.6wt% (**Table 2-1**). Previously, we observed that the PBI mostly covered surface of multi-walled carbon nanotubes



Scheme 2-1. Schematic of the preparation of (a) AB/Pt and (b) AB/PBI/Pt. TEM images of AB/Pt and AB/PBI/Pt were also displayed. (orange— PBI, blue circle – Pt particle, gray circle – acetylene black (AB))

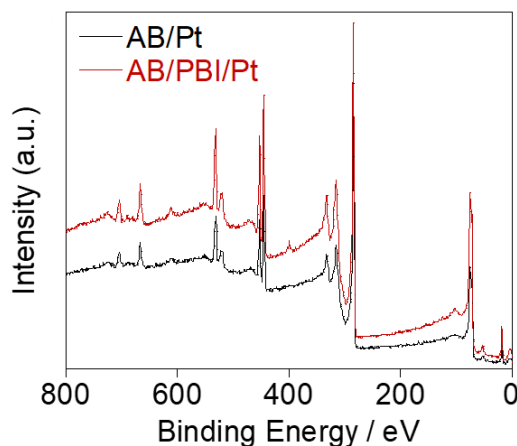


Figure 2-1 XPS curves of AB/Pt (black) and AB/PBI/Pt (red).

(MWCNTs)²⁵ and their coating thickness was around 0.3 nm²⁶. Although our attempt to visualize PBI on AB surface was not successful due to the non-uniform shape of the AB particles, we consider that the PBI coating morphology on AB was similar to that of MWCNTs because AB has highly graphitized surface similar with MWCNTs. AB and AB/PBI were subjected to the Pt depositions using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and EG as a Pt source and reducing agent, respectively (**Scheme 2-1**), to fabricate AB/Pt and AB/PBI/Pt, respectively²⁴. X-ray photoelectron spectroscopy (XPS) survey scans of the catalysts evidenced the presence of Pt for both composites by the presence of Pt 4f_{7/2} and Pt 4f_{5/2} at 71.5 and 75.0 eV, respectively. In addition, the presence of N in AB/PBI/Pt was confirmed by the presence of N 1s at 402 eV in the XPS survey scan (**Figure 2-1**). The amounts of Pt in the catalysts were estimated by thermogravimetric analysis (TGA) and the Pt loading ratio of AB/Pt and AB/PBI/Pt determined based on the residual amount at 900 °C were 44.6 and 44.5 wt%, respectively (**Figure 2-2**). From the transmission electro microscope (TEM),

homogeneous dispersion of the Pt nanoparticles for both on AB/Pt and AB/PBI/Pt was observed (**Scheme 2-1**). Pt particle size of AB/Pt and AB/PBI/Pt were determined as 4.4 ± 1.2 nm and 3.4 ± 0.7 nm, respectively. We explained the reason of the smaller particle size as well as the narrower diameter distribution of Pt in AB/PBI/Pt as an efficient anchoring effect of Pt on PBI layer compared to that of bare carbon surface²⁴. Such a difference supported our speculation that PBI mostly coated the surface of AB of AB/PBI/Pt.

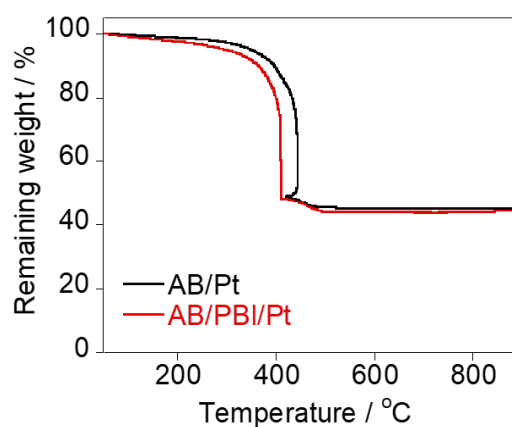


Figure 2-2 TGA survey scans of AB/Pt (black) and AB/PBI/Pt (red).

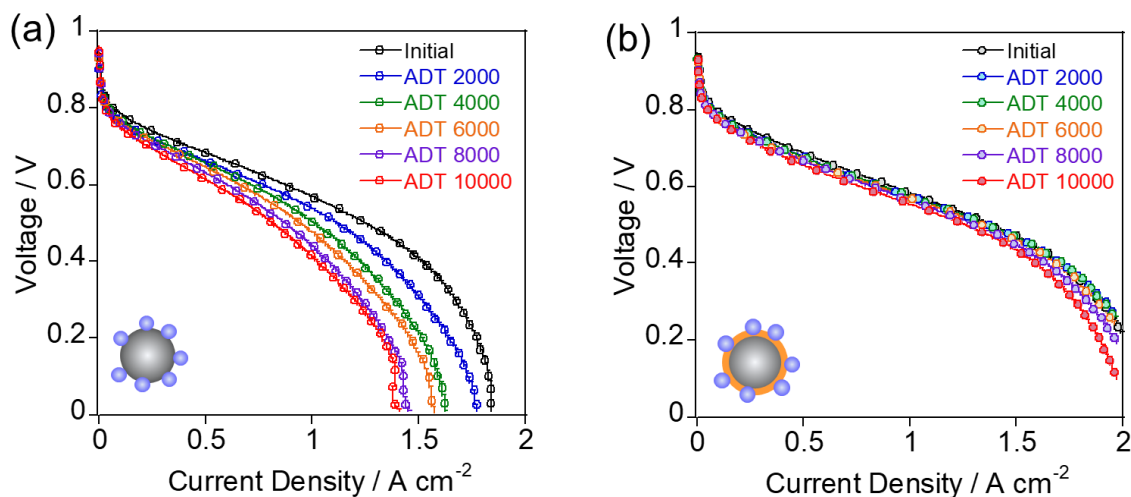


Figure 2-3 Polarization curves of (a) MEA_{AB} and (b) MEA_{AB/PBI} during ADT recorded at every 2000 potential cycles (blue; after 2000, green; after 4000, orange; after 6000, purple; after 8000, red; after 10000)

2.3.2. Durability test

Two MEAs containing AB/Pt (denoted as MEA_{AB}) and AB/PBI/Pt (denoted as MEA_{AB/PBI}) in both anode and cathode were prepared by spray coating of the catalysts onto Nafion membranes with Pt loading of 0.2 mg cm^{-2} . To study the stability of the Pt catalysts, MEA_{AB} and MEA_{AB/PBI} were subjected to the accelerated durability tests (ADT) protocol designed by Fuel Cell Commercialization Conference Japan (FCCJ), where the potential cycles between 0.6 and 1.0 V are applied with a holding time for 3 s at each potentials to mimic load cycling conditions in PEMFC²⁷. Then, polarization of these MEAs were measured at every 2000 cycles under 100% relative humidity (RH) at 80 °C. At the beginning of the test, the maximum power density of

MEA_{AB/PBI} (705 mW cm⁻²) was higher than that of MEA_{AB} (632 mW cm⁻²) as calculated from **Figure 2-3** a and b. Higher initial performance of MEA_{AB/PBI} than MEA_{AB} was explained in two effects; namely, 1) smaller Pt particle size of AB/PBI/Pt (3.4 ± 0.7 nm) than AB/Pt (4.4 ± 1.2 nm) as discussed above (**Scheme 2-1**) and 2) homogeneous distribution of the ionomer in the catalyst layer (CL) of MEA_{AB/PBI} led by the strong interaction between PBI and ionomer as reported ^{24, 27}. Electrical impedance spectroscopy (EIS) revealed that the gas diffusion resistance (R_g) of MEA_{AB/PBI} were much lower than that of MEA_{AB} especially at higher current density regions (**Figure 2-4**). We reported that the homogeneous ionomer distribution in PBI-coated catalyst offered connective pore network and facilitated the gas diffusion, that resulted in higher maximum power density for PBI-coated Vulcan systems (700 mW cm⁻²) compared to that of the non-coated systems (580 mW cm⁻²) ²⁸. Similar effect might be taken place for the AB-based MEA. It is worth mentioning that charge transfer resistance (R_c) of MEA_{AB/PBI} were slightly higher than that of MEA_{AB} for all the current density regions, while ohmic resistance (R_Ω) was comparable between two MEAs. Such a higher charge transfer resistance for MEA_{AB/PBI} might be an effect of insulating PBI layer.

During ADT cycles, we observed the faster deterioration of the performance for MEA_{AB} compared to MEA_{AB/PBI} in their maximum power density (**Figure 2-5 a and b**). The reduction of the maximum power density at the end of the test for MEA_{AB} was 34%, while that of MEA_{AB/PBI} was only 8% (**Figure 2-5 c**).

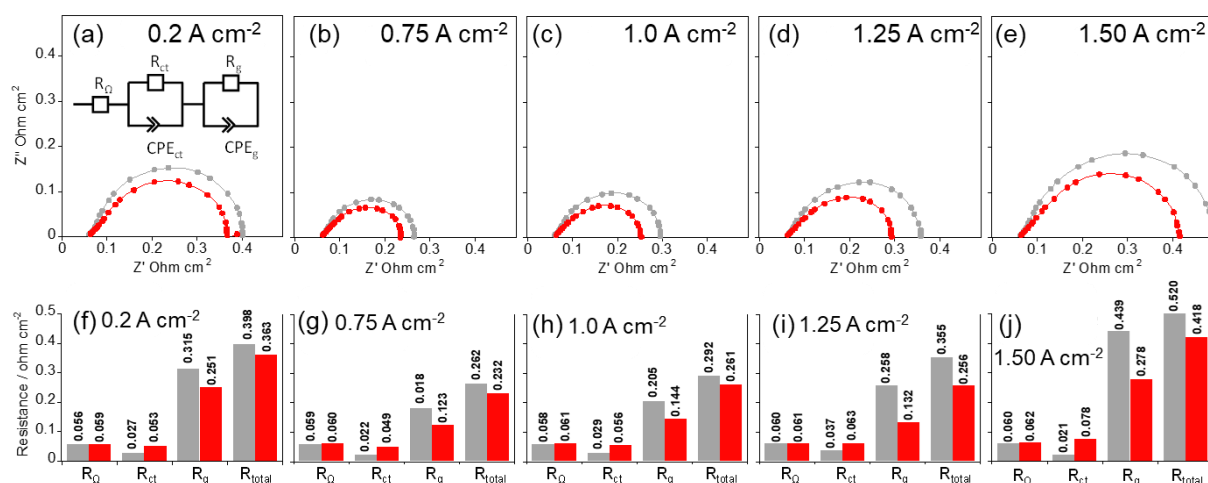


Figure 2-4 (a-e) EIS Nyquist plots of MEA_{AB} (gray) and MEA_{AB/PBI} (red) at different current density regions. Inset) Equivalent circuit used for curve fitting composed of ohmic resistance (R_Ω), charge transfer resistance (R_c) and gas diffusion resistance (R_g). (f-j) R_Ω , R_c and R_g values of MEA_{AB} (gray) and MEA_{AB/PBI} (red) obtained from the fitting at different current density regions. Total resistance (R_{total}) are also displayed.

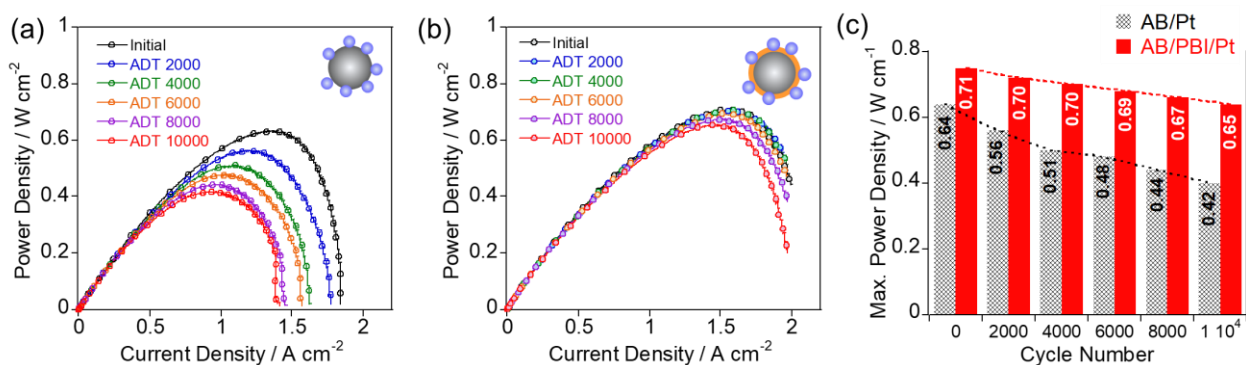


Figure 2-5 Power density curves of a) MEA_{AB} and b) MEA_{AB/PBI} during ADT at every 2000 potential cycles (blue; after 2000, green; after 4000, orange; after 6000, purple; after 8000, red; after 10000). c) Maximum power density of AB/PBI/Pt (red) and AB/Pt (black) upon ADT.

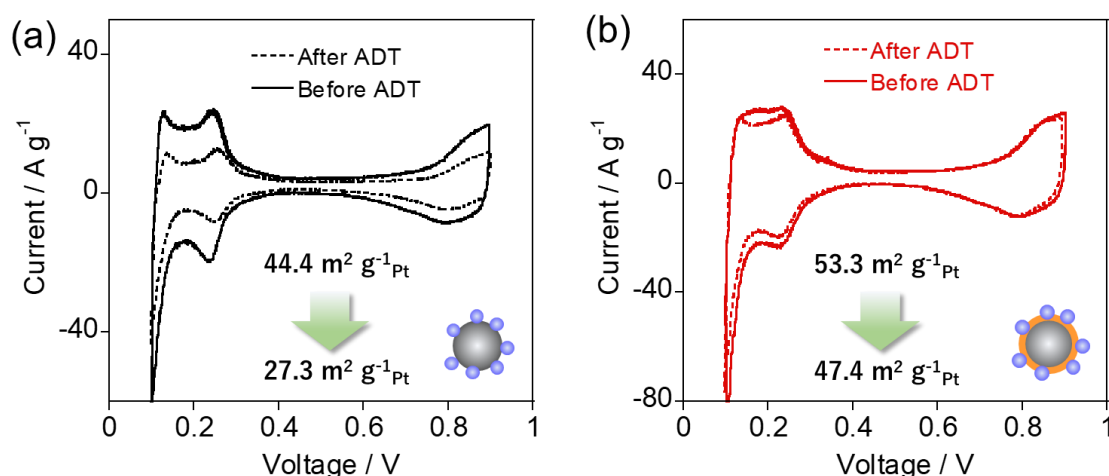


Figure 2-6 CV curves of (a) MEA_{AB} and b) MEA_{AB/PBI} before (solid line) and after (dotted line) ADT. ECSA values before and after ADT were displayed in the graphs.

Figure 2-6 (a) and (b) shows in-situ cyclic voltammograms (CV) of MEA_{AB} and MEA_{AB/PBI}, respectively, before (solid lines) and after (dotted lines) ADT measured using H₂ and N₂ for anode and cathode, respectively, at 40 °C. The characteristic peaks in 0.1–0.4 V are attributable to atomic

hydrogen adsorption and desorption on the Pt surfaces. Electrochemically active surface area (ECSA) calculated based on the desorption peak of hydrogen for MEA_{AB} and MEA_{AB/PBI} before ADT were 44.4 and 53.3 m² g⁻¹ of Pt, respectively. The results are consistent with the fact that size of Pt in MEA_{AB/PBI} is smaller than that in MEA_{AB}. After ADT, we observed 39% decrease of the hydrogen adsorption peak for MEA_{AB} (**Figure 2-6 a**), while the decrease in MEA_{AB/PBI} was only by 11% (**Figure 2-6 b**).

Similar decrease of the ECSA was also observed in the durability tests on GC electrode in half-cell condition using HClO₄ as the electrolyte (**Figure 2-7**). In there, initial ECSA of AB/Pt (25.4 m² g⁻¹) was reduced by 47% to 13.5 m² g⁻¹ after 10000 potential cycling between 0.6 and 1.0 V_{RHE} (**Figure 2-7a**). On the other hand, in the case of AB/PBI/Pt (**Figure 2-7 b**), the ECSA was reduced from 53.7 to 47.1 m² g⁻¹ and the decrease was only 15%. To evaluate proton (H⁺) conductivity of the CL before and after ADT, impedance spectra of the MEA_{AB} and

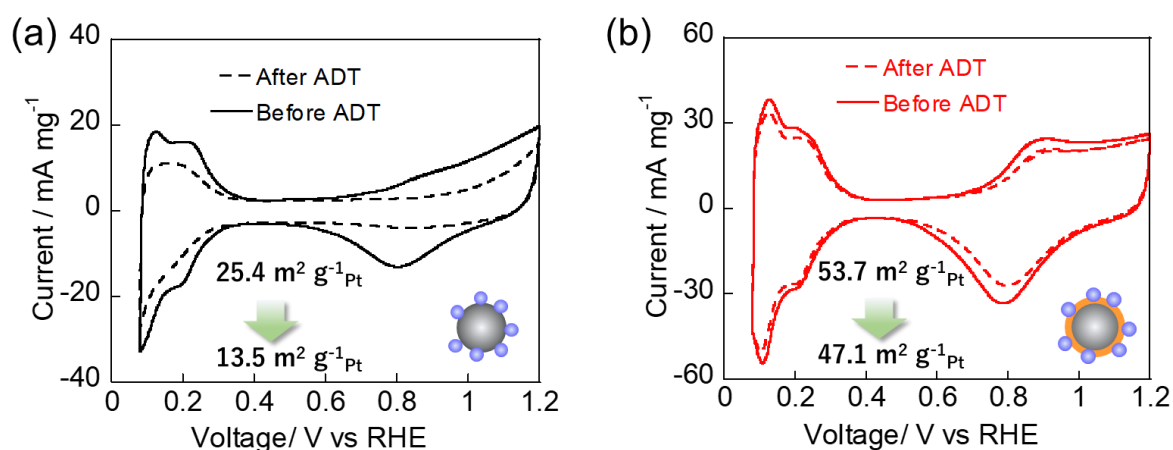


Figure 2-7 CV curves of (a) AB/Pt and (b) AB/PBI/Pt on GC electrode before (solid line) and after (dotted line) ADT measured 0.1 M HClO₄.

MEA_{AB/PBI} was measured using H₂ and air as anode and cathode, respectively. Based on the linear slop of the high frequency region of impedance spectra, H⁺ resistances of the MEA before and after the ADT were calculated^{29, 30}. We found that the H⁺ resistance of the MEA_{AB} was significantly increased from 52 to 75 mΩ cm² after ADT (**Figure 2-8 a**). On contrary, the H⁺ resistance of MEA_{AB/PBI} before and after the ADT was almost unchanged (~50 mΩ cm²). Since both MEA used the same Nafion membrane, the difference of the impedance changes should come from the changes of the CL. From the above results, both the decrease of the ECSA of Pt and the decrease of the H⁺ conductivity of the CL were determined as the reason of the decrease of the cell performance.

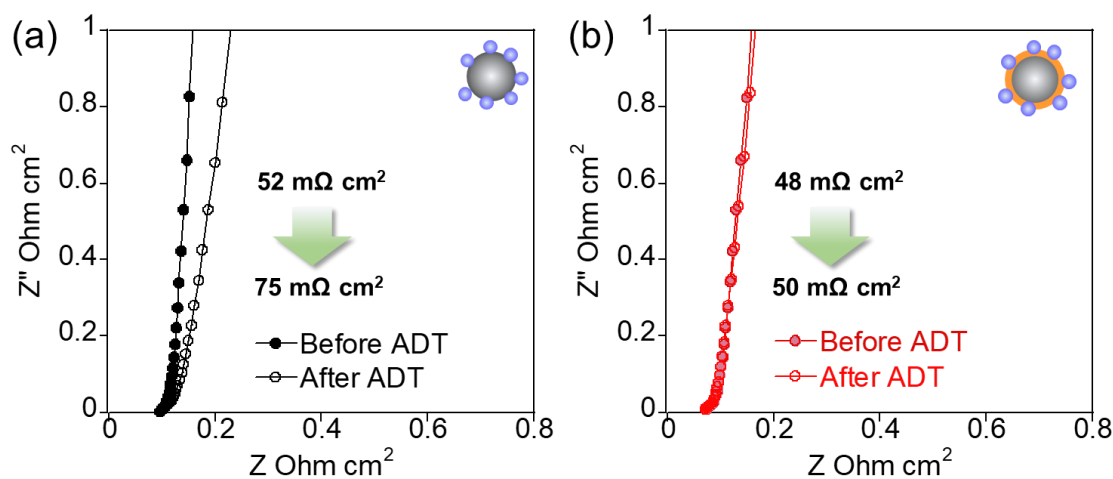


Figure 2-8 Nyquist impedance spectra response at 0.45 V of (a) MEA_{AB} and (b) MEA_{AB/PBI} before and after potential cycling between 0.6 and 1.0 V_{RHE}. Calculated H⁺ resistance of MEA_{AB} and MEA_{AB/PBI} before and after ADT were displayed in the graphs.

2.3.3. Analysis of the catalyst after ADT

To investigate the morphology changes of catalysts, TEM of the AB/Pt and AB/PBI/Pt taken from both anode and cathode CLs after ADT were measured (**Figure 2-9**). After the ADT, large Pt particles was observed for AB/Pt (**Figure 2-9 a**). On the other hand, the dispersion and their diameter distribution (3.4 ± 0.5 nm) were not significantly changed for AB/PBI/Pt (**Figure 2-9 b**). Uchida et al. reported that the narrower diameter distribution of the Pt affords longer stability due to the suppression of the electrochemical Ostwald ripening³¹. We consider that the same effect is

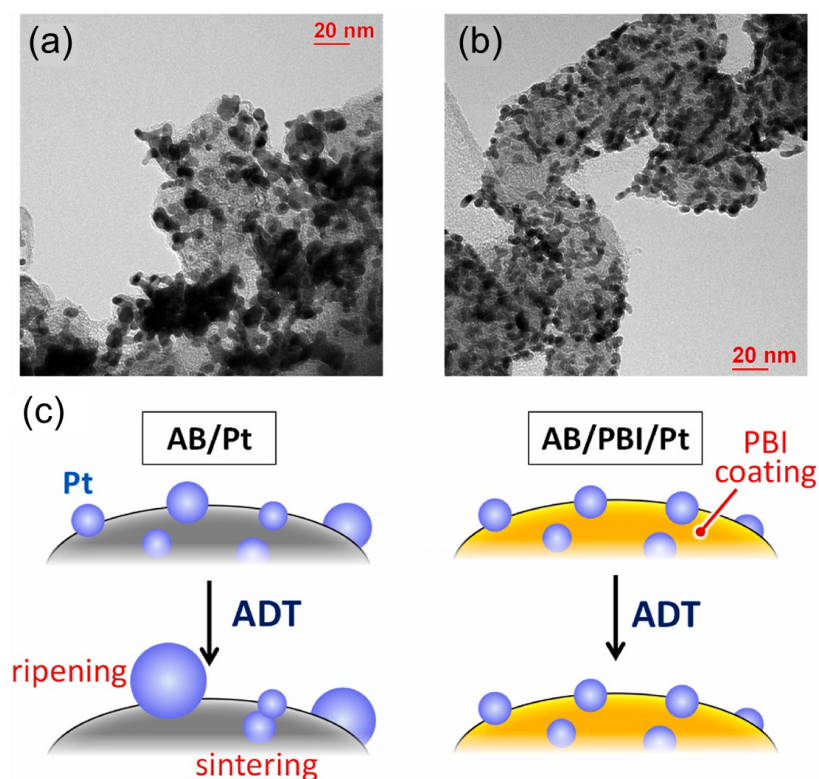


Figure 2-9 TEM images of (a) AB/Pt and (b) AB/PBI/Pt after the ADT. (c) Schematic illustration of the changes of Pt after ADT.

the one of the reasons of the superior ECSA stability for AB/PBI/Pt. Meanwhile, from the TEM image, Pt agglomeration is also recognized for AB/Pt after ADT, indicating that not only Ostwald ripening but the sintering was occurred for AB/Pt. We considered that the strong interaction between Pt and PBI prevents the diffusion of Pt particles for AB/PBI/Pt³²⁻³⁵, whereas weaker interaction between Pt and graphitic AB surface allows the diffusion of the Pt nanoparticles^{11, 12}. As far as we know, this is the first finding that the polymer-coating on carbon supports can mitigate the sintering of the Pt particles (**Figure 2-9 c**).

Further comparisons of the catalysts before and after the ADT were carried out by XPS of the CLs for both cathode (**Figure 2-10**) and anode (**Figure 2-11**). It is noted that intensity of the

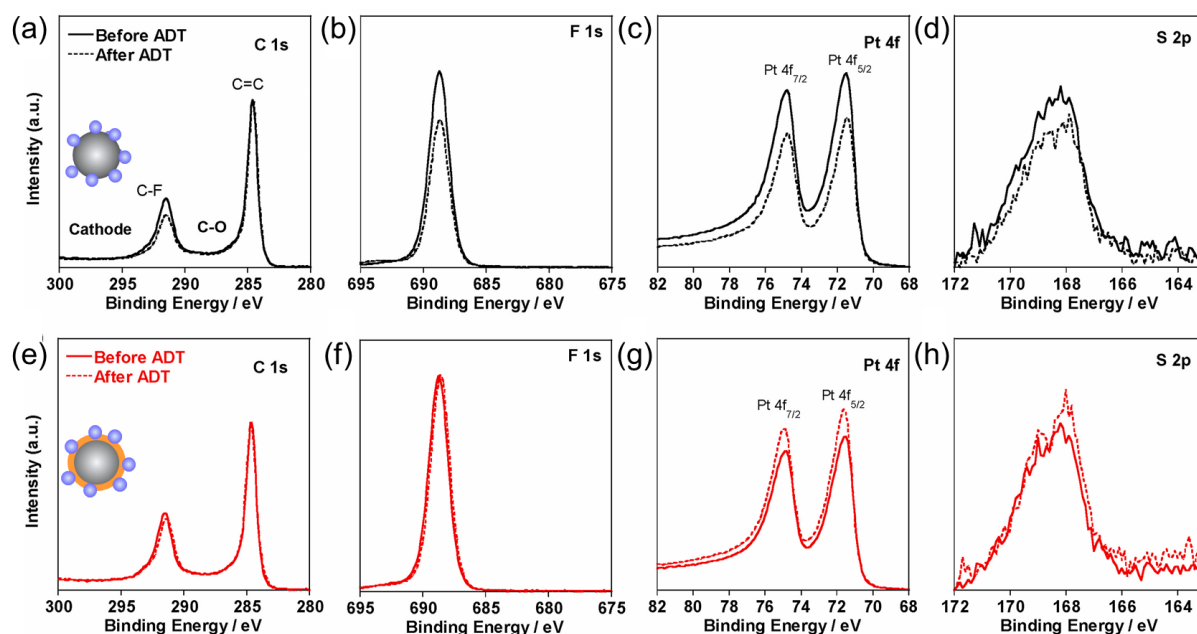


Figure 2-10 XPS narrow scans of (a-d) AB/Pt and (e-h) AB/PBI/Pt before (solid lines) and after (dotted lines) the ADT at cathode.

peaks is normalized to the C1s at 284.6 eV attributed to the core absorption of C=C. No significant increase of the C1s peaks due to C–O (286.2 eV) was observed for both AB/Pt and AB/PBI/Pt. This confirms that carbon oxidation was negligible after the ADT. Interestingly, we observed the decrease of C1s attributed to C–F bond at 291.5 eV for AB/Pt (**Figure 2-10 a**), while no such change was observed for AB/PBI/Pt (**Figure 2-10 b**). The result was well agreed with the clear decrease of the F1s peak at 687 eV for AB/Pt (**Figure 2-10 c**), whereas no loss of the peak was observed for AB/PBI/Pt (**Figure 2-10 d**). Similar decreases of the fluorine peaks were also observed for AB/Pt in anode (**Figure 2-11**). For the decreases of fluorine peaks for AB/Pt, two mechanisms can be considered ³⁶, namely, 1) chemical decomposition of the ionomer mainly by radical attack and 2) leaching of ionomer by dissolution. For chemical decomposition of ionomer, the radical such as •OH generated by Fe-catalyzed reaction attacks to Nafion and leads to the chemical decomposition especially for the loss of side chain ^{37, 38}. In this mechanism, suppression of the radical generation is the key to prevent the loss of fluorine, but, at this moment, such a suppression of the radical generation via PBI-mediated pathway is not considered. On the other hand, the loss of ionomer by dissolution, the interaction between PBI and Nafion ionomer based on the basic PBI and acidic Nafion might prevent the leaching. Such mechanism can nicely explain the maintenance of ionomer of MEA_{AB/PBI} in anode and cathode. We consider that the decrease of the proton conductivity for MEA_{AB} (**Figure 2-8 a**) was due to the loss of ionomer from the CL.

For Pt 4f peaks, decrease of the intensity for AB/Pt were observed (**Figure 2-10c**), while the intensity of Pt 4f for AB/PBI/Pt was comparable after ADT (**Figure 2-10g**). We consider that the decrease of the Pt peak in AB/Pt agreed with the leaching of the Pt ion by oxidation for AB/Pt as observed in **Figure 2-6 a**. Based on the results obtained above, we conclude that the enhancement of the PEM durability for MEA_{AB/PBI} is due to the enhancement of the Pt stability and ionomer stability due to the stronger binding at PBI–Pt interface and PBI–ionomer interface compared to carbon–Pt interface and carbon–ionomer interface, respectively. We previously reported that PBI coating increases the Pt utilization efficiency (mass activity) due to the homogeneous distribution of the ionomer in the CL facilitated by the interaction between PBI and ionomer, which resulted

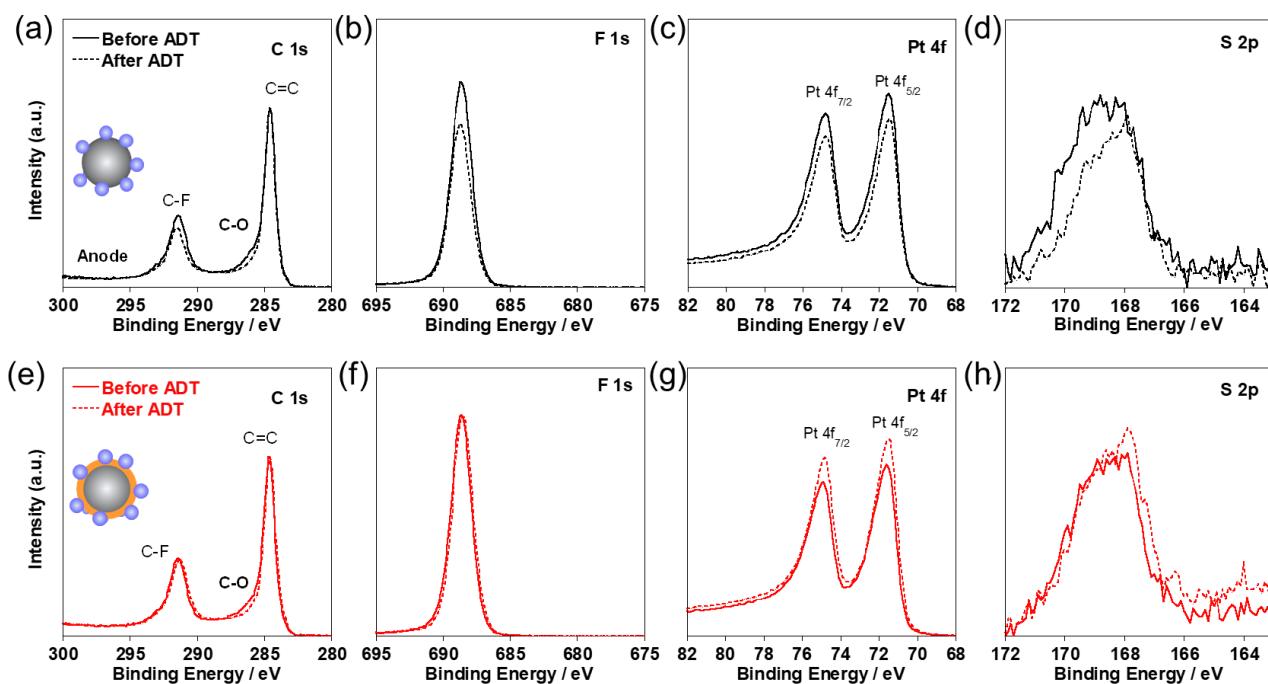


Figure 2-11 XPS narrow scans of (a-d) AB/Pt and (e-h) AB/PBI/Pt before and after the ADT at anode.

in the increase of the maximum power density ^{24, 39}. Thus, we can conclude that PBI wrapping approach is effective for the enhancements of both durability and the power generation efficiency.

2.4. Conclusion

Pt catalyst loaded on PBI-coated AB (AB/PBI/Pt) and the Pt catalyst on AB (AB/Pt) were fabricated to study the effect of PBI coating for the stability of Pt nanoparticles during fuel cell operation. By applying potential cycles between 0.6 and 1.0 V to accelerate Pt oxidation, we found that the MEA containing AB/PBI/Pt (MEA_{AB/PBI}) showed greater stability than the MEA fabricated with AB/Pt (MEA_{AB}). Comparison of the Pt morphology before and after the ADT revealed that the enhancement of the Pt dispersion stability by PBI coating. We consider that the strong binding between Pt and PBI contributed to the inhibition of Pt diffusion. In addition, Pt nanoparticles with narrower diameter distribution in AB/PBI/Pt that was realized by the strong binding between PBI and Pt effectively hamper the Ostwald ripening of Pt. Both effects afford higher stability of Pt compared to that in AB/Pt and thus higher stability for MEA_{AB/PBI}. Interestingly, ionomer content in the CLs in anode and cathode was almost unchanged for MEA_{AB/PBI}, while that of MEA_{AB} was largely decreased. We consider that the strong binding between PBI and ionomer through acid-base interaction prevent the loss of ionomer from the CLs upon ADT, consequently contributed to the durability of the MEA_{AB/PBI}. The present results clearly suggest the positive impact of PBI coating to improve the fuel cell durability and the activity.

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Chapter 3

Creating Electron Conductive Polymer-Coated Carbon Catalysts to Reduce Overpotential in Polymer Electrolyte Membrane Fuel Cell

3.1. Introduction

As discussed in **Chapter 1**, PBI coating can improve mass activity of Pt because strong interaction between PBI and the ionomers lead a homogeneous ionomer distribution in cathode catalyst layer, thereby generating a well-connected proton path and porous network for O₂ diffusion to the catalyst surface ^{1, 2}. In addition, in **Chapter 2**, we proposed improvement of the durability after the PBI wrapping ³. However, one of the drawbacks of the PBI wrapping is slightly larger charge transfer resistance (R_{ct}). We assumed such a higher charge transfer resistance for PBI-coated catalyst might be an effect of insulating PBI layer. Indeed, as discussed in **Chapter 4**, CB/PBI has lower conductivity (2.99 Ω cm, resistivity value) than that of CB (1.01 Ω cm). Also, CB/PBI-PS has lower conductivity (1.21 Ω cm).

Therefore, in this chapter, we employed electron conductive polymer which also interact with ionomer as the adhesive layer. As the electron conductive polymer with ionomer interaction, we focused on the use of polythiophene grafted with sulfonic acid group (S-PEDOT). This polymer was developed by Okuzaki et al. ^{4,5} as the advanced model of the conventional electron conductive polymer such as poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate) (PEDOT: PSS) ⁶. The chemical structures of PEDOT: PSS and S-PEDOT as shown in **Figure 3-1** (a) and (b),

respectively. For PEDOT:PSS, excess amount of PSS as the dopant of PEDOT often act as the insulator depending on their domain structure ⁷. Sulfonic acid in S-PEDOT was covalently grafted in PEDOT main-chain and act as the dopant. Therefore, higher conductivity can be expected independent on the nano phase structure. Because sulfonic acid group interact with PEDOT main-chain via charge transfer, similar interaction can be expected with sulfonic acid in ionomer (Nafion). Thereby, homogeneous ionomer distribution can be expected for S-PEDOT similar with PBI. In addition, we expected the proton conductivity for S-PEDOT due to the high graft density of acid group.

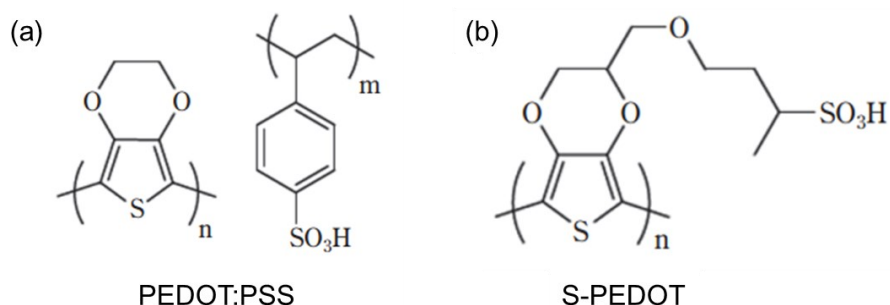


Figure 3-1 The chemical structures of (a) PEDOT: PSS and (b) S-PEDOT.

3.2. Experimental

3.2.1. Materials

Hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), ethylene glycol (EG), and ethanol (99.5%), 1-propanol and 2-propanol were purchased from the FUJIFILM Wako Pure

Chemical (Tokyo, Japan). Vulcan XC-72R (CB) purchased from Cabot Chemical Co., Ltd., (Boston, USA) was used as CB. CB/Pt (Vulcan/Pt: TEC10V30E) was purchased from Tanaka Kikinzoku Kogyo (Tokyo, Japan). self-doped Poly(3,4-ethylenedioxythiophene) (PEDOT) (commercial product name is SELFTRON A, chemical name donated as S-PEDOT) was purchased from the Tosoh Co. (Tokyo, Japan). Nafion solution (5%) and Nafion® 212 membranes were purchased from MilliporeSigma (St. Louis, USA). Gas diffusion layers (SIGRACET® GDL 22BB) was purchased from SGL Carbon SE (Wiesbaden, Germany). 0.1 μm PTFE film, 50 μm Kapton film and 1 mm silicon film were purchased from AS ONE Co. (Tokyo, Japan).

3.2.2. Material characterization

Thermogravimetric analysis (TGA) was performed using an NEXTA STA200 analyzer (Hitachi High-Technologies) at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under air flow of 100 mL min^{-1} with protection gas N_2 flow of 100 mL min^{-1} . Transmission electron microscopy (TEM) was executed using a JEOL 2010 microscope (JEOL, Tokyo) operating at 120 kV. X-ray photoelectron spectroscopy (XPS) was conducted using an AXIS-ULTRA^{DLD} spectrometer (Shimadzu, Tokyo).

3.2.3. Preparation of CB/S-PEDOT composite and CB/S-PEDOT/Pt catalyst

1000 mg of Vulcan XC-72 (CB) was added to 250 mL of a 50% v/v water/ethanol solution and sonicated for 20 minutes to disperse the CB powder. Subsequently, 16.25 mL of SELFTRON A solution (1 wt% S-PEDOT in ethanol) was mixed with 70 mL of ethanol and combined with the dispersed Vulcan solution. The mixture was shaken in a shaking incubator for 3 hours. The resulting CB/S-PEDOT composite was obtained through filtration using a hydrophilic PTFE filter membrane (pore size 0.2 μm), followed by washing with a large amount of Milli-Q water to remove excess S-PEDOT, and then washing with a small amount of methanol to facilitate rapid solvent evaporation under vacuum at 80°C for 12 hours.

Pt was loaded onto CB/S-PEDOT using a polyol reduction method, employing a 60% (v/v) ethylene glycol (EG) aqueous solution as the reducing agent and 5 wt% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution as the Pt precursor⁸. CB/S-PEDOT (100 mg) was dispersed in 400 mL of 60% (v/v) EG aqueous solution using a bath sonicator. The target Pt loading amount (30 wt%) was achieved by adding 2.276 g of 5 wt% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution to a three-neck round-bottom flask, which was refluxed at 140°C for 6 hours under an N_2 atmosphere. After cooling to room temperature, the obtained composites were collected by filtration using a hydrophobic PTFE filter membrane (pore size 0.2 μm), followed by washing with plenty of Milli-Q water and dried under vacuum at 80°C for overnight.

3.2.4. Fabrication of MEA

In this chapter, different from **chapter 2**, the CB/S-PEDOT/Pt catalyst was used to fabricate the MEA via the decal transfer method. CB/S-PEDOT/Pt catalyst inks were prepared with Nafion, maintaining an ionomer-to-carbon (I/C) ratio of 0.6. Additionally, a commercial CB/Pt catalyst (TEC 10V30E) was used for comparative experiments under the same Nafion I/C ratio of 0.6. Firstly, as shown in **Figure 3-2**, the catalyst ink was prepared using CB/S-PEDOT/Pt with a Pt loading of 26 wt% 1-Propanol and 2-propanol were separately added as dispersion solvents. Additionally, ethylene glycol (EG) was introduced to enhance the adhesive properties of the ink for coating onto a 0.1 μm PTFE film. Nafion was then added to achieve an I/C ratio of 0.6, followed

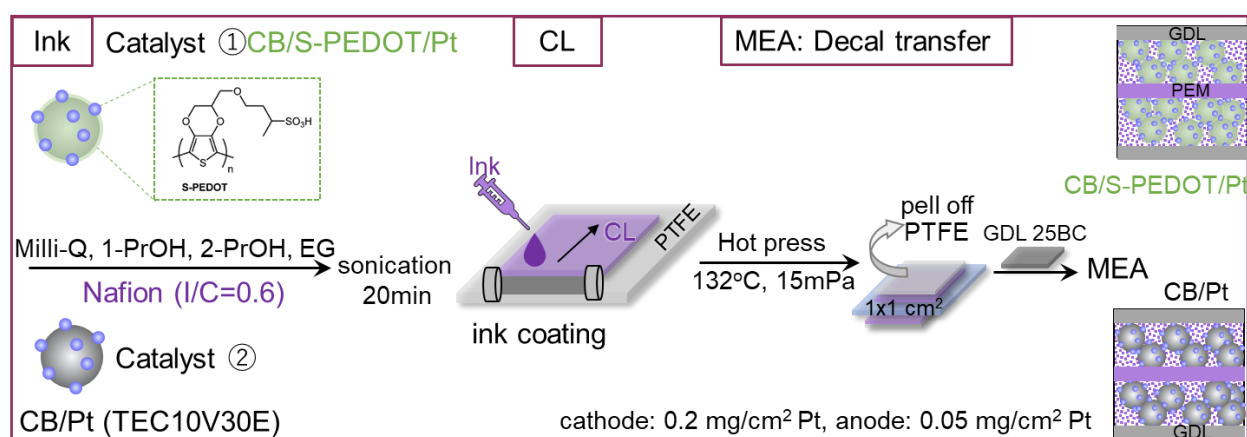


Figure 3-2 Schematic of MEA fabrication method in this study

by 20 minutes of sonication to ensure uniform dispersion of the catalyst ink. Thereafter, the rod Mini coater (MC-20, Hohsen Corp., Japan) was used to coat inks onto a 0.1 μm PTFE film, which served as the decal transfer substrate. After coating the ink on the PTFE substrate, the catalyst

layer (CL) with the PTFE substrate was vacuum-dried at 120°C for 1 hour to evaporate solvent. Subsequently, the decal transfer method was applied, where two pieces of CLs were transferred from the PTFE substrate to a Nafion 212 membrane through hot pressing. The Pt loading in the cathode was controlled at 0.2 mg cm⁻², while at the anode, it was set to approximately 0.05 mg cm⁻² to address cost optimization concerns. This lower Pt loading at the anode is feasible due to the faster reaction kinetics of the hydrogen oxidation reaction (HOR) compared to the oxygen reduction reaction (ORR) at the cathode^{9, 10 11}. The successfully transferred CL coated Nafion® 212 membrane were directly laminated with gas diffusion layers (GDL) when setting in 1×1 cm JARI cell-II (Ex-2C type) to fabricate membrane electrode assembly (MEA). The catalyst areas in MEAs were 1.0 × 1.0 cm².

3.2.5. Fuel cell measurements

The CV curves were performed by feeding with humidified H₂ at a flow rate of 100 mL min⁻¹ and humidified N₂ at a flow rate of 200 mL min⁻¹ at 80 °C at the anode and cathode, respectively. To activate the MEA, 99 potential cycles from 0.05 to 0.9 V vs. RHE at a scan rate of 50 mV s⁻¹ controlled by a SP-240 (Toyo Corporation) were carried out. Five cycles were recorded under N₂ stop-flow conditions for CV data analysis. The ECSA was determined as described in **Chapter 2**.

The H⁺ impedance measurements of the MEAs were carried out 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 100 kHz. The proton conduction resistance (R_p)

of a CL can be quantified based on the reports ^{12, 13}. The linear slope of the high-frequency region (10^3 – 10^5 Hz) represents the contributions from protonic resistance and the CV curve double-layer charging capacitance of the CL expressed by **Eq. (3-1)** ¹².

$$|Z| = \sqrt{R_p/C_{dl}} * \omega^{-1/2} \rightarrow K = \sqrt{R_p/C_{dl}} \dots\dots\dots \mathbf{Eq. (3-1)}$$

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 CL, and ω is the frequency of the harmonic signal equal to $2\pi f$ (f = linear frequency). Considering **Eq. (3-1)**, plotting $|Z|$ vs. $\omega^{-1/2}$ gives the slope K , which is the ratio of R_p to C_{dl} .

The I–V curves of each MEAs were obtained by feeding humidified H₂ (flow rate: 100 mL min⁻¹) and air (flow rate: 200 mL min⁻¹) to the anode and cathode at 80 °C, respectively. The electrochemical impedance spectroscopy (EIS) was recorded in the 10 mHz to 100 kHz frequency range with a sinusoidal amplitude of 10 mV. The humidified air (flow rate: 200 mL min⁻¹) and humidified H₂ (flow rate: 100 mL min⁻¹) were supplied into the cathode and anode, respectively.

3.3. Results and discussion

3.3.1. Material properties analysis

Figures 3-3 (a) show XPS survey of CB/S-PEDOT, and the narrow scans of S 2p (Figure 3-3 (b)) peaks was observed at 164 eV, 165 eV and 168 eV, respectively, evidencing a presence of S-PEDOT in the composite.

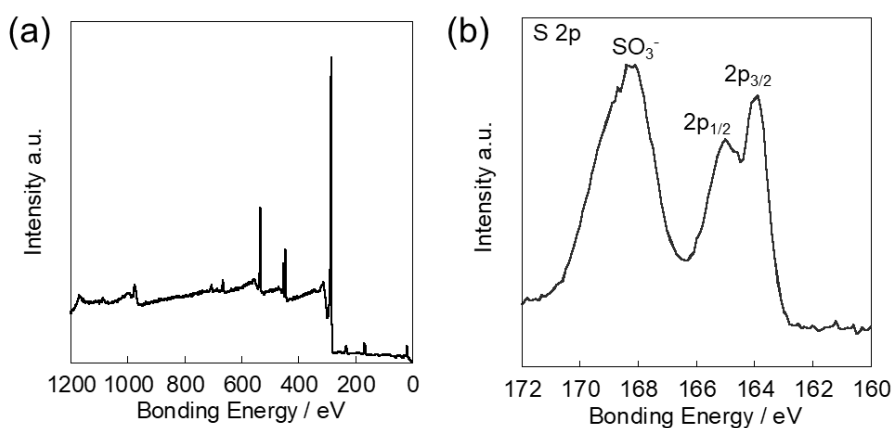


Figure 3-3 X-ray photoelectron spectroscopy (XPS) of (a) survey scan and (b) S 2p narrow scan

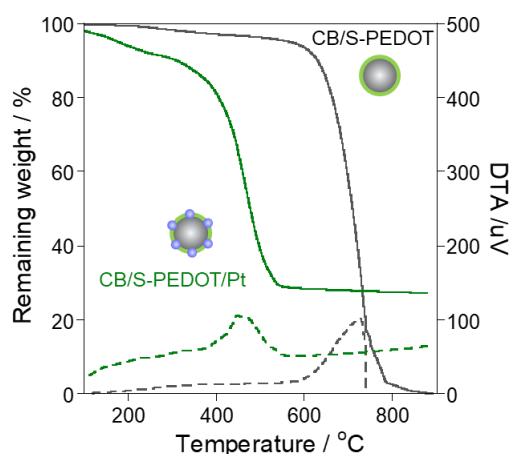


Figure 3-4 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of CB/S-PEDOT (black line), CB/S-PEDOT/Pt (green line)

Furthermore, **Figure 3-4** presents the TGA and DTA curves for CB/S-PEDOT (gray line) and CB/S-PEDOT/Pt (green line). The CB/S-PEDOT composite began to degrade at approximately 210 °C, with CB combustion occurring around 700 °C. In the case of CB/S-PEDOT/Pt, a minor mass loss was observed near 100 °C, which can be attributed to the evaporation of water molecules present in the sample. The Pt loading amount was evaluated based on the weight residue at 900 °C, indicating that the Pt content was approximately 26 wt%.

Figure 3-5 is the TEM images of CB/S-PEDOT/Pt, indicating that Pt particles were homogeneously loaded on CB/S-PEDOT. The size distribution of Pt on CB/S-PEDOT/Pt is 2.35 ± 0.43 nm.

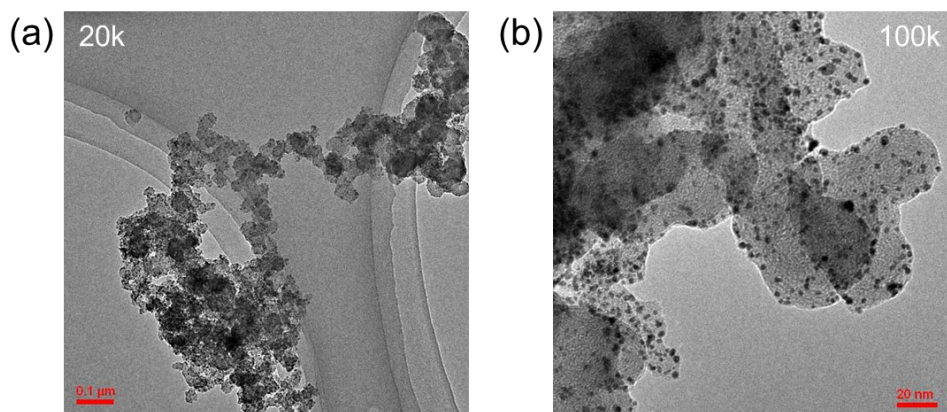


Figure 3-5 Transmission electron microscopy (TEM) images of CB/S-PEDOT/Pt in (a) 20k and (b) 100k magnification.

3.3.2. Electrical resistivity of the composites

Table 3-1 summarizes the electrical resistivity of each sample in powder form. In powder form, the electrical conductivity measurements are not influenced by the complex interactions present in MEAs or CL, such as electrochemical reactions and PEM-CL interfaces. This simplification allows for a clearer understanding of the intrinsic electrical properties of the material. CB/S-PEDOT exhibited much lower resistivity ($0.68 \Omega \cdot \text{cm}$) compared to AB/PBI ($2.68 \Omega \cdot \text{cm}$) and the value was even lower than Vulcan ($1.01 \Omega \cdot \text{cm}$).

Table 3-1. Resistivity of sample in powder form

Powdered sample	Resistivity ($\Omega \cdot \text{cm}$)
Vulcan	1.01
CB/S-PEDOT	0.68
AB/PBI	2.68

3.3.3. Single Cell Measurements

Two MEA having CB/S-PEDOT/Pt as the catalyst was fabricated and MEA having commercial CB/Pt catalyst was also fabricated as the comparison. For both MEAs, the Nafion content was set to an ionomer-to-carbon (I/C) ratio of 0.6. The Pt loading in the cathode was 0.2 mg/cm², while the anode was set to 0.05 mg/cm².

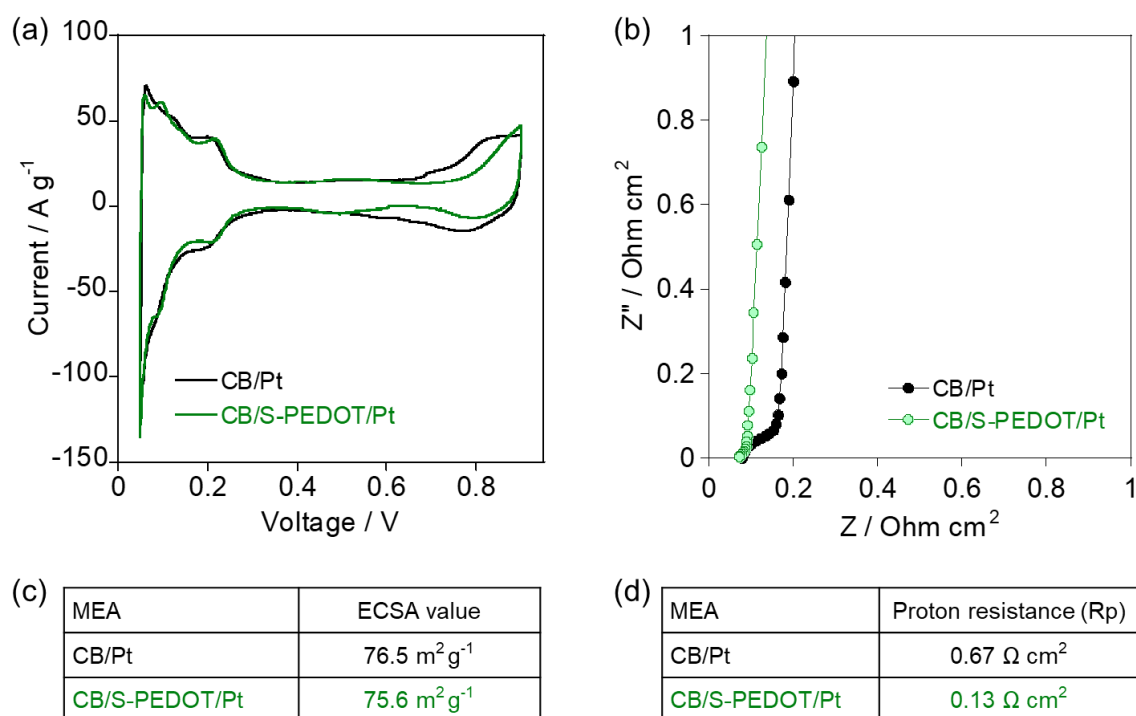


Figure 3-6 (a) CV curves, (b) Nyquist impedance spectra response at 0.45 V (c) calculated ECSA value (d) calculated proton resistance (R_p) of CB/Pt (black) and CB/S-PEDOT/Pt (green) MEAs.

Figure 3-6 (a) shows the CV curves of CB/Pt (black line) and CB/S-PEDOT/Pt (green line), showing that both MEAs demonstrated almost equivalent ECSA values: 76.5 m²/g for CB/Pt and 75.6 m²/g for CB/S-PEDOT/Pt (**Figure 3-6 c**). This similarity likely arises from the comparable Pt particle sizes for CB/S-PEDOT/Pt (2.35 ± 0.43 nm) and CB/Pt (2.03 ± 0.29 nm). Additionally, in the high potential region, the Pt oxidation peak of the CB/S-PEDOT/Pt MEA is not prominent or has been shifted. This phenomenon has been reported in the literature, where at potentials below the Pt oxidation potential (~0.9 VRHE), it is attributed to the interaction between Pt surface atoms and adsorbates such as R-SO₃⁻, OH, or O¹⁴. Furthermore, it has been suggested that cycling up to 1.2 V is preferable, as at 1 V (near OCV), some contaminants may not be oxidized or removed¹⁵. Therefore, we believe that the phenomenon may be attributed to an excess of -SO₃⁻ impurities

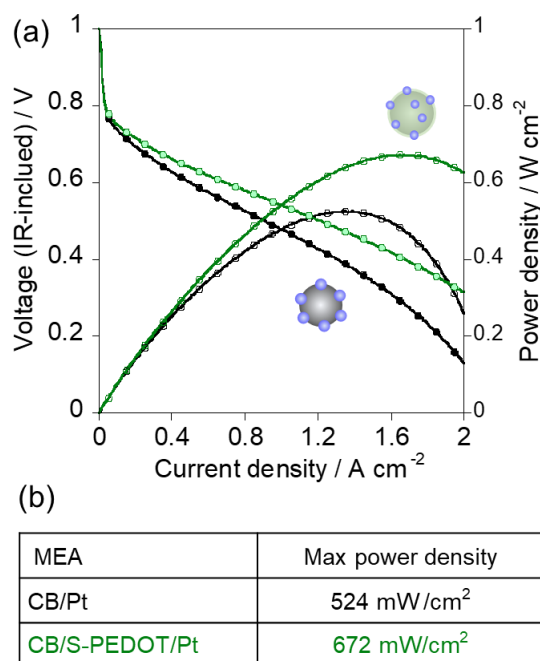


Figure 3-7 (a) Polarization curves and (b) max power density value of CB/Pt (black) and CB/S-PEDOT/Pt (green) MEAs.

provided by the S-PEDOT polymer on the carbon surface, which could be responsible for this behavior. Consequently, in future work, we plan to conduct half-cell testing to confirm this hypothesis.

Figure 3-6 (b) shows the impedance analysis carried out under H_2 (anode)/ N_2 (cathode) condition. By analyzing the curve and calculated the proton conduction resistance value (R_p) using **Eq 3-1**, it was found that the R_p of the CB/S-PEDOT/Pt was $0.13 \Omega \text{ cm}^2$, which is significantly lower than that of CB/Pt ($0.67 \Omega \text{ cm}^2$), as shown in **Figure 3-6** (d). This notable difference may be attributed to the additional proton conduction in CB/S-PEDOT/Pt due to the $-SO_3^-$ groups in S-PEDOT. Further studies such as ionomer-free ($I/C=0$) condition are required to determine whether this mechanism contributes to the enhanced proton conductivity observed. **Figure 3-7** a shows I-

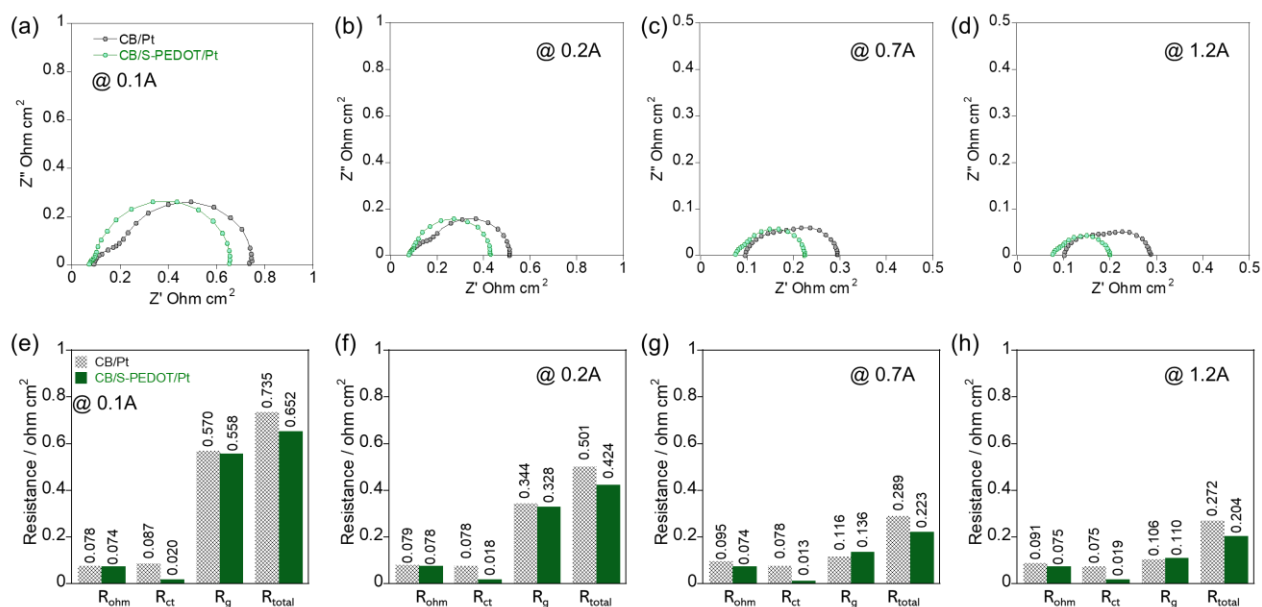


Figure 3-8 EIS curve (up) and fitting value (down: bar chart) of (a) CB/Pt (black) and (b) CB/S-PEDOT/Pt (green) MEAs with $I/C=0.6$ at (a, e) 0.1A, (b, f) 0.2A, (c, g) 0.7A and (d, h) 1.2A.

V performance of the MEAs measured under 100 mL/min hydrogen to the anode and 200 mL/min air to the cathode was fed at 100% humidity and 80 °C. Interestingly, CB/S-PEDOT/Pt still demonstrated superior cell performance compared to the MEA having CB/Pt. Specifically, the maximum power density of CB/S-PEDOT/Pt was 672 mW/cm², which is 28% higher than CB/Pt (524 mW/cm²) (**Figure 3-7 b**).

Furthermore, in the EIS (**Figure 3-8**), the two MEAs exhibited similar ohmic resistance (R_{ohm}) at low current densities (0.1 A and 0.2 A). However, the CB/S-PEDOT/Pt MEA demonstrated slightly lower R_{ohm} at middle and high current densities (0.7 A and 1.2 A). Notably, compared to the CB/Pt MEA, the CB/S-PEDOT/Pt MEA showed significantly lower charge transfer resistance (R_{ct}) across both low and high current density ranges. This improvement can be attributed to the lower resistivity of CB/S-PEDOT (0.68 $\Omega \cdot cm$) compared to CB (1.01 $\Omega \cdot cm$), as discussed in Section 3.3.2 (Table 3-1). Consequently, the CB/S-PEDOT/Pt MEA exhibited a reduced total resistance (R_{total}). Additionally, when comparing the fitted R_{ct} values of CB/S-PEDOT/Pt MEA with those of AB/PBI/Pt MEA (Chapter 2, **Figure 2-4**), a significant decrease in R_{ct} was observed for CB/S-PEDOT/Pt MEA. This result confirms that replacing the insulated PBI with the electron-conductive polymer S-PEDOT for wrapping the carbon surface effectively reduced the charge transfer (e^-) resistance.

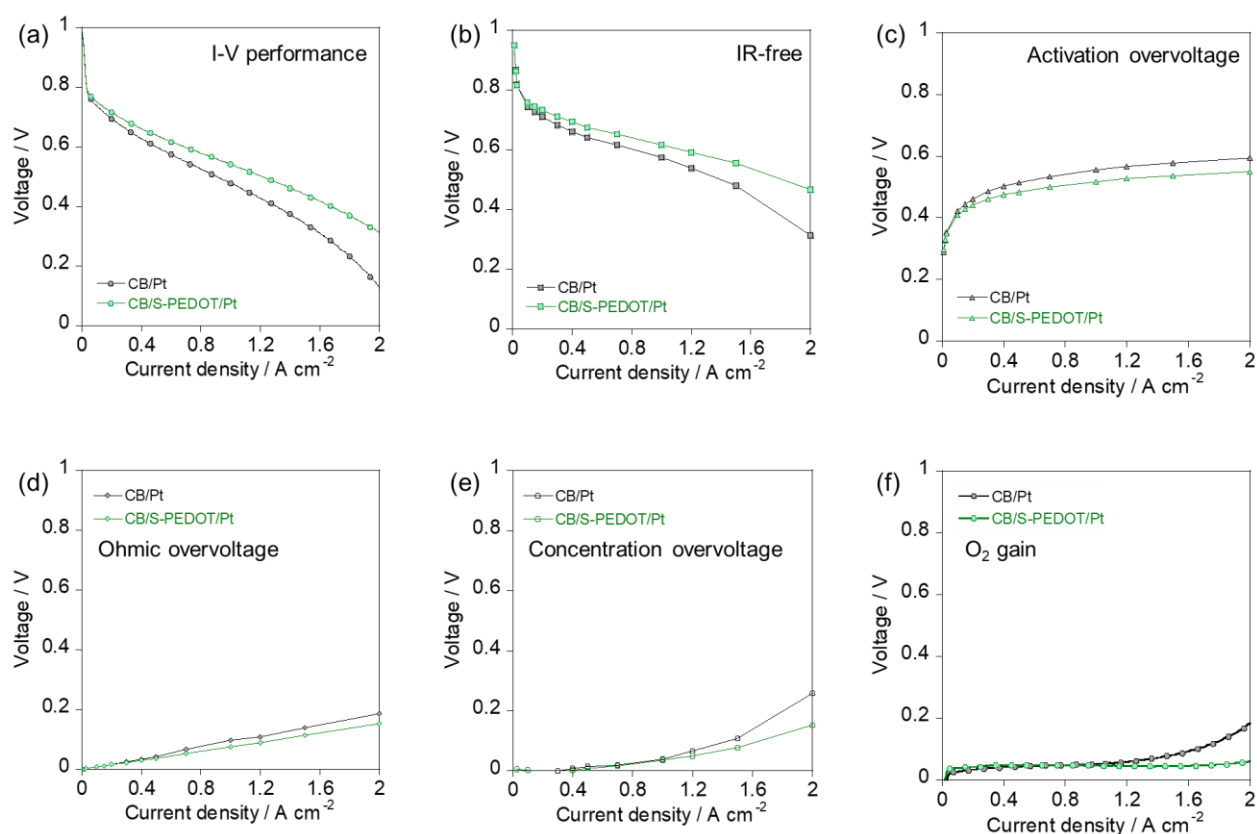


Figure 3-9 (a) IR-included I-V performance, (b) IR-free I-V performance, (c) activation overvoltage, (d) ohmic overvoltage, (e) concentration overvoltage and (f) O₂ gain of CB/Pt (black) and CB/S-PEDOT/Pt (green) MEAs

Figure 3-9 (a-e) shows IR-included I-V performance, IR-free I-V performance, activation overvoltage, ohmic overvoltage, and concentration overvoltage of two MEAs. Same as IR-included cell performance in **Figure 3-9** (a), a higher IR-free performance (**Figure 3-9** b) for CB/S-PEDOT/Pt corresponds to lower ohmic overvoltage (**Figure 3-9** d). In addition to the contribution from the lower ohmic overvoltage (**Figure 3-9** d) in CB/S-PEDOT/Pt agreed with the lower proton resistance values as shown in **Figure 3-6** (b), lowering of the activation overvoltage

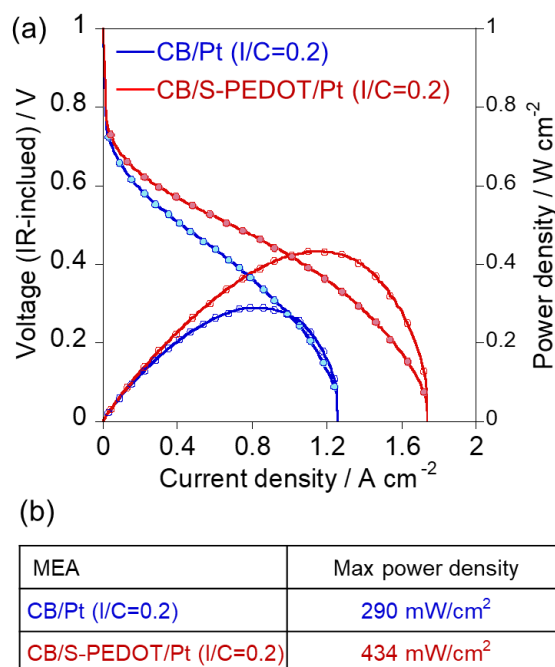


Figure 3-10 (a) Polarization curves and (b) max power density value of CB/Pt (blue) and CB/S-PEDOT/Pt (red) MEAs at I/C=0.2.

(**Figure 3-9 c**) of CB/S-PEDOT/Pt was observed. This effect might be due to the faster reaction kinetics¹⁶ due to higher proton conduction for CB/S-PEDOT/Pt catalyst. To verify this hypothesis, the I/C ratio was decreased to 0.2. **Figure 3-10** (a) shows I-V performance of the MEAs measured under 40 mL/min hydrogen to the anode and 90 mL/min air to the cathode was fed at 100% humidity and 80 °C. Interestingly, CB/S-PEDOT/Pt still demonstrated higher cell performance compared to the MEA of CB/Pt. Specifically, the maximum power density of CB/S-PEDOT/Pt was 434 mW/cm², which is 49% higher than CB/Pt (290 mW/cm²) (**Figure 3-10 b**). This provides evidence that additional proton conduction facilitated by the -SO₃⁻ groups in S-PEDOT.

Figure 3-9 (f) shows O_2 gain results calculated from the subtraction of $H_2(\text{anode})/O_2(\text{cathode})$ and $H_2(\text{anode})/\text{air}(\text{cathode})$ measurements. Obviously, CB/S-PEDOT/Pt CL has higher gas diffusivity than CB/Pt CL especially at high current density region. We have reported in the PBI system that the effective interaction between PBI and Nafion inomer resulted in the homogeneous distribution of ionomer and offered higher O_2 diffusivity due to higher porosity in the cathode CL^{12 8}. Therefore, we consider that the S-PEDOT also has interaction with Nafion inomer and offered the superior porosity structure for O_2 diffusion (especially for Knudsen diffusion) for CB/S-PEDOT/Pt. In future work, we plan to further investigate interaction with CB/S-PEDOT/Pt and Nafion ionomer through various methods carried out in our group.^{17 18 19}

3.4. Conclusion

Successfully enhanced the electron conductivity by coating electron conductive polymer S-PEDOT on carbon surface. Homogeneous deposition of Pt particles on the CB/S-PEDOT surface resulted in a 28% higher maximum power density compared to the conventional CB/Pt catalyst, which can be attributed to the significantly lower electron resistivity of CB/S-PEDOT ($0.68 \Omega \cdot \text{cm}$) compared to CB ($1.01 \Omega \cdot \text{cm}$). Additionally, the proton conduction resistance of the CB/S-PEDOT/Pt MEA was measured at $0.13 \Omega \cdot \text{cm}^2$, much lower than that of the CB/Pt MEA ($0.67 \Omega \cdot \text{cm}^2$). This improvement is likely due to the additional proton conduction facilitated by the SO_3^- groups in S-PEDOT.

To further confirm this mechanism, future investigations under ionomer-free conditions ($I/C = 0$) are required. Furthermore, the superior gas diffusion structure of the CB/S-PEDOT/Pt MEA contributed to lower concentration overvoltage and reduced ohmic overvoltage, which in turn resulted in a lower activation overpotential in the PEMFC system. These findings highlight the potential of self-doped electron-conductive polymers like S-PEDOT to simultaneously enhance proton and electron conductivity, offering a promising pathway for improved catalyst and MEA designs in PEMFC applications.

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Chapter 4

Development of Proton-conductive Carbon Support via Polymer Coating Method for Fuel Cell Electrocatalyst

4.1. Introduction

Recent advancements in catalyst design emphasize optimizing three-dimensional hierarchical structures to minimize various impedances, such as those caused by proton (H^+) and oxygen (O_2) diffusion, particularly within the cathode catalyst layer (CL). A critical impedance identified in cathode CL is the substantial O_2 diffusion resistance at the Pt/ionomer interface, referred to as film diffusion resistance. However, the ionomer is essential for facilitating H^+ diffusion, making its use unavoidable. In addition, this resistance becomes even more pronounced in low-Pt-loading regions (low roughness factor regions), posing a significant obstacle to achieving low-Pt targets. Jinnouchi et al. developed a new ionomer with higher oxygen permeability, called HOPI (high oxygen permeability ionomer), which successfully reduced O_2 diffusion impedance at the Pt/ionomer interface, thereby improving the mass activity of Pt catalysts ¹.

Previously, we proposed an ionomer-free catalyst structure in which no ionomer is added to the CL. To achieve this, the carbon support surface was covalently modified with sulfonic acid groups to facilitate proton conduction in the cathode CL, and Pt was loaded onto this acid-modified carbon black (SCB) ². Single-cell I-V measurements revealed that the absence of ionomer reduced O_2 diffusion overvoltage at high current densities, primarily due to decreased Knudsen diffusion resistance. However, the low proton conductivity of SCB increased activation overvoltage, rendering the ionomer-free structure's impact at the Pt interface unclear. Moreover, the covalent

modification of acid groups on the carbon surface disrupted the sp^2 carbon structure, significantly reducing the thermal stability of the carbon black. Since thermal stability correlates with the electrochemical stability of PEMFCs, this approach risks compromising PEMFC durability ³. Therefore, developing a novel modification method to enhance the proton conductivity of acid-modified carbons without compromising the sp^2 structure is critical.

In this chapter, we developed a non-covalent acid modification method. This approach employs polybenzimidazole (PBI) with acid functional groups as side chains, which are used to coat the carbon surface and introduce acid groups. PBI was chosen for its strong adsorption onto carbon materials via non-covalent interactions and its exceptional thermal stability due to its rigid main-chain structure as discussed in **chapter 1 (Figure 1-16)**. Our recent research demonstrated that PBI grafted with trifluorosulfonimide (PBI-TFSI) exhibited excellent proton conductivity ⁴, especially at low humidity and high temperatures, attributed to the strong acidity ($pK_a \approx -20$) of the TFSI group. However, we employed PBI grafted with sulfonic acid (PBI-PS) for its higher potential for hydrogen bonding with water molecules. Although our previous study showed that PBI-PS membranes exhibited lower proton conductivity due to neutralization of the acid by the basic imidazole in the PBI main chain, they displayed greater water uptake compared to PBI-TFSI membranes. Consequently, PBI-PS was used as a wrapping polymer for carbon. The resulting acid-modified carbons (CB/PBI-PS) were used to support Pt nanoparticles. The strategy of this study and chemical structure of PBI-PS as shown in **Figure 4-1 (a, b)**. This interfacial design

ensures that the Pt surface remains uncovered by ionomer, thereby avoiding O_2 diffusion impedance and preventing poisoning by SO_3^- groups on the Pt surface. Synthesis of PBI grafted by sodium 3-bromopropanesulfonate (PS-Na) was conducted by grafting PS-Na to PBI followed by acid treatment, as shown in **Figure 4-1** (c). The graft ratio of PS-Na was controlled by controlling the feeding ratio of the PS-Na unit.

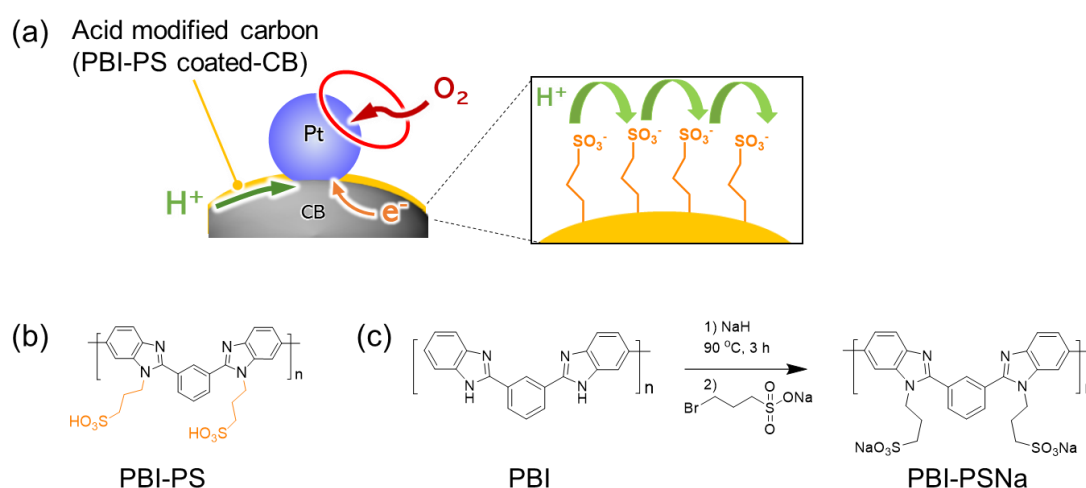


Figure 4-1 (a) Strategy of this study, (b) chemical structure of PBI-PS and (c) synthesis of PBI-PSNa.

4.2 Experimental

4.2.1. Materials

Vulcan XC-72R purchased from Cabot Chemical Co., Ltd., (Boston, USA) was used as carbon black (CB). For comparison, commercially available Pt catalyst on Vulcan (TEC10V30E) was purchased from Tanaka Kikinzoku Kogyo (Tokyo, Japan) and used as CB/Pt. 5% Nafion

dispersion (DE520 CS type), hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), dimethyl sulfoxide (DMSO), ethylene glycol (EG), 1-propanol and 2-propanol were purchased from the FUJIFILM Wako Pure Chemical (Tokyo, Japan). Nafion[®] 212 membrane was purchased from Millipore Sigma (St. Louis, USA). Gas diffusion layers (SIGRACET[®] GDL 22BB) was purchased from SGL Carbon SE (Wiesbaden, Germany). 0.1 μm PTFE film, 50 μm Kapton film and 1 mm silicon film were purchased from AS ONE Co. (Tokyo, Japan). PBI was purchased from SATO LIGHT Co. (Mie, Japan). As shown in **Figure 4-1** (c), grafting of PBI to prepare propanesulfonic acid-grafted PBI (PBI-PS) was synthesized according to the previous report ⁴.

4.2.2. Material Characterization

CHN elemental analyses were performed using a CHN Corder MT-6 (Yanaco). Thermogravimetric analysis (TGA) was performed using an NEXTA STA200 analyzer (Hitachi High-Technologies, Japan) at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under air flow of 100 mL min^{-1} with protection gas N_2 flow of 100 mL min^{-1} . Transmission electron microscopy (TEM) was executed using a 2010 microscope (JEOL, Tokyo, Japan) operating at 120 kV. X-ray photoelectron spectroscopy (XPS) was conducted using an AXIS-ULTRA^{DLD} spectrometer (Shimadzu, Tokyo, Japan). The morphology of the CL was observed by scanning electron microscopy (SEM) using a SU9000 microscope (Hitachi High-Technologies, Japan) at an operating voltage of 20 kV.

4.2.3. Preparation of CB/PBI-PS/Pt catalysts

Potassium form of PBI-PSNa (44 mg) dissolved in DMSO (200 mL) was added to CB (200 mg). The mixture was dispersed using a bath sonicator for 10 minutes and then shaken in a shaking incubator at 80 °C for 3 h. The resulting solutions were filtered using a 0.2 µm PTFE filter membrane and washed with DMSO. The obtained solids were dispersed in DMSO (200 mL) by sonication for 1 minute and stirred at 80°C for 12 hours to dissolve unbounded PBI-PS. After cooling the solution, the mixture was filtered and washed with DMSO. This washing step was repeated one more time to ensure the removal of unbounded PBI-PS. Finally, 1M HCl (100mL) was used to replacement the potassium ion (Na^{2+}) in PBI-PSNa. Subsequently, the obtained solid was treated with 1 M HCl (100 mL) to convert PBI-PS from potassium form to proton form. Finally, the composite (CB/PBI-PS) was washed extensively with Milli-Q water, filtered using a PTFE membrane, and dried under vacuum at 80°C for 12 h in the presence of P_2O_5 . CB/PBI-PS was prepared in the similar manner.

Pt was loaded onto CB/PBI-PS using a polyol reduction method, which employs 60 v/v% EG aqueous solution as the reducing agent and 5% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution as the Pt precursor and detailed procedure can be found in previous study ⁶.

4.2.4. Fabrication of MEA and Fuel Cell Measurements

The catalyst inks were prepared by dispersing CB/PBI-PS/Pt into the mixture of water, 1-propanol and 2-propanol, ethylene glycol by sonication for 20 min. It is noted that these inks have

no ionomer in the dispersion and it can be called as “ionomer-free” inks. As the comparison, a commercial catalyst, CB/Pt (TEC10V30E) was dispersed in the same solvent with Nafion ionomer in the ionomer/carbon ratio (I/C) of 0.6.

Thereafter, the rod Mini coater (MC-20, Hohsen Corp., Japan) was used to cast the inks onto a PTFE sheet (thickness: 0.1 μm) used as the decal transfer substrate. Especially, for the ionomer-free catalyst ink, the of PTFE sheets was treated by O_2 plasma for 5 minutes prior to the casting. After the coating, the sheets were vacuum dried at 120 $^{\circ}\text{C}$ for 1 h to evaporate the solvent. Subsequently, two square sheets (1.0 cm $\times$ 1.0 cm) were hot pressed with Nafion 211 membrane to transfer the catalysts for both side of the membrane. The Pt amount in the cathode and anode was 0.1 mg cm^{-2} and 0.03 mg mg cm^{-2} , respectively. The obtained membranes with the catalysts were directly laminated with gas diffusion layers (GDL; 1.1 cm $\times$ 1.1 cm) when setting in 1 $\times$ 1 cm JARI cell-II (Ex-2C type) to fabricate membrane electrode assembly (MEA).

4.2.5. Single-cell measurements

All the measurements were carried out as described in **Chapter 3**.

4.3. Results and Discussion

4.3.1 Material properties analysis

Table 4-1 Elemental analysis of CB, CB/PBI-PS.

Element analysis	H (%)	C (%)	N (%)	Polymer amount
CB	0.05	97.95	0.07	0
CB/PBI-PS	0.22	96.84	0.22	2.36wt%

Figure 4-2 show X-ray photoelectron spectroscopy (XPS) narrow scans of CB/PBI-PS. N 1s (**Figure 4-2 a**) and S 2p (**Figure 4-2 b**) peaks that was not detected for Vulcan was observed at 402 eV and 168 eV, respectively, evidencing a presence of PBI-PS in the composites. From the elemental analysis, atomic content of nitrogen in CB coated by PBI-PS (CB/PBI-PS) was 0.22% (**Table 4-1**). According to the ^1H NMR measurement, grafting ratio of acid groups in PBI-PS was about 100%, indeed, the molecular weight for per unit for PBI-PS can be calculated as 582.1. Therefore, PBI-PS content in the composites can be estimated 2.36 wt% (**Table 4-1**). Based on the content of the polymers, number of acid groups per 1g of the composites were 4.8×10^{19} for CB/PBI-PS. In the coating of polybenzimidazole (PBI: unit molecular weight = 324.1) on CB, 7.3 wt% of PBI was coated⁷ with the coating coverage and thickness of 69% and ca 0.52 nm, respectively⁸. Suppose that the coating thickness is similar for all the coating, the coverage ratio of the CB/PBI-PS must be less than 30%.

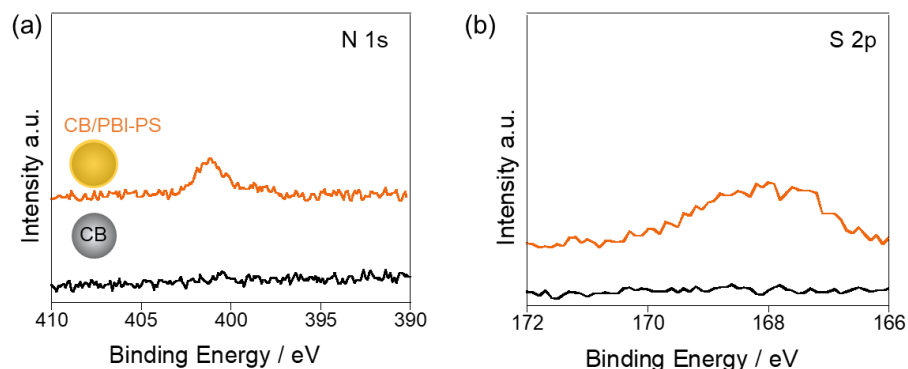


Figure 4-2 X-ray photoelectron spectroscopy (XPS) narrow scans of (a) N 1s, (b) S 2p for CB (black line) and CB/PBI-PS (orange line).

Figure 4-3 shows thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of CB/PBI-PS (orange line). Three step weight reductions starting from 250 °C and 600 °C were observed. By comparing the TGA curve of CB (black line), weight reductions starting at 600 °C is assignable to the combustions of CB. It is noted combustion temperature of CB in the CB/PBI-PS was identical to that of CB, guaranteed the thermal stability of CB was maintained

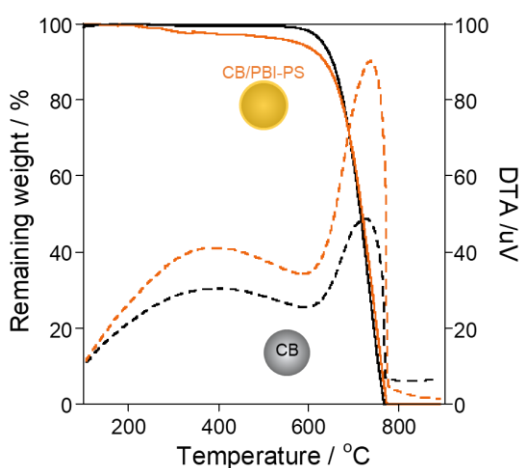


Figure 4-3 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of CB (black line), CB/PBI-PS (orange line).

after coating. Previously, we reported covalent modification of $\text{-SO}_3\text{H}$ group on CB led to the severe decrease of the combustion temperature by $100\text{ }^\circ\text{C}$ ². The thermal stability of the carbon supporting materials is a good indicator of the electrochemical stability of PEMFC operation³ and, therefore, comparable thermal stability indicates the comparable PEMFC durability for CB/PBI-PS.

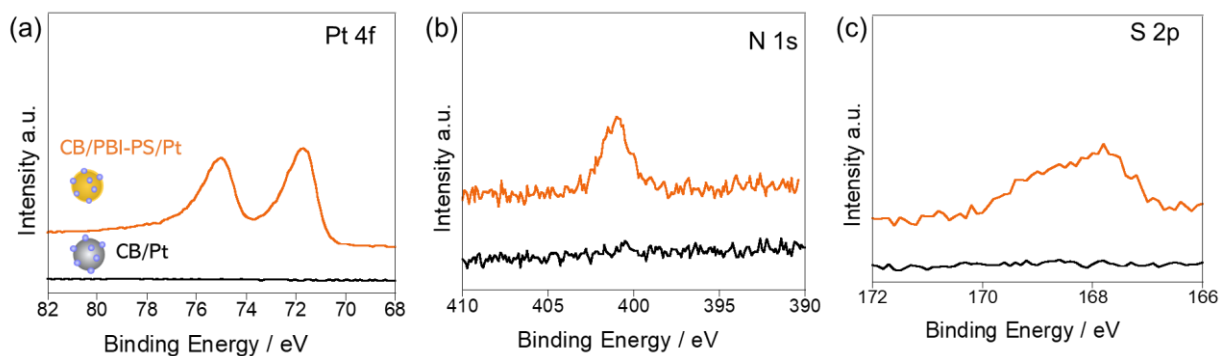


Figure 4-4 XPS narrow scans of (a) Pt 4f, (b) N 1s and (c) S 2p for CB (black line), CB/PBI-PS (orange line).

Pt loading on CB/PBI-PS was conducted using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and EG as a Pt source and reducing agent, respectively. XPS survey scans of the catalysts evidenced the presence of Pt for both composites by the presence of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ at 71.5 and 75.0 eV, respectively (**Figure 4-4 a**). In addition, the presence of N 1s and S 2p supported the PBI-PS coating was stable upon the Pt loading (**Figure 4-4 b and c**). In TGA of CB/Pt and CB/PBI-PS/Pt, only one step weight reduction due to the combustion of supporting materials was observed. Pt loading amount was estimated based on the residual amount at 900 °C and it were determined 29wt% and 20wt% for CB/Pt and CB/PBI-PS/Pt, respectively (**Figure 4-5**). From the transmission electron microscope (TEM), homogeneous dispersion of the Pt nanoparticles was observed for both composites (**Figure 4-6**). Pt particle size of CB/PBI-PS/Pt was determined as 1.93 ± 0.34 nm, which is slightly smaller than that of CB/Pt used as reference (2.03 ± 0.29 nm)

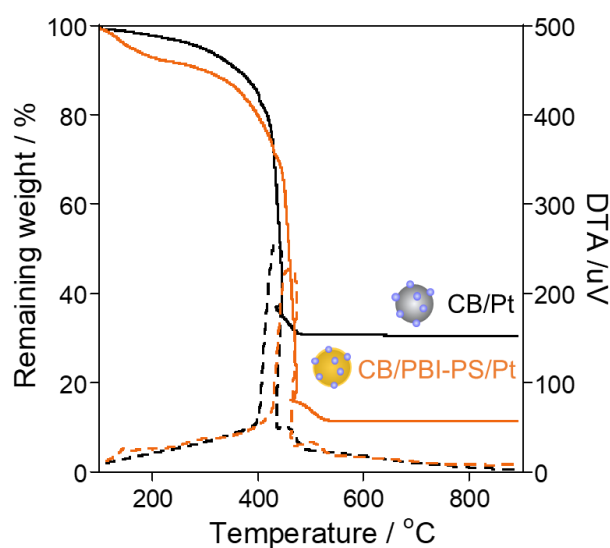


Figure 4-5 TGA and DTA curves of CB/PBI-PS/Pt (orange line) and CB/ Pt (black line).

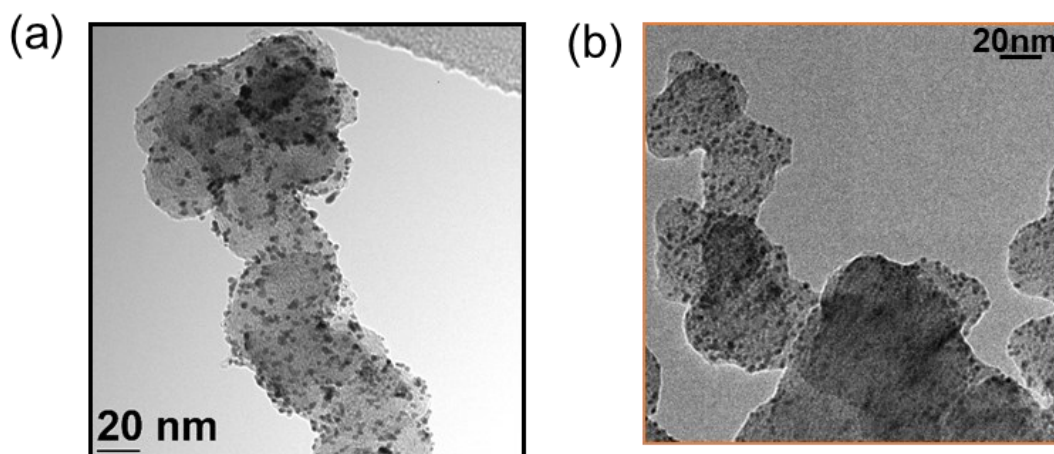


Figure 4-6 TEM images of (a) CB/Pt and (b) CB/PBI-PS/Pt in 100k magnification.

4.3.2 Electrical resistivity of the composites

Previously, we observed the larger charge transfer resistance for AB/PBI/Pt catalyst compared to the AB/Pt catalyst in the single cell measurements⁹. We considered that the electrical insulating of PBI increased the contact at CB/PBI-CB/PBI interface. Therefore, this time, we measured the electrical resistivity of polymer-coated CBs using the method described in Chapter 3, Section 3.3.2. **Table 4-2** summarizes the electrical resistivity of the polymer-coated CB. As

Table 4-2 Resistivity of CB, CB/PBI, CB/PBI-PS in powder form

Element analysis	Resistivity (Ω cm)
CB	1.01
CB/PBI	2.99
CB/PBI-PS	1.21

considered, CB/PBI showed higher resistivity (2.99 Ωcm) compared to the CB (1.01 Ωcm). On the other hand, CB/PBI-PS showed lower resistivity than CB/PBI, probably due to the smaller coverage of the polymers.

4.3.3 Single Cell Measurements

To prepare the CL for MEA, CB/PBI-PS/Pt ink without containing any ionomer was casted to PTFE sheet and transferred to both sides of Nafion films to prepare MEAs (denoted as MEA_{PS}). As the comparison, CB/Pt dispersed in Nafion solution in 30wt% was used to prepare MEA (MEA_{ref}). We noticed that the not all the catalyst composites were transferred to Nafion membrane for CB/PBI-PS/Pt. This is probably due to the absence of ionomer that serves as the glue/binder for the conventional catalysts. Therefore, Pt amounts on the CL were limited in the range from 0.1 to 0.2 mg cm⁻², which are acceptable for next generation targets (ex. 0.125 mg cm⁻² for 2040¹⁰). **Figure 4-7** shows SEM of the casted catalysts on PTFE, in which this side is transferred as PEM/CL interface. Compared to the CL of CB/Pt having Nafion ionomer (I/C=0.6), CL of

CB/PBI-PS/Pt (w/o Nafion) surface showed similar morphology that means the two MEAs can fairly compare.

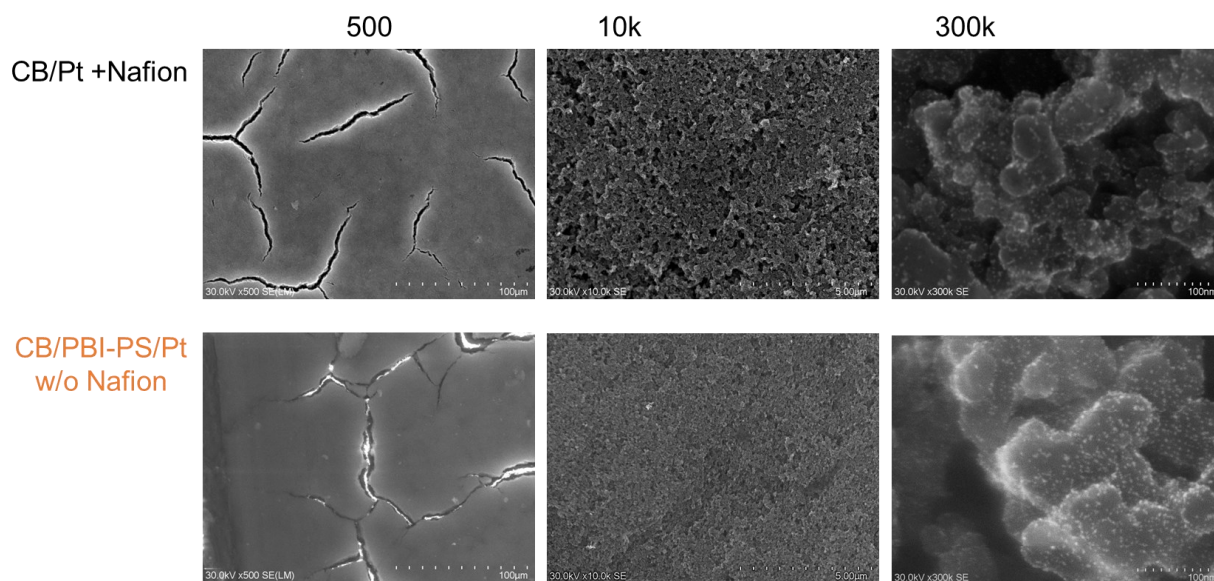


Figure 4-7 SEM images of CB/Pt with Nafion (up) and CB/PBI-PS/Pt without Nafion (down) under 500, 10k and 300k magnifications.

Figure 4-8 (a) shows the CV of cathode CL in MEA_{ref} and MEA_{PS}. Clear hydrogen adsorption and desorption peaks were observed. From the adsorption peak, ECSA were calculated and the ECSA of CB/PBI-PS/Pt in cathode CL was determined as $83.6 \text{ m}^2 \text{ g}^{-1}$, which is slightly higher than that of CB/Pt ($75.8 \text{ m}^2 \text{ g}^{-1}$). The difference is probably due to the size of Pt on CB/PBI-PS/Pt is smaller than that of CB/Pt. We noticed that the Pt oxidation peak was suppressed or positively shifted for both for CB/PBI-PS/Pt. One possibility is the Pt was grown inside the coating layer and the surface of Pt was covered by polymers, which hampered the O₂ adsorption.

To estimate the proton conductivity of the catalysts, impedance of the cathode CL was measured at 0.45 V by feeding H₂ and N₂ for anode and cathode, respectively **Figure 4-8** (b). Proton resistivity of MEA_{PS} cathodes is 0.55 Ωcm², while MEA_{ref} cathode has proton resistivity of 0.26 Ωcm² much lower than others reports which using ethanol or alcohol-rich solvent ^{7 11} but similar as the report of using 2-propanol solvent in catalyst ink ². As we discussed in **chapter 5**, the solvent and alcohol content in catalyst extremely affect the cell performance. Although the values in ionomer-free catalyst of CB/PBI-PS/Pt was slightly larger than that of MEA_{ref} having ionomer, these values were much lower than that of SCB (2.9 Ω cm²) ². We consider that the -

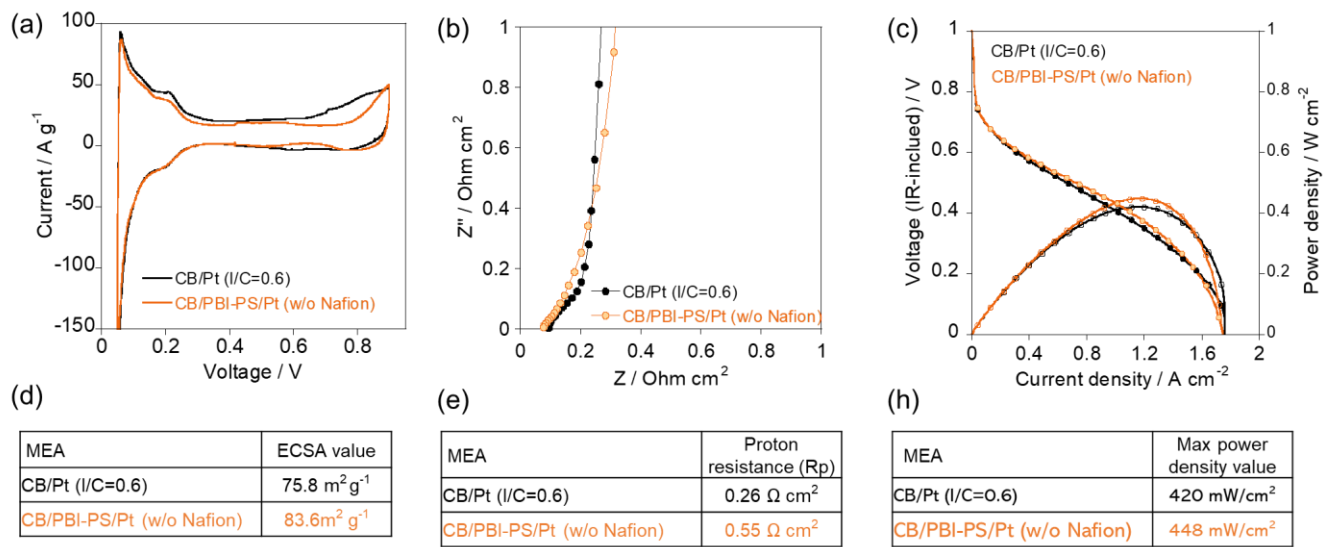


Figure 4-8 (a) CV curves, (b) protonic resistance (R_p), (c) polarization curves, (d) calculated ECSA value (e) calculated proton resistance (R_p) and (h) max power density value of MEA_{ref} (black) with Nafion, MEA_{PS} (orange) without Nafion

SO₃H group is grafted in the polymer backbone and the distance between -SO₃H become closer compared to the chemical grafting onto CB, resulted in the higher proton conductivity.

Figure 4-8 (c) shows I-V curve of MEAs operated at 80 °C under 100% RH. Of interest, MEA_{PS} exhibited the comparable performance with MEA_{ref} at 100%RH even though the MEA_{PS} has lower proton conductivity. Indeed, in the EIS (**Figure 4-9**), similar ohmic resistance (R_{ohm}) were observed for two MEAs. However, much lower gas diffusion resistance (R_g) was observed for MEA_{PS}, especially at low current density. In addition, the charge transfer resistance (R_{ct}) in two MEAs also comparable may due to the resistivity in CB/PBI-PS (1.21Ω cm) is similar with CB

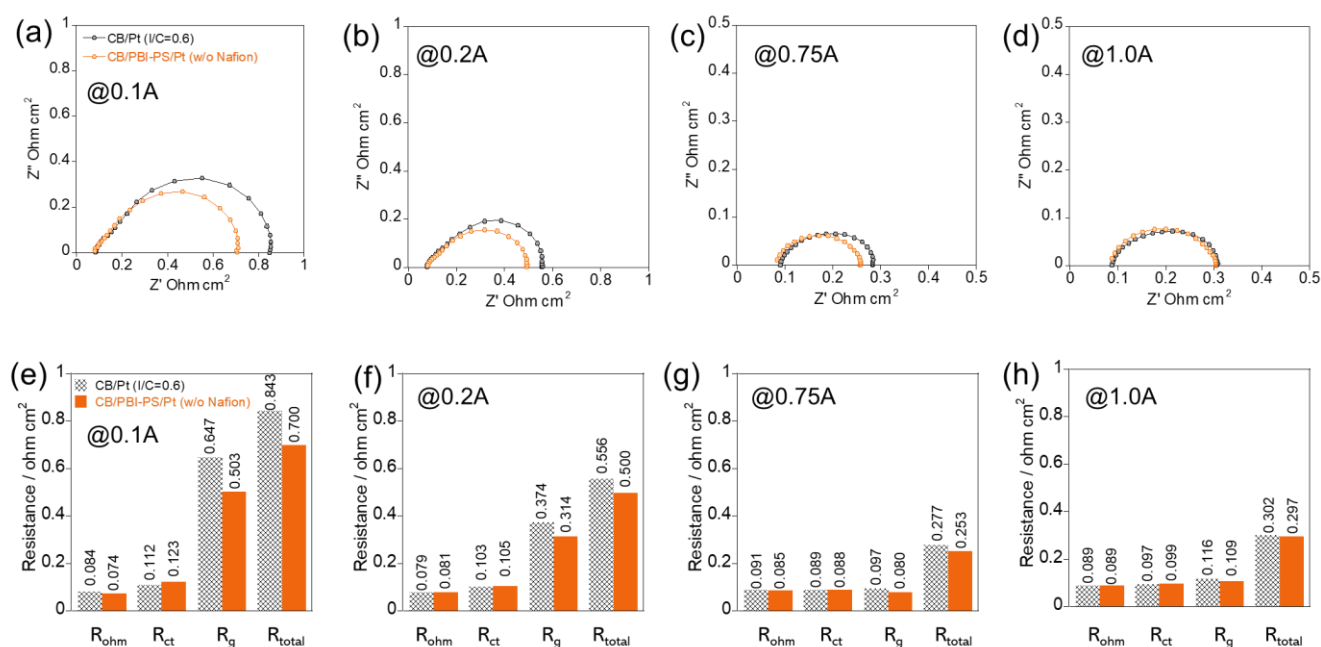


Figure 4-9 EIS curve (up) and fitting value (down: bar chart) of MEA_{ref} (black) with Nafion and MEA_{PS} (orange) without Nafion at (a, e) 0.1A, (b, f) 0.2A, (c, g) 0.75A and (d, h) 1.0A.

($1.01\Omega\text{ cm}$), as discussed in section 4.3.2 (**Table 4-2**). Therefore, finally showed a lower total resistance value (R_{total}) for MEA_{PS}, hence, obtained a slightly higher max power density value in MEA_{PS} ($448\text{mW}/\text{cm}^2$) compare with MEA_{ref} ($420\text{mW}/\text{cm}^2$), because in the ionomer-free catalyst, absence of ionomer provides superior space for O_2 diffusion and resulted in the lower O_2 diffusion resistance². **Figure 4-10** (a-e) shows IR-included I-V performance, IR-free I-V performance, activation overvoltage, ohmic overvoltage, and concentration overvoltage of MEA_{PS}, and MEA_{ref}. Similar to IR-included cell performance shown in **Figure 4-10** (a), the slightly higher IR-free cell performance (**Figure 4-10** b) of MEA_{PS} corresponds to lower ohmic overvoltage (**Figure 4-10** d)

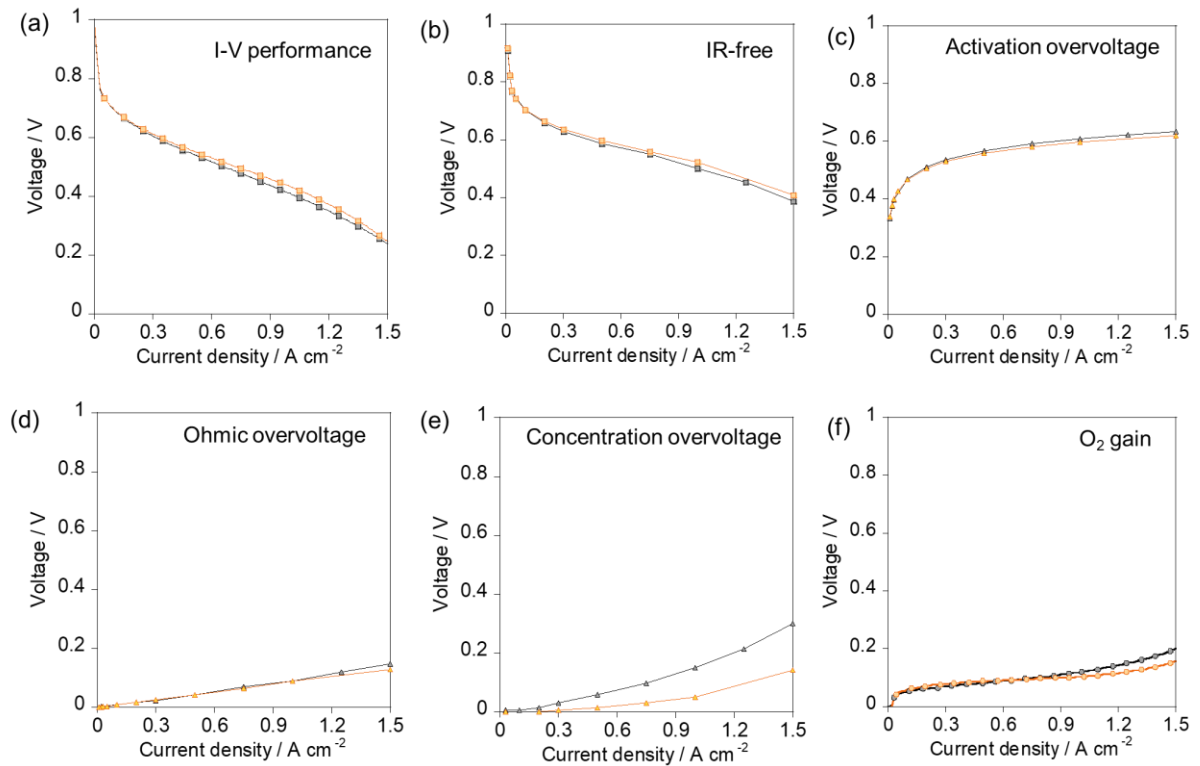


Figure 4-10 (a) IR-included I-V performance, (b) IR-free I-V performance, (c) activation overvoltage, (d) ohmic overvoltage, (e) concentration overvoltage and (f) O_2 gain of MEA_{ref} (black line and marks) and MEA_{PS} (orange line and marks).

of CB/PBI-PS/Pt, especially over 1.0A current density range. In addition, the slightly lower activation overvoltage observed for MEA_{PS} may indicates the effect of ionomer-free catalyst for reduce overpotential (**Figure 4-10 c**). As discussed above, much lower concentration overvoltage (**Figure 4-10 e**) for MEA_{PS} correspond to superior gas diffusion space due to the absence of ionomer. This result is good agreement with O₂ gain measurement showing lower O₂ gain for MEA_{PS} (**Figure 4-10 f**), indicated the higher O₂ diffusion.

Figure 4-11 showed the I-V performance of MEA_{PS} measured at 80 °C at different humidity from 20%RH to 100%RH. As decrease of humidity, we observed drop of I-V performance for MEA_{PS}, while MEA_{ref} showed gradual decrease of the I-V performance. Therefore, proton conduction via PBI-PS layer might be highly dependent on water adsorption environment. We assumed that the PBI-PS layer is not sufficiently connected so that optimization of the coating

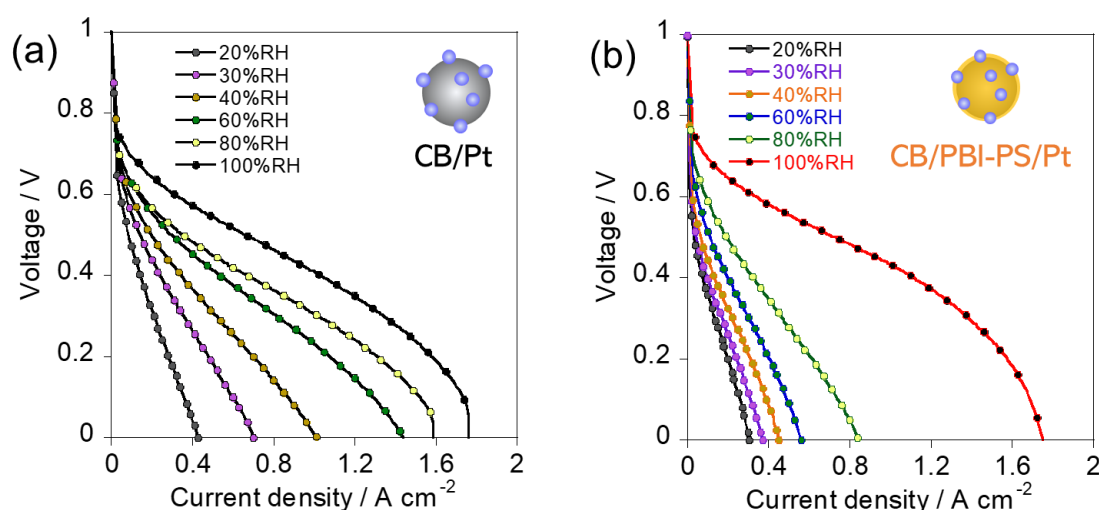


Figure 4-11 I-V performance measured at 80 °C at different humidity from 20%RH to 100%RH. of MEA_{ref} (a) with Nafion and MEA_{PS} (b) without Nafion

morphology and tuning of the $-\text{SO}_3\text{H}/-\text{SO}_3\text{H}$ distance will offer improvement of the I-V performance.

4.4. Conclusion

CB was successfully modified by sulfonic acid group ($-\text{SO}_3\text{H}$) without deteriorating the thermal stability of the CB, where CB was non-covalently coated by PBI-PS has proton conductivity. Pt nanoparticles were deposited on CB/PBI-PS to fabricate ionomer-free catalyst composite (CB/PBI-PS/Pt). The composite even without ionomer addition and allow us to fabricate CL on Nafion membrane through decal transfer method. MEA having CB/PBI-PS/Pt (MEA_{PS}) without containing ionomer showed comparable I-V performance of the MEA having CB/Pt with Nafion ($\text{I/C}=0.6$) at 80 °C under 100%RH. Although proton conductivity of CL in MEA_{PS} was lower than that of MEA_{ref} , superior gas diffusion structure of ionomer-free MEA_{PS} offers lower concentration overvoltage. Large drop of I-V performance at lower RH suggests that the optimization of the coating morphology and/or acid/acid distance on carbon surface can further improve I-V performance. These findings provide important information to realize novel ionomer-free MEA system, that will contribute both for cost reduction and improvement of mass activity.

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Chapter 5

Effect of alcohol content on the ionomer adsorption of polymer electrolyte membrane fuel cell catalysts

5.1. Introduction

As discussed in **chapter 1**, to control the 3D structure of the CL, including the distribution of its ionomers and pores, the dispersion compositions of the Pt/C with ionomer, referred to as “ink,” and their casting conditions for the CL preparation are highly important ¹. One of a critical parameter that determines the CL structure is the amount of ionomer in the inks (i.e., carbon-to-ionomer weight ratio, I/C). Various researchers have optimized I/C depending on the type of carbon supports, ionomer structure, and ink concentration ²⁻¹¹. General trend is that an increase in I/C increases the proton conductivities but decreases O₂ diffusivity, while decreasing I/C improves the O₂ diffusivity but decreasing the proton conductivity because of disconnection of the ionomer networks ³. The type of solvents in the ink also affects the PEMFC performance ¹²⁻²⁰. In particular, the binary mixture of water and alcohols, such as methanol, ethanol, isopropyl alcohol, and 1-propanol, has been extensively studied to tune the ink properties ^{14, 19, 21-24}. Further, the amount of ionomer adsorption onto Pt/C and their adsorption morphology vary depending on the solvent systems, thereby affecting the ionomer distribution ¹⁴, 3D porous structure ¹⁸, microscale voids ¹⁹, and millimeter-scale cracks ¹² in the CL, which affect the PEMFC power density. Thus, the ionomer morphology in the bulk solution plays a key role on the morphology of Pt/C and ionomer distribution in the CL ¹⁴.

The morphology of Nafion dramatically changes depending on the dielectric constant (ϵ) and solubility parameter (δ) of the solvents based on the response of two Nafion chemical compositions, i.e., hydrophobic fluorocarbon backbone and hydrophilic side chain acids ($pK_a = -6$)²⁵. In water, Nafion forms rod-like colloidal clusters (diameter of 4 – 5 nm and length of ~30 nm) with a backbone assembly as the core and negatively charged side chains as the shell^{14, 26-28}. When the alcohol content is increased, the Nafion clusters tend to disassemble owing to the high affinity of alcohol to the backbone (similar δ). Moreover, the dissociation of $-\text{SO}_3\text{H}$ decreased because of the lower ϵ ¹⁴.

Several studies have noted that the adsorption of Nafion is dependent on the alcohol content in the inks. In the presence of carbons or Pt/C, the backbone of Nafion tends to adsorb on the carbon surface in water or water-rich solvents owing to the hydrophobic interactions, which renders the orientation of the $-\text{SO}_3\text{H}$ group to outside^{29, 30}. Several attempts have systematically illustrated the relationship between the Nafion morphology in the ink, adsorption morphology on Pt/C, and CL performance depending on the alcohol content^{14, 19, 22-24}.

Ngo et al. reported a higher PEMFC performance in water-rich (80 wt% water) inks, whereby highly charged large Nafion aggregations deposited on the of Pt/C surface lower the Nafion contact on the Pt/C surface and facilitate O_2 access¹⁴. Meanwhile, in alcohol-rich solvents, weakly charged small Nafion particles exhibit strong contact with the Pt/C surface and shielded the contact with H_2/O_2 gas, resulting in a lower performance. In contrast, Orfanidi et al. reported a lower

performance in water-rich (65 wt%) ink than in alcohol-rich (16 wt%) ink. They explained that the large ionomer aggregation in the water-rich ink covers the macropores of the CL, thereby hampering the O₂ diffusion. Meanwhile, under alcohol-rich conditions, the ionomers are distributed more homogeneously because of the small ionomer aggregation, which leads to good ionomer connection on the C/Pt surface, thereby resulting in the good performance²². These studies clearly indicate that the interactions among Nafion ionomer, solvent molecules, and carbon surface in inks are important in controlling the final distribution of Nafion in the CL. However, the systematic and quantitative analysis of Nafion adsorption onto carbons or Pt/C depending on the solvent composition is yet to be analyzed.

The quantitative analysis of Nafion adsorption onto carbons or Pt/C in water has been evaluated by adsorption isotherm measurements^{29, 31-35}. In addition, several methods have been used to quantify Nafion concentration, including gravimetric methods³¹, density measurement²⁹, and fluorine-19 nuclear magnetic resonance spectroscopy (¹⁹F-NMR)³²⁻³⁵. Based on the adsorption isotherm, the Nafion adsorption for various carbon materials, including CB, carbon nanofiber, carbon nanotube, and Pt/CB, in water exhibits Langmuir type adsorption isotherms and a multilayer adsorption for high Nafion concentrations³²⁻³⁵. Thoma et al. investigated the adsorption of PFSA ionomers with different graft densities of the acid side chains onto CB surface, whereby an increase in the side chain density decreased the number of adsorbed PFSA ionomer per CB surface²⁹. These results confirm that the adsorption isotherm is a powerful tool for

analyzing the adsorption behavior, however, existing experiments have been carried out in water, and the effects of alcohol are yet to be considered. In particular, as binary mixtures of water/alcohol are used in the actual fabrication of PEMFCs, the adsorption isotherm using the binary mixtures of water/alcohol as the solvents could provide practical information to optimize the PEMFC performance.

Recently, Ott et al. reported the control of the adsorption and ionomer distribution in the CL by the surface modification of CB, thereby improving the PEMFC performance³⁶. In our previous studies, the PEMFC performance is improved by the surface coating of carbons with polybenzimidazole (PBI) in alcohol-rich solvents³⁷⁻⁴⁰. In that system, the PBI was coated onto CB surface through non-covalent interaction, then Pt was directly loaded on the surface of the PBI-coated CB (CB/PBI) to form a new catalyst of CB/PBI/Pt. Thus, we assumed that the PBI coating supports a homogeneous ionomer distribution due to the strong interaction between PBI and the ionomers, thereby generating a well-connected proton path and porous network for O₂ diffusion^{39, 40}. However, the degree of interaction and adsorption amounts of ionomers are yet to be quantitatively determined.

In this chapter, we evaluated the adsorption isotherm of Nafion onto CB and their Pt composites in water-rich (80 wt% water) and alcohol-rich (13 wt% water) binary mixtures. As an alcohol, ethanol was chosen because of the easy evaporation at the practical fabrication process of membrane-electrode-assembly (MEA) compared to the other alcohols having higher boiling point such as ethylene glycol. As the catalyst composites, Pt-loaded CB and Pt-loaded polymer-wrapped CB were compared to study the effects of the alcohol contents on the interaction between ionomer and the surface of the carbon supports. The control of the interaction between the ionomers and catalyst composites is crucial in controlling the PEMFC performance (**Figure 5-1**).

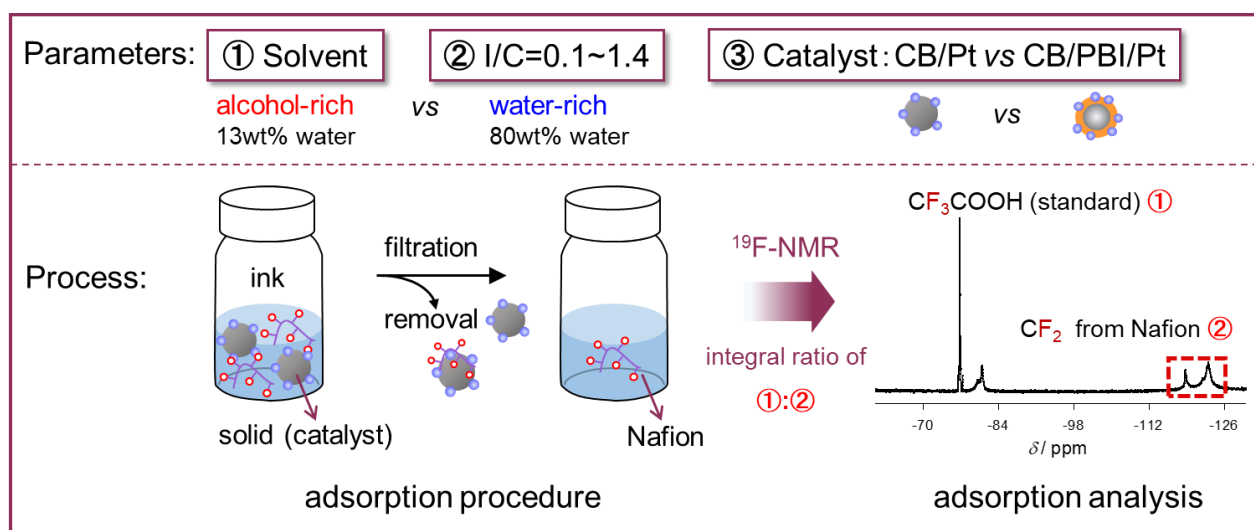


Figure 5-1 Overview of this study

5.2. Experimental

5.2.1. Materials

Hydrogen hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), *N,N*-dimethylacetamide (DMAc), trifluoroacetic acid (98.0%), deuterium oxide (99.9%), ethylene glycol (EG), and ethanol

(99.5%) were purchased from FUJIFILM Wako Pure Chemicals Ltd. (Tokyo, Japan). Vulcan XC-72R purchased from Cabot Chemical Co., Ltd., (Boston, USA) was used as CB. CB/Pt (Vulcan/Pt: TEC10V50E) was purchased from Tanaka Kikinzoku Kogyo (Tokyo, Japan). Nafion solution (5%) in lower aliphatic alcohols and water was purchased from MilliporeSigma (St. Louis, USA). Polybenzimidazole (PBI) (containing 23.4 wt% DMAc) was provided by Sato Light Industrial Co. Ltd (Kameyama, Japan). All solutions were prepared with Milli-Q ultra-pure water with a resistance of 15 M Ω ·cm (Milli-Q, Elix).

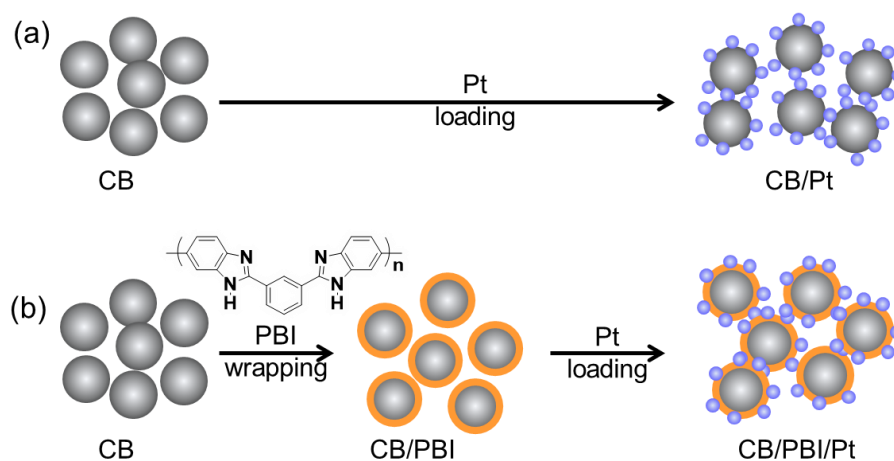
5.2.2. Material characterization

Thermogravimetric analysis (TGA) was performed using EXSTAR TG/DTA6300 analyzer (Hitachi High-Technologies Corp., Tokyo, Japan) at a heating rate of 10 °C·min⁻¹ under an air flow of 100 mL min⁻¹. ¹⁹F-NMR experiments were performed in a JEPL 400 MHz (JNM-ECZ400S). The size distribution of the catalyst particles in the catalyst ink was investigated by dynamic light scattering (DLS) measurements with a particle size analyzer (DLS, PHOTAL ELS8000, Otsuka Electronics) using an ink diluted ten folds. The surface charge of the composites in the inks was determined by the zeta potential measurements using the same instrument of DLS with the same dilution ratio. The CB/Pt and CB/PBI/Pt ink dispersions with Nafion (I/C of 0.6 and 1.0) in the water- and alcohol-rich solvents were sprayed on polyethylene terephthalate (PET) substrates to prepare the CL. The zeta potential of the sprayed CL surfaces was measured using

SiO₂ monitor particles (diameter of 500 nm). The DLS results of the ink dispersion and zeta potential of their CL were modeled using the Smoluchowski equation. The morphology of the CL was observed by scanning electron microscopy (SEM) using a SU9000 microscope (Hitachi High-Technologies) at an operating voltage of 20 kV with magnifications of 1300×, 10,000×, and 300,000×.

5.2.3. Preparation of CB/PBI/Pt

The detailed preparation methods of the Pt catalyst on the PBI-coated CB (CB/PBI/Pt) and CB (CB/Pt) were reported in our previous works (**Scheme 5-1**)^{38,39}. In brief, CB/PBI was prepared by mixing CB (20.0 mg) and PBI (13.0 mg) in DMAc (20.0 mL) under sonication. Pt was loaded onto CB/PBI and CB using a polyol reduction method, which employs 60 v/v% EG aqueous solution as the reducing agent and 5% H₂PtCl₆·6H₂O solution as the Pt precursor.



Scheme 5-1 Preparation of (a) CB/Pt and (b) CB/PBI/Pt

5.2.4. Adsorption isotherm

CB (6.13 mg) was dispersed in aqueous ethanol solutions (87 or 20 wt%, 2.0 mL) with different amounts of Nafion (I/C = 0.1–1.4) by sonicating for 30 min and shaking for 24 h at programed temperatures. The dispersions were filtered with a syringe filter (pore size of 0.2 μm), and the filtrates were measured with ^{19}F -NMR at 25 $^{\circ}\text{C}$ to calculate the amount of adsorption. For ^{19}F -NMR, 0.6 mL filtrates were added to 20 μL trifluoroacetic acid and 20 μL heavy water used as internal standard and deuterium solvent, respectively. The amount of Nafion was calculated based on the integral ratio of the largest peaks of Nafion ranging from -115 to -130 ppm in reference to the trifluoroacetic acid peak at -75.5 ppm, in which the calibration curves were prepared separately. To prepare the adsorption isotherm, the adsorption amount (Γ) of Nafion was plotted as a function of the equilibrium concentration (C_e). The maximum adsorption amount (Γ_{max}) and Langmuir constant (K_L) were determined based on the Langmuir equation **Eq. (5-1)**:

$$\frac{C_e}{\Gamma} = \frac{C_e}{\Gamma_{\text{max}}} + \frac{1}{\Gamma_{\text{max}}K_L} \dots\dots\dots \text{Eq. (5-1)}$$

where C_e : Equilibrium concentration ($\text{g}\cdot\text{L}^{-1}$), Γ : Adsorption amount ($\text{g}\cdot\text{g}^{-1}$), Γ_{max} : Maximum adsorption amount per monolayer ($\text{g}\cdot\text{g}^{-1}$) and K_L : Langmuir constant. The same procedure was applied for CB/PBI, CB/Pt, and CB/PBI/Pt and each experiment were repeated at least three times.

5.2.5. Preparation of inks

CB/Pt or CB/PBI/Pt (11.23 mg) was dispersed in 87 wt% ethanol (alcohol-rich) or 20 wt% ethanol (water-rich) solvents. Subsequently, 5.0 wt% Nafion solution and solvent were mixed to obtain a total volume of 10 mL. The concentration of the solution was adjusted to achieve an I/C of 0.2–1.4. After the addition of 5.0 wt% Nafion solution, the solution was sonicated for 30 min and shook for 24 h to prepare the ink solutions. For the DLS and zeta potential measurements, the inks were diluted 10 times using the solvents. For the sedimentation experiments, the inks were stored in glass tubes (inner diameter of 4.0 mm) for 2 weeks.

5.2.6. Membrane electrode assembly (MEA) preparation

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. The amount of Nafion ionomer was 28 wt% (ionomer/carbon; I/C = 0.72). The 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 to get a MEA. The Pt loading of the catalyst-coated membrane was 0.3 mg cm⁻² and its geometric area was 1.0 cm².

5.2.7. Fuel cell operation

All the measurements were carried out as described in **Chapter 2**.

5.3. Results and discussion

5.3.1. Ionomer adsorption on CB and CB/Pt

Figure 5-2 (a) show the adsorption isotherms of CB in the binary mixture of water and ethanol in the water-rich (blue) and alcohol-rich (black) solvents at 25 °C. The Nafion adsorption on CB was measured at different I/C and plotted as a function of the equilibrium concentration (C_e) of Nafion. The amount of adsorbed Nafion and C_e were evaluated based on the ^{19}F -NMR spectra (Figure 5-3), where the peak area integrations of the CF_2 peaks at -115 to -130 ppm were used to estimate the Nafion concentration using trifluoroacetic acid as the internal standard. Two-step adsorption profiles were observed under water- and alcohol-rich conditions, indicating the multilayer adsorption of Nafion³²⁻³⁵. According to previous reports, the primary adsorption can be fitted following a Langmuir type adsorption³²⁻³⁵. However, theoretically, polymer adsorption onto a solid surface should not follow Langmuir adsorption because Nafion is not homogenous in terms of molecular weight, and the adsorption sites on CB are not equivalent. However, in our

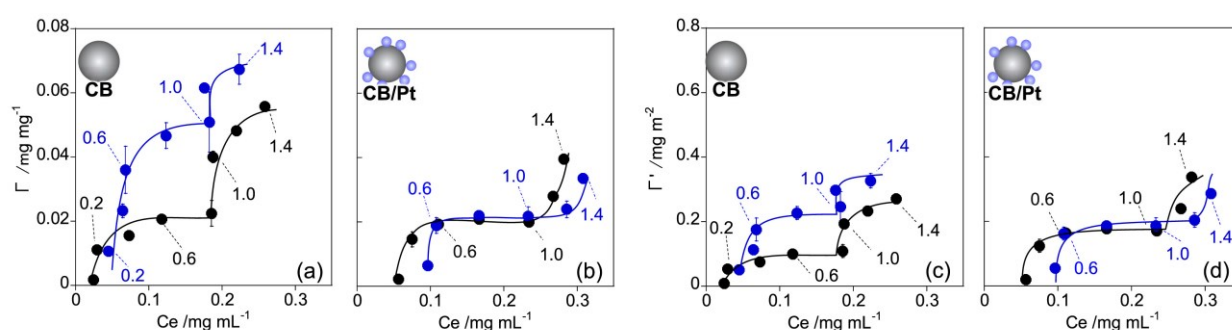


Figure 5-2 (a–d) Adsorption isotherm of Nafion onto (a, c) CB and (b, d) CB/Pt in the water-rich (blue) and alcohol-rich (black) solvents at 25 °C for (a, b) Γ and (c, d) Γ' . The numbers in the figures represent I/C.

Table 5-1. K_L , $\Gamma_{\max}$, and $\Gamma'_{\max}$ for CB and CB/Pt in water- and alcohol-rich solvents.

	CB		CB/Pt	
	Water	Alcohol	Water	Alcohol
K_L	89	32	29	25
$\Gamma_{\max}$ [mg·mg ⁻¹]	0.043	0.024	0.022	0.021
$\Gamma'_{\max}$ [mg·m ⁻²]	0.209	0.116	0.188	0.179

system, as we compared the same polymers, we considered the comparison based on the Langmuir type fitting is effective enough to determine the adsorption trend, which allows a quantitative comparison for various ink systems. In addition, the R_2 values of the Langmuir fitting was over 0.95, suggesting a reasonable fitting. Based on the fitting of **Figure 5-2 a**, the K_L of the first layer adsorption of Nafion onto CB in the water- and alcohol-rich solvents were calculated as 89 and 32, respectively, which indicates the stronger interaction of Nafion to the CB surface in the water-rich solvent. In addition, the $\Gamma_{\max}$ for the first layer was determined to be 0.043 and 0.024 mg mg⁻¹ in the water- and alcohol-rich solvents, respectively (**Table 5-1**). The superior adsorption of Nafion onto the CB surface in the water-rich solvent indicates hydrophobic interaction as the major driving force of the adsorption, whereby the hydrophobic CF₂ backbones are preferentially adsorbed onto the CB surface ²⁹. Of interest, for the water-rich solvent, the primary adsorption

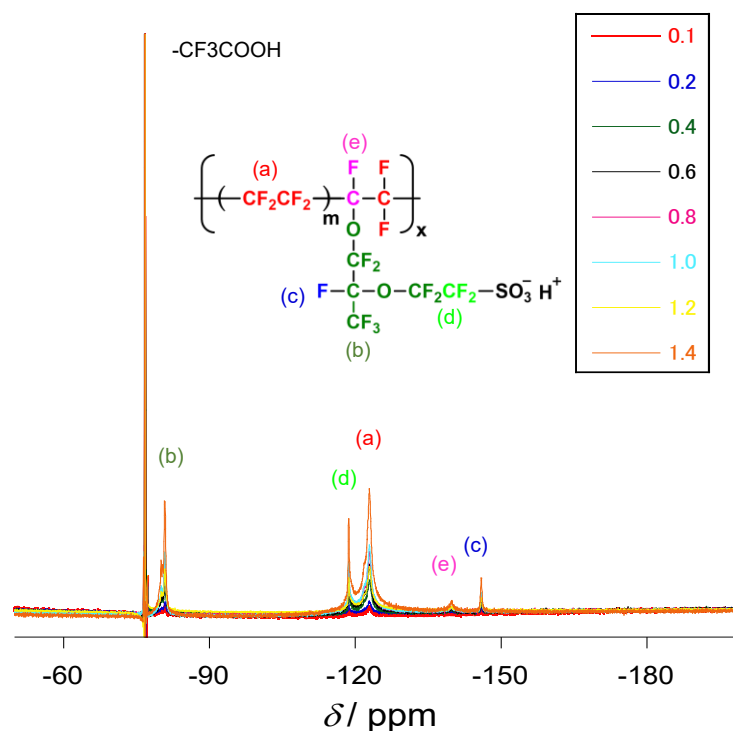


Figure 5-3 ^{19}F -NMR spectra of Nafion at various I/C ratio in alcohol-rich solvents.

started at C_e of around 0.04 mg mL^{-1} that is higher than that of the alcohol-rich solvent with around 0.02 mg mL^{-1} . We consider that effective concentration of Nafion differs depending on the solvent system due to the difference of the aggregation state and the difference of the effective Nafion concentration between water-rich solvent and alcohol-rich solvent might cause the shift of the isotherm profiles. As evidenced from several papers, Nafion forms large bundle in water-rich solvent because of the strong hydrophobic interaction between the CF_2 backbones, while only small bundles are formed in alcohol-rich solvent owing to the strong solvation of CF_2 backbones by the alcohol molecules^{28, 41}. As the matter of fact, in the ^{19}F -NMR measurements, the intensity of the CF_2 signals was significantly weaker in the water-rich solvents than in the alcohol-rich solvents (**Figure 5-4 a**), which clearly indicates the lower mobility of the Nafion backbones in the

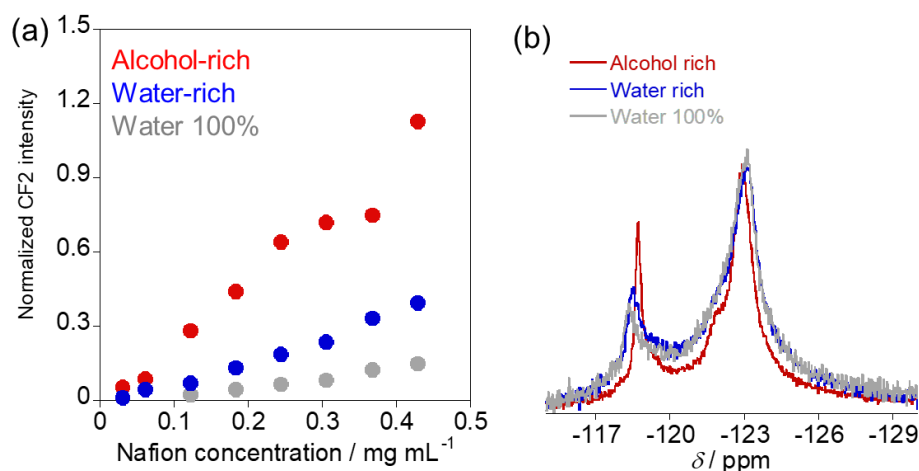


Figure 5-4 (a) Integral ratio of CF₂ peaks normalized by that of CF₃COOH in alcohol-rich (red), water-rich (blue) and 100% water (gray) solvents. (b) CF₂ peaks between -115 to -130 ppm normalized by the peak at -123 ppm.

water-rich solvent owing to the Nafion assembly⁴². In addition, the CF₂ signals from the Nafion side chain (-123 ppm) in the alcohol-rich solvent were sharper than those in the water-rich solvents (**Figure 5-4 b**), which further evidences the lower mobility of Nafion in the water-rich solvents⁴³,⁴⁴. In an alcohol-rich solvent, isolated Nafion may weakly cover the CB surface through the interactions of the backbone and side chains onto CB surface. In contrast, in water-rich solvent, the CF₂ backbone in Nafion assembly is strongly adsorbed onto the CB surface owing to the strong hydrophobic interaction between CF₂ and carbon, while exposing the side chains to the outer surface due to hydration and charging of SO₃⁻²⁹. In addition to this efficient interaction of the Nafion backbone, the adsorption of the large Nafion assembly onto CB also resulted in the higher $\Gamma_{\max}$ values under water-rich conditions.

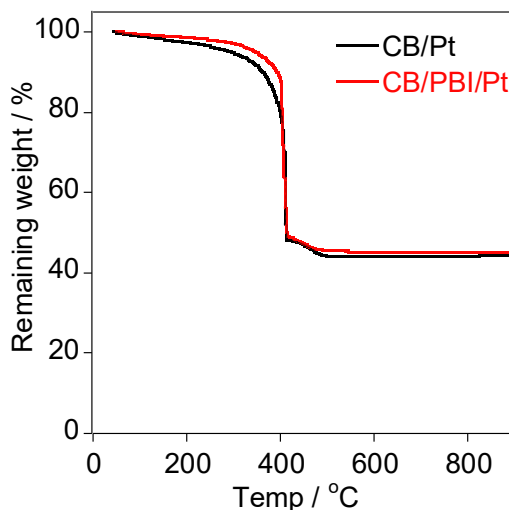


Figure 5-5 TGA curves of CB/Pt (black) and CB/PBI/Pt (red), showing both composites have Pt loading of 46 wt%.

The adsorption isotherm of Nafion on Pt-loaded CB (CB/Pt) was also evaluated for the water-rich (blue) and alcohol-rich (black) dispersions (**Figure 5-2 b**), in which the Pt loading amount on CB/Pt was separately determined by thermogravimetric analysis (TGA) to be 46 wt% (**Figure 5-5**). The K_L in the water- and alcohol-rich solvents are 29 and 25, respectively (**Table 5-1**), which were lower than those of CB. The results suggest that the Nafion affinity to Pt was lower than that of the CB surface regardless of the alcohol content. Ma et al. reported that the K_L of Nafion on Pt black was significantly lower (1.29) than that of Vulcan (22.36) in water³². In addition, the $\Gamma_{\max}$ values in CB and CB/Pt significantly decreased for water-rich solvents (**Figure 5-2 b**). One possible reason for lower $\Gamma_{\max}$ values is an underestimation due to the incorporation of heavy atoms, i.e. Pt. Therefore, to compare the Nafion adsorption amount per surface area rather than weight, we newly defined Γ' (mg m^{-2}) instead of Γ ($\text{mg} \cdot \text{mg}^{-1}$). The Γ' (mg m^{-2}) was determined

by dividing Γ (mg mg^{-1}) by Brunauer–Emmett–Teller (BET) surface area ($\text{m}^2 \text{g}^{-1}$) estimated from N_2 adsorption measurements (**Figure 5-2 c and d**), in which the BET values of 206 and $117 \text{ m}^2 \text{g}^{-1}$ for CB, CB/Pt were used for the calculation³⁷. In water-rich solvent, the maximum Γ' (Γ'_{max}) of CB/Pt (0.188 mg m^{-2}) was smaller than that of CB (0.209 mg m^{-2}), which confirms the preferential absorption of Nafion onto the CB rather than Pt surface (**Table 5-1**). On the other hand, Γ'_{max} of CB/Pt (0.179 mg m^{-2}) was larger than that of CB (0.116 mg m^{-2}) in alcohol-rich condition, suggesting the Nafion adsorb preferentially on Pt surface than CB surface in alcohol-rich solvent (**Table 5-1**). Similar to CB, the isotherm of CB/Pt in the water-rich solvent started at a higher concentration than those of the alcohol-rich solvents (**Figure 5-2 b and d**), reflecting the difference of the effective Nafion concentration as discussed above.

The zeta potential (ζ) of CB (**Figure 5-6 a**) and CB/Pt (**Figure 5-6 b**) in the water-rich (blue) and alcohol-rich (black) solvents was measured at 25°C . In the absence of Nafion ($I/C = 0$), ζ was difficult to measure owing to the immediate aggregation and sedimentation of the particles. Above

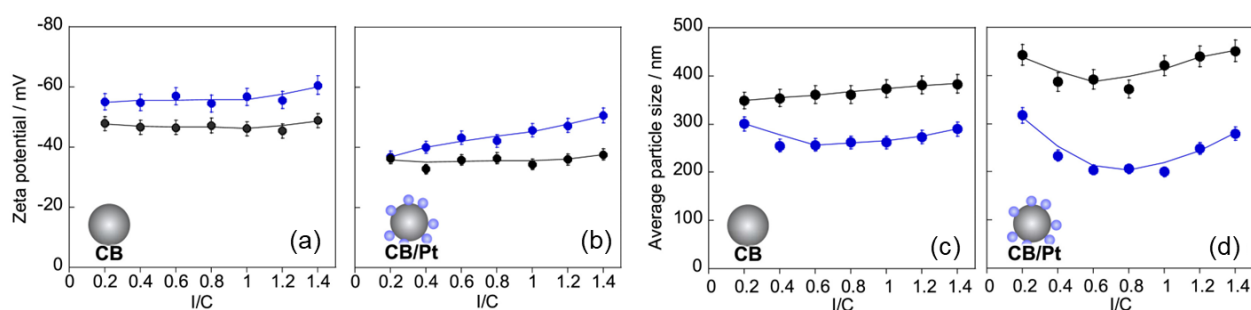


Figure 5-6 (a, b) Zeta potential of (a) CB and (b) CB/Pt for different I/C values in the water-rich (blue) and alcohol-rich (black) solvents. (c, d) Average particle size of (c) CB and (d) CB/Pt depending on I/C in the water-rich (blue) and alcohol-rich (black) solvents.

I/C = 0.2, the negative values of ζ clearly indicate that these composites are surrounded by SO_3^- groups, and stable colloidal dispersion was obtained by these negative charges. Although the isotherm experiments revealed the increase in the amount of adsorbed Nafion with the increase in I/C, the ζ values were almost constant regardless of the I/C values. This can be considered that the CB and CB/Pt particles were surrounded by bound and unbound Nafion and the adsorption measurement only estimated bound Nafion whereas ζ measurements monitored the surface including unbound Nafion layer. The more negative values of ζ under water-rich conditions than that under alcohol-rich conditions for CB and CB/Pt are ascribed to the higher dissociation constant of the $-\text{SO}_3\text{H}$ groups in the water-rich solvent because of the higher ϵ values of water¹⁴. Meanwhile, the absolute ζ values of CB/Pt were lower than those of CB for the water- and alcohol-rich solvents (**Figure 5-6 b**). In the presence of Pt, the $-\text{SO}_3\text{H}$ groups interact with the Pt surface⁴⁵, which may decrease the net negative charges from the composites and ζ for CB/Pt.

The average particle sizes of the CB (**Figure 5-6 c**) and CB/Pt (**Figure 5-6 d**) in water-rich (blue) and alcohol-rich (black) solvents was measured by DLS. Since the CB/Pt often show flocculation by time ⁴⁶, the inks were sonicated before the measurements to initialize the dispersion state. The diameter distribution of these solutions is provided in **Figure 5-7**. For CB and CB/Pt, the water-rich solvent resulted in smaller average size and narrower diameter distribution than the alcohol-rich solvent. This can be ascribed that stronger adsorption and higher charging of Nafion adsorbed on CB and CB/Pt in the water-rich solvent may prevent the clustering of particles. In the

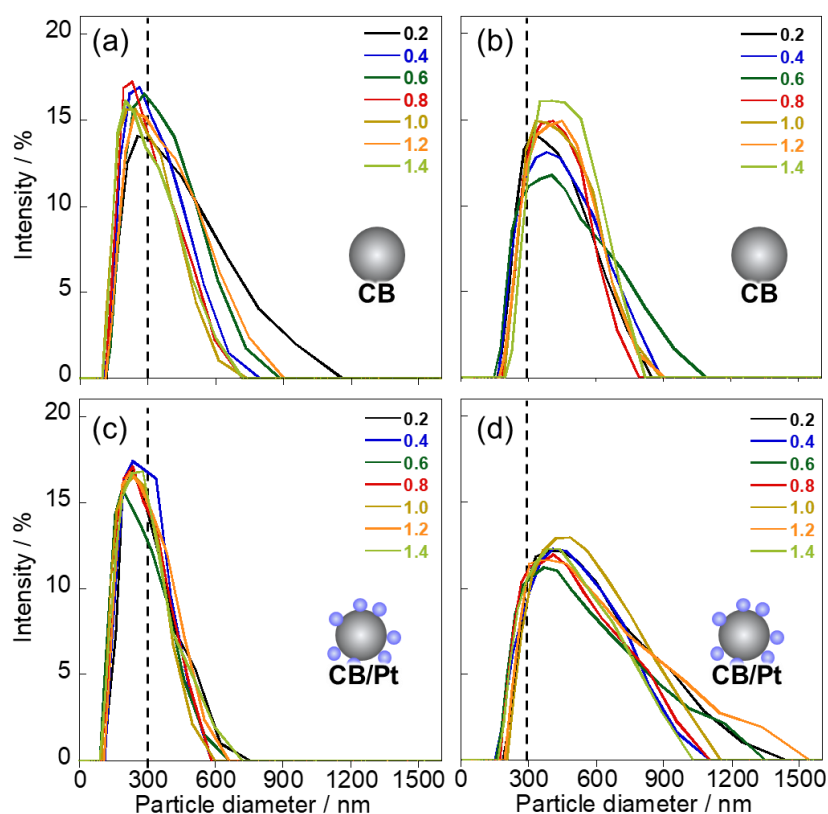


Figure 5-7 The size distribution of (a, b) CB and (c, d) CB/Pt in (a, c) water-rich and (b, d) alcohol-rich solvents.

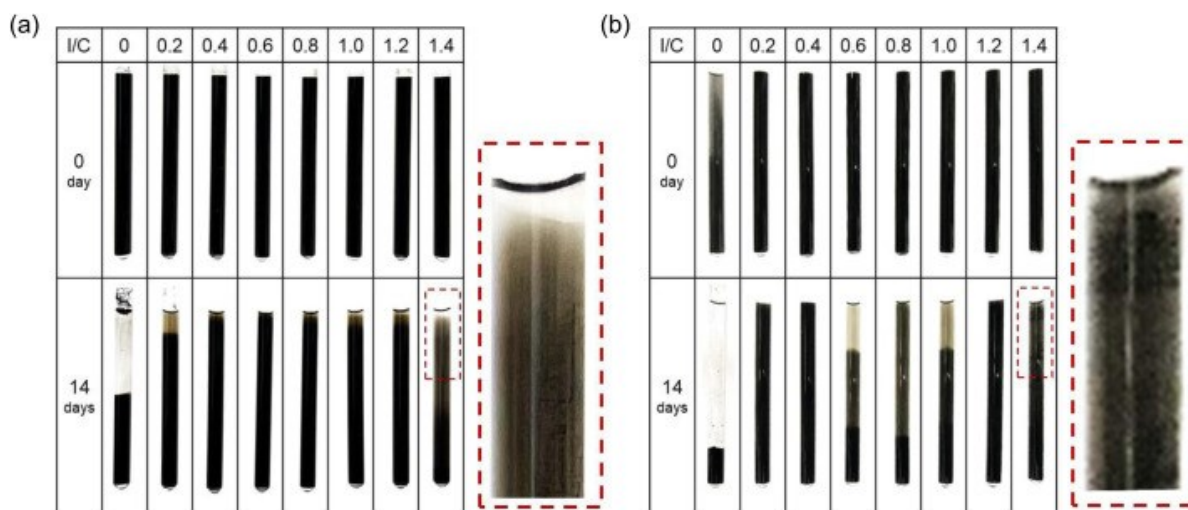


Figure 5-8 CB/Pt dispersions with different I/C in the (a) water-rich solvent and (b) alcohol-rich solvent after preparation (upper panels) and after 14 days (lower panels). The upper line of the solvents is 40 mm from the bottom. The magnified images of the inks after 14 days are displayed in the dotted frames.

alcohol-rich solvents, larger particles of over 1.0 μm were observed for CB/Pt (**Figure 5-7 d**). To further estimate the flocculation behavior, the time course of the clustering of CB/Pt was monitored by the sedimentation of the inks for 14 days (**Figure 5-8**). Without ionomers (I/C=0), sedimentation immediately occurred to the CB/Pt dispersions in the water- and alcohol-rich solvents, which clearly indicates the essential role of Nafion for the dispersion. For CB/Pt, the dispersions remained stable in the water-rich solvent and less stable in the alcohol-rich solvent with small flocculation (**Figure 5-8**, magnified images), and sedimentation was observed with I/C of 0.2–1.0. Generally, higher absolute ζ values indicate a higher colloidal stability; an absolute ζ value of more than 50 mV offer stable electrostatic dispersion⁴⁷. In the water-rich solvent, the stronger Nafion adsorption onto CB/Pt and higher charging over 50 mV enables a stable colloidal

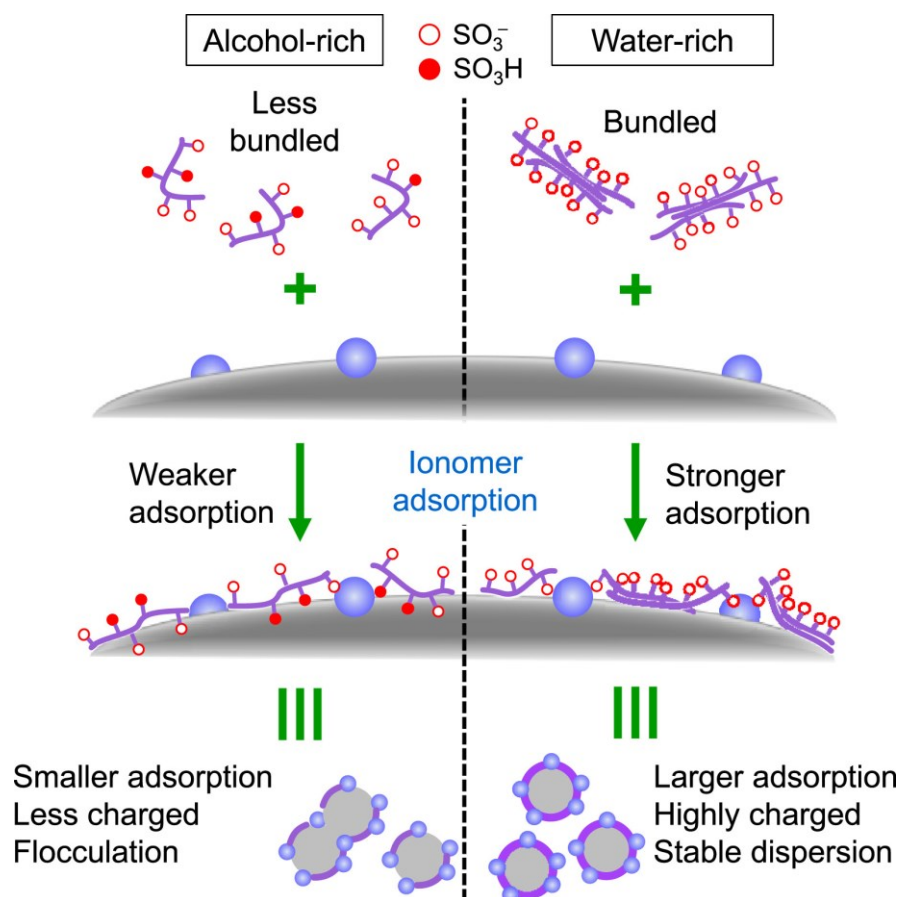


Figure 5-9 Schematic of the ionomer adsorption of CB/Pt in the alcohol-rich (left) and water-rich (right) solvents.

dispersion, whereas the weak Nafion adsorption and lower charging of SO_3^- groups in the alcohol-rich dispersion might induce flocculation (**Figure 5-9**). In addition to the smaller adsorption of the Nafion and weaker dissociation of the $-\text{SO}_3\text{H}$ groups, random orientation of the $-\text{SO}_3\text{H}$ groups may also decrease the surface charge in the alcohol-rich solvent, whereas exposed orientation of highly dissociated SO_3^- groups together with the larger adsorption of the ionomer may contribute to the stable colloidal dispersion in the water-rich solvent (**Figure 5-9**).

5.3.2. Ionomer adsorption on the CB/PBI and CB/PBI/Pt

Table 5-2 K_L , $\Gamma_{\max}$, and $\Gamma'_{\max}$ for CB/PBI and CB/PBI/Pt in water- and alcohol-rich solvents.

	CB/PBI		CB/PBI/Pt	
	Water	Alcohol	Water	Alcohol
K_L	82	55	44	43
$\Gamma_{\max}$ [mg·mg ⁻¹]	0.043	0.034	0.033	0.026
$\Gamma'_{\max}$ [mg·m ⁻²]	0.485	0.388	0.277	0.218

PBI-coated CB (CB/PBI) was prepared according to our previous reports^{37 38 40} and **Scheme 5-1**, the adsorption isotherms were measured in water- and alcohol-rich solvents (dsorption, K_L was calculated as 82 and 55 in the water- and alcohol-rich solvents, respectively (**Figure 5-10 a–d**), in which the BET values of 88 and 119 m² g⁻¹ for CB/PBI and CB/PBI/Pt, respectively, were used for the calculation of Γ' ³⁷. For the first layer adsorption, K_L was calculated as 82 and 55 in the water- and alcohol-rich solvents, respectively (**Figure 5-10 a, Table 5-2**). Comparing these values with those of CB (**Table 5-1**), clear increase of the K_L in the alcohol-rich solvent from 32 (CB) to 55 (CB/PBI) was obtained, whereas the K_L values in the water-rich solvent were almost comparable between CB (89) and CB/PBI (82). In addition, the $\Gamma_{\max}$ of the first layer in the alcohol-rich solvents increased from 0.024 mg mg⁻¹ (CB) to 0.034 mg mg⁻¹ (CB/PBI), while that

in water-rich solvents were comparable between CB (0.043 mg mg^{-1}) and CB/PBI (0.043 mg mg^{-1}). Both results clearly indicate the stronger interaction between PBI and Nafion compared to the interaction between CB and Nafion in alcohol-rich solvents, while strong interaction in water-rich solvents was still maintained. A similar trend was also observed for Pt-loaded CB/PBI (CB/PBI/Pt), namely, the K_L (43) and Γ'_{max} (0.218 mg m^{-2}) were larger than those of CB/Pt ($K_L = 25$ and $\Gamma'_{\text{max}} = 0.179$) in the alcohol-rich solvent, while in water-rich solvent, K_L (44) and Γ'_{max} (0.277 mg m^{-2}) of CB/PBI/Pt were very high similar to CB/Pt ($K_L = 29$ and $\Gamma'_{\text{max}} = 0.188 \text{ mg m}^{-2}$). On the other hand, when we compare Γ'_{max} values of CB/PBI (Figure 5-10 c) and CB/PBI/Pt (Figure 5-10 d), the decrease of the CB after Pt loading in the water-rich and alcohol-rich solvents were observed (Figure 5-2), suggesting the Nafion adsorption onto Pt surface is inferior for PBI systems regardless of alcohol content.

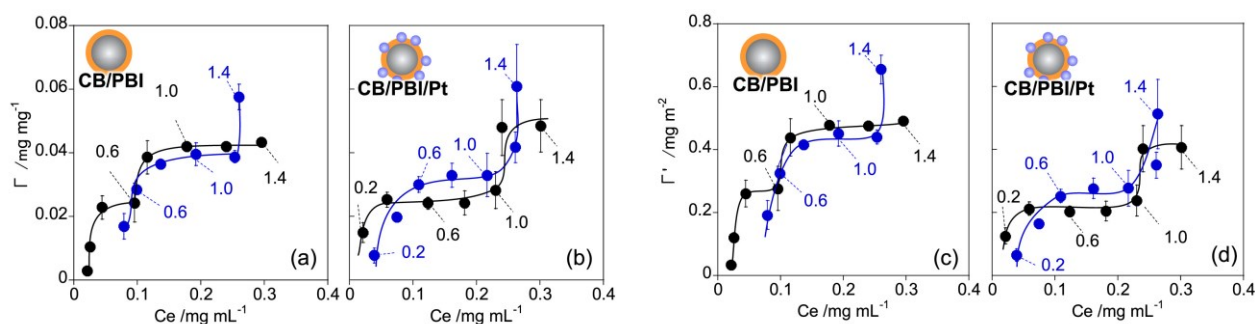


Figure 5-10 (a–d) Adsorption isotherm of Nafion onto (a, c) CB/PBI and (b, d) CB/PBI/Pt in the water-rich (blue) and alcohol-rich (black) solvents at 25 °C plotted for (a, b) Γ and (c, d) Γ' . The numbers in the figures represent the I/C value.

Figure 5-10 e and f shows ζ of CB/PBI and CB/PBI/Pt, respectively. Interestingly, CB/PBI and CB/PBI/Pt possessed almost comparable ζ with the CB and CB/Pt, respectively, in water-rich and alcohol-rich solvents. In our previous reports using alcohol-rich solvent, we consider the acid-base or electrostatic interaction between $-\text{SO}_3\text{H}$ in Nafion and basic imidazole in PBI as the driving force of the strong adsorption^{38 39 40}. This mechanism may decrease ζ for PBI-coated composites due to the adsorption of negatively charged side chains (SO_3^-) onto the positively charged PBI surface and induce the exposure of the hydrophobic Nafion backbone. Thus, comparable ζ values of PBI-coated and non-coated composites suggested the adsorption of the second Nafion layer based on the hydrophobic interaction between 1st and 2nd Nafion bundle layers.

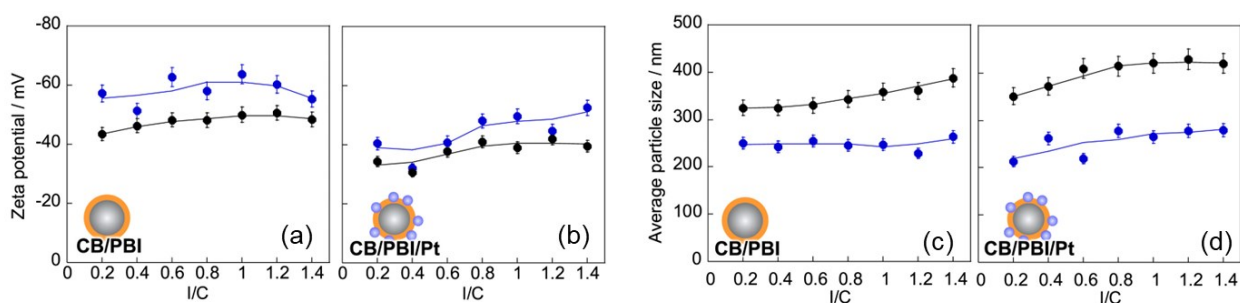


Figure 5-11 (a, b) Zeta potential of (a) CB/PBI and (b) CB/PBI/Pt for different I/C in water-rich (blue) and alcohol-rich (black) solvents. (c, d) Average particle size of (c) CB/PBI and (d) CB/PBI/Pt depending on the I/C in water-rich (blue) and alcohol-rich (black) solvents.

Figure 5-11 c and d shows average particle diameter of CB/PBI (Figure 5-11 c) and CB/PBI/Pt (Figure 5-11 d) for water-rich (blue plots) and alcohol-rich (black plots) solvents. The diameter range of CB/PBI and CB/PBI/Pt are comparable to that of CB (Figure 5-6 c) and CB/Pt (Figure 5-6 d), respectively. In addition, similar to CB and CB/Pt, average particle size of CB/PBI and CB/PBI/Pt was smaller in water-rich solvents. Of interest, the CB/PBI and CB/PBI/Pt exhibited a narrow diameter distribution especially in the alcohol-rich solvent (Figure 5-12) compared to CB and CB/Pt, respectively (Figure 5-7). Strong interaction between PBI and Nafion might enable the good dispersion of CB/PBI/Pt regardless of the alcohol content. As the matter of

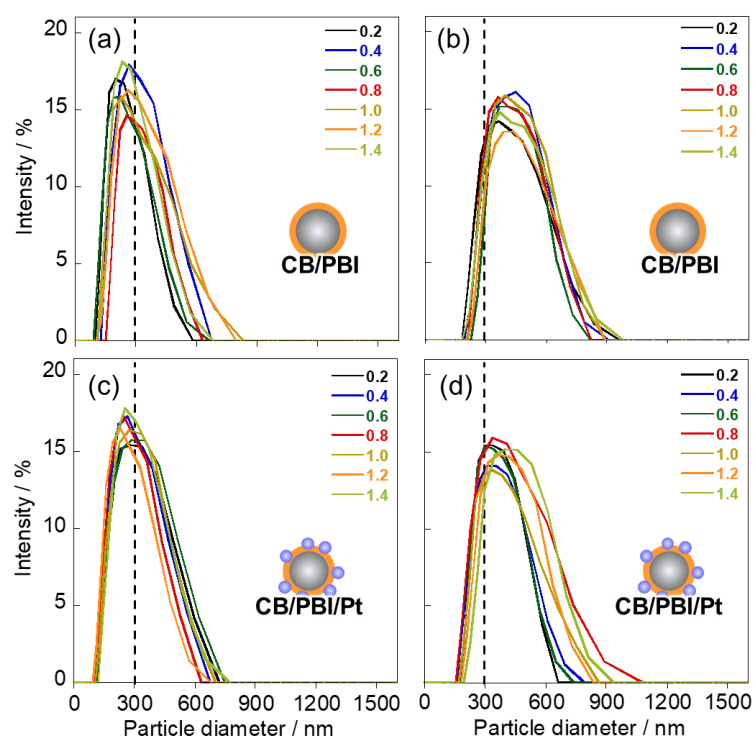


Figure 5-12 The size distribution of (a, b) CB/PBI and (c, d) CB/PBI/Pt in (a, c) water-rich and (b, d) alcohol-rich solvents.

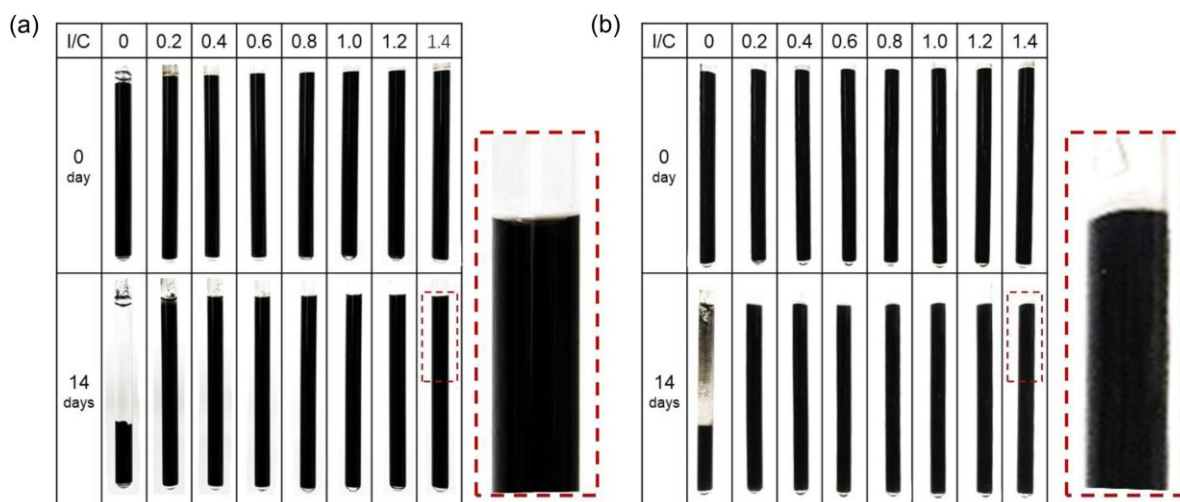


Figure 5-13 Photographs of the CB/PBI/Pt dispersions with different I/C values (a) in the water-rich solvent and (b) alcohol-rich solvent after the preparation (upper panels) and after 14 days (lower panels). The magnified images of the inks after 14 days are displayed in the dotted flames.

fact, in the sedimentation experiment in **Figure 5-13**, CB/PBI/Pt formed very stable inks for both water-rich and alcohol-rich solvents in any I/C ratio except $I/C = 0$ and no visible flocculation was observed in the magnified images.

In the preparation of the ink for the PBI coating system, the isolated Nafion in the alcohol-rich and bundled Nafion in the water-rich solvents was strongly adsorbed onto the CB/PBI/Pt surface owing to the strong interaction between PBI and Nafion based on acid-base interaction. The 2nd Nafion layer adsorption provides outside orientation of SO_3^- groups and offers highly

charged particles that enables stable dispersion in the water-rich and alcohol-rich solvents (**Figure 5-14**).

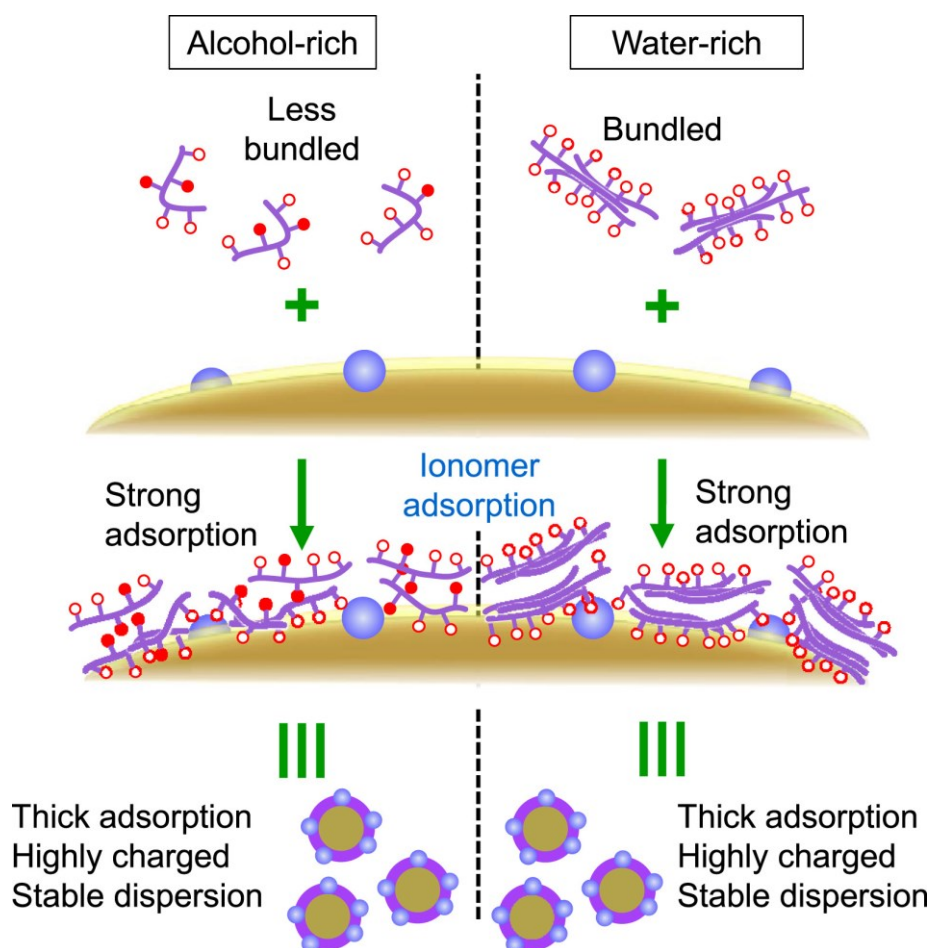


Figure 5-14 Schematic of the ionomer adsorption of for CB/PBI/Pt in the alcohol-rich (left) and water-rich (right) solvents. The isolated ionomer in the alcohol-rich and bundled ionomer in the water-rich solvents were strongly adsorbed onto the CB/PBI/Pt surface based on acid-base interaction. The larger adsorption of ionomer and exposed orientation of the SO_3H groups in the water-rich solvent afforded a stable colloidal dispersion.

5.3.3. Ink coating

Table 5-3 Surface ζ of the CL prepared from water-rich and alcohol-rich dispersion of CB/Pt and CB/PBI/Pt.

	I/C	Water-rich	Alcohol-rich
CB/Pt	0.6	-8.3 ± 0.9	-3.3 ± 1.2
	1.0	-10.7 ± 0.3	-4.5 ± 0.3
CB/PBI/Pt	0.6	-10.0 ± 0.8	-3.9 ± 1.8
	1.0	-14.5 ± 1.2	-4.8 ± 0.4

The CB/Pt and CB/PBI/Pt dispersions containing Nafion (I/C = 0.6 and 1.0) in the water-rich and alcohol-rich solvents were sprayed on the polyethylene terephthalate substrates to measure the ζ of the sprayed catalyst layer (CL). In these measurements, ζ of the coated substrates prepared from water-rich and alcohol-rich solvents were measured in water. Interestingly, we found that the ζ of the CL sprayed from the water-rich solvent with I/C of 0.6 and 1.0 were -8.3 and -10.7 mV for CB/Pt, respectively, whereas those from the alcohol-rich solvent were -3.3 and -4.5 mV, respectively (**Table 5-3**). The difference between the CLs prepared from the water-rich and alcohol-rich solvents clearly indicates the enrichment of the SO_3^- groups for the CL in the water-rich solvent. Upon spraying, the adsorbed and unbound Nafion were deposited, where the unbound Nafion can be moved away from the surface and concentrated in between aggregation of CB/Pt

owing to the capillary force upon drying. Therefore, the result indicates the Nafion tend to move from the surface upon drying in the alcohol-rich solvent owing to the weak interactions, resulting in the lower SO_3^- group density on the CL surface. The increase of I/C from 0.6 to 1.0 increased the absolute surface ζ potential with similar trends. Meanwhile, the ζ of the CB/PBI/Pt sprayed from the water-rich and alcohol-rich conditions were more negative than those of the corresponding CB/Pt for I/C of 0.6 and 1.0 (**Table 5-2**). The increase of the Nafion adsorption amount assisted by PBI can reduce ζ for CB/PBI/Pt than that of CB/Pt.

5.3.4. Fuel cell study using CB/Pt as the catalyst

To study the relationship between the Nafion adsorption onto the composites and PEMFC performance, MEA containing CB/Pt as the electrode catalyst (MEA_{CB}) were prepared using water-rich (w-MEA) and alcohol-rich (a-MEA) inks, in which an I/C of 0.72 was selected since $\text{I/C} = 0.72$ is in the adsorption plateau region (**Figure 5-2, Figure 5-10 b**) and also used in our previous optimization⁴⁰. **Figure 5-15** a–f shows the SEM images of the CL surface of w-MEA_{CB} and a-MEA_{CB} . At SEM images of lower magnifications, we observed many microvoids only in the w-MEA_{CB} surface (**Figure 5-15 a and b**). The possible formation mechanism of these pores is that the residual of the water drops might work as the template¹⁹. Other microstructure such as cracks were hardly observed for MEAs regardless of the solvent conditions. The

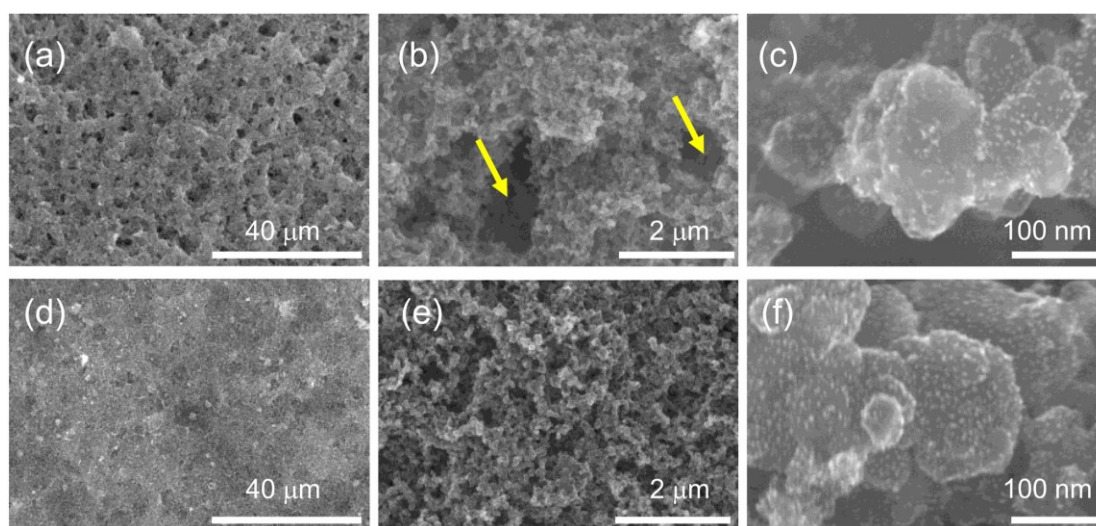


Figure 5-15 SEM images of the CL surface for (a–c) w-MEACB and (d–f) a-MEACB with magnifications of (a, d) 1300 $\times$, (b, e) 20,000 $\times$, and (c, f) 300,000 $\times$. The voids are indicated as yellow arrows.

polarization (I–V) curves of the w-MEA_{CB} and a-MEA_{CB} are shown in **Figure 5-17 a**, in which the data of a-MEA_{CB} was adapted from our previous report ³⁹. w-MEA_{CB} (blue line) offered higher potential at all the current density regions with the maximum power density (750 mW cm⁻²) that was 29% higher than that of a-MEA_{CB} (580 mW cm⁻²). From the impedance spectroscopy results (**Figure 5-16**), the proton conduction resistance (R_p) of w-MEA_{CB} and a-MEA_{CB} were determined as 0.35 and 1.26 Ω cm⁻¹ ⁴⁰, respectively (**Figure 5-16 b**). **Figure 5-17 c** and **Figure 5-17 d** shows the *in-situ* CV for w-MEA_{CB} and a-MEA_{CB} under nitrogen and H₂ flows at the cathode and anode, respectively. Clear hydrogen adsorption/desorption (HAD) peaks were observed at 0.1–0.3 V. Electrochemically active surface area (ECSA) determined from HAD peak using MEAs is an important parameter demonstrating the accessible Pt surface area in the CL ⁴⁸. For w-MEA_{CB} and a-MEA_{CB} to be 75.1 and 49.3 m² g⁻¹_{Pt}, respectively. The lower R_p and larger ECSA for w-MEA_{CB} are ascribed to the larger Nafion adsorption onto the CB/Pt surface that creates well

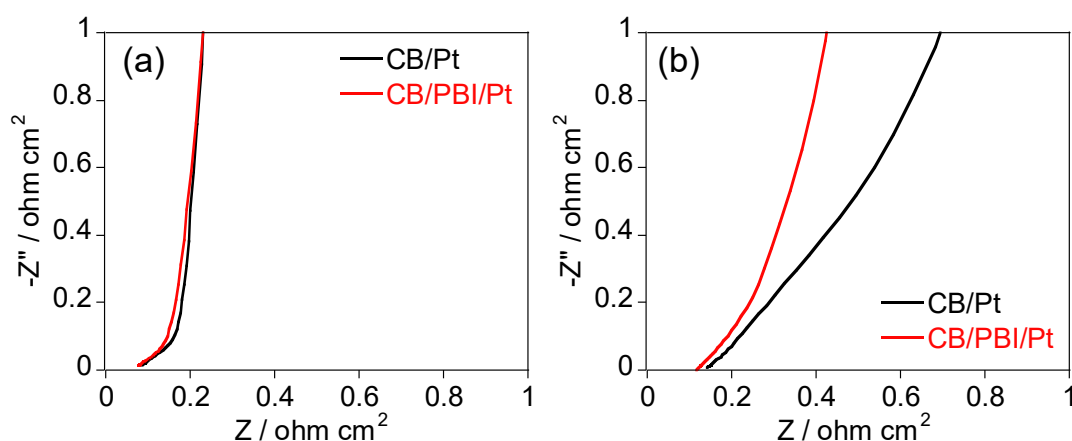


Figure 5-16. High frequency region (10^5 - 10^3 Hz) of Nyquist plot of CB/Pt (black) and CB/PBI/Pt (red) in (a) water-rich and (b) alcohol-rich solvents.

developed ionomer network and facilitates proton delivery to the Pt surface (**Figure 5-18**, right panel)¹⁴. Meanwhile, the insufficient interaction of Nafion onto CB/Pt in the alcohol-rich solvents may result in the agglomeration of the Nafion to form discontinuous ionomer networks during casting of the ink (**Figure 5-18**, left panel)⁴⁹. A similar increase of ECSA¹⁴ and decrease of R_p ^{13,14}⁵⁰ by decreasing the alcohol content was also reported. For the oxygen reduction reaction (ORR) at the cathode, not only proton diffusion but O₂ diffusion resistance in CL is also involved, in which both the O₂ diffusion through ionomer on the Pt surface and the O₂ diffusion in the bulk space in the CL are included in the total O₂ resistance. In addition, the ionomer coverage on the Pt surface suppresses the adsorption of the O₂ molecules on to the Pt surface^{19, 51 52} and negatively

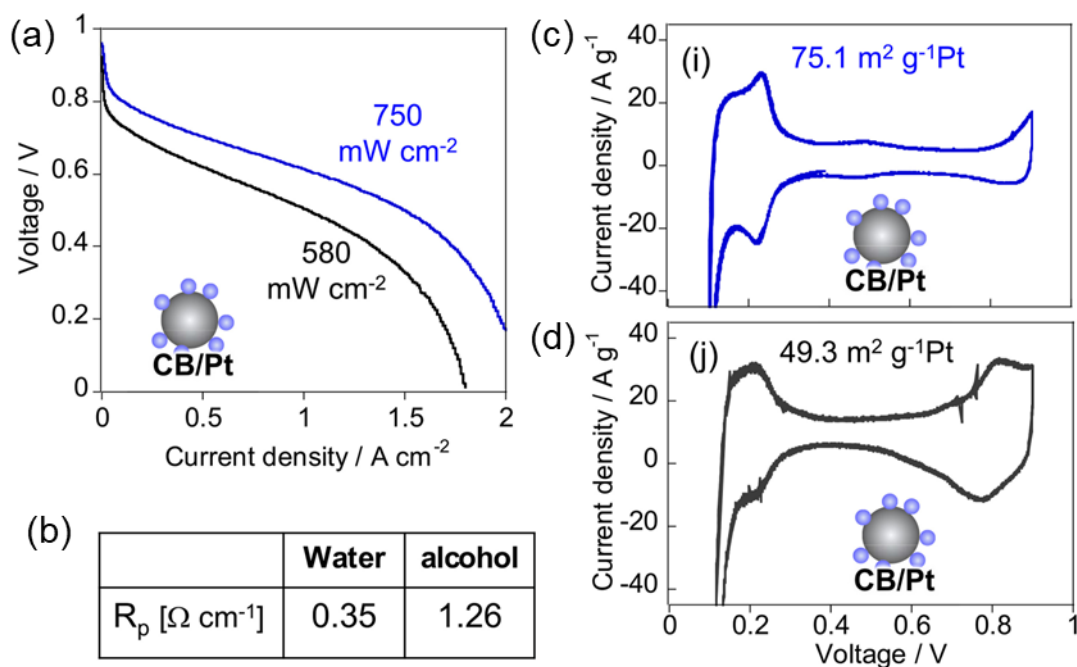


Figure 5-17. (a) Polarization (I–V) curves of w-MEACB (blue) and a-MEACB (black). (b) Proton conduction resistance (R_p) of w-MEACB and a-MEACB. (c, d) In-situ CV curves of (c) w-MEACB (blue) and (d) a-MEACB (black).

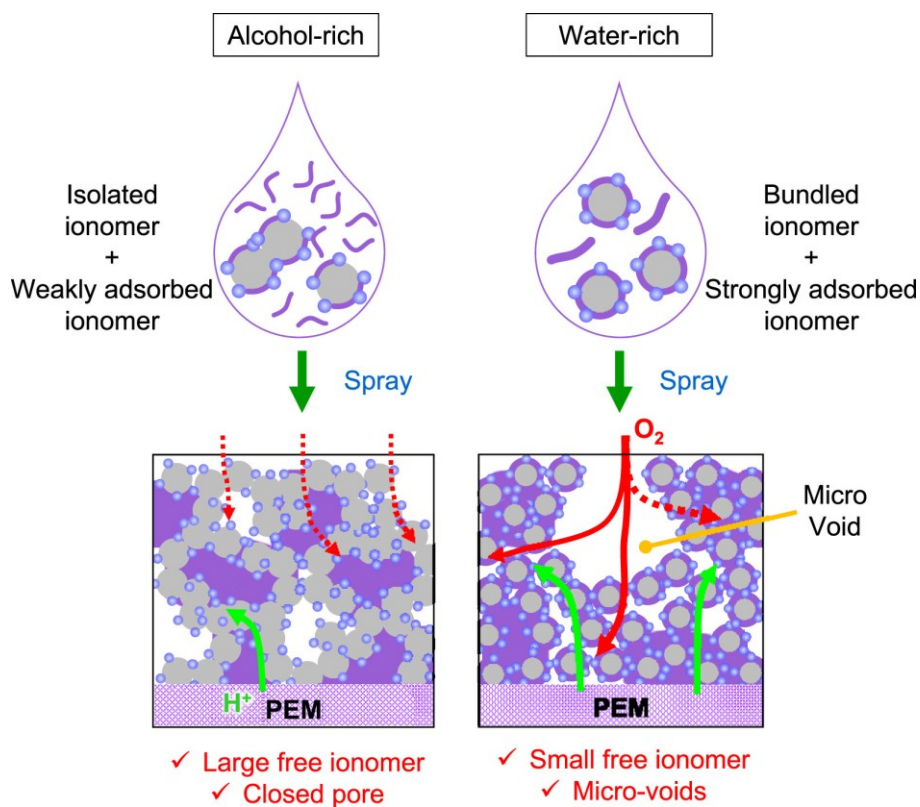


Figure 5-18 Schematic of the formation of the CL using alcohol-rich (left) and water-rich (right) inks. O_2 and H^+ diffusions in the CL are indicated as red and green arrows, respectively.

impacts ORR in the cathode CL. Under alcohol-rich conditions, large primary agglomerations of CB/Pt were formed due to the poor ionomer coverage and generated the large secondary agglomerations with closed pore structures (**Figure 5-18**, left panel). On the other hand, owing to the strong ionomer adsorption, CB/Pt formed small primary agglomerations in water-rich condition and created the small secondary agglomerate with small pores homogeneously distributed in the CL. We consider that these pores were interconnected with the aid of microvoids in w-MEA_{CB} (**Figure 5-18**, right panel), which facilitated the O_2 diffusion and lowered the total O_2 diffusion resistance¹⁹. Overall, w-MEA_{CB} exhibited lower proton conduction resistance and

O₂ diffusion resistance than a-MEA_{CB} and possessed lower the overpotential at a low current and high current density regions (**Figure 5-17 a**).

5.3.5. Fuel cell study using CB/PBI/Pt as the catalyst

To study the effects of PBI on the PEMFC performance, a MEA having CB/PBI/Pt as the electrode catalyst (MEA_{CB/PBI}) was prepared using water-rich (w-MEA_{CB/PBI}) and alcohol-rich (a-MEA_{CB/PBI}) inks. **Figure 5-19** a–f shows the SEM images of the CL surface of w-MEA_{CB/PBI} and a-MEA_{CB/PBI}. From the low-magnification SEM images, micro voids were also observed in w-MEA_{CB/PBI}. From the low-magnification SEM images, micro voids were also observed in w-MEA_{CB/PBI} (**Figure 5-19** a and b), similar to w-MEA_{CB}. In the polarization measurement, w-MEA_{CB/PBI} exhibited higher cell potential at all current density regions compared to a-

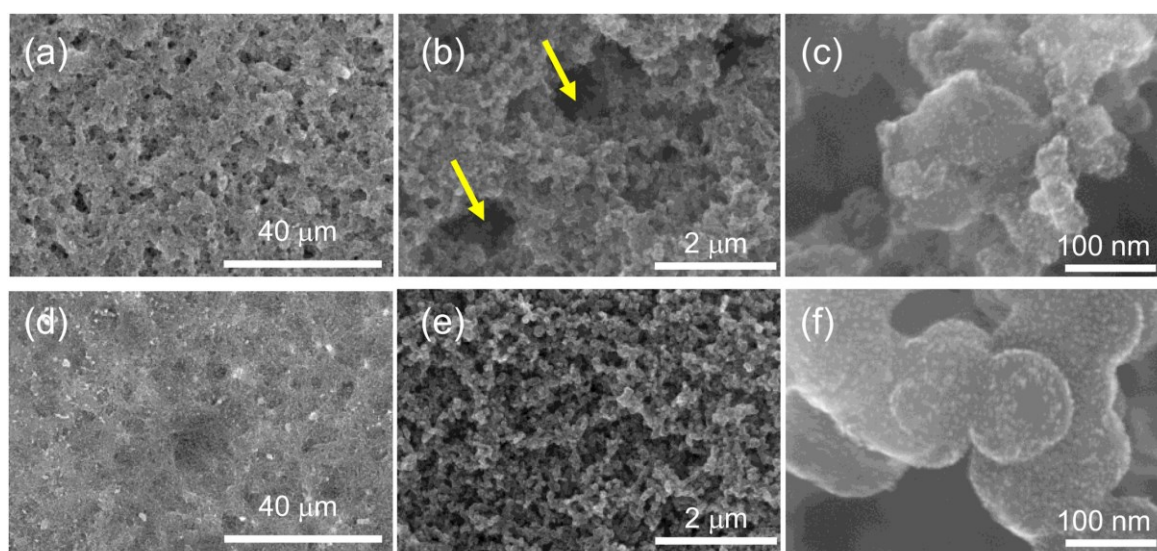


Figure 5-19 SEM images of the CL surface for (a–c) w-MEA_{CB/PBI} and (d–f) a-MEA_{CB/PBI} at magnifications of (a, d) 1300 $\times$, (b, e) 20,000 $\times$, and (c, f) 300,000 $\times$. The voids are indicated by the yellow arrows.

MEA_{CB/PBI} (**Figure 5-20 a**). However, the difference of the maximum power density between w-MEA_{CB/PBI} and a-MEA_{CB/PBI} was 13%. This small difference suggests that the Pt utilization efficiency does not largely depend on the solvent composition in the case of the PBI system, unlike the MEA_{CB} systems. Indeed, w-MEA_{CB/PBI} and a-MEA_{CB/PBI} showed relatively low R_p of 0.33 and $0.44 \Omega \text{ cm}^{-1}$ ⁴⁰, respectively (**Figure 5-20 b**). In addition, in the *in-situ* CV measurements, both w-MEA_{CB/PBI} and a-MEA_{CB/PBI} exhibited relatively high ECSA values of 75.5 and $62.4 \text{ m}^2 \text{ g}^{-1} \text{ Pt}$, respectively (**Figure 5-20 c and d**). Such a low R_p values and high *in-situ* ECSA for two MEAs clearly supports the higher Nafion adsorption aided by PBI yielding a good proton conduction path even in an alcohol-rich solvent (**Figure 5-21**). We previously reported that the effect of the

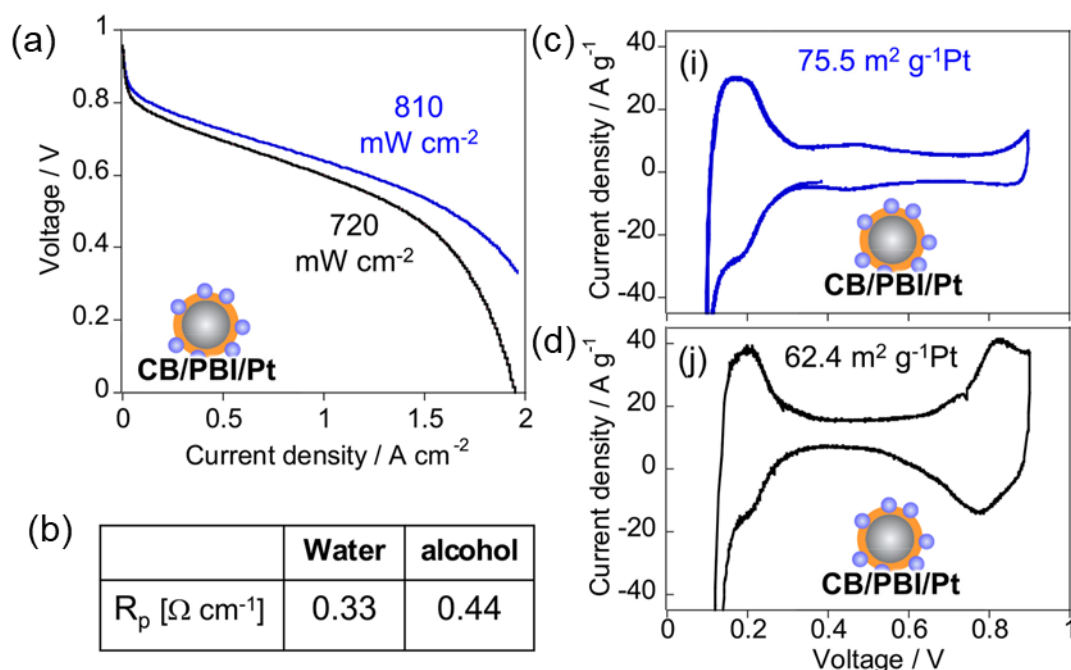


Figure 5-20 (a) Polarization curves of w-MEA_{CB/PBI} (blue) and a-MEA_{CB/PBI} (black). (b) Protonic resistance (R_p) of w-MEA_{CB/PBI} (blue) and a-MEA_{CB/PBI} (black). (c, d) *in-situ* CV of (c) w-MEA_{CB/PBI} (blue) and (d) a-MEA_{CB/PBI} (black).

homogeneous Nafion coating by the aid of PBI layer was quite obvious especially at low I/C, namely, a-MEA_{CB/PBI} exhibited high maximum power density of 750 mW cm⁻² even at I/C = 0.2, while a-MEA_{CB} showed low maximum power density of 190 mW cm⁻² at I/C = 0.2.

When we compare two MEAs prepared from water-rich inks, the maximum power density of w-MEA_{CB/PBI} (810 mW cm⁻²) was higher than that of w-MEA_{CB} (750 mW cm⁻²), indicating the advantages of the PBI coating over the conventional system using unmodified CB. The electrochemical impedance spectroscopy (EIS) results showed a gas diffusion resistance (R_g) of w-MEA_{CB} was higher than that of w-MEA_{CB/PBI} at both 0.05 and 0.1 A cm⁻², while ohmic

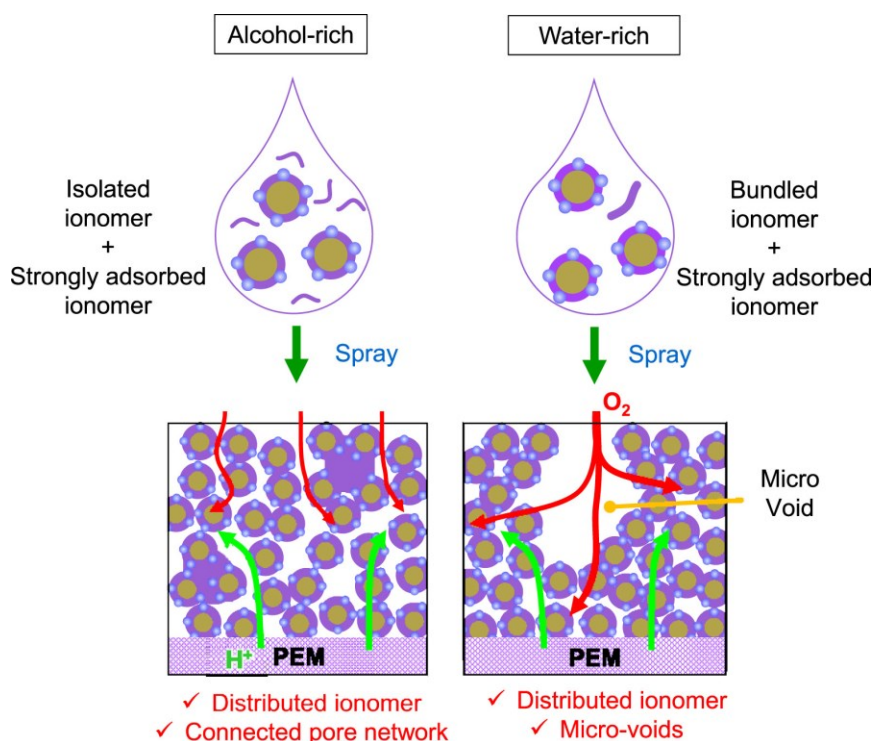


Figure 5-21 Schematic illustration of the formation of CL of CB/PBI/Pt using alcohol-rich (left) and water-rich (right) inks. O_2 and H^+ diffusions in the CL are indicated as red and green arrows, respectively.

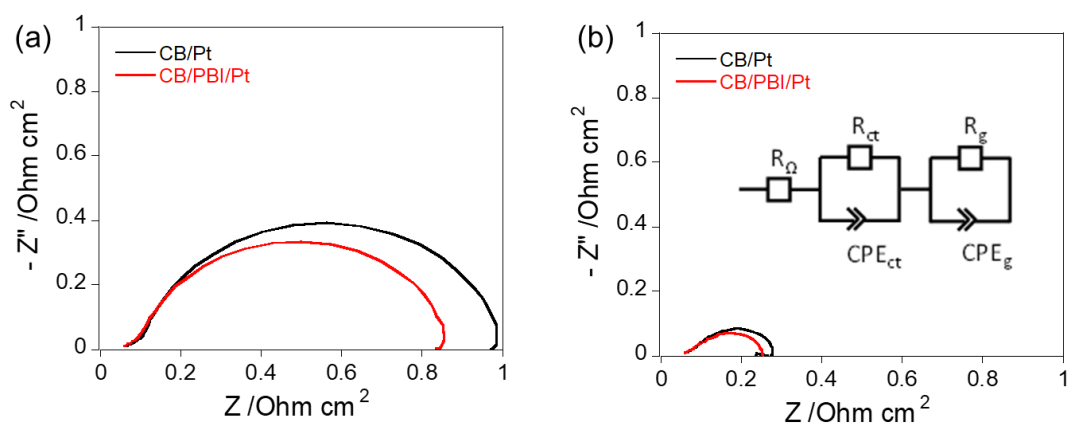


Figure 5-22 Impedance spectroscopy (air and H₂ flowed) measured at (a) 0.05 and (b) 1.0 A cm⁻² of CB/Pt (black) and CB/PBI/Pt (red) in water-rich solvents condition.

Table 5-4. Ohm resistance (R_{Ω}), charge resistance (R_{ct}) and gas diffusion resistance (R_g) values of CB/Pt and CB/PBI/Pt (pink) obtained from the fitting at different current density regions at 0.05 and 1.0 A cm⁻².

Current density	R_{Ω} / ohm cm ²		R_{ct} / ohm cm ²		R_g / ohm cm ²	
0.05 A cm ⁻²	CB/Pt	0.058	CB/Pt	0.065	CB/Pt	0.860
	CB/PBI/Pt	0.050	CB/PBI/Pt	0.075	CB/PBI/Pt	0.722
1.0 A cm ⁻²	CB/Pt	0.059	CB/Pt	0.069	CB/Pt	0.167
	CB/PBI/Pt	0.054	CB/PBI/Pt	0.062	CB/PBI/Pt	0.138

resistance (R_{Ω}) and charge resistance (R_{ct}) were almost constant (**Figure 5-22** and **Table 5-4**). We assumed that gas diffusion space is consecutively remained in between CB/PBI/Pt aggregates in w-MEA_{CB/PBI} due to the greater Nafion adsorption capacity (i.e. smaller unbound Nafion) onto CB/PBI/Pt ($\Gamma = 0.277$ mg m⁻²) (**Figure 5-21**, right panel), while parts of space between CB/Pt

aggregates are clogged by unbound Nafion for w-MEA_{CB} due to smaller Nafion adsorption capacity (i.e. larger unbound Nafion) onto CB/Pt ($\Gamma = 0.188 \text{ mg m}^{-2}$) (**Figure 5-18**, right panel).

When compared two MEAs prepared from alcohol-rich inks, the maximum power density of a-MEA_{CB/PBI} (720 mW cm^{-2}) was much higher than that of a-MEA_{CB} (580 mW cm^{-2}), which also indicates the advantages of the PBI coating system. In the case of a-MEA_{CB}, due to the weak adsorption of Nafion onto CB/Pt in alcohol-rich condition ($\Gamma = 0.179 \text{ mg m}^{-2}$), CB/Pt forms closed pores with large primary agglomerates which are often filled with unbound Nafion (**Figure 5-18**, left panel). On the other hand, for a-MEA_{CB/PBI}, CB/PBI/Pt forms small primary agglomerates coated with thicker Nafion layer due to large Nafion adsorption on CB/PBI/Pt ($\Gamma = 0.218 \text{ mg m}^{-2}$), where well-developed slits preferable to gas diffusion are also formed (**Figure 5-21**, left panel). Such a larger pore size in a-MEA_{CB} as well as better pore connectivity in a-MEA_{CB/PBI} were reported in our cross-sectional SEM observations of the corresponding CLs

40.

The use of carbon support materials modified with nitrogen-containing groups induces the interaction with Nafion and promotes its homogeneous distribution, thereby increasing the higher PEMFC power density^{36 53}. Unlike these covalent modifications, in the PBI coating approach, the sp^2 structure on carbon surface remains intact since the PBI coating is based on non-covalent adsorption on carbon surface^{37 54}, which is advantageous over covalent modification methods or atomic doping³⁶ for durability of PEMFC because the introduction of sp^3 carbon lowers thermal

and electrochemical stability of carbon materials ⁵⁵. In our study, Nafion adsorption can be increased by increasing the water content. However, the PBI modification can ensure the superior adsorption regardless of alcohol/water compositions, which can widen the preparation conditions of CL and is beneficial in the MEA fabrication process. Such a better ionomer network is effective especially under low humidity condition and the MEA analysis under low humidity condition are currently investigating.

5.4. Conclusion

The Nafion adsorption analysis (adsorption isotherm, zeta potential, particle size, and sedimentation experiments) and MEA analysis (impedance, in-situ CV, and polarization analyses) revealed the crucial role of the interaction between Nafion and carbon surface on the MEA performance. The use of water-rich solvent and/or PBI-coated CB offers the stronger interaction between Nafion and carbon supports than alcohol-rich solvent, resulting in the homogenous distribution of Nafion in the CL and thereby higher power densities. In the PBI system, the solvent composition does not significantly affect the MEA performance and alcohol-rich solvent can be used, which is advantageous to the process of CL fabrication.

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Chapter 6

Conclusions and perspectives

6.1. 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 PEMFC was discussed. However, low durability and high overpotential due to the monogenous ionomer distribution on Pt-ionomer, Pt-carbon and carbon-ionomer interface. Therefore, enhance catalyst durability and catalyst interface control is highly required. Furthermore, although optimized ionomer distribution on carbon/Pt interface, the specifical adsorption between Pt and $-\text{SO}_3\text{H}$ group belongs ionomer lead a low Pt utilization and Pt posing.

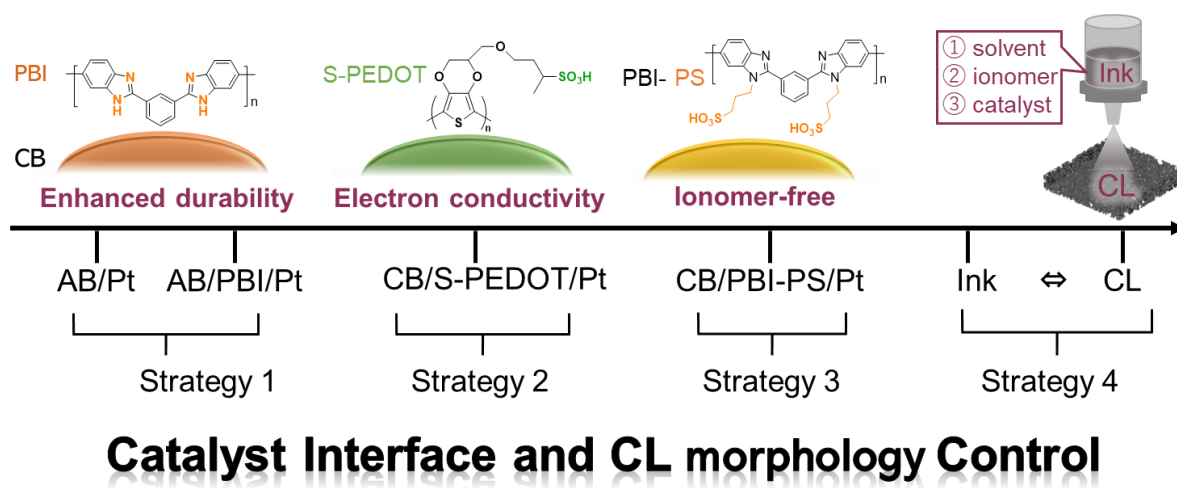


Figure 6-1 Overview of 4 strategies in this study

To achieve this, 4 strategies (**Figure 6-1**) were considered via catalyst interface controlling. Strategy 1; enhance the catalyst durability by PBI wrapping technology (chapter 2), strategy 2; employ an electron conductive polymer replace PBI to decreasing the charge transfer resistance (chapter 3) , strategy 3; develop a ionomer-free catalyst which design a non-covalent acid modification carbon to enhance the proton conductivity, avoiding O₂ diffusion impedance and preventing poisoning by sulfonic acid groups on the Pt surface to decrease the overpotential and strategy 4; evaluate the adsorption isotherm of ionomer onto CB and their Pt composites in water-rich and alcohol-rich binary mixtures aims to gain insights into how ionomer adsorption behavior varies under different solvent conditions.

In chapter 2, it was revealed that Pt catalyst loaded on PBI-coated AB (AB/PBI/Pt) and the Pt catalyst on AB (AB/Pt) were fabricated to study the effect of PBI wrapping for the stability of Pt nanoparticles during fuel cell operation. By applying potential cycles between 0.6 and 1.0 V to accelerate Pt oxidation, we found that the MEA containing AB/PBI/Pt (MEA_{AB/PBI}) showed greater stability than the MEA fabricated with AB/Pt (MEA_{AB}). Comparison of the Pt morphology before and after the ADT revealed that the enhancement of the Pt dispersion stability by PBI coating. We consider that the strong binding between Pt and PBI contributed to the inhibition of Pt diffusion. In addition, Pt nanoparticles with narrower diameter distribution in AB/PBI/Pt that was realized by the strong binding between PBI and Pt effectively hamper the Ostwald ripening of Pt. Both effects afford higher stability of Pt compared to that in AB/Pt and thus higher stability for

MEA_{AB/PBI}. Interestingly, ionomer content in the CLs in anode and cathode was almost unchanged for MEA_{AB/PBI}, while that of MEA_{AB} was largely decreased. We consider that the strong binding between PBI and ionomer through acid-base interaction prevent the loss of ionomer from the CLs upon ADT, consequently contributed to the durability of the MEA_{AB/PBI}. The present results clearly suggest the positive impact of PBI coating to improve the fuel cell durability and the activity.

Chapter 3

In chapter 3, successfully enhanced the electron conductivity by coating electron conductive Polymer S-PEDOT on carbon surface. Homogeneous deposition of Pt particles on the CB/S-PEDOT surface resulted in a 28% higher maximum power density compared to the conventional CB/Pt catalyst, which can be attributed to the significantly lower electron resistivity of CB/S-PEDOT ($0.68 \Omega \cdot \text{cm}$) compared to CB ($1.01 \Omega \cdot \text{cm}$). Additionally, the proton conduction resistance of the CB/S-PEDOT/Pt MEA was measured at $0.13 \Omega \cdot \text{cm}^2$, much lower than that of the CB/Pt MEA ($0.67 \Omega \cdot \text{cm}^2$). This improvement is likely due to the additional proton conduction facilitated by the $-\text{SO}_3^-$ groups in S-PEDOT. Furthermore, the superior gas diffusion structure of the CB/S-PEDOT/Pt MEA contributed to lower concentration overvoltage and reduced ohmic overvoltage, which in turn resulted in a lower activation overpotential in the PEMFC system. These findings highlight the potential of self-doped electron-conductive polymers like S-PEDOT to simultaneously enhance proton and electron conductivity, offering a promising pathway for improved catalyst and MEA designs in PEMFC applications.

In chapter 4, Vulcan was successfully modified by sulfonic acid group ($-\text{SO}_3\text{H}$) without deteriorating the thermal stability of the CB, where CB was non-covalently coated by PBI-PS has proton conductivity. Pt nanoparticles were deposited on CB/PBI-PS and CB/PBI-TFSI to fabricate ionomer-free catalyst composites (CB/PBI-PS/Pt). The composite showed remarkable dispersion stability even without ionomer addition and allow us to fabricate CL on Nafion membrane through Decal transfer method. MEA having CB/PBI-PS/Pt (MEA_{PS}) without containing ionomer showed comparable I-V performance of the MEA having CB/Pt with Nafion ionomer ($I/C=0.6$) at $80\text{ }^\circ\text{C}$ under 100%RH. Although proton conductivity of CL in MEA_{PS} was lower than that of MEA_{ref} , superior gas diffusion structure of ionomer-free MEA_{PS} offers lower concentration overvoltage that compensated the higher ohmic overvoltage. Lower activation overvoltage of MEA_{PS} and large drop of I-V performance at lower RH suggest that the optimization of the coating morphology and/or acid/acid distance on carbon surface can further improve I-V performance. These findings provide important information to realize novel ionomer-free MEA system, that will contribute both for cost reduction and improvement of mass activity.

In chapter 5, the Nafion adsorption analysis (adsorption isotherm, zeta potential, particle size, and sedimentation experiments) and MEA analysis (impedance, in-situ CV, and polarization analyses) revealed the crucial role of the interaction between Nafion and carbon surface on the MEA performance. The use of water-rich solvent and/or PBI-coated CB offers the stronger interaction between Nafion and carbon supports than alcohol-rich solvent, resulting in the

homogenous distribution of Nafion in the CL and thereby higher power densities. In the PBI system, the solvent composition does not significantly affect the MEA performance and alcohol-rich solvent can be used, which is advantageous to the process of CL fabrication.

6.2. Perspective

This dissertation underscores the importance of catalyst interface control in addressing PEMFC challenges. The strategies explored offer pathways to enhance catalyst durability, optimize ionomer distribution, and reduce overpotentials, contributing to the development of cost-effective and high-performance PEMFC systems. Future research should focus on further refining ionomer-free catalysts and exploring novel materials and fabrication methods to push the boundaries of PEMFC technology.

6.3. Future work

6.3.1 Future work 1

In Chapter 3, it was demonstrated that the proton conduction resistance of CB/S-PEDOT/Pt ($0.13 \Omega \cdot \text{cm}^2$) was significantly lower than that of CB/Pt ($0.67 \Omega \cdot \text{cm}^2$). This improvement is likely due to the additional proton conduction facilitated by the $-\text{SO}_3\text{H}$ groups in S-PEDOT. Building on this finding and the ionomer-free approach studied in Chapter 4, we propose utilizing S-PEDOT as a dual-function electron and proton conductor coating on carbon surfaces to develop a novel ionomer-free catalyst (**Figure 6-2**). This strategy aims to enhance performance further by addressing the limitations of conventional ionomer-based systems and promoting efficient proton and electron transport within the catalyst layer.

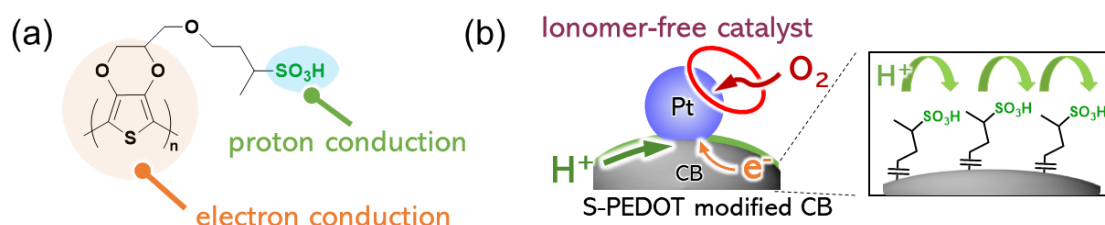


Figure 6-2 Overview of future work 1, (a) electron conduction and proton conduction function part in S-PEDOT (b) strategy of future work 1.

6.3.2 Future work 2

Furthermore, in Chapter 4, we demonstrated that the acid-grafted PBI polymer, PBI-PS, exhibits higher cell performance at 100%RH. However, lower activation overvoltage of MEA_{PS} and large drop of I-V performance at lower RH suggest that the optimization of the coating morphology and/or acid/acid distance on carbon surface can further improve I-V performance. Based on this insight, future work 2 will focus on using a more hydrophilic polymer with high proton conductivity of poly(2,5-benzimidazole) (ABPBI)-PS to replace the PBI-PS wrapping on the carbon surface (**Figure 6-3**). This approach aims to create a high-performance ionomer-free catalyst, further enhancing the efficiency and durability of PEMFC systems.

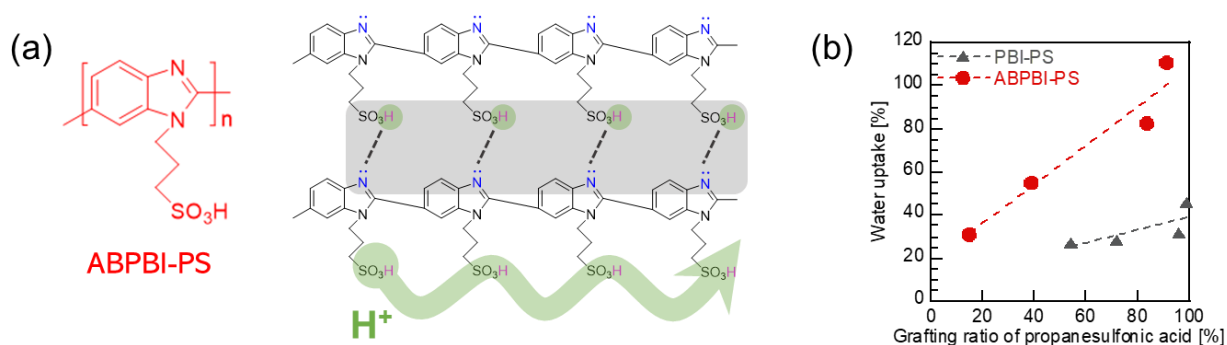


Figure 6-3 Overview of future work 2, (a) structure of poly(2,5-benzimidazole) (ABPBI)-PS, (b) water uptake of PBI-PS and ABPBI-PS polymers depended on grafting ratio of propanesulfonic acid.

Chapter 7

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