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<td>井殿, 大</td>
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Analysis of Mass Transport Properties and Microstructure of Catalyst Layers for Polymer Electrolyte Fuel Cell

（固体高分子形燃料電池触媒層の物質輸送特性と微細構造の解析）

Hiroshi Iden

井 殿 大

May 2014

Doctoral Thesis at Osaka Prefecture University
Analysis of Mass Transport Properties and Microstructure of Catalyst Layers for Polymer Electrolyte Fuel Cell

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Chapter 1 General introduction
1.1. Background

In the 21st century, it is said that climate change is the greatest common issue for all humankind. It is worried that global warming may cause great increase of famine in Africa and severe damage in agricultural sector due to drought and frequent typhoons in Asia. Glaciers have been melting and changing river flow. About 50% of glacier on Alps in Europe had disappeared before 1980. In China, highland glaciers equivalent to the total water amount of the Yellow River are melting in a year, and there is a fear of water shortage in western China where over 30 million people live in. Sea level is rising 3 mm each year due to rise of sea temperature and melt of glaciers since 1992, while the rise had been 1~2 mm each year over past hundreds years. Low areas such as islands and coastal cities are now in danger of erosion and flooding. Global warming may also cause epidemic of communicable diseases such as malaria and dengue fever. As described above, the climate change is a major issue that is closely associated with lives of people all around the world.

Intergovernmental Panel on Climate Change (IPCC) reported the following things [1]. 1) There is no doubt about the warming of the climate system and many of the changes which have been observed after 1950s are unprecedented. 2) It is highly likely that human activities have caused the warming observed since 1950s. 3) The total cumulative anthropogenic carbon emission is proportional to the ratio of global mean surface temperature change. According to the report, it seems safe to say that CO₂ emissions through human activities are the main cause of recent climate change. Consecutive greenhouse gas (GHG) emission may cause temperature rise and change in various part of the climate system. To restrain the climate change, significant and constant reduction of GHG emissions is indispensable.

According to the report issued by Greenhouse Gas Inventory Office of Japan [2], CO₂ accounted for 94.9% of the total amount of GHGs emissions in Japan in 2011. Therefore, reducing CO₂ emissions is an urgent matter. The report also said that the transport sector accounted for 17.9% of the total CO₂ emissions in Japan in 2011, and over 90% the CO₂ emissions from the transport sector was from automobile (Table 1.1.1). Accordingly, reducing CO₂ emissions from automobile is quite important.
Table 1.1.1. Trends in CO₂ emissions and removal in each sector [2].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Fuel combustion</td>
<td>1,068,280</td>
<td>1,143,799</td>
<td>1,280,064</td>
<td>1,217,697</td>
<td>1,193,093</td>
<td>1,089,805</td>
<td>1,161,982</td>
<td>1,180,904</td>
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<tr>
<td>Public electricity and heat production</td>
<td>299,074</td>
<td>318,599</td>
<td>336,805</td>
<td>338,921</td>
<td>335,199</td>
<td>330,705</td>
<td>327,941</td>
<td>329,529</td>
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<tr>
<td>Petroleum refining</td>
<td>13,893</td>
<td>16,956</td>
<td>17,383</td>
<td>16,441</td>
<td>14,334</td>
<td>14,364</td>
<td>15,658</td>
<td>14,223</td>
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<tr>
<td>Manufacturer of solid fuels and other energy industries</td>
<td>11,266</td>
<td>12,992</td>
<td>9,426</td>
<td>10,677</td>
<td>11,225</td>
<td>14,272</td>
<td>10,994</td>
<td>12,856</td>
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<tr>
<td>Iron and steel</td>
<td>140,880</td>
<td>151,162</td>
<td>150,776</td>
<td>151,341</td>
<td>148,260</td>
<td>134,610</td>
<td>151,804</td>
<td>147,564</td>
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<td>Non-ferrous metals</td>
<td>5,092</td>
<td>4,770</td>
<td>3,042</td>
<td>2,654</td>
<td>2,333</td>
<td>2,210</td>
<td>2,975</td>
<td>1,999</td>
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<td>Chemicals</td>
<td>94,796</td>
<td>84,800</td>
<td>67,216</td>
<td>58,050</td>
<td>53,325</td>
<td>52,949</td>
<td>51,582</td>
<td>52,983</td>
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<td>Pulp, paper and print</td>
<td>21,825</td>
<td>20,440</td>
<td>20,953</td>
<td>36,553</td>
<td>22,845</td>
<td>21,242</td>
<td>20,320</td>
<td>30,816</td>
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<tr>
<td>Food processing beverages and tobacco</td>
<td>13,129</td>
<td>14,407</td>
<td>13,168</td>
<td>13,216</td>
<td>8,862</td>
<td>8,761</td>
<td>9,128</td>
<td>9,296</td>
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<tr>
<td>Other</td>
<td>111,929</td>
<td>107,385</td>
<td>118,567</td>
<td>119,838</td>
<td>106,991</td>
<td>98,761</td>
<td>101,785</td>
<td>102,412</td>
</tr>
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<td>A.3. Transport</td>
<td>212,204</td>
<td>235,127</td>
<td>250,058</td>
<td>247,050</td>
<td>226,600</td>
<td>232,948</td>
<td>221,460</td>
<td>232,133</td>
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<td>Civil aviation</td>
<td>7,162</td>
<td>10,728</td>
<td>10,677</td>
<td>10,599</td>
<td>10,277</td>
<td>9,718</td>
<td>9,193</td>
<td>9,001</td>
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<td>Road transportation</td>
<td>189,238</td>
<td>235,981</td>
<td>232,827</td>
<td>222,032</td>
<td>205,938</td>
<td>202,018</td>
<td>204,981</td>
<td>201,973</td>
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<tr>
<td>Railway</td>
<td>932</td>
<td>929</td>
<td>797</td>
<td>644</td>
<td>600</td>
<td>596</td>
<td>170</td>
<td>568</td>
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<tr>
<td>Navigation</td>
<td>13,731</td>
<td>14,487</td>
<td>14,885</td>
<td>13,913</td>
<td>13,288</td>
<td>10,883</td>
<td>10,716</td>
<td>10,928</td>
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<td>A.4. Other sectors</td>
<td>101,641</td>
<td>179,113</td>
<td>188,585</td>
<td>193,419</td>
<td>188,485</td>
<td>189,500</td>
<td>191,605</td>
<td>192,065</td>
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<td>Commercial and institutional</td>
<td>61,303</td>
<td>70,369</td>
<td>101,408</td>
<td>110,078</td>
<td>98,706</td>
<td>93,365</td>
<td>91,994</td>
<td>93,407</td>
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<td>Residential</td>
<td>56,638</td>
<td>65,124</td>
<td>68,089</td>
<td>67,381</td>
<td>59,023</td>
<td>57,792</td>
<td>61,074</td>
<td>58,965</td>
</tr>
<tr>
<td>Agriculture, forestry, fisheries</td>
<td>21,380</td>
<td>19,526</td>
<td>16,307</td>
<td>15,518</td>
<td>16,657</td>
<td>10,425</td>
<td>14,048</td>
<td>15,176</td>
</tr>
<tr>
<td>B. Fugitive emissions from fuels</td>
<td>37</td>
<td>51</td>
<td>36</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
<td>38</td>
</tr>
<tr>
<td>Industrial processes</td>
<td>52,036</td>
<td>62,553</td>
<td>33,887</td>
<td>40,963</td>
<td>45,813</td>
<td>40,199</td>
<td>41,734</td>
<td>43,133</td>
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<td>Minerals products</td>
<td>55,581</td>
<td>56,756</td>
<td>50,746</td>
<td>46,714</td>
<td>42,389</td>
<td>37,180</td>
<td>38,177</td>
<td>38,341</td>
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<td>Chemical industry</td>
<td>4,209</td>
<td>4,258</td>
<td>3,893</td>
<td>3,867</td>
<td>3,747</td>
<td>2,488</td>
<td>2,737</td>
<td>2,629</td>
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<tr>
<td>Mining, quarrying</td>
<td>18,036</td>
<td>15,507</td>
<td>19,548</td>
<td>14,242</td>
<td>17,290</td>
<td>14,752</td>
<td>13,912</td>
<td>14,623</td>
</tr>
<tr>
<td>Total (including LULUCF)</td>
<td>1,073,228</td>
<td>1,104,023</td>
<td>1,155,412</td>
<td>1,195,277</td>
<td>1,223,871</td>
<td>1,095,489</td>
<td>1,115,267</td>
<td>1,155,249</td>
</tr>
<tr>
<td>Total (excluding LULUCF)</td>
<td>1,344,138</td>
<td>1,229,097</td>
<td>1,257,451</td>
<td>1,258,917</td>
<td>1,220,858</td>
<td>1,144,465</td>
<td>1,191,088</td>
<td>1,240,584</td>
</tr>
</tbody>
</table>

From the aspect of GHG emissions, it is important to use a methodology known as “Well-to-Wheel (WTW) analysis.” This approach considers not only the GHGs produced when a fuel is used in the vehicle (“Tank-to-Wheel” – TTW), but also the GHGs emitted in the fuel’s production and distribution (“Well-to-Tank” – WTT). Mobility 2030 (the final report of the World Business Council for Sustainable Development: WBCSD’s Sustainable Mobility project) shows an estimate of WTW emissions for various fuel/powertrain combinations some 10-20 years (or more) in the future, with each combination being separated into its WTT and TTW components [3]. As Fig. 1.1.1 shows, all combinations using internal combustion engines (ICE) and any fuel other than hydrogen have relatively high TTW emissions. The CO₂ savings from biomass-derived fuels occurs in the WTT part of the product chain as plants absorb CO₂ from the atmosphere during growth. As fuel cell electric vehicles (FCEV) using hydrogen as its fuel exhaust water only, there is no TTW emission. Therefore, WTW emissions can be reduced significantly with FCEVs though it depends on hydrogen production process. For this reason, the practical use of FCEV is highly expected.
1.2. Fuel cell (FC)

A fuel cell is a device that converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. Building blocks of polymer electrolyte fuel cell (PEFC) are shown in Fig. 1.2.1 as an example. The basic building block, which is called as single cell, is consisting of a polymer electrolyte membrane (PEM), electrodes on both sides of the membrane and flow channels for fuel and oxidizing agent. A fuel cell combines fuel (ex. Hydrogen) and oxidation agent (ex. Oxygen) to produce electricity. The electrochemical reactions can be expressed as follows:

Hydrogen oxidation reaction (HOR) at the anode

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]  \hspace{1cm} (1.2.1)
Oxygen reduction reaction (ORR) at the cathode

\[
\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (1.2.2)
\]

Overall reaction

\[
H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \quad \Delta G^\circ = -237.2 \text{ kJ mol}^{-1} \quad (25 \text{ °C}) \quad (1.2.3)
\]

Through the reactions, electrical energy equal to the change in Gibbs free energy ($\Delta G^\circ$) can be supplied. The theoretical efficiency ($\varepsilon$) is defined as the ratio of the converted electrical energy to the chemical energy of the fuel ($\Delta H^\circ$).

\[
\varepsilon = \frac{\Delta G^\circ}{\Delta H^\circ} \quad (1.2.4)
\]

As $\Delta H^\circ$ for HOR is $-285.8$ kJ mol$^{-1}$ at 25 °C, $\varepsilon$ is calculated to be 83%. This high theoretical efficiency is one of the reasons for high expectations for practical use of the fuel cell. The theoretical electromotive force, $E^\circ$, of the fuel cell is the difference in standard electrode potentials of the anode where fuel oxidation occurs and the cathode where reduction of oxidizing agent occurs, and is expressed as follows:

\[
E^\circ = -\frac{\Delta G^\circ}{nF} \quad (1.2.5)
\]

where $n$ is the number of electrons and $F$ is the Faraday constant (96485.3 C mol$^{-1}$).

---

**Fig. 1.2.1. Building blocks of polymer electrolyte fuel cell single cell.**

Fuel cells can be categorized as alkaline fuel cell (AFC), molten carbide fuel cell (MCFC), solid oxide fuel cell (SOFC), phosphoric acid fuel cell (PAFC) and PEFC by the kind of electrolyte. Among them, PEFC has the following features. 1) short start-up time thanks to a high proton conductive PEM and relatively low operation temperature (room temperature ~ 100°C), 2) thin electrolyte membrane as the electrolyte does not
scatter, resulting in high power density, 3) impervious to vibration and easy assembling as PEFC is composed of solid materials. With these features, PEFC is thought to be the most suitable for automotive use, and research and development of PEFC and automobile that utilizes PEFC have been being carried out in Japan, North America and Europe. Although some car manufacturers have already brought PEFC to market as lease, there are still many issues regarding infrastructure such as consolidation of hydrogen filling station and performance, durability and cost of PEFC and its peripherals.

1.3. Structure and performance of polymer electrolyte fuel cell (PEFC)

The basic structure of PEFC is composed of a PEM, two catalyst layers on its both sides, two gas diffusion layers (GDL) next to the catalyst layers and two bipolar plates outside the GDLs. This is called as single cell and structure which has single cells piled in series is called as stack. The structures of a PEFC stack and a single cell are shown in Fig. 1.3.1 and Fig. 1.2.1, respectively. Functions of the PEM include proton conduction, mechanical and chemical stability and gas barrier property. Especially, high proton conductivity at a low RH condition is necessary to simplify PEFC system. In the catalyst layers, high catalyst surface area and paths of proton, gas and electron towards the catalyst have to be secured so that electrochemical reactions (1.2.1) and (1.2.2) can occur consecutively. Therefore, the catalyst layer consists of catalyst particles deposited on a high surface area carbon support which has high electroconductivity, polymer electrolyte (ionomer) for proton conduction and pores for gas transport. In general, the GDLs are composed of a carbon paper which is water-repellent treated with polytetrafluoroethylene (PTFE) and a micro porous layer based on the mixture of carbon and PTFE. Gas and water transport, electroconductivity and thermal conductivity are required for the GDLs. Bipolar plates work as a current collector, a gas supply media and a separator between the anode and the cathode, whereas they have ribs for current collection and channels for gas supply.
Fig. 1.3.1. The structures of a PEFC stack.

PEFC performance is typically expressed as current–voltage curve (I–V curve) like Fig. 1.3.2. Actual cell voltage is below the theoretical electromotive force for several reasons and the gap, which is called as overpotential, becomes larger with increasing the current. The sources of the voltage loss can be classified roughly into three, namely, ohmic loss, activation overpotential and concentration overpotential. The ohmic loss is caused by proton transport resistance of the PEM, electric resistance of the GDLs and the bipolar plates and their contact resistance. The activation overpotential is the potential difference above the equilibrium value required to produce a current which depends on the activation energy of electrochemical reactions. As HOR is very fast on Pt catalyst, the overpotential at the anode is usually negligible. On the other hand, ORR is slow even on Pt, resulting in high overpotential. Therefore, reducing the overpotential for ORR is necessary to obtain better performance. When transport of reactant is slow, the concentration of reactant at electrode surface decreases. As the rate of electrochemical reactions depends on the reactant concentration, like chemical reactions, the decrease in reactant concentration causes the decrease in reaction rate, resulting in the increase of overpotential. This is called as concentration overpotential. Drainage of the GDLs and gas transport resistance of the GDLs and the catalyst layers affect the concentration overpotential. Aside from these overpotentials, gas crossover and electrical short can cause voltage loss. The relation among the sources of voltage loss, their impact on cell voltage and governing factor was summarized in Table 1.3.1.
Fig. 1.3.2. An I–V curve of PEFC and sources of voltage loss.

Table 1.3.1. Sources of voltage loss, their impact on cell voltage and governing factor.

<table>
<thead>
<tr>
<th>Loss</th>
<th>Impact</th>
<th>Governing factor of components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Activation overpotential</td>
<td>Catalytic activity of catalyst</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Concentration overpotential</td>
<td>Low</td>
<td>Gas diffusivity in GDL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas permeability in catalyst layer</td>
</tr>
<tr>
<td>Cathode</td>
<td>Activation overpotential</td>
<td>Catalytic activity of catalyst</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td></td>
</tr>
<tr>
<td>Concentration overpotential</td>
<td>Medium</td>
<td>Gas diffusivity in GDL</td>
</tr>
<tr>
<td></td>
<td>(High at a high current density)</td>
<td>Water drainability of GDL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gas permeability in catalyst layer</td>
</tr>
<tr>
<td>Ohmic loss</td>
<td>Medium</td>
<td>Proton conductivity of membrane</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electric conductivity of GDL and bipolar plate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Contact resistance of electroconductors</td>
</tr>
<tr>
<td>Gas crossover/shorting</td>
<td>Low</td>
<td>Gas barrier ability of membrane</td>
</tr>
<tr>
<td></td>
<td>(High at a low current density)</td>
<td>Electric shorting resistance</td>
</tr>
</tbody>
</table>

1.4. Issues of PEFC for commercialization of fuel cell electric vehicle (FCEV)

To use the PEFC as an automotive power source, balance of plant (BOP) parts such as hydrogen tank, air compressor, stack temperature controller and humidifier need improvement. However, these parts are to help the stack exercise its top performance, therefore, improvement of PEFC performance itself is necessary for full-scale commercialization of FCEVs.

As securing interior comfort and load capacity of the FCEV is required, the volume of the PEFC stack has to be as small as possible. In other words, high power density (power to volume) is required, and the I–V performance mentioned in Sec. 1.3 is
a governing factor to determine the power density. High durability is also required as automobile is a consumer durable. As Automobile Inspection and Registration Information Association in Japan reported that the average age of passenger vehicles is over 12 years in 2013 [4], the PEFC stack has to last for such a long time. At cold regions where the temperature goes below zero, water generated from the PEFC stack or water in a humidifier can freeze during shut down period. The frozen water might cause physical destruction of the bipolar plates or membrane electrode assemblies (MEAs) and clogging in the GDLs which might results in a start-up failure due to high gas transport resistance. As the FCEVs are expected to experience subzero temperatures like conventional vehicles with an ICE, the PEFC stack has to be able to survive and operate under such conditions.

In addition to the three issues above, cost reduction of PEFC is also necessary. From an industrial point of view, reducing the FCEV’s cost to affordable level for vehicle users is indispensable for its commercialization. The Department of Energy (DOE) in the United States updated the fuel cell system cost analysis. The analysis indicates that the fuel cell stack would account for 64% and 49% of the total system cost at 1,000 and 500,000 systems per year, respectively [5]. A breakdown of stack component cost in 2013 is shown in Fig. 1.4.1. Of the various components, catalyst and bipolar plates are dominated by commodity materials costs (platinum and stainless steel, respectively), which are relatively insensitive to manufacturing volume. The rest of the component costs stem more from specialty materials and processing costs, which are more sensitive to volume. Thus, an increase in volume causes the membrane and GDL cost elements to decrease from 32% and 18% of system cost at 1,000 systems per year to 11% and 5% of system cost at 500,000 systems per year, respectively, while the catalyst and bipolar plate cost elements increase from 16% and 14% to 49% and 22% of total system cost, respectively. The analysis suggests that reducing metal loading, especially Pt loading, is a key issue for the cost reduction.
1.5. The role of catalyst layers and its importance

At Nissan, development work on FCEVs is proceeding toward a target market introduction in the late 2010s. Research and development work on Nissan FCEVs has been under way since 1996. As mentioned above, the main issues that must be addressed to commercialize FCEVs include: (1) to increase power density, (2) to prevent performance decay, (3) to improve subzero start-up capability and (4) to develop technologies for reducing costs. Fundamental research activities at Nissan undertaken to resolve these issues have elucidated various phenomena such as mass transport mechanism [6-10] and degradation mechanism [11-17] in the membrane electrode assembly (MEA) and corrosion on metal bipolar plates [18,19]. These activities have resulted in a new Nissan fuel cell stack (developed in 2011) that achieves a power density of 2.5 kW L\(^{-1}\) and a lower cost by reducing the amount of Pt loading used by one-fourth compared with the previous stack model developed in 2005 [20]. The performance and the durability of the new stack are close to satisfying the requirements for real-world use, except the cost.

In order to accomplish a reduction of the Pt loading, it will be necessary to make more effective use of Pt contained in the catalyst layer of the MEA. Naturally, it is important to increase the catalytic activity and the active surface area of the Pt contributing to the electrochemical reactions to use it more effectively. In terms of the catalytic activity, core–shell catalysts have been in the spotlight recently [21-23]. The electrochemically active surface area is related to Pt utilization [24-26]. It is
indispensable to understand more deeply ORR at the metal/electrolyte interface for further Pt reduction, such as modeling approach of elementary kinetics model for ORR [27,28]. It is also essential to design the fuel cell so as to maintain a higher concentration of reactants transported to the Pt surface and to ensure a homogeneous reaction distribution as much as possible within the catalyst layer, related to Pt effectiveness [29–32]. Such measures can achieve high I–V performance with a lower Pt loading. Accordingly, in order to promote more effective use of Pt, it is necessary to understand the effects on the reaction distribution and potential loss (polarization) occurring in the catalyst layer. Other issues involved here include ascertaining the transport properties and the enabling microstructures, as they determine the reaction distribution.

Considering fuel cell operation condition, applying high current density is more effective in reducing cost because the number of cells in a stack can be reduced. Therefore, optimizing the catalyst layers for better mass transport is necessary. However, it is difficult to characterize and model the catalyst layers because they have a very complicated microstructure and the transport of water, gas and protons and the electrochemical reactions occur simultaneously there.

1.6. Objective of this work

As has been mentioned above, practical use of FCEVs has been demanded for reducing CO₂ emissions and preventing further climate change. However, there are still challenges to be addressed in the commercialization of FCEVs, including power density, durability, sub-zero startup, and cost reductions. The greatest challenge of all from an industrial point of view is cost reduction. According to a U.S. DOE report, Pt in the catalyst layer accounts for about a quarter of the total fuel system cost [5]. The most effective measure for this issue is to reduce the loading of the Pt noble metal. For reducing the Pt loading, using Pt more effectively and improving performance dramatically are indispensable. To achieve this, improving catalyst activity and enhancing mass transport of gas and proton are effective. Considering fuel cell operation condition, optimizing the catalyst layer structure for better mass transport is thought to be more effective. The objectives of this study are 1) developing evaluation techniques for proton and gas transport and microstructure of the catalyst layers, 2) analyzing the mass transport properties and microstructure of the catalyst layers to understand their key factors and 3) obtaining an idea about an optimized catalyst layer from the aspect of mass transport.
References

[1] Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2013*.
Chapter 2 Proton transport analysis
2.1. Analysis of proton transport in pseudo catalyst layers

2.1.1. Introduction

The greatest challenge for commercialization of FCEVs is the cost reduction from industrial point of view. Based on the cost reduction, operation in low humidity and high current density is desirable. Though it is reported that operation in low humidity leads the electrolyte to deteriorate [1,2], to remove humidifier from FCEV is thought to be effective to simplify FC system. Moreover, operation in high current density makes it possible to reduce the number of MEAs and bipolar plates of a FC stack. However, the increase of IR loss is concerned in such condition. Especially, decrease of proton conductivity in the catalyst layer could cause the decrease of the catalyst utilization due to heterolytic distribution of current density [3,4]. Therefore, it is important to understand proton transport phenomena in the catalyst layers. In this section, the proton transport phenomena in the catalyst layers were focused on. Various factors such as the distribution of the current density, water and heat production, mass transport, electroosmotic drag (EOD) and the structural factors (ionomer coverage, network structure etc.), among others, affect proton transport phenomena in the catalyst layers. The influence of the factors related to the microstructure on the electrochemical reaction and transport properties should be investigated. However it is not fully understood. Especially, the relationship between proton transport and the microstructure of the catalyst layers has not been clarified yet.

In recent years, a lot of studies for modeling the proton transport properties in the catalyst layers have been conducted, where percolative models [5,6] or the Bruggeman correction [7-9] were used. It is necessary to measure proton transport resistance of the actual catalyst layers to validate the models. Electrochemical impedance spectroscopy (EIS) and analyses based on the finite transmission line models have been adopted [10-13]. In general, capacitance and resistance elements were regarded as equal in each section in the transmission line circuits to analyze. However, it is reported that a profile of a Nyquist plot depends on the distribution of the capacitance and the resistance despite that total capacitance and resistance are the same [12,14]. So, it is difficult to apply the technique in the case that the capacitance and/or the ionomer resistance are distributed non-uniformly. In addition, there are some experimental problems such as elimination of inductance or increase of frequency to apply EIS to the sample with small double layer capacitance or proton transport resistance. Therefore, it is necessary to develop another technique which can be applied
to more practical samples and conditions.

In this section, a new evaluation technique of the proton transport with pseudo catalyst layers, which consisted of carbon support and ionomer, was examined. A quantitative characterization of microstructure of the catalyst layers, in particular, the ionomer coverage and thickness was also carried out. According to Bruggeman correction equation, the effective conductivity ($\sigma_{eff}$) can be expressed as follows:

$$\sigma_{eff} = \sigma_{bulk} \varepsilon^{\gamma}_{ion}$$

(2.1.1)

where $\sigma_{bulk}$ is the proton conductivity of the ionomer as bulk, $\varepsilon_{ion}$ is the volume fraction of ionomer and $\gamma$ is the Bruggeman factor ($\approx 1.5$) which is related to the tortuosity of the conductor [7-9,15]. The relationship between the microstructure and the proton transport in the catalyst layers was analyzed using the information obtained with above techniques.

### 2.1.2. Experimental

**Preparation of MEA**

Table 2.1.1 and Table 2.1.2 show the MEA specifications used in this study. Two samples shown in Table 2.1.1 (denoted as samples 1 and 2) with different carbon materials and perfluorosulfonic acid (PFSA) membranes (Nafion® NR211, thickness = 25 $\mu$m) were used to measure proton transport resistance. Other two samples shown in Table 2.1.2 were used to investigate electrochemical characteristics of pseudo catalyst layers (PCLs). Catalyst and pseudo catalyst inks were prepared respectively by mixing Pt/C (catalyst: 46 wt.%, TEC10E50E, TKK) or carbon (ketjen black (KB) or graphitized ketjen black (GKB)) and the Nafion® ionomer solution (D2020, EW1000, DuPont) together so that the weight ratio of the ionomer content was 0.9 relative to the carbon support. A propylene glycol solution (50 wt.%) was also added to the ink to keep its solid content at 19 wt.% for the catalyst layers and at 12 wt.% for the PCLs. The electrocatalyst layers and PCLs were fabricated on polytetrafluoroethylene (PTFE) substrates using a screen-printing technique. The square electrocatalyst layers measured 50 mm on one side and had a Pt loading of 0.35 mg cm$^{-2}$ and the PCLs had a C loading of 0.70 mg cm$^{-2}$. These layers were heat treated on the PTFE substrates for 30 min at 130°C to remove the organic solvent.
To fabricate the samples shown in Table 2.1.2, a catalyst layer and a pseudo catalyst layer were decal-transferred to a square membrane (72 mm on one side). In addition, to prepare the samples shown in Table 2.1.1, the other catalyst layer was also decal-transferred to another membrane. The catalyst-coated membranes (CCMs) were then hot-pressed together with the PCL located in the center of the MEA. To extract proton transport resistance of the PCLs, an MEA without PCL was necessary. The sample was also fabricated by hot-pressing two half CCMs. The decal-transfer and hot-press conditions were 150°C, 10 min, and 0.8 MPa. Polyethylene naphthalate (PEN) films (Q51, 25 μm, Teijin-DuPont) were bonded on the surrounding areas of the
electrocatalyst layers and the pseudo catalyst layer as reinforcement. Gas diffusion layers (GDLs) with microporous layers (24BC, SGL Carbon) were used in this study. The MEA was formed by assembling the GDLs on both sides of the CCMs. The MEA was assembled in a single cell between bipolar plates with a straight flow field made of graphite and gaskets made of silicone rubber. The compression pressure was kept uniform by measuring it with pressure-sensitive paper (Prescale, Fuji Film).

**Measurement of proton transport resistance**

Proton transport resistances were measured under the conditions shown in Table 2.1.3. Hydrogen under ambient pressure was fed to both the anode and cathode. By means of a hydrogen pump technique [16], voltage drops were measured under various current densities and RH conditions. The overall resistances were obtained from the slopes at the lower current densities, ignoring the water distribution due to EOD and temperature rise produced by the IR drop. The overall resistances of the samples with and without the PCL were evaluated (Fig. 2.1.1). The difference in resistance between them was found to be mainly due to the proton transport resistance of the PCL (measurement technique 1).

<table>
<thead>
<tr>
<th>Anode gas</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode gas</td>
<td>H₂</td>
</tr>
<tr>
<td>Back pressure</td>
<td>Ambient</td>
</tr>
<tr>
<td>Cell temperature / °C</td>
<td>80</td>
</tr>
<tr>
<td>Anode humidity / % RH</td>
<td>30, 40, 50, 60, 70, 80, 90, 100</td>
</tr>
<tr>
<td>Cathode humidity / % RH</td>
<td>30, 40, 50, 60, 70, 80, 90, 100</td>
</tr>
<tr>
<td>Anode flow rate / NL min⁻¹</td>
<td>4.0</td>
</tr>
<tr>
<td>Cathode flow rate / NL min⁻¹</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Another technique of subtracting HFR (high-frequency resistance) from the overall resistance was also examined (measurement technique 2). HFR was measured by electrochemical impedance spectroscopy (EIS) simultaneously with the operation of the hydrogen pump. The EIS measurements were conducted with a current perturbation of 0.04 A cm$^{-2}$ at frequencies ranging from 0.1 to 15,000 Hz. HFR was obtained at the point where impedance spectra intersected with the x-axis in Nyquist plots. If the double layer capacitance of the PCL is large, the proton transport resistance of the PCL is not included in the HFR. Therefore, if the electronic resistance of the PCL is negligible, the difference between the overall resistance obtained with the hydrogen pump technique and the HFR includes the proton transport resistance of the PCL and resistances of the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER). The HOR and HER resistances are presumed to be markedly lower [17] than the proton transport resistance of the PCL, so they might be negligible. The RH dependence of the proton transport resistance of the PCL was evaluated with the two techniques and the results were compared. The details of the analysis will be described in the following section.

*Measurement of proton conductivity and expansion of Nafion® membrane*

Proton conductivity of the Nafion® membrane at 80°C was measured by a four-point probe method using a Solartron 1260 Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz to 1 MHz under different RH conditions. The membrane
was equilibrated in a humidity-temperature oven (ETAC, TH 203HA) at the specified RH and temperature for at least thirty minutes before the measurement. The expansion of the membrane was also studied using a dynamic mechanical analyzer DVA-220/L2/HiHT (IT keisokuseigyō). The membrane was cut into size of about 3 mm x 40 mm. The length was measured with a low static load of 0.04 N under different relative humidity at 80°C after a waiting period.

Cyclic voltammetry

To investigate electric double layer capacitance \( C_{dl} \) of the PCLs, cyclic voltammetry was carried out using the same single cell set-up at 80°C. Pure \( \text{H}_2 \) and \( \text{N}_2 \) were fed to the counter and reference electrode and a working electrode (PCL) respectively. After a waiting period, the cathode potential was scanned between 0.2 and 0.6 V vs. RHE at a scan rate of 50 mV s\(^{-1}\) for a few cycles. HZ-3000 electrochemical measurement system (Hokuto Denko, Japan) was used to carry out the cyclic voltammetry.

Water uptake measurement

Water adsorption onto KB, GKB, PCLs and membrane was carried out using an automatic vapor adsorption apparatus (Belsorp 18 Plus-HT, Nihon Bell) at 80°C. 0.03~0.05 g of the samples was placed in a glass sample tube. As preconditioning, the sample tube was evacuated for 5 hours at 80°C after that it was kept at 80°C. Water vapor was then introduced until the relative pressure, \( \frac{P}{P_s} \) (\( P_s \), saturated vapor pressure, 47.416 kPa at 80°C).

2.1.3. Results and discussion

Comparison of the two techniques

The hydrogen pump results for sample 1 with a PCL having a carbon support of ketjen black (KB) are described in this section. The relationship between the voltage drop and current density under various RH conditions is shown in Fig. 2.1.2. The voltage drop showed good linearity as a function of the current density. The overall resistances obtained from the slopes are shown in Fig. 2.1.3 as a function of RH. As shown in Fig. 2.1.3, HFR was not so large compared to the overall resistance. As mentioned in the previous section, the proton transport resistance of the PCL cannot be included in the HFR. So, this result indicates that the resistance of the sample with the PCL was mainly due to the proton transport resistance of the PCL and that proton
transport resistance markedly increased with decreasing RH. The proton transport resistance was also estimated by the subtraction of the HFR obtained by EIS from the overall resistance of sample 1. The results obtained with both techniques are compared in Fig. 2.1.4. It is seen that almost the same resistances were obtained with both techniques.

Fig. 2.1.2. Voltage drop as a function of current density in different RH conditions at 80°C (With a pseudo catalyst layer).
Fig. 2.1.3. RH dependency of HFR and the resistivity of the MEA with the PCL (dashed line: proton transport resistivity of the PCL obtained by subtracting HFR from overall resistance of the MEA).

Fig. 2.1.4. Comparison of the proton transport resistivity of the PCL obtained with techniques 1 and 2.
Fig. 2.1.4 also indicates that $R_{\text{bulk}}$ (electronic resistance of bulk of cell hardware), $R_{\text{contact}}$ (contact resistance) and $R_{\text{mem}}$ (proton transport resistance of membrane) of the sample with the PCL were almost the same as those of the sample without the layer and that $R_{\text{HOR}}$ and $R_{\text{HFR}}$ (reaction resistance of hydrogen oxidation and hydrogen evolution) had little influence on the overall resistance of the PCL. With measurement technique 2, it is not necessary to consider the differences of $R_{\text{bulk}}$, $R_{\text{contact}}$ and $R_{\text{mem}}$ because HFR is measured simultaneously with the operation of the hydrogen pump. Moreover, it is not necessary to fabricate and evaluate a sample without a PCL. Measurement technique 2 is preferable due to its convenience. However, measurement technique 1 was used because the double layer capacitance of the PCL consisting of a GKB support and ionomer was very low as will be explained in following section (Fig. 2.1.10).

**Comparison of the two different MEAs**

Another sample (sample 2) with a PCL having a GKB carbon support was also evaluated. Resistivities of the PCLs with the different carbon supports are shown in Fig. 2.1.5. Effective proton conductivities of the samples were calculated from their resistivities and thicknesses (Fig. 2.1.6). The average thickness was measured from SEM images of the PCLs (Table 2.1.4). A comparison revealed that sample 2 showed higher conductivity. The difference was analyzed in detail with Eq. (2.1.1).

![Fig. 2.1.5. Comparison of resistivities of the PCLs with different carbon supports.](image-url)
Fig. 2.1.6. Comparison of effective proton conductivities of the PCLs with different carbon supports.

Table 2.1.4. Properties of carbon blacks and PCLs.

<table>
<thead>
<tr>
<th>Carbon support</th>
<th>Average thickness of PCL / µm</th>
<th>$\epsilon_{\text{ion}}$ / -</th>
<th>$s_{\text{carbon}}$ / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 Ketjen black</td>
<td>22</td>
<td>0.17</td>
<td>718</td>
</tr>
<tr>
<td>Sample 2 Graphitized ketjen black</td>
<td>20</td>
<td>0.19</td>
<td>151</td>
</tr>
</tbody>
</table>

The volume fraction of the ionomer, $\epsilon_{\text{ion}}$, was obtained with following process. First, the volumes of the PCLs were calculated from their geometric area and thickness. The weight of the ionomer was calculated from the I/C (ionomer/carbon) weight ratio. The volume of the ionomer was then estimated from its weight and density. The density was estimated based on the relationship between $\lambda$ ($\text{H}_2\text{O}/\text{SO}_3\text{H}$, the ratio of the number of moles of water to sulfonic acid group) and the density of the Nafion® membrane reported by Morris et al. (1.91 g cm⁻³ at 25°C and 30% RH) [18]. Then, $\epsilon_{\text{ion}}$ was obtained from the volume of the PCL and ionomer. These values are shown in Table 2.1.4.

Assuming that the ionomer swells and shrinks as the membrane does, $\epsilon_{\text{ion}}$ depends on temperature and RH. To estimate this influence, the expansion of a membrane (Nafion® NR211) was measured under various temperature and RH conditions. Measured expansion ratio was not so far from the value in Ref. 19. Assuming that the expansion of the membrane was equal in all directions and was the same as that of the ionomer, $\epsilon_{\text{ion}}$ was corrected based on the expansion of the membrane. The
proton conductivity of the membrane was measured under various temperature and RH conditions and regarded as $\sigma_{\text{bulk}}$. The values obtained are shown in Fig. 2.1.7. They were also not so far from the values in the literature [20].

![Proton conductivity and expansion of membrane (Nafion® NR211) as a function of relative humidity at 80°C.]

Fig. 2.1.7. Proton conductivity and expansion of membrane (Nafion® NR211) as a function of relative humidity at 80°C.

The Bruggeman factor, $\gamma$, of the samples was calculated with these values. $\gamma$ of the samples is shown in Fig. 2.1.8 as a function of RH. $\gamma$ slightly decreased with increasing RH. This tendency was also mentioned in Ref. 21. The increase in the thickness of the ionomer due to its swelling might have caused this tendency, which will be discussed later. The tortuosity of the proton path probably depends on the surface area covered with the ionomer, assuming that it is thin enough and covers the outer surface of the carbon support almost uniformly. The area depends on the coverage of the ionomer, $\theta$, and the surface area of the carbon support, $S_{\text{carbon}}$, because the Bruggeman factor is originally derived from the ratio between one-half of the circumference and the diameter ($\pi/2 \approx 1.5$) [15]. The average diameter of the carbon supports for the PCLs was obtained from the SEM images (Fig. 2.1.9), and it was found to be almost the same ($\approx 40$ nm). Then, to grasp covering state of the ionomer, SEM images of KB and the PCL consisting of KB and the ionomer were compared in Fig. 2.1.9. The outline of the PCL was not sharply defined as that of KB without ionomer. It is inferred that the ionomer is thin enough and covers the outer surface of the carbon support almost uniformly. Surely, it is difficult to know that definitely from SEM images only, but it is regarded that the
ionomer coverage could be estimated roughly. Therefore, the ratio of the Bruggeman factor of the samples in this study was expressed as shown in Eq. (2.1.2) below,

\[
\frac{\gamma_{KB}}{\gamma_{GKB}} = \frac{l_{KB}'}{l_{GKB}'} = \frac{l_{KB}'}{l_{GKB}'} = \sqrt{\frac{S_{KB}\theta_{KB}}{S_{GKB}\theta_{GKB}}}
\]  

(2.1.2)

where \(l\) is the average diameter and \(l'\) is the one-half of the circumference of the carbon support. \(S_{\text{carbon}}\) was measured by the BET N\(_2\) adsorption method, and \(\theta\) was determined from the change in the double layer capacitance (\(C_{\text{dl}}\)) of the PCL (Table 2.1.5). Here, \(S_{\text{carbon}}\theta_{\text{carbon}}\) means the total area covered with the ionomer. So, the ratio of square root of \(S_{\text{carbon}}\theta_{\text{carbon}}\) can be regarded as the ratio of the length of proton paths. \(C_{\text{dl}}\) of the PCL was obtained from a cyclic voltammogram (CV) of the MEA shown in Table 2.1.2. CVs of the PCLs obtained under a 100% RH condition at 80°C were shown in Fig. 2.1.10. In both cases, CV showed square like shape. It is considered that only charge or discharge of the electric double layer occurred in the PCL. However, some slight peaks which might be due to redox reactions of functional groups of KB surface were observed from 0.4 to 0.6V. Then, \(C_{\text{dl}}\) was calculated with the current at 0.3V. RH dependency of \(C_{\text{dl}}\) of the PCLs was measured and shown in Fig. 2.1.11. \(C_{\text{dl}}\) of sample 2 did not depend on RH. The surface area covered with the ionomer presumably works as \(C_{\text{dl}}\) even in a drier case. In contrast, \(C_{\text{dl}}\) of sample 1 was strongly affected by RH. It implies that the interface between the carbon support and adsorbed water worked as \(C_{\text{dl}}\) in higher RH conditions, based on the results of water adsorption isotherms (discussed later).

![Fig. 2.1.8. Relationship between \(\gamma\) of the PCLs and relative humidity.](image)
Fig. 2.1.9. SEM images of the carbon supports and pseudo catalyst layer.

Table 2.1.5. Ionomer coverage and average thickness of the samples.

<table>
<thead>
<tr>
<th>Carbon support</th>
<th>Ionomer coverage /</th>
<th>Average thickness of PCL / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 Ketjen black</td>
<td>0.34</td>
<td>1.9</td>
</tr>
<tr>
<td>Sample 2 Graphitized ketjen black</td>
<td>1</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Fig. 2.1.10. Cyclic voltammograms of the PCLs with different carbon supports under a 100% RH condition at 80°C.

Fig. 2.1.11. RH dependency of double layer capacitances of the PCLs with different carbon supports.

Therefore, it is presumed that the carbon surface was almost entirely covered with the ionomer or water under a 100% RH condition. The carbon surface was probably covered with the ionomer only at lower RH conditions. Accordingly, \( \theta \) was expressed as \( C_{dl\text{-dry}}/C_{dl\text{-wet}} \). \( C_{dl} \) due to the water-carbon interface was not large at 30% RH, based on
the results in Fig. 2.1.11 and the water adsorption isotherm of KB (see Fig. 2.1.14), so $C_{dl}$ in that condition was regarded as $C_{dl-dry}$. $C_{dl}$ at 100% RH was also regarded as $C_{dl-wet}$, corresponding to that at $\theta = 1.0$. In order to validate this assumption, the specific capacitances of KB and GKB were estimated from $S_{carbon}$ and $C_{dl}$ in a 100% RH condition. $C_{dl-KB}$ was found to be 7.56 $\mu$F cm$^{-2}$carbon and $C_{dl-GKB}$ to be 2.23 $\mu$F cm$^{-2}$carbon. Although this comparison is not precise because of the differences in various conditions, $C_{dl}$ of KB and GKB showed values close to that of carbon black in Refs. 22 and 23. Therefore, $\theta$ might be around 1 in a 100% RH condition. In addition, the average thickness of the ionomer was also calculated from $S_{carbon}$, I/C ratio and the density of the ionomer as shown in Table 2.1.5.

The effective conductivity of sample 2 was corrected with $\gamma_{KB}/\gamma_{GKB}$ (1.23) and compared with that of sample 1 (Fig. 2.1.12). However, a difference still remained between the two samples. The reasons for this difference were then investigated. One possible cause of the difference is that the correction of $\gamma$ was not reasonable. For instance, $\gamma$ of the two samples with different ionomer thicknesses might have differed. Presumably, $\gamma$ becomes smaller when the ionomer is thicker as shown in Fig. 2.1.13. Moreover, $\gamma_{KB}/\gamma_{GKB}$ would be larger, if $\theta$ of sample 2 is smaller than 1. That would reduce the difference between the experimental data for sample 1 and the calculated results for sample 2.

![Graph of effective proton conductivities](image)

Fig. 2.1.12. Comparison of effective proton conductivities of the PCLs with different carbon support (Solid line: experimental data; dashed line: corrected result of sample 2 with $\epsilon_{ion}$ and the ratio of $\gamma$ of the samples).
Another possibility is that $\sigma_{\text{bulk}}$ of the samples might have been different, i.e., $\sigma_{\text{bulk}}$ of sample 1 might have been lower than that of sample 2. To investigate this possibility, water adsorption isotherms for the carbon supports and the PCLs were evaluated (Fig. 2.1.14). The amount of water adsorbed on KB increased from a lower water activity condition, which might be ascribable to hydrophilicity of the functional groups on the surface. It was found that the amount of adsorbed water of sample 1 was less than that of sample 2. Although a simple subtraction might not be exactly appropriate, the amount of water adsorbed on the ionomer was approximated from the difference between the compounds and the carbon. The equilibrium adsorption of water vapor for the ionomer is shown in Fig. 2.1.15 as a function of water activity. The results indicate that $\lambda$ of the ionomer of sample 1 was lower than that of sample 2. In addition, $\lambda$ of the ionomer of sample 2 showed almost the same value as that of the membrane prepared by casting ionomer solution (Nafion® D2020). Actual value of equivalent weight (EW, defined as the weight of polymer (in molecular mass) per sulfonic acid group) of that membrane was evaluated by combustion ion chromatography and found to be 1046. Accordingly, it is inferred that $\sigma_{\text{bulk}}$ of sample 1 might have been lower than that of sample 2. When the calculated results of sample 2 shown in Fig. 2.1.12 correspond to the experimental data of sample 1, the amount of adsorbed water for ionomer of sample 2 is expressed as the chained line in Fig. 2.1.15.
In general, it is said that a lot of functional groups such as carboxyl groups are on the surface of the KB used in sample 1 [22,23]. According to the calculation based on molecular dynamics, it was suggested that ionized carboxyl groups on the carbon surface interacted the sulfonic groups of Nafion® and water strongly [24]. In this study,
such kind of functional groups might exist on KB surface and have affinity with the sulfonic groups of the ionomer as well as Ref. 24. As a result, water adsorbability of the sulfonic groups of the ionomer could become weaker than without the functional groups. In contrast, the graphitized carbon used in sample 2 probably does not have so many functional groups as sample 1, so such interaction would be much less. Such differences in the properties of the carbon surface might have caused the difference in $\sigma_{\text{bulk}}$. Another possible reason for the difference in $\sigma_{\text{bulk}}$ is that it might have been affected by the cluster size of the ionomer. In short, a smaller cluster would form when the ionomer is thinner, as estimated in Table 2.1.5. In such cases, $\sigma_{\text{bulk}}$ might be smaller.

As another factor contributing to the difference in $\sigma_{\text{eff}}$, the connectivity of the ionomer might change depending on the carbon support. Though $\gamma$ in Bruggeman correction equation could be regarded as a factor that includes the connectivity, only the tortuosity was considered as the factor related to $\gamma$ in this study.

### 2.1.4. Conclusion

The overall resistance of samples with and without a pseudo catalyst layer between two membranes was evaluated with a hydrogen pump technique. The difference seen in their resistance was mainly attributed to the proton transport resistance of the pseudo catalyst layer. Another technique of subtracting HFR from the overall resistance was examined. It was found that the proton transport resistance of the pseudo catalyst layer can be determined with this technique if the double layer capacitance of the layer is large. We used these measurement techniques to examine the influence of the ionomer network structure on proton transport in the pseudo catalyst layer.

A comparison was made of the effective proton conductivities of pseudo catalyst layers with different types of carbon supports. A layer with a carbon support of graphitized ketjen black (sample 2) showed higher proton conductivity than that of a layer with a ketjen black carbon support (sample 1). The experimental data for sample 2 were initially corrected using the difference in the Bruggeman factor of the samples, obtained from their ionomer coverage and carbon surface area. However, the corrected results still did not correspond with the data for sample 1.

One possible reason for the difference is that the correction of $\gamma$ was not reasonable. For instance, $\gamma$ of the two samples with different ionomer thicknesses might have differed. $\gamma$ might become smaller when the ionomer is thicker. Moreover, $\gamma_{\text{KB}}/\gamma_{\text{GKB}}$ would be larger if $\theta$ of sample 2 is smaller than 1. Accordingly, the difference between
the experimental data for sample 1 and the calculated results for sample 2 would be smaller.

As another possibility, $\sigma_{\text{bulk}}$ of the samples might have differed, i.e., $\sigma_{\text{bulk}}$ of sample 1 might have been lower than that of sample 2. To investigate this possibility, water adsorption isotherms for the carbon supports and the PCLs were evaluated. The amount of water adsorbed on the ionomer was estimated from the difference between the compounds and the carbon. The results indicated that $\lambda$ of the ionomer of sample 1 might have been lower than that of the ionomer of sample 2. In addition, $\lambda$ of the ionomer of sample 2 showed almost the same value as that of the membrane, suggesting that $\sigma_{\text{bulk}}$ of sample 1 might have been lower than that of sample 2. Functional groups on the carbon surface can interact strongly with the sulfonic groups of the ionomer, thereby lessening the water adsorbability of the sulfonic groups compared with the case without the functional groups. The difference of such interactions could have caused the difference in $\sigma_{\text{bulk}}$. 
References


2.2. Relationship among microstructure, ionomer property and proton transport in pseudo catalyst layers

2.2.1. Introduction

As mentioned in the previous section, the greatest challenge for commercializing FCEVs from an industrial point of view is to reduce the cost. Fuel cell operation at low humidity and high current density is desirable because it would allow the FC stack and system to be simplified, resulting in lower cost. However, the increase in IR loss stemming from proton transport under such conditions is an issue of concern. A decrease in proton conductivity in the catalyst layers in particular could cause a decline in catalyst utilization due to heterolytic distribution of the current density [1,2]. Therefore, it is essential to understand proton transport phenomena in the catalyst layers.

In recent years, a lot of studies concerning the modeling of proton transport properties in the catalyst layers have been conducted, in which percolative models [3,4] or the Bruggeman correction [5-7] was used. It is necessary to measure the proton transport resistance of actual catalyst layers to validate such models. Electrochemical impedance spectroscopy (EIS) and analyses based on finite transmission line models have been used for measuring proton transport in the catalyst layers [8-11]. Capacitance and resistance elements were regarded as being equal in each section of the transmission line circuits analyzed. However, it is reported that the profile of a Nyquist plot depends on the distribution of the capacitance and the resistance, although the total capacitance and resistance are the same [10]. Therefore, it is difficult to apply such techniques if the capacitance or the ionomer resistance is distributed nonuniformly. There are also some experimental problems that arise in trying to apply EIS to samples with a small double-layer capacitance or proton-transport resistance such as the need to eliminate inductance or the increase in frequency. Therefore, a non-EIS method and a technique using a cast thin film have been developed for evaluation of proton transport resistance of the ionomer [12,13].

I also established a new method of evaluating proton transport resistance using a PCL consisting of the carbon support and the ionomer, which was shown in the previous section (2.1) [14]. This method makes it easier to understand proton transport and used for prediction of proton conductivity [15]. The results obtained so far indicate that not only structural parameters such as the volume fraction and tortuosity but also water adsorbability of the ionomer can affect proton transport. There are some reports
about the influence of the ionomer content on proton transport resistance [6,16]. However, the influence of the ionomer content on structural parameters and ionomer properties has not been investigated thoroughly.

In this study, we measured proton transport resistance of PCLs with different types of carbon support and ionomer content using the method in the previous section. In order to estimate the structural parameters, an investigation was made of electrochemical characteristics such as the electric double layer capacitance of the PCLs. To estimate ionomer properties, various analyses were performed such as water adsorption measurement and titration. However, I previously reported that it is difficult to estimate structural parameters and ionomer properties based on experimental data only (see the previous section). Therefore, a heterogeneous Do-Do model [17] was applied to gain a more detailed understanding of water adsorption behavior. The influence of the ionomer content was examined using these techniques.

2.2.2. Experimental

Preparation of MEA

Tables 2.2.1 and 2.2.2 show the MEA specifications used in this study. The samples shown in Table 2.2.1 with different carbon materials and perfluorosulfonic acid (PFSA) membranes (Nafion® NR211, thickness = 25 μm) were used to measure proton transport resistance. The other samples shown in Table 2.2.2 were used to investigate the electrochemical characteristics of the PCLs.

<table>
<thead>
<tr>
<th>Anode and Cathode</th>
<th>Pseudo catalyst layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Pt/C (46 wt.%, TKK)</td>
</tr>
<tr>
<td>Carbon support</td>
<td>KB</td>
</tr>
<tr>
<td>Loading</td>
<td>0.35 mg·Pt cm⁻²</td>
</tr>
<tr>
<td>Ionomer</td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
</tr>
<tr>
<td>Ionomer/Carbon</td>
<td>0.9</td>
</tr>
<tr>
<td>weight ratio</td>
<td></td>
</tr>
<tr>
<td>Electrode area / cm²</td>
<td>25</td>
</tr>
<tr>
<td>GDL</td>
<td>Carbon Paper with MPL (24BC, SGL Carbon)</td>
</tr>
</tbody>
</table>

- 37 -
Table 2.2.2. Specifications of MEAs for measurement of electrochemical characteristics.

<table>
<thead>
<tr>
<th>Counter and reference electrode</th>
<th>Working electrode (Pseudo catalyst layer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Pt/C (46 wt. %, TKK)</td>
</tr>
<tr>
<td>Carbon support</td>
<td>KB, GKB</td>
</tr>
<tr>
<td>Loading</td>
<td>0.35 mg·Pt cm$^{-2}$</td>
</tr>
<tr>
<td>Ionomer</td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
</tr>
<tr>
<td>Ionomer/Carbon weight ratio</td>
<td>0.9</td>
</tr>
<tr>
<td>Electrode area / cm$^2$</td>
<td>25</td>
</tr>
<tr>
<td>GDL</td>
<td>Carbon Paper with MPL (24BC, SGL Carbon)</td>
</tr>
</tbody>
</table>

All MEAs were prepared using the same method as in the previous section. Catalyst and pseudo catalyst inks were prepared respectively by mixing Pt/C (catalyst: 46 wt. %, TEC10E50E, Tanaka Kikinzoku Kogyo KK) or carbon (ketjen black (KB) or graphitized ketjen black (GKB)) and the Nafion® ionomer dispersion (D2020, EW1000, DuPont) together so that the weight ratio of the ionomer content was 0.7, 0.9 or 1.3 relative to the carbon support. A propylene glycol solution (50 wt. %) was also added to the ink to keep its solid content at 19 wt. % for the catalyst layers and at 12 wt. % for the PCLs. The electrocatalyst layers and PCLs were fabricated on polytetrafluoroethylene (PTFE) substrates using a screen-printing technique. The square electrocatalyst layers measured 50 mm on one side and had a Pt loading of 0.35 mg cm$^{-2}$ and the PCLs had a C loading of 0.70 mg cm$^{-2}$. These layers were heat treated on the PTFE substrates for 30 min at 130°C to remove the organic solvent.

To fabricate the samples shown in Table 2.2.2, a catalyst layer and a pseudo catalyst layer were decal-transferred to a square membrane (72 mm on one side). To prepare the samples shown in Table 2.2.1, the other catalyst layer was also decal-transferred to another membrane. The catalyst-coated membranes (CCMs) were then hot-pressed together with the PCL located in the center of the MEA. To determine the proton transport resistance of the PCLs, an MEA without a PCL was necessary. The sample was also fabricated by hot-pressing two half CCMs. The decal-transfer and hot-press conditions were 150°C, 10 min, and 0.8 MPa. Polyethylene naphthalate (PEN) films (Q51, 25 μm, Teijin-DuPont) were bonded on the surrounding areas of the electrocatalyst layers and the PCL as reinforcement. Gas diffusion layers (GDLs) with
microporous layers (24BC, SGL Carbon) were used in this study. The MEA was formed by assembling the GDLs on both sides of the CCMs. The MEA was assembled in a single cell between bipolar plates with a straight flow field made of graphite and gaskets made of silicone rubber. The compression pressure was kept uniform by measuring it with pressure-sensitive paper (Prescale, Fuji Film).

**Measurement of proton transport resistance**

The proton transport resistance of the MEAs described in Table 2.2.1 was measured under the conditions shown in Table 2.2.3. The same measurement technique as that used in the previous section was applied. Hydrogen under ambient pressure was fed to both the anode and cathode. By means of a hydrogen pump technique [18], voltage drops between the anode and cathode were measured under various current densities and RH conditions. The overall resistance was obtained from the slopes at the lower current densities, ignoring the water distribution due to electro-osmotic drag (EOD) and the temperature rise produced by the IR drop. The overall resistance of the samples with and without the PCL was evaluated (Fig. 2.2.1(a)). The difference in resistance between them was found to be mainly due to the proton transport resistance of the PCL. The RH dependency of the proton transport resistance of the PCL was evaluated with the same technique. The details of the analysis will be described in the following section.

<table>
<thead>
<tr>
<th>Hydrogen pump</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode gas</td>
<td>H(_2)</td>
</tr>
<tr>
<td>Cathode gas</td>
<td>H(_2)</td>
</tr>
<tr>
<td>Back pressure</td>
<td>Ambient</td>
</tr>
<tr>
<td>Cell temperature / °C</td>
<td>80</td>
</tr>
<tr>
<td>Anode humidity / % RH</td>
<td>30, 40, 50, 60, 70, 80, 90, 100</td>
</tr>
<tr>
<td>Cathode humidity / % RH</td>
<td>30, 40, 50, 60, 70, 80, 90, 100</td>
</tr>
<tr>
<td>Anode flow rate / NL min(^{-1})</td>
<td>4.0</td>
</tr>
<tr>
<td>Cathode flow rate / NL min(^{-1})</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Cyclic voltammetry

To measure the electric double layer capacitance ($C_{dl}$) of the PCLs, cyclic voltammetry was carried out using the same single cell set-up at 80 °C and MEAs described in Table 2.2.2 and Fig. 2.2.1 (b). Pure H$_2$ and N$_2$ were fed to the counter and reference electrodes (normal catalyst layer) and working electrode (PCL), respectively. After a certain waiting period, the cathode potential was scanned between 0.2 and 0.6 V vs. the reversible hydrogen electrode (RHE) at a scan rate of 50 mV s$^{-1}$ for a few cycles. An HZ-3000 electrochemical measurement system (Hokuto Denko, Japan) was used to perform cyclic voltammetry.
**Water uptake measurement**

In order to investigate ionomer properties, the adsorption isotherms of water for KB (particles), GKB (particles), PCLs and the dispersion-cast Nafion® ionomer membrane were measured by means of a volumetric method using an automatic vapor adsorption apparatus (Belsorp 18 Plus-HT, Nihon Bell) at 80°C. Nafion® commercial dispersion, D2020, was used for preparation of the membrane. 0.03~0.05 g of the samples was placed in a glass sample tube. As preconditioning, the sample tube was evacuated for 5 hours at 90°C before the measurement.

**Determination of acidity of carbon surface**

The acidity of the KB surface was determined by titration to determine the surface concentration of primary adsorption sites for water. First, 5 ml of 0.05 M sodium carbonate (Na₂CO₃) was added to 0.1 g of KB. Then, titration was done with 0.1 M hydrogen chloride (HCl). Methyl orange was used as the indicator.

**2.2.3. Results and discussion**

**The influence of ionomer content in the GKB system**

The influence of the ionomer content on proton transport in the GKB system is discussed in this section. The relationship between the voltage drop and current density of samples with an I/C ratio of 0.9 under various RH conditions is shown in Fig. 2.2.2. The voltage drop showed good linearity as a function of the current density. The overall resistances obtained from the slopes at the lower current densities in Fig. 2.2.2 are shown in Fig. 2.2.3 as a function of RH. The overall resistance of the sample without the PCL was also evaluated and is shown in Fig. 2.2.3. The proton transport resistance of the PCL was calculated as the difference in overall resistance between the samples with and without the PCL. This process was the same as that shown in the previous section. As shown in Fig. 2.2.3, the overall resistance of the sample with the PCL was mainly due to the proton transport resistance of the PCL and proton transport resistance markedly increased with decreasing RH.
Fig. 2.2.2. Voltage drop between the anode and cathode as a function of current density for different RH conditions at 80°C (for PCLs with an I/C ratio of 0.9 and a GKB carbon support).

Proton transport resistivities of PCLs with different I/C ratios were also evaluated with the same technique. Effective proton conductivities of the samples were then calculated from their resistivities and thicknesses (Fig. 2.2.4). To obtain the average thickness, the cross-section surface of another PCL was observed with an optical microscope. An observation was made over about half of the PCL width (2.5 cm) and the thickness was measured along the length at 20 points; the average thickness was then calculated (see Table 2.2.4). It was found that the effective proton conductivity
of the PCL increased with increasing ionomer content. The difference was analyzed in detail with the Bruggeman correction equation (2.2.1).

\[
\sigma^{\text{eff}} = \sigma^{\text{bulk}} \varepsilon^{\text{ion}}
\]  

(2.2.1),

where \(\sigma^{\text{eff}}\) indicates effective proton conductivity, \(\sigma^{\text{bulk}}\) the proton conductivity of the ionomer as bulk, \(\varepsilon^{\text{ion}}\) the volume fraction of the ionomer and \(\gamma\) the Bruggeman factor (\(\approx 1.5\)), which is related to the tortuosity of the conductor [5-7,10]. In concrete, tortuosity, \(\tau\) is considered as \(\tau^{-1} = \varepsilon^{\text{ion}}\) in Eq. (2.2.1). It is necessary to obtain these values in order to analyze proton transport properties.

Fig. 2.2.4. Effective proton conductivities of PCLs consisting of GKB and different ionomer contents (solid line: experimental data; dashed line: calculation with \(\varepsilon^{\text{ion}}, \gamma (= 1.6)\) and \(\sigma^{\text{bulk}}\) of the PCLs).

First, the volume fraction of the ionomer, \(\varepsilon^{\text{ion}}\), was obtained using the same process as that in the previous section. Then, \(\varepsilon^{\text{ion}}\) was corrected based on the expansion of the membrane. The proton conductivity of the membrane was measured under various RH conditions at 80°C and regarded as \(\sigma^{\text{bulk}}\).

Then, \(\sigma^{\text{bulk}}\) of the PCLs was estimated by evaluating the water adsorption behavior of GKB and PCLs consisting of GKB and different ionomer contents at 80°C. The results are shown in Fig. 2.2.5 as a function of water activity. Although a simple subtraction might not be exactly appropriate, it seemed roughly correct because the amount of water adsorbed on GKB was much lower compared with the PCLs. Therefore, the apparent equilibrium adsorption of water vapor for the ionomer, \(\lambda^{\text{app}}\), of the PCLs
was approximated from the difference between the compounds and the carbon. The equilibrium adsorption of water vapor for the ionomer is compared with that of the solution-cast Nafion® ionomer membrane in Fig. 2.2.6. As seen in the figure, $\lambda_{\text{app}}$ of the ionomer did not depend on the ionomer content and showed almost the same value as that of the membrane. This suggests that $\sigma^{\text{bulk}}$ of the ionomer was the same as that of the membrane even though the ionomer content differed.

Fig. 2.2.5. Water adsorption isotherms for GKB and PCLs consisting of GKB and different ionomer contents at 80°C.

Fig. 2.2.6. Apparent equilibrium adsorption of water vapor for solution-cast Nafion® ionomer membrane and the ionomer of PCLs consisting of GKB and different ionomer contents as a function of water activity at 80°C.
The Bruggeman factor, $\gamma$, of the samples was then estimated by comparing experimentally obtained $\sigma_{\text{eff}}$ and calculated values (dashed lines in Fig. 2.2.4) with $\sigma_{\text{bulk}}$ and $\varepsilon_{\text{ion}}$ estimated in above. When 1.6 was applied to $\gamma$, there was not so much of a difference between the calculated results and experimental data. The experimental data of the PCL whose I/C was 1.3 diverged from the calculated results under a high RH condition. The experimental data apparently contained some error because the resistance due to the PCL of the sample was sufficiently low compared with that attributable to other components. So, the signal-to-noise ratio should be low. It is necessary to reduce the resistance due to other components in order to determine the proton transport resistance of the PCL accurately when the latter is low enough. Except for this point, the calculated results corresponded well with the experimental data for all I/C values. This result implies that the estimation of $\varepsilon_{\text{ion}}$ and $\sigma_{\text{bulk}}$ was roughly correct.

The influence of ionomer content in the KB system

The influence of the ionomer content on proton transport in the KB system was also investigated. The process was the same as for the GKB system. $\sigma_{\text{eff}}$ of the PCLs with KB are shown in Fig. 2.2.7. $\sigma_{\text{eff}}$ also increased with increasing ionomer content in the KB system. The difference was analyzed with Eq. (2.2.1) in the same way as for the GKB system. At first, $\sigma_{\text{eff}}$ of the PCLs was calculated from $\varepsilon_{\text{ion}}$, $\gamma$ (regarded as the same as that of GKB system = 1.6) and $\sigma_{\text{bulk}}$ (regarded as that of the bulk membrane) and compared with the experimental data in Fig. 2.2.7. There was a large gap between the experimental and calculated results for all I/C values. The difference in $\gamma$ and $\sigma_{\text{bulk}}$ was considered to be a possible cause.
Fig. 2.2.7. Effective proton conductivities of PCLs consisting of KB and different ionomer contents (solid line: experimental data; dashed line: calculation with $\varepsilon_{\text{ion}}$, $\gamma$ (assumed as the same as that of GKB system) and $\sigma_{\text{bulk}}$ (assumed as the same as that of bulk membrane) of the PCLs).

First, $\gamma$ in the KB system was estimated. In order to estimate it, the ratio of the tortuosity was examined. As reported in the previous section, it was considered that the ionomer is thin enough and covers the outer surface of the carbon support almost uniformly. Then, the tortuosity of the proton path probably depends on the surface area covered with the ionomer assuming that the structure of the PCL is macroscopically homogeneous. The area depends on the coverage of the ionomer, $\theta$, and the surface area of the carbon support, $S_{\text{carbon}}$, because the tortuosity of the sphere can be regarded as the ratio between one-half of the circumference and the diameter [19]. The ratio of the tortuosity in this section was expressed as shown in Eq. (2.2.2) because the average diameter of the carbon supports was almost the same as shown in the previous section.

$$\frac{\tau_1}{\tau_2} = \frac{l_1/l_1'}{l_2/l_2'} = \frac{l_1'}{l_2'} = \frac{S_1\theta_1}{S_2\theta_2}$$  \hspace{1cm} (2.2.2)

where $l$ is the average diameter and $l'$ is one-half of the circumference of the carbon support. $S_{\text{carbon}}$ was measured by the BET N$_2$ adsorption method, and it was found that $S_{\text{GKB}}$ was 151 m$^2$ g$^{-1}$ and $S_{\text{KB}}$ was 718 m$^2$ g$^{-1}$. $\theta$ was determined from RH dependence of the double layer capacitance ($C_{\text{dl}}$) of the PCL (Table 2.2.4) considering that the change in $C_{\text{dl}}$ shows the contribution of an interface between the carbon support and adsorbed water to total. $C_{\text{dl}}$ of the PCLs was obtained from cyclic voltammograms of the MEAs described in Table 2.2.2. The transition of $C_{\text{dl}}$ of the PCLs containing GKB is shown in
Fig. 2.2.8 as a function of RH. To make it simple to see its change, $C_{dl}$ in Fig. 2.2.8 was normalized by $C_{dl}$ at 100% RH condition. As seen in the figure, $C_{dl}$ of the PCLs with GKB did not depend on RH. In addition, the absolute value of $C_{dl}$ was almost the same regardless of the ionomer content. This result indicated that the surface of GKB was almost completely covered with the ionomer. So, $\theta$ of the PCLs was approximated as 1 (Table 2.2.4), regardless of the difference in the ionomer content. To verify that $\theta$ was 1, the specific capacitances of GKB were also estimated from $S_{carbon}$ and $C_{dl}$ under a 100% RH condition (2.23 $\mu$F cm$^{-2}$carbon) and were found to be close to that of carbon black in Refs. 19 and 20. The average thickness of the ionomer was also calculated from $S_{carbon}$, the I/C ratio and the density of the ionomer as shown in Table 2.2.4. It was found that $\theta$ of the PCLs was almost the same regardless of the ionomer content and implied that only the thickness of the ionomer changed with the difference in the ionomer content.

Table 2.2.4. Properties of PCLs consisting of GKB and ionomer.

<table>
<thead>
<tr>
<th>I/C ratio</th>
<th>Average thickness of PCLs / $\mu$m</th>
<th>$\theta_{ion}$/ -</th>
<th>$\theta$/ -</th>
<th>Average thickness of ionomer / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>21.9</td>
<td>0.15</td>
<td>1</td>
<td>2.4</td>
</tr>
<tr>
<td>0.9</td>
<td>18.9</td>
<td>0.22</td>
<td>1</td>
<td>3.2</td>
</tr>
<tr>
<td>1.3</td>
<td>17.5</td>
<td>0.35</td>
<td>1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

*at 30% RH and 80°C

Fig. 2.2.8. $C_{dl}$ of PCLs consisting of GKB and different ionomer contents as a function of RH at 80°C.
$C_{dl}$ of the PCLs with KB was also evaluated under different RH conditions (Fig. 2.2.8). As shown in Fig. 2.2.8, $C_{dl}$ of the PCLs strongly depended on RH. As mentioned in our previous paper, adsorption of water on the carbon surface seems to be a dominant factor of this tendency (see the previous section). More concretely, only the interface between the carbon support and the ionomer might work as $C_{dl}$ under lower RH conditions. In contrast, the interface between the carbon support and adsorbed water can be formed and also work as $C_{dl}$ under higher RH conditions. The specific capacitance of KB estimated from $S_{carbon}$ and $C_{dl}$ under a 100% RH condition was found to be 7.56 $\mu$F cm$^{-2}$. Although the comparison is not precise because of the differences in various conditions, this value is close to that of carbon black in Refs. 19 and 20. This implies that almost the whole carbon surface was covered with either the ionomer or water in this condition. In addition, the influence of adsorbed water on $C_{dl}$ was not large at 30% RH, based on the results in Fig. 2.2.8 and the water adsorption isotherm of KB shown in Fig. 2.2.9. Accordingly, $\theta$ can be expressed as $C_{dl@30\%RH}/C_{dl@100\%RH}$. $\theta$ of the PCLs was obtained and is shown in Table 2.2.5. The average thickness and $\varepsilon_{ion}$ of the PCLs were also estimated (Table 2.2.5). It was found that $\theta$ of the PCLs was almost the same regardless of the ionomer content and only the thickness of the ionomer changed with the difference in the ionomer content. $\gamma_{KB}/\gamma_{GKB}$ was calculated as ca. 1.23 with obtained $S_{carbon}$ and $\theta$. This value indicates the ratio of the tortuosity when the ionomer is thin enough because $C_{dl}$ is reflected in the state of the interface. So, $\gamma_{KB}$ was calculated with $\varepsilon_{ion}$ of the PCL whose I/C ratio was 0.7 and $\gamma_{GKB}$, and found to be ca. 1.78.

![Water adsorption isotherms for KB and PCLs consisting of KB and different ionomer contents at 80°C.](image)

Fig. 2.2.9. Water adsorption isotherms for KB and PCLs consisting of KB and different ionomer contents at 80°C.
Table 2.2.5. Properties of PCLs consisting of KB and ionomer.

<table>
<thead>
<tr>
<th>I/C ratio</th>
<th>Average thickness of PCLs / μm</th>
<th>εion* / -</th>
<th>θf / -</th>
<th>Average thickness of ionomer / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>27.7</td>
<td>0.12</td>
<td>0.3</td>
<td>1.7</td>
</tr>
<tr>
<td>0.9</td>
<td>22.4</td>
<td>0.20</td>
<td>0.32</td>
<td>2.0</td>
</tr>
<tr>
<td>1.3</td>
<td>18.4</td>
<td>0.35</td>
<td>0.32</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*at 30% RH and 80°C

Then, $\sigma_{\text{bulk}}$ in the KB system was estimated. To estimate $\sigma_{\text{bulk}}$ of the ionomer of the PCL in the KB system, the water adsorption behavior of KB and PCLs consisting of KB and different ionomer contents was evaluated at 80°C and the results are shown in Fig. 2.2.9 as a function of water activity. In the KB system, a simple subtraction looked inappropriate because the amount of water adsorbed on the surface of KB was not negligible. In order to estimate more accurately, it is necessary to understand water adsorption behavior, which was then analyzed with a heterogeneous Do-Do model (HDDM).

The Do-Do model is a semi-empirical model developed for analysis of water adsorption for activated carbon [21]. The Do-Do model is applied not only for activated carbon but for nano-sized carbon like single-wall carbon nanotubes (SWNT) [22]. An improved Do-Do model developed by Furmaniak et al. [17], i.e., the HDDM, was used in this study to analyze water adsorption behavior of the PCLs based on KB. In the Do-Do model, water adsorption for porous carbon like activated carbon is considered to consist of two stages and is described as two terms. In the first stage, water molecules adsorb on the primary adsorption site by hydrogen-bonding and form a cluster. In the second stage, five molecules fall away from the cluster and fill micropores when the number of molecules reaches six [17]. Neitsch et al. generalized this idea (i.e., micropore filling by the m-mers) and expressed it as

$$a = a_0 \frac{\sum_{n=1}^{N} n h^n}{1 + K_f \sum_{n=1}^{N} h^n} + a_{\text{sat}} \frac{K_f h^m}{1 + K_p h^m}$$

(2.2.3)

where $N$ is the maximum number of water molecules adsorbed on the surface sites, $a_0$ is the concentration of surface active groups, $a_{\text{sat}}$ is the saturation concentration in the micropores, $K_f$ is the chemisorption and $K_p$ is the micropore equilibrium constant, respectively, and $h$ is the relative pressure (equal to $p/p_s$ where $p$ is the equilibrium and $p_s$ the saturation pressure of water, respectively). The HDDM is an expanded Do-Do
model based on this idea and another idea that several functional groups with different adsorption force are present on the activated carbon. The model is expressed as

\[
a = a_{\text{prime}} \left( 1 + \frac{\sum_{n=1}^{N} nK_{h}^{n}}{1 + \sum_{n=1}^{N} K_{h}^{n}} \right) + a_{\mu} + \frac{Kh^{m}}{1 + Kh^{m}}
\]  

(2.2.4),

where \(a_{\text{prime}}\) is the total number of water molecules adsorbed on primary sites and expressed as

\[
a_{\text{prime}} = \sum_{i} a_{\text{prime},i} = \sum_{i} \frac{a_{mL,i}K_{L,i}h}{p_{s} + K_{L,i}h}
\]  

(2.2.5),

where \(a_{\text{prime},i}\) is the number of water molecules adsorbed on the \(i\) th kind of functional group, and \(K_{L,i}\) is the Langmuir constant for adsorption. The first term in Eq. 2.2.4 signifies the primary adsorption and its accompanying secondary adsorption. Secondary adsorption is regarded as adsorption on primary adsorbed water molecules by hydrogen-bonding and is expressed as

\[
a_{\text{sec}} = \frac{a_{\text{prime}}}{1 + \sum_{n=1}^{N} K_{h}^{n}} = \sum_{i} \frac{a_{mL,i}K_{L,i}h}{1 + \sum_{n=1}^{N} K_{h}^{n}}
\]  

(2.2.6),

where \(K_{h}\) is the adsorption force of secondary adsorption.

Table 2.2.6. Parameters for HDDM.

<table>
<thead>
<tr>
<th>(K_{h}/\text{Pa}^{-1})</th>
<th>(K'/\text{Pa}^{-1})</th>
<th>(N'/)</th>
<th>(m'/)</th>
<th>(a_{\mu}/\text{mmol g}^{-1}\text{carbon})</th>
<th>(a_{\text{mL,fg}}/\text{mmol g}^{-1}\text{carbon})</th>
<th>(a_{\text{mL,C}}/\text{mmol g}^{-1}\text{carbon})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
<td>6</td>
<td>5</td>
<td>17.4</td>
<td>0.16</td>
<td>9.5</td>
</tr>
</tbody>
</table>

To understand the water adsorption behavior in the catalyst layer in detail, a curve fitting of the experimental water adsorption isotherm was done with the HDDM. In the calculation, it was assumed that there were two kinds of primary adsorption sites on the KB surface, i.e., the functional groups and the bare carbon surface. The total number of water molecules adsorbed on the functional groups of the carbon surface, \(a_{\text{prime,fg}}\), was obtained from the surface concentration of the functional groups, \(a_{mL,fg}\) determined by the acidity of the KB surface (0.16 mmol g\(^{-1}\text{carbon}\)) assuming that one water molecule adsorbs on each functional group. The total number of water molecules adsorbed on the KB surface, \(a_{\text{prime,C}}\), was also obtained from the surface concentration of the primary adsorption sites, \(a_{mL,C}\) determined by the N\(_2\)-BET specific surface area.
regarding that the area occupied by water molecule is 0.125 nm$^2$ as shown in the literature [23]. The saturation concentration in the micropores, $a_{\text{\textmu s}}$, was determined by the micropore volume calculated by the MP-method (0.347 cm$^3$ g$^{-1}$carbon) [24]. In addition, $m$ and $N$ were regarded as 5 and 6 respectively assuming that five molecules of water fall away from the cluster and fill micropores when the number of molecules reaches six as mentioned before [17]. $K$ and $K_p$ were fitting parameters. The parameters used in the calculation are shown in Table 2.2.6. The calculated results obtained with the HDDM are compared with the experimental water adsorption isotherm in Fig. 2.2.10. The total amount of adsorption coincided well below 0.8 of water activity. The difference in the higher activity region could be ascribable to capillary condensation, which was not considered in the HDDM. The dotted line in Fig. 2.2.10 shows the amount of adsorption on the entire surface, including functional groups, and corresponds to the first term of Eq. 2.2.4. The solid line shows the amount of adsorption for micropores except for that on the micropore surface and corresponds to the second term of Eq. 2.2.4. In concrete terms, total amount of the adsorbed water for the carbon support can be divided as

$$a_c = a_{\text{surface}} + a_{\text{micropores}}$$

Here, the amount of adsorption on the entire surface, $a_{\text{surface}}$, means the sum of the amount of adsorbed water for the outer surface of the carbon, $a_{\text{surface,outside}}$, and that for the surface of micropores, $a_{\text{surface,inside}}$. $a_{\text{surface,inside}}$ can be expressed as $a_{\text{surface}} \times (1 - \theta)$.

Water in the micropores seemed not to contribute to proton transport in the through-plane direction because a pH of the KB (3.4) determined by the titration was quite high compared to that of the solution-cast Nafion® ionomer membrane (0.29 ~ 0.09) calculated from water adsorption (Fig. 2.2.6) as reported in the literature [25]. Therefore, proton transport through the pores should be negligible. Then, $\lambda_{\text{app}}$ of the PCLs was estimated by subtracting the amount of adsorbed water of the micropores from that of the PCLs.
The equilibrium adsorption of water vapor for the ionomer was corrected in two different ways and compared with that of the solution-cast Nafion® ionomer membrane in Fig. 2.2.11. \( \lambda_{\text{app}} \) in Fig. 2.2.11 (a) was obtained by simply subtracting the water adsorption of the KB from that of the PCLs. It was lower than \( \lambda_{\text{app}} \) in Fig. 2.2.11 (b), which was corrected with the HDDM. The difference increased under higher RH conditions. Water adsorbed on the outer surface of the KB and water generated by capillary condensation could have caused the difference. As seen in these figures, \( \lambda_{\text{app}} \) of the ionomer showed lower values than that of the membrane. The possibility that functional groups on the KB surface affect water adsorbability of the ionomer was suggested in the previous section. Such interaction is presumably one cause of the difference in \( \lambda_{\text{app}} \) between the ionomer and the membrane. Water adsorbability of the ionomer was probably reduced by the interaction with the functional groups on the KB surface. A simulation based on molecular dynamics also suggested that ionized carboxyl groups on the carbon surface strongly interacted with the sulfonic groups of Nafion® and water [26]. Based on the results in Fig. 2.2.11, water adsorbability of the ionomer seemed to decrease with decreasing ionomer content. In order to ascertain the difference more clearly, the maximum, minimum and average values of \( \lambda_{\text{app}} \) of the ionomer at 50% RH were found and are plotted in Fig. 2.2.12. Here, the maximum value means \( \lambda_{\text{app}} \) estimated with the HDDM and the minimum value means \( \lambda_{\text{app}} \) obtained by simple subtraction. Although the difference was not so pronounced, \( \lambda_{\text{app}} \) decreased with decreasing ionomer content. It is inferred that the ionomer on the carbon support around the interface is probably influenced by the carbon surface (or functional groups).
However, the ionomer distant from the interface shows transport properties similar to the bulk membrane. This implies that the ionomer with lower content (i.e., thinner) could show lower adsorbability. Figure 2.2.11 also indicates that $\sigma_{\text{bulk}}$ of the ionomer of the PCLs is lower than that of the membrane. To verify that the difference in $\lambda_{\text{app}}$, i.e., the difference in $\sigma_{\text{bulk}}$, is the cause of the gap in $\sigma_{\text{eff}}$ in Fig. 2.2.7, $\sigma_{\text{bulk}}$ was also calculated with Eq. 2.2.1 so as to close the gap. Then, another $\lambda_{\text{app}}$ was obtained from the relationship among $\lambda$, $\sigma$ and RH of the membrane reported in the previous section and is also shown in Fig. 2.2.11 (b). Here, it was found that the ionomer in the KB system adsorbed less water compared with that of the membrane. Then expansion of the ionomer should be lower. So, $\delta_{\text{ion}}$ was corrected with the relationship between the expansion and $\lambda_{\text{app}}$ in the KB system obtained from HDDM and used for $\lambda_{\text{app}}$ estimation. The relation among the expansion, $\lambda$ and RH was shown in the previous section. Both $\lambda_{\text{app}}$ coincided well except for the high water activity region. Under such conditions, although water generated by capillary condensation should be taken account, the difference in the amount between the KB powder and that of the PCLs was not considered here.
Fig. 2.2.11. Apparent equilibrium adsorption of water vapor for dispersion-cast Nafion®
ionomer membrane and the ionomer of PCLs consisting of KB and different ionomer
contents as a function of water activity at 80°C. (a) obtained by subtracting water
adsorption for KB from that for the PCLs; (b) experimental data corrected with the
HDDM (solid line) and calculated results for the gap in Fig. 2.2.7 (dashed line)).
Effective proton conductivity $\sigma^{\text{eff}}$ increased with increasing ionomer content in both the GKB and KB systems. An analysis was made using the Bruggeman correction equation to investigate the influence of the ionomer content on the effective proton conductivity. To estimate the Bruggeman factor, $\gamma$, which is related to the tortuosity of the proton path, the ionomer coverage $\theta$ of the PCL was obtained by analysis of the electric double layer capacitance. It was found that ionomer coverage did not depend on the ionomer content and that $\gamma$ of the PCLs was almost the same regardless of the ionomer content in both systems. In the GKB system, the difference in $\varepsilon_{\text{ion}}$ and $\gamma$ accounted for the difference in $\sigma^{\text{eff}}$ of the PCLs with different ionomer contents. $\varepsilon_{\text{ion}}$ was the most dominant factor. However, such structural differences did not account for the difference in $\sigma^{\text{eff}}$ of the PCLs with different types of carbon support. Therefore, the proton conductivity of the ionomer as bulk $\sigma^{\text{bulk}}$ of the samples may have been different. An analysis of water adsorption behavior based on the experimental data and results calculated with the HDDM implied that $\lambda_{\text{app}}$ of the ionomer in the KB system was lower than that of the GKB system and bulk membrane. This result suggested that $\sigma^{\text{bulk}}$ of the ionomer in the KB system is lower than that of the GKB system and bulk membrane. Functional groups on the KB surface probably interact with the side chains of the Nafion® ionomer and weaken its water adsorbability. In the KB system, both structural differences and ionomer properties varied with the ionomer content.
References


Chapter 3 Microstructure analysis
3.1. An in-situ technique for analyzing ionomer coverage in catalyst layers

3.1.1. Introduction

As mentioned in the previous chapters, the greatest challenge for commercialization of fuel cell electric vehicles (FCEVs) from an industrial point of view is to reduce the cost. According to a U.S. DOE report, Pt accounts for about a quarter of the total system cost [1]. The most effective measure for this issue is to reduce Pt loading and to use Pt more effectively.

Catalyst layers could play an important role in resolving these challenges, especially cost reductions. However, it is difficult to characterize and model the catalyst layers. For one reason, the transport of water, gas and protons and the electrochemical reactions occur simultaneously in the catalyst layers. In addition, the catalyst layers have a very complicated microstructure, characterized by a microporous structure consisting of Pt, its support (basically carbon) and a proton conductive ionomer. To design optimized catalyst layers, it is necessary to develop methods of evaluating and gaining an in-depth understanding of the phenomena involved [2]. While the ionomer is necessary for proton conduction, it is reported that the ionomer may affect gas transport [3,4] and electrochemical activity [5,6]. In recent reports, it was proved that Nafion® adsorption changes voltammogram of Pt single crystal [7] and blocks other species from adsorbing on the interface [8,9]. In this way, the understanding of the interaction between the ionomer and Pt surface is growing in importance. Therefore, it is indispensable to understand the relation between the state of the ionomer, such as its thickness and coverage, and various performance parameters of the actual catalyst layers.

The thickness of the ionomer on Pt/C or highly oriented pyrolytic graphite (HOPG) has been observed by transmission electron microscopy (TEM) [10] and atomic force microscopy (AFM) [11] and found to be less than a few nm. Although these techniques are helpful in visualizing the microstructure, they do not provide information that can be linked with performance. The reason is that such methods examine only a small area under particular conditions, which may be somewhat different from the actual operating conditions of a fuel cell. Therefore, it is necessary to have an in-situ method capable of evaluating the state of the ionomer under actual operating conditions. I previously established an in-situ technique that makes it possible to estimate the average thickness and coverage of the ionomer, \( \theta_{\text{ion}} \) (2.1 and 2.2 in this thesis) [12,13]. This method, however, uses PCLs consisting of the carbon
support and the ionomer and is not applicable to actual Pt catalyst layers. This is because the method distinguishes the electric double layer capacitance, $C_{dl}$, due to the carbon/water interface and that of the carbon/ionomer interface based on the RH dependence of $C_{dl}$. With actual catalyst layers, it may not be that simple as Pt should also contribute to the RH dependence of $C_{dl}$.

In this chapter, an in-situ method of analyzing the ionomer coverage on Pt and the carbon support was investigated. The drawback of the previous method is that it was not possible to extract the contribution of Pt and the carbon support to RH dependence of total $C_{dl}$ separately. However, if one of the interfaces is deactivated, the previous method will be applicable. It is well known that carbon monoxide (CO) adsorbs specifically on Pt and deactivates it. With CO adsorption, not only the electrochemical surface area (ECA), but also $C_{dl}$ is suppressed [14]. Therefore, we attempted to apply the previous method to actual catalyst layers by deactivating Pt through CO adsorption. This new method was used to evaluate the ionomer coverage of catalyst layers having two different types of carbon support.

### 3.1.2. Experimental

**Preparation of MEA**

Tables 3.1.1 and 3.1.2 show the membrane electrode assembly (MEA) specifications used in this study. The samples shown in Table 3.1.1 with different carbon materials and perfluorosulfonic acid (PFSA) membranes (Nafion® NR211, thickness = 25 μm) contained Pt. The other samples shown in Table 3.1.2 had PCLs on one side. Catalyst and pseudo catalyst inks were prepared respectively by mixing one of the following materials: a) ketjen black (KB); b) graphitized ketjen black (GKB); c) Pt/KB (catalyst: 46 wt. %, TEC10E50E, TKK); and d) Pt/GKB (catalyst: 46 wt. %) and the Nafion® ionomer dispersion (D2020, EW1000, DuPont) together so that the weight ratio of the ionomer content was 0.9 relative to the carbon support. A propylene glycol solution (50 wt. %) was also added to the ink to keep its solid content at 19 wt. % for the catalyst layers and at 12 wt. % for the PCLs. The electrocatalyst layers and PCLs were fabricated on polytetrafluoroethylene (PTFE) substrates using a screen-printing technique. The square electrocatalyst layers measured 50 mm on one side and had a Pt loading of 0.35 mg cm$^{-2}$ and the PCLs had a carbon loading of 0.70 mg cm$^{-2}$. These layers were heat treated on the PTFE substrates for 30 min at 130°C to remove the organic solvent.
Table 3.1.1. Specifications of the MEAs with Pt-containing cathode.

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Cathode</th>
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<tbody>
<tr>
<td><strong>Catalyst</strong></td>
<td>TEC10E50E</td>
<td>TEC10E50E</td>
</tr>
<tr>
<td></td>
<td>Pt/C (46 wt. %, TKK)</td>
<td>(Pt 46 wt. %, TKK)</td>
</tr>
<tr>
<td><strong>Carbon support</strong></td>
<td>KB</td>
<td>KB</td>
</tr>
<tr>
<td><strong>Loading</strong></td>
<td>0.35 mg·Pt cm⁻²</td>
<td>0.35 mg·Pt cm⁻²</td>
</tr>
<tr>
<td><strong>Ionomer</strong></td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
</tr>
<tr>
<td><strong>Ionomer/Carbon weight ratio</strong></td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Electrode area / cm²</strong></td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td><strong>GDL</strong></td>
<td>Carbon Paper with MPL</td>
<td>Carbon Paper with MPL</td>
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<tr>
<td></td>
<td>(24BC, SGL Carbon)</td>
<td>(24BC, SGL Carbon)</td>
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</table>

Table 3.1.2. Specifications of the MEAs with pseudo catalyst layer.

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Cathode</th>
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<tbody>
<tr>
<td><strong>Catalyst</strong></td>
<td>TEC10E50E</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pt/C (46 wt. %, TKK)</td>
<td>-</td>
</tr>
<tr>
<td><strong>Carbon support</strong></td>
<td>KB</td>
<td>KB</td>
</tr>
<tr>
<td><strong>Loading</strong></td>
<td>0.35 mg·Pt cm⁻²</td>
<td>0.70 mg·C cm⁻²</td>
</tr>
<tr>
<td><strong>Ionomer</strong></td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
</tr>
<tr>
<td><strong>Ionomer/Carbon weight ratio</strong></td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Electrode area / cm²</strong></td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td><strong>GDL</strong></td>
<td>Carbon Paper with MPL</td>
<td>Carbon Paper with MPL</td>
</tr>
<tr>
<td></td>
<td>(24BC, SGL Carbon)</td>
<td>(24BC, SGL Carbon)</td>
</tr>
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</table>

A catalyst layer for the anode was decal-transferred to a square membrane (72 mm on one side) and then another catalyst layer for the cathode or a PCL was also decal-transferred to the other side of the membrane. The decal-transfer conditions were 150°C 10 min, and 0.8 MPa. Polyethylene naphthalate (PEN) films (Q51, 25 μm, Teijin-DuPont) were bonded on the surrounding areas of the electrocatalyst layers and the PCLs as reinforcement. Gas diffusion layers (GDLs) with microporous layers (24BC,
SGL Carbon) were used in this study. The MEA was formed by assembling the GDLs on both sides of the catalyst coated membrane (CCM). The MEA was assembled in a single cell between bipolar plates with a straight flow field made of graphite and gaskets made of silicone rubber. The compression pressure was kept uniform by measuring it with pressure-sensitive paper (Prescale, Fuji Film).

**CO adsorption**

To deactivate Pt, 1% CO gas balanced with N₂ was used. All of the measurements using CO were carried out at 30°C to enhance CO adsorption. As it is difficult to control RH by heating a bubbler tank at such low temperature, it was controlled by mixing dry gas with the wet gas which goes through the bubbler. The flow system used in this study is illustrated in Fig. 3.1.1. Flow rates of the dry and wet gases were controlled with mass flow controllers to prepare the specified RH condition in Table 3.1.3 and then mixed in a mixer tube right before reaching the cell. The same system was used for the other gases as well. Before CO was supplied, pure H₂ and N₂ were fed to the anode and the cathode, respectively. The anode filled with pure H2 was used as the reversible hydrogen electrode (RHE) for all the electrochemistry in this study. The cathode potential was then set at 0.05 V vs. RHE and the current was monitored during CO supply. When the current reached almost zero, CO in the system was purged with N₂ for at least 15 min via the cathode valves before the cell closed. After that, N₂ was supplied to the cathode side to purge the remaining CO in the cell. Various electrochemical measurements described in this section were then performed. An HZ-3000 electrochemical measurement system (Hokuto Denko, Japan) was used to perform all the electrochemical measurements.

<table>
<thead>
<tr>
<th>Table 3.1.3. Test conditions for various electrochemical measurements.</th>
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<tbody>
<tr>
<td><strong>Anode gas</strong></td>
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<tr>
<td><strong>Cathode gas</strong></td>
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<tr>
<td><strong>Back pressure</strong></td>
</tr>
<tr>
<td><strong>Cell temperature / °C</strong></td>
</tr>
<tr>
<td><strong>Anode humidity / % RH</strong></td>
</tr>
<tr>
<td><strong>Cathode humidity / % RH</strong></td>
</tr>
<tr>
<td><strong>Anode flow rate / NL min⁻¹</strong></td>
</tr>
<tr>
<td><strong>Cathode flow rate / NL min⁻¹</strong></td>
</tr>
</tbody>
</table>
Fig. 3.1.1. A schematic diagram of the flow system used in this study.

**Measurement of electric double layer capacitance**

To measure $C_{dl}$ of the catalyst layers and PCLs, electrochemical impedance spectroscopy (EIS) was performed using the same single cell set-up and the same electrochemical system with an FRA 5020A frequency response analyzer (NF Corporation, Japan). The impedance spectra were recorded in a frequency range of 20 kHz to 10 mHz with an ac signal of ± 15 mV amplitude (± 30 mV for drier cases) under the various conditions shown in Table 3.1.3. The cathode potential was held at 0.45 V vs. RHE during the EIS measurement. After the CO treatment, however, the potential was held at 0.15 V in order to minimize CO desorption during the measurement.

**Measurement of electrochemical surface area (CO stripping voltammetry)**

To measure the electrochemical area (ECA) of the catalyst layer, CO stripping voltammetry was carried out under various conditions as shown in Table 3.1.3. After CO adsorption, the cathode potential was scanned between 0.02 and 0.95 V vs. RHE at a scan rate of 5 mV s$^{-1}$ for five cycles. The quantity of electricity due to CO oxidation, $Q_{CO}$, was calculated from the difference in the voltammograms. The roughness factor of a Pt disk electrode with a diameter of 5 mm (AFE2M050PT, PINE instrument Co.) was also obtained by CO stripping voltammetry. For the Pt disk electrode, 0.1 M of perchloric acid and a three-compartment electrochemical cell consisting of an RHE, a Pt wire counter electrode and the Pt disk working electrode was used. The potential of the working electrode was scanned between 0.02 and 1.2 V vs. RHE at a scan rate of 50 mV s$^{-1}$ for 5 cycles.
Measurement of electrochemical surface area (Potential step CO stripping voltammetry)

Under low RH conditions, CO stripping was conducted by a potential step method because the CO stripping voltammogram obtained with the method described above might have been skewed due to extremely low proton conductivity. After CO adsorption, the cathode potential was held at 0.3 V vs. RHE for three minutes and then stepped to 1.0 V and kept for fifteen minutes. The same measurement was also carried out without any CO treatment to obtain the background. \( Q_{CO} \) was obtained from the difference between the voltammogram and the background.

Measurement of electrochemical surface area (cyclic voltammetry)

The ECA of the catalyst layer was also measured by cyclic voltammetry (CV) under the same conditions as CO stripping voltammetry. Pure \( H_2 \) and \( N_2 \) were fed to the counter electrode and working electrode, respectively. After a certain waiting period, the cathode valves were closed to reduce the \( N_2 \) partial pressure at the cathode during the measurement. Right after that, the cathode potential was scanned between 0.02 and 0.9 V vs. RHE at a scan rate of 50 mV s\(^{-1}\) for several cycles. The ECA was obtained from the amount of protons which were underpotentially deposited on Pt, \( H_{UPD} \), and the Pt loading. The amount of \( H_{UPD} \) was calculated by extracting the quantity of electricity due to hydrogen evolution reaction (HER) from total reduction current below the potential where the double layer region was observed. The Tafel curve for HER was calculated using a Tafel slope and an intercept approximated at low potential region (usually below 0.07 V vs. RHE) where the voltammogram is logarithmically linear. The roughness factor of the Pt disk electrode was also obtained by CV. The same electrolyte and cell as described above was used. The potential of the working electrode was scanned between 0.02 and 1.2 V vs. RHE at a scan rate of 50 mV s\(^{-1}\) for several cycles. The same calculation method as the catalyst layer was used to calculate the quantity of electricity due to \( H_{UPD} \).

Water uptake measurement

In order to investigate water adsorption behavior, the adsorption isotherms of water for Pt/KB and Pt/GKB were measured by means of a volumetric method using an automatic vapor adsorption apparatus (Belsorp 18 Plus-HT, Nihon Bell) at 30°C. 0.03–0.05 g of the samples was placed in a glass sample tube. To reduce the Pt surface, the sample tube was dosed with hydrogen for fifteen minutes at 100°C. As preconditioning, the sample tube was evacuated for over an hour at 100°C before the measurement.
Measurements were performed with and without hydrogen treatment for both Pt/KB and Pt/GKB.

3.1.3. Results and discussion

Ionomer coverage in KB system

In a simple Randles circuit like that in Fig. 3.1.2, an impedance, $Z$, is expressed as

$$Z = R_{\text{mem}} + \frac{R_{\text{ct}}}{1 + \omega^2 R_{\text{ct}}^2 C_{\text{dl}}^2} - j \omega R_{\text{ct}}^2 C_{\text{dl}}$$

(3.1.1),

where $R_{\text{mem}}$ and $R_{\text{ct}}$ are the proton transport resistance of the membrane and the charge transfer resistance of the catalyst layer, respectively. When $R_{\text{ct}}$ is high enough and can be regarded as infinite, (3.1.1) can be simplified as

$$Z = R_{\text{mem}} - \frac{j}{\omega C_{\text{dl}}}$$

(3.1.2).

EIS was carried out under an inert gas atmosphere at 0.45 V vs. RHE. In such cases, very little Faradic current, i.e., limiting current due to crossover hydrogen through the membrane, is observed. As a consequence, $R_{\text{ct}}$ is notably high. For a more accurate analysis, however, $C_{\text{dl}}$ was calculated in a different way. The imaginary part in Eq. (3.1.1), $Z_{\text{img}}$, can be expressed as

$$-\frac{1}{\omega Z_{\text{img}}} = \frac{1}{\omega^2 R_{\text{ct}}^2 C_{\text{dl}}} + C_{\text{dl}}$$

(3.1.3)

when $R_{\text{ct}}$ is not negligible. According to eq. (3.1.3), the relation between $-\omega Z_{\text{img}}^{-1}$ and $\omega^2$ should give $C_{\text{dl}}$. The catalyst layer should be expressed as a much more complicated model such as a transmission line model [15] because it has a complex microporous structure. However, it can be simplified as shown in Fig. 3.1.2 in the low frequency region because the current distribution is negligible. Therefore, $C_{\text{dl}}$ was obtained on the basis of the relation between $-\omega Z_{\text{img}}^{-1}$ and $\omega^2$ in the low frequency region.
Fig. 3.1.2. A simple Randles circuit consisting of the proton transport resistance of the membrane ($R_{\text{mem}}$), charge transfer resistance ($R_{\text{ct}}$) and the electric double layer capacitance ($C_{\text{dl}}$).

An impedance spectrum of the KB-based catalyst layer was obtained at 100% RH and 30°C (Fig. 3.1.3). The Nyquist plot was very similar to ones reported in the literature [15,16]. As the counter electrode was also used as the reference electrode in this system instead of a typical three electrode configuration, the influence of the anode could appear in the spectrum. However, it is said that the kinetics of hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) on Pt are very high and the current density is very low when the frequency is low. Accordingly, the cell configuration probably does not matter to low frequency region. In addition, it is also said that adsorbed protons can works as pseudo capacitance [17]. Therefore it probably does not greatly affect the analysis even under the high frequency region. Capacitance plots are shown in Fig. 3.1.4 as a function of $\omega^{-2}$. As can be seen, capacitance increased with decreasing frequency (increasing $\omega^{2}$). Although the plots looked stable at low frequency region, $C_{\text{dl}}$ was obtained by extrapolating the plots up to $\omega^{2} = 0$ from the low frequency region (high $\omega^{2}$ region). For comparison, capacitance plots obtained with the CO treatment and the KB-based PCL are also shown in Fig. 3.1.4. With the CO treatment, decreased to the same level as that of the PCL. This result indicates that almost the entire surface of Pt became inactive and did not work as $C_{\text{dl}}$ any more due to CO adsorption. If so, the difference between $C_{\text{dl}}$ with and without the CO treatment would correspond to $C_{\text{dl}}$ of Pt. To verify this assumption, the specific capacitance of Pt was estimated from the ECA and the gap of $C_{\text{dl}}$. The ECA was measured by CO stripping voltammetry. As shown in Fig. 3.1.5, the CO stripping voltammogram exhibited a clear peak due to CO oxidation around 0.75 V in the first cycle. $Q_{\text{CO}}$ was obtained from the difference between the voltammograms. Though it was not so large, the difference between the voltammograms was also calculated up to the 5th cycle. The ECA was then obtained as 69.1 m$^2$ g$^{-1}$ using a charge to the Pt surface area conversion factor of 420 $\mu$C cm$^{-2}$Pt and $Q_{\text{CO}}$. As a result, the specific capacitance of Pt was estimated as 80.2 $\mu$F.
cm$^2_{\text{Pt}}$, which corresponded well with the value reported in the literature [18]. Consequently, it is reasonable to assume that $C_{\text{dl}}$ due to Pt can be simply obtained by CO adsorption.

Fig. 3.1.3. A Nyquist plot of a KB-based catalyst layer at 100% RH and 30°C.
Fig. 3.1.4. Capacitance plots of a KB-based catalyst layer and a PCL at 100% RH and 30°C.

Fig. 3.1.5. CO stripping voltammograms of a catalyst layer with a KB support at 100% RH and 30°C.
The total double layer capacitance, \( C_{d\text{,total}} \), is assumed to consist of \( C_{d\text{l}} \) derived from Pt, \( C_{d\text{l}\text{,Pt}} \), and that derived from the carbon support, \( C_{d\text{l}\text{,C}} \). Moreover, considering the two kinds of electrolyte used, namely the ionomer and water, each of these two sources can be further divided. Consequently, the following four kinds of interfaces: i) Pt/ionomer (\( C_{d\text{l}\text{,Pt/i}} \)); ii) Pt/water (\( C_{d\text{l}\text{,Pt/w}} \)); iii) carbon/ionomer (\( C_{d\text{l}\text{,C/i}} \)); and iv) carbon/water (\( C_{d\text{l}\text{,C/w}} \)) contribute to \( C_{d\text{l\text{,total}}} \). All of them contribute to \( C_{d\text{l}} \) under a wet condition without the CO treatment. Accordingly, the contribution of Pt may be regarded as negligible with the CO treatment, in other words, iii) and iv) work as \( C_{d\text{l}} \). Meanwhile, the contribution of water may be regarded as negligible under a dry condition because the ionomer works as an electrolyte even in a dry state. In this case, i) and iii) work as \( C_{d\text{l}} \). Only iii) works as \( C_{d\text{l}} \) under a dry condition with the CO treatment.

The contributions of each of the above four kinds of interfaces can be separated respectively by obtaining \( C_{d\text{l}} \) in those four cases. Assuming that the specific capacitance derived from the different electrolytes, namely, the ionomer and water, is the same, the difference of \( C_{d\text{l}} \) between dry and wet conditions should be attributed to the difference of Pt surface which is covered with the ionomer or water. In that case, the ionomer coverage on Pt, \( \theta_{\text{ion,Pt}} \), can be simply expressed as

\[
\theta_{\text{ion,Pt}} = \frac{C_{d\text{l}\text{,Pt/i}}}{C_{d\text{l}\text{,Pt/i}} + C_{d\text{l}\text{,Pt/w}}}
\]

Likewise, the ionomer coverage on carbon, \( \theta_{\text{ion,C}} \), is

\[
\theta_{\text{ion,C}} = \frac{C_{d\text{l}\text{,C/i}}}{C_{d\text{l}\text{,C/i}} + C_{d\text{l}\text{,C/w}}}
\]

The verification of this assumption will be discussed later.

The RH dependence of \( C_{d\text{l}} \) was then investigated with and without the CO treatment (Fig. 3.1.6). For comparison, \( C_{d\text{l}} \) of the KB-based PCL is also shown in Fig. 3.1.6. \( C_{d\text{l}} \) after the CO treatment was almost the same as that of the PCL at high RH conditions such as 90 or 100% where interfaces consisting of either water or the ionomer should work, although they were different at lower RH probably because of different water adsorption behavior. As mentioned before, this indicated that the entire Pt surface was covered with CO and \( C_{d\text{l}} \) due to Pt became almost zero after the CO treatment. It also indicated that the carbon surface property of the CO-treated catalyst layer was the same as that of the PCL even after Pt deposition and the CO treatment. The implications of these observations will be discussed later. \( C_{d\text{l}} \) started to increase with an increase in RH from 10% and saturated in the high RH region in both cases. Presumably, \( C_{d\text{l}} \) was sufficiently low at 5% RH and water did not contribute to \( C_{d\text{l\text{,total}}} \). As long as the support was KB (or GKB), the amount of water was markedly small at
5% RH, after drying at 90°C for five hours as described in 2.1 and 2.2 in this thesis. This suggests that adsorbed water does not affect $C_{dl}$ at 5% RH. However, whether this is true for Pt/C is still unclear.

Fig. 3.1.6. RH dependence of a KB-based PCL and a catalyst layer with and without CO treatment at 30°C.

To clarify this issue, water adsorption isotherms for Pt/C were measured at 30°C (Fig. 3.1.7). Pt/C showed a considerable amount of water even at 5% RH. The hydrophilic characteristic of Pt probably produced that amount of adsorption. In this respect, water could still contribute to $C_{dl}$ even at such low RH and make the analysis difficult. The Pt surface state, however, was probably different. While the atmosphere right before the water adsorption measurement was air and the Pt surface must have been oxidized, that of the cathode during $C_{dl}$ measurement was H$_2$/N$_2$ due to crossover hydrogen and the Pt surface must have been bare. Therefore, the influence of the Pt surface state on the water adsorption isotherms was investigated. Pt/C was exposed to hydrogen at 100°C for fifteen minutes, and after evacuation for over an hour at 100°C, water adsorption behavior was measured again. The results revealed that the onset of water adsorption shifted to the higher water activity side and that the amount of water adsorbed at 5% RH was much smaller: less than 3 mg g$^{-1}$ carbon in the KB system and less than 2 mg g$^{-1}$ carbon in the GKB system. Though the influence of adsorbed water on $C_{dl}$
varies depending on the double layer structure (thickness of water, ratio of adsorption on Pt to that on carbon and so on), such a small amount of water will probably not affect the result. Without any hydrogen treatment, a Pt oxide presumably was formed and its higher hydrophilicity contributed to higher water adsorption than the bare Pt surface. Based on this investigation, the amount of water in the catalyst layer at 5% RH under the actual experimental environment seemed low enough, and it was concluded that applying $C_{\text{dl}}$ at 5% RH to the estimation of $\theta_{\text{ion}}$ did not matter. Furthermore, it is well known that CO adsorption interferes with water adsorption on bare Pt [19,20]. Considering this, it is reasonable to say that water adsorption at 5% RH with the CO treatment was negligibly small.

Therefore, the values of $C_{\text{dl}}$ at 5 % RH and 100% RH were used for estimating $\theta_{\text{ion}}$. As a result, it was found that $\theta_{\text{ion,Pt}}$ and $\theta_{\text{ion,C}}$ were 0.39 and 0.25 respectively. $\theta_{\text{ion,C}}$ of the PCL was also calculated from Fig. 3.1.6 as ca. 0.3 at 30°C. The estimated values are summarized in Table 3.1.4. $\theta_{\text{ion,C}}$ of the catalyst layer was a little smaller than $\theta_{\text{ion,Pt}}$ and $\theta_{\text{ion,C}}$ obtained with the PCL. These results suggest that Pt is a little more likely to be deposited on the outer surface of the KB support rather than inside the primary pores. Moreover, Pt on the outer surface may have caused the difference seen in
between the catalyst layer and the PCL because the voids between Pt particles and the carbon support were so small that the ionomer could not penetrate into them. Pt particles in primary pores may not matter because the ionomer apparently does not penetrate into such pores as reported in 2.1 and 2.2 in this thesis. This was also suggested by simulations based on coarse-grained molecular dynamics [21,22].

<table>
<thead>
<tr>
<th>Table 3.1.4. Ionomer coverage on Pt and carbon.</th>
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<tr>
<td></td>
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<tr>
<td><strong>Pt/KB catalyst layer</strong></td>
</tr>
<tr>
<td>$\theta_{\text{ion},\text{Pt}}$</td>
</tr>
<tr>
<td>$\theta_{\text{ion},\text{C}}$</td>
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<tr>
<td><strong>KB-based pseudo catalyst layer</strong></td>
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<tr>
<td>$\theta_{\text{ion},\text{Pt}}$</td>
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<tr>
<td>$\theta_{\text{ion},\text{C}}$</td>
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<tr>
<td><strong>Pt/GKB catalyst layer</strong></td>
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<tr>
<td>$\theta_{\text{ion},\text{Pt}}$</td>
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<tr>
<td>$\theta_{\text{ion},\text{C}}$</td>
</tr>
<tr>
<td><strong>GKB-based pseudo catalyst layer</strong></td>
</tr>
<tr>
<td>$\theta_{\text{ion},\text{Pt}}$</td>
</tr>
<tr>
<td>$\theta_{\text{ion},\text{C}}$</td>
</tr>
</tbody>
</table>

*Refs. [12,13].

For further verification of $\theta_{\text{ion},\text{Pt}}$, the RH dependence of ECA was evaluated by CO stripping voltammetry (Fig. 3.1.8). Here, the same charge to Pt surface area conversion factor was used for all RH conditions assuming that the CO coverage for both Pt/ionomer and Pt/water interfaces is the same. To verify this assumption, the roughness factor and $C_{\text{dl}}$ of a Pt disk electrode with a diameter of 5 mm were compared with and without a Nafion® film. Without the Nafion® film, the roughness factor was obtained by measuring the amount of the underpotential deposition of protons, $H_{\text{UPD}}$, and the amount of CO respectively, after polished the Pt disk electrode well with an alumina polishing suspension (MicroPolish® Alumina, BUEHLER). $C_{\text{dl}}$ was determined from the cyclic voltammogram for $H_{\text{UPD}}$ estimation. As a result, roughness factors were determined to be 1.50 (by $H_{\text{UPD}}$) and 1.63 (by CO stripping) and $C_{\text{dl}}$ was 0.162 mF cm$^{-2}$. For preparing a Nafion® film, the same Nafion® ionomer dispersion (D2020) as used for preparing the catalyst ink was diluted with water ($H_2O$) and propan-2-ol (iso propyl alchol, IPA) so that the weight ratio of those three materials was D2020: $H_2O$: IPA = 7: 20: 15. The Nafion® film was then made by dropping 10 µl of the diluted dispersion onto the Pt disk electrode after being polished well again and dried in a fumehood over fifteen minutes. With the electrode, the roughness factors and $C_{\text{dl}}$ were 1.62 (by $H_{\text{UPD}}$), 1.76 (by CO stripping) and 0.173 mF cm$^{-2}$. The ratios of the roughness factors and $C_{\text{dl}}$ with the Nafion® film to those without the film were 1.08 (by $H_{\text{UPD}}$), 1.08 (by CO stripping) and 1.07 ($C_{\text{dl}}$). Consequently, it was found that the Nafion® film did not matter to CO adsorption. In this way, the assumption was verified.
Fig. 3.1.8. RH dependence of ECA of a KB-based catalyst layer obtained by CO stripping voltammetry at 30°C.

Under low RH conditions of 5, 10, or 20% RH, however, CO stripping was conducted by the potential step method. Under low RH and low temperature, CV was skewed due to extremely low proton conductivity, making quantification difficult. It was found that ECA strongly depended on RH and decreased with decreasing RH. The same tendency was reported by Shinozaki et al. [23]. Disappearance of the proton path consisting of water might produce such a trend. To verify this assumption, another CO stripping was carried out. RH was raised to 100% without any additional CO supply after CO stripping at 5% RH. CO stripping voltammetry was then performed again and the ECA determined by the remaining CO was calculated. The ECA values are compared in Fig. 3.1.9. The sum of the ECA at 5% RH and 5-100% RH corresponded well to that normally obtained at 100% RH. This result confirmed that a proton path consisting of water was present and caused the RH dependence of the ECA and $C_{dl}$. Consequently, the specific capacitance of $C_{dl, Pt}$ and $C_{dl, Pt/w}$ was obtained from Figs. 3.1.6 and 3.1.8 as 77.8 and 81.5 $\mu$F cm$^{-2}$Pt, respectively. The values are close to each other and consistent with the literature [18]. If the water content of the ionomer had greatly changed specific capacitance, those three values would not have been consistent with each other. Therefore, the different water content of the ionomer does not have a significant effect on the analysis. Consequently, the aforementioned assumption about
specific capacitance is presumably valid. At the same time, the foregoing ideas that the carbon surface property was the same and that CO covered the Pt surface completely also hold true. Moreover, the ratio of the ECA at 5% RH to that at 100% RH was found to be ca. 0.34. There is not much difference between this value and $\theta_{\text{ion,Pt}}$ obtained from the $C_{\text{dl}}$ analysis. Jinnai et al. reported that about 70% of the Pt particles were deposited inside the primary pores of KB, based on transmission electron microtomography (TEMT), although the observed area was limited [24]. According to this result, about 30% of Pt was on the outer surface of the KB support. The obtained $\theta_{\text{ion,Pt}}$ and the ratio of the ECA (dry to wet) were not so far from their result.

![Fig. 3.1.9. RH dependence of ECA of KB-based catalyst layer obtained by CO stripping voltammetry at 30°C.](image)

**Ionomer coverage in GKB system**

$\theta_{\text{ion,Pt}}$ in the GKB system was also evaluated in the same manner as that of the KB system. Figure 3.1.10 shows the RH dependence of $C_{\text{dl}}$ of the GKB-based catalyst layer with and without the CO treatment. $\theta_{\text{ion,Pt}}$ and $\theta_{\text{ion,C}}$ were estimated to be ca. 0.34 and 0.91, respectively. In order to verify the validity of $\theta_{\text{ion}}$, the RH dependence of $C_{\text{dl}}$ of the GKB-based PCL was investigated. Though the temperature was different (80°C), the results are shown in Fig. 3.1.10 for comparison and were also reported in 2.1 and 2.2 in this thesis. $C_{\text{dl}}$ of the PCL at 100% RH and 30°C (3.8 F g$^{-1}$carbon) was almost the same.
as that at 100% RH and 80°C (4.0 F g\(^{-1}\)carbon). In addition, it did not depend on RH. Therefore, it was concluded that using the data at 80°C as a comparison target would not affect the analysis. \(C_{dl}\) of the catalyst layer was larger than that of the PCL even after the CO treatment. Two hypotheses for the difference can be suggested. One is that Pt deposition gave rise to different carbon surface properties. The other is that a portion of the Pt surface was not covered with CO.

![Graph showing RH dependence of catalyst layer with and without CO treatment](image)

Fig. 3.1.10. RH dependence of a GKB-based catalyst layer with and without CO treatment at 30°C and that of a GKB-based PCL at 80°C.

To investigate these hypotheses, the specific capacitance of Pt was investigated. For calculating the specific capacitance, however, it is necessary to know the ECA. Applying the ECA obtained from CO stripping did not seem appropriate in this case because CO may not have covered the entire Pt surface as mentioned above. For this reason, the ECA of the GKB-based catalyst layer was evaluated by both CO stripping and a conventional method that uses the underpotential deposition of protons, \(H_{\text{UPD}}\) (Fig. 3.1.11). CO stripping was conducted by the potential step method with RH of 5, 10, and 20% for the same reason as with the KB system. A comparison of the results obtained with the two methods revealed that CO stripping showed a lower ECA value, and this trend did not contradict the second hypothesis. The specific capacitance of Pt was calculated from the ECA evaluated from the amount of \(H_{\text{UPD}}\) and the difference in
with and without the CO treatment. It was found to be only 58 \( \mu \text{C cm}^{-2\text{Pt}} \) and much smaller than that given in the literature [18]. Even if the first hypothesis about the different carbon surface properties is correct, it would not explain the decrease in the specific capacitance of Pt. For that reason, the second hypothesis was deemed reasonable. For further verification, \( C_{dl} \) due to uncovered Pt was calculated from the difference in the ECA values in Fig. 3.1.11 and the specific capacitance of Pt (80 \( \mu \text{F cm}^{-2\text{Pt}} \)). It was found to be 5.66 F g\(^{-1}\)carbon and corresponded well with the difference in between the CO-treated catalyst layer and the PCL (5.50 F g\(^{-1}\)carbon). Therefore, it is reasonable to assume that \( C_{dl} \) of carbon is almost the same as that of the PCL. As verified above, CO probably did not cover the entire Pt surface. Taking this into account, the actual \( \theta_{\text{ion},C} \) may be larger than the \( \theta_{\text{ion},C} \) noted above because it might include the RH dependence of non-CO-covered Pt when all the sites were not covered by the ionomer. Therefore, \( \theta_{\text{ion},C} \) in the GKB system was presumed to be larger than 0.91. Meanwhile, \( \theta_{\text{ion},C} \) in the GKB system was reported to be 1 in 2.1 and 2.2 in this thesis. Though the exact value of \( \theta_{\text{ion},C} \) was not certain, \( C_{dl} \) due to carbon was very small in this case and had little influence on the analysis. Actually, the value of \( \theta_{\text{ion},Pt} \) was estimated to be 0.49 and did not change with different \( \theta_{\text{ion},C} \) values (0.91 and 1).

\[ \text{Fig. 3.1.11. RH dependence of ECA of a GKB-based catalyst layer obtained by CO stripping and amount of underpotential deposition of proton at 30°C.} \]
A comparison of $\theta_{\text{ion,Pt}}$ with different carbon supports revealed that GKB showed a higher value. This seems reasonable because the number of primary pores in GKB is very small, so Pt particles should be deposited on its outer surface. Even so, the value still seemed too small compared with $\theta_{\text{ion,C}}$ of the GKB system. In order to examine this difference, the microstructure of Pt/C was observed under a scanning transmission electron microscope (HD-2000, Hitachi High-Technologies Corporation). STEM images are shown in Fig. 3.1.12. Both SEM and TEM images showed that Pt particles agglutinated and formed clusters on the GKB surface. Although it was difficult to measure the voids of the clusters exactly from these images, they were assumed to be smaller in size than the Pt particles (2~3 nm). It is quite unlikely that the ionomer can penetrate into such small voids easily and cover the entire Pt surface. Assuming it can not, Pt/water interface can be formed inside of the Pt clusters and work as $C_{\text{dl}}$ under high RH conditions just like inside of the primary pores in the KB system. In other words, the voids of the Pt clusters could account for the RH dependence of $C_{\text{dl},\text{Pt}}$ and ECA. The difference in $\theta_{\text{ion,Pt}}$ and $\theta_{\text{ion,C}}$ in the GKB system is probably attributable to the poor dispersibility of Pt.

![Fig. 3.1.12. (Left) scanning electron microscope and (right) transmission electron microscope images of Pt/KB and Pt/GKB.](image-url)
This does not, however, explain the RH independence of the ECA obtained by CO stripping. The ECA values calculated from the amount of $H_{\text{UPD}}$ showed RH dependence. The measured CVs used in the ECA calculation are shown in Fig. 3.1.13. In fact, the CVs under low RH conditions skewed severely because of markedly low proton conductivity, so the ECA under such conditions was probably not evaluated accurately. However, the ECA still seemed to depend on RH aside from the skewed CVs such as the values at 5, 10, and 20% RH. It is well known that adsorbed CO diffuses on the Pt surface and its diffusivity has been investigated in various ways [25–28]. This likely explains the reason why CO stripping did not show any RH dependence of the ECA. Specifically, CO molecules adsorbed at a site isolated from proton network can move to other sites due to surface diffusion. When CO reaches sites connected to the proton network in the system, it can then be oxidized at a high potential probably via a so-called Langmuir-Hinshelwood mechanism [28–30] involving adsorbed CO and an oxygen-containing species such as PtOH. The surface diffusion coefficient, $D_{\text{CO}}$, on Pt/GC (particle size: 3.1 nm) at 298 K was calculated to be $3 \times 10^{-14}$ cm$^2$ s$^{-1}$ [27]. The mean diffusion length of adsorbed CO was simply estimated from this $D_{\text{CO}}$ and the result showed that it can diffuse to adjacent particles in less than four seconds when the Pt particle size is 3 nm. This seems rapid enough considering the scan rate for CO stripping voltammetry (5 mV s$^{-1}$). It is even more so for the low RH cases in this study because the potential was kept at 1.0 V for fifteen minutes under such conditions. In contrast, the ECA of Pt/KB depended on RH despite the same CO stripping procedure. In the case of Pt/KB, Pt particles dispersed well on the carbon surface as can be seen in the SEM and TEM images in Fig. 3.1.12. In such cases, CO surface diffusion should not affect the ECA measurement by CO stripping. On these grounds, it is inferred that $C_{\text{dl}}$ and the ECA of Pt/GKB depend on RH due to the voids in the Pt clusters on the GKB surface. In addition, an ECA evaluation using CO stripping voltammetry may result in an overestimation depending on the microstructure of the sample and RH condition because of the surface diffusion of adsorbed CO.
3.1.4. Conclusions

An in-situ technique was developed for analyzing $\theta_{\text{ion,Pt}}$ and $\theta_{\text{ion,C}}$ in actual fuel cell catalyst layers using CO adsorption and the RH dependence of $C_{dl}$. This method was used to investigate $\theta_{\text{ion}}$ of catalyst layers with different types of carbon support. For the KB-based catalyst layers, $\theta_{\text{ion,Pt}}$ and $\theta_{\text{ion,C}}$ were found to be ca. 0.39 and 0.25, respectively. The validity of the analysis was verified on the basis of various analyses and experiments, namely, water adsorption analysis, analysis of specific capacitance and ECA analysis by CO stripping voltammetry.

In the case of the GKB-based catalyst layer, the results suggested the possibility that CO did not cover the entire Pt surface, making the analysis more complex. That possibility was verified by undertaking the following experiments: I) a comparison with $C_{dl}$ of the GKB-based PCL; II) specific $C_{dl}$ analysis; and III) a comparison of ECA values obtained with different methods. As a result, the possibility was deemed appropriate and $\theta_{\text{ion,Pt}}$ of the GKB-based catalyst layer was estimated to be ca. 0.49 using the $C_{dl}$ of the GKB-based PCL.

Although the number of primary pores in GKB is very small, $\theta_{\text{ion,Pt}}$ was small compared with $\theta_{\text{ion,C}}$. SEM and TEM images revealed that Pt particles formed clusters...
on the GKB surface. The voids of the Pt clusters, which are very narrow, probably contributed to the low $\theta_{\text{on,Pt}}$. Although this contradicted the RH independence of the ECA shown by CO stripping, the difference can be explained by considering the surface diffusion of adsorbed CO on the Pt surface. This analysis also suggested that CO stripping voltammetry may result in overestimation of the ECA depending on the microstructure of the sample and RH condition.
References

Chapter 4 Gas transport analysis
4.1. Relationship between Gas Transport Resistance in the Catalyst Layer and Effective Surface Area of the Catalyst

4.1.1. Introduction

As mentioned in the previous chapters, to design optimized catalyst layers, it is necessary to develop methods of evaluating and gaining an in-depth understanding of the phenomena involved [1].

The greatest challenge of all from an industrial point of view is to reduce the cost [2, 3]. The most effective way to do that is to reduce the amount of Pt used. Fuel cell operation under low humidity and high current density is also desirable because it would allow the FC stack and its associated system to be simplified [4], resulting in lower cost. However, the increase in gas transport resistance, $R_{\text{gas}}$, stemming from lower Pt loading is an issue of concern [5, 6]. Mass transport in the cathode catalyst layers in particular could cause performance loss under high current density. Moreover, improved performance under low RH conditions is required for dry operation. Therefore, it is essential to understand the gas transport properties of low Pt loading catalyst layers, especially through the ionomer, and their RH dependence.

In recent years, a method of evaluating gas transport in the catalyst layers, $R_{\text{CL}}$, by measuring the limiting current of diluted gases has been developed [7] and applied [5,6]. This method has good reproducibility and the advantage of enabling simultaneous evaluation of both gas transport resistance in the gas diffusion layer, $R_{\text{GDL}}$, and $R_{\text{CL}}$. This method provides a basic understanding of phenomena in ideal RH conditions (e.g., 70 - 90 % RH). However, it is not universally applicable. For one thing, the limiting current is uncertain when the proton conductivity of the catalyst layers is not high enough (with a low ionomer content or under low RH) because of the potential distribution attributed to the IR drop in the catalyst layers. For this reason, the RH dependence of $R_{\text{gas}}$ has not been investigated thoroughly, although a low RH is essential for dry operation. What is more, the concentration distribution of the reactant from the inlet to the outlet makes it difficult to analyze this dependence.

In this chapter, a new method for evaluating gas transport resistance based on gas crossover through the Nafion® membrane was investigated. Using gas crossover as a reactant source has several advantages. Specifically, it allows the method to be applied to low proton conductive conditions because the amount of the reactants is extremely small compared with that of the previous method [7], resulting in small limiting current densities (gas crossover: less than 1.6 mA cm$^{-2}$ for hydrogen and 1.8 mA
cm⁻² for oxygen, previous method: less than 0.3 A cm⁻² and 0.2 A cm⁻² for oxygen). The concentration distribution in the gas flow direction can also be ignored because the flow direction does not matter for gas crossover from the counter electrode side. With this method, the RH dependence of \( R_{\text{CL}} \) was investigated and analyzed for both hydrogen and oxygen.

### 4.1.2. Experimental

**Preparation of MEA**

Table 4.1.1 shows the membrane electrode assembly (MEA) specifications used in this study. Two catalyst inks were prepared respectively by mixing Pt black (manufactured by TKK, Japan) with the Nafion® ionomer dispersion (D2020, EW1000, DuPont), and Pt/GKB (catalyst: 46 wt.%) with the Nafion® ionomer dispersion so that the weight ratio of the ionomer content was 0.17 relative to the Pt black and 0.9 to the carbon support. In this study, oxygen transport resistance was measured using the gas crossover. Thereby, water electrolysis occurred on the counter side. If a carbon support had been applied, the carbon would have corroded. Therefore, Pt black was applied to the reference and counter electrodes, so as not to cause the morphological change in water electrolysis. Graphitized ketjen black, which has a very small number of primary pores, was used as the support in order to ignore gas transport in the primary pores.

<table>
<thead>
<tr>
<th>Counter and reference electrodes</th>
<th>Working electrode (Pseudo catalyst layer)</th>
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<tbody>
<tr>
<td>Catalyst</td>
<td>Pt black</td>
</tr>
<tr>
<td>Carbon support</td>
<td>Pt/GKB (46 wt.%)</td>
</tr>
<tr>
<td>Loading</td>
<td>0.6 mg·Pt cm⁻²</td>
</tr>
<tr>
<td>Ionomer</td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
</tr>
<tr>
<td>Ionomer/Carbon weight ratio</td>
<td>0.17 (I/Pt)</td>
</tr>
<tr>
<td>Electrode area / cm²</td>
<td>10</td>
</tr>
<tr>
<td>GDL</td>
<td>Carbon Paper with MPL (25BCH, SGL Carbon)</td>
</tr>
<tr>
<td></td>
<td>Carbon Paper without MPL (TGP H120, Toray)</td>
</tr>
</tbody>
</table>
The counter electrode consisted of a Pt black catalyst layer that was spray-coated on a square perfluorosulfonic acid (PFSA) membrane (Nafion® NR211, thickness = 25 µm) measuring 72 mm on one side and then dried for 30 min at 80°C to remove the organic solvent. The working electrode, consisting of Pt/C, was then fabricated on the other side and dried. The membrane was masked beforehand with a 25-µm-thick polyethylene naphthalate (PEN) film (Q51, Teijin-DuPont) having a 10 cm² open area (2 cm vertical x 5 cm horizontal) on both sides so as to prevent any gap between the film and the catalyst layer. This was done because gas crossover through the gap might affect the analysis, albeit not so significantly. The film also provided reinforcement. Pt loadings on the counter electrode and the working electrode were 0.6 and 0.12 mg cm⁻², respectively. The Pt loading of the counter electrode was determined from an engineering point of view. The catalyst layer of the counter electrode is quite thin when approximately the same Pt loading is applied to both the counter and working electrodes because the former electrode does not have a carbon support. Therefore, high Pt loading was applied to the counter electrode to prevent the gas diffusion layer (GDL) from attacking the membrane directly. The thickness of the catalyst layer was observed using a scanning electron microscope (SEM) and found to be around 2 µm.

GDLs with a microporous layer (25BCH, SGL Carbon) and without a microporous layer (TGP-H120, Toray) were used for the counter electrode and the working electrode, respectively. A GDL without a microporous layer was desirable for the working electrode to make it easier to analyze gas transport phenomena. The MEA was formed by assembling the GDLs on both sides of the catalyst coated membrane (CCM). It was assembled in a single cell between bipolar plates with a straight flow field made of graphite and gaskets made of silicone rubber. The compression pressure was kept uniform by measuring it with pressure-sensitive paper (Prescale, Fuji Film). A schematic image of the MEA is shown in Fig. 4.1.1 with the experimental setup.
Fig. 4.1.1. A schematic image of an MEA and an experimental setup.

**Principle of the measurement and analysis**

Crossover hydrogen has generally been measured electrochemically with inert gas flowing to the working electrode [8]. Strictly speaking, crossover hydrogen can exit the system through the cathode GDL and gas channels in this case because the cathode side is not hermetically closed. Usually, this should not matter because the GDLs are much thicker than the catalyst layers, in other words, gas transport resistance in the GDLs, $R_{GDL}$, is much larger than that in the catalyst layers, $R_{CL}$. Both the thickness and Pt loading are key factors of $R_{CL}$ because $R_{CL}$ is a function of the Pt surface area as reported in the literature [5,6]. It was found that $R_{CL}$ increased when the Pt loading was reduced. Accordingly, the amount of gas crossover detected in the catalyst layer should decrease when the Pt loading is reduced even if the same membrane and GDLs are used.

An equivalent circuit model for gas transport in the MEA and a schematic diagram of the flux of each component are shown in Fig. 4.1.2. The relationship among the flux that goes through the GDLs, $N_{GDL}$, the flux that is consumed in the catalyst layer, $N_{CL}$, $R_{CL}$ and $R_{GDL}$ is expressed as

$$\frac{N_{CL}}{N_{GDL}} = \frac{R_{GDL}}{R_{CL}} \quad (4.1.1)$$

Therefore, it is possible to obtain $R_{CL}$ using $R_{GDL}$, $N_{GDL}$ and $N_{CL}$. Here, $N_{CL}$ can be simply measured by the conventional method [8] and $N_{GDL}$ is obtainable from the flux through the membrane, $N_{total}$, and $N_{CL}$. In Fig. 4.1.2, $R_{CL}$ is expressed as a parallel circuit consisting of gas transport resistance in the through-plane direction, which corresponds to gas transport resistance in the macropores of the catalyst layer, $R_{macro}$,
and the gas transport resistance toward the Pt surface, namely, gas transport resistance through the ionomer, \( R_{\text{micro}} \). \( R_{\text{CL}} \) was calculated with this type of equivalent circuit model having 100 segments in the catalyst layer region. When \( R_{\text{GDL}} \) is infinite all the reactant should be consumed in the catalyst layer. Such a condition can be created just by closing the inlet and outlet valves on the working electrode side. In this way, \( N_{\text{total}} \) was measured by consuming all the reactant leaked through from the counter electrode side with the valves on the working electrode side closed. \( N_{\text{CL}} \) can be measured with inert gas flowing to the working electrode. In both cases, the valves on the counter electrode side were opened to maintain homogeneity. \( N_{\text{GDL}} \) was then simply obtained from the difference between \( N_{\text{total}} \) and \( N_{\text{CL}} \).

Fig. 4.1.2. An equivalent circuit model for gas transport in the MEA and a schematic diagram of the flux of each component.

**Measurement of gas transport resistance for hydrogen**

\( R_{\text{CL}} \) for hydrogen was measured by potential step voltammetry under the conditions shown in Table 4.1.2. In the measurement, pure \( \text{H}_2 \) and \( \text{N}_2 \) were fed to the counter and reference electrodes and to the working electrode, respectively, at 80°C. After a certain waiting period, the potential was held at 0.95 V vs. RHE for ten minutes and then set at 0.9 V for five minutes. After that, it was stepped to 0.2 V in 0.1 V increments at five-minute intervals. \( N_{\text{total}} \) was measured in the same way by closing the valves on the working electrode side. An HZ-3000 electrochemical measurement system (Hokuto Denko, Japan) and the same single cell setup were used to perform all the measurements in this study.
Table 4.1.2. Test conditions for gas transport resistance measurements.

<table>
<thead>
<tr>
<th>Counter electrode gas</th>
<th>H₂</th>
</tr>
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<tbody>
<tr>
<td>Working electrode gas</td>
<td>N₂ (with or without flow)</td>
</tr>
<tr>
<td>Back pressure</td>
<td>Ambient</td>
</tr>
<tr>
<td>Cell temperature / °C</td>
<td>80</td>
</tr>
<tr>
<td>Counter electrode humidity / % RH</td>
<td>20, 40, 70, 90</td>
</tr>
<tr>
<td>Working electrode humidity / % RH</td>
<td>20, 40, 70, 90</td>
</tr>
<tr>
<td>Counter electrode flow rate / NL min⁻¹</td>
<td>4.0</td>
</tr>
<tr>
<td>Working electrode flow rate / NL min⁻¹</td>
<td>8.0 (with flow)</td>
</tr>
</tbody>
</table>

Measurement of gas transport resistance for oxygen

$R_{Cl}$ for oxygen was also measured under the same conditions as for hydrogen. However, potential step voltammetry was not appropriate for oxygen because pure O₂ was fed to the counter electrode, which meant that it did not work as a reference electrode. For this reason, linear sweep voltammetry (LSV) was used instead in the $R_{Cl}$ measurement for oxygen. First, pure O₂ and N₂ were fed to the counter and working electrodes, respectively, at 80°C. The cell voltage (counter electrode: negative; working electrode: positive) was then scanned from -0.2 to -1.8 V at a scan rate of 1 mV s⁻¹ after a certain waiting period. After that, the same LSV measurement was carried out by closing the valves on the working electrode side. The cut-off current density was set at 5.0 mA cm⁻² to protect the MEA from differential pressure due to too much hydrogen evolution.

Cyclic voltammetry

To measure the electrochemical area (ECA) of the catalyst layer, cyclic voltammetry was carried out before the $R_{gas}$ measurement using the same single cell set-up and the electrochemical measurement system at 80°C. Pure H₂ and N₂ were fed to the counter electrode and working electrode, respectively. After a certain waiting period, the cathode valves were closed to reduce the N₂ partial pressure at the cathode during the measurement. Right after that, the working electrode potential was scanned between 0.02 and 0.9 V vs. RHE at a scan rate of 50 mV s⁻¹ for several cycles.

Pt oxide measurement

To estimate the amount of Pt oxides of the catalyst layer, LSV was also carried out using another MEA with the same single cell set-up and the electrochemical measurement system at 80°C. Pure H₂ and N₂ were fed to the counter electrode and working electrode, respectively. After a certain waiting period, the working electrode
potential was set at the same levels as in the $R_{\text{gas}}$ measurement for the hydrogen oxidation reaction (HOR), namely, 0.95, 0.9, 0.8, 0.7, 0.6, or 0.5 V for three minutes and then scanned to 0.05 V vs. RHE respectively, at a scan rate of 250 mV s$^{-1}$.

4.1.3. Results and discussion

Gas transport resistance for hydrogen

The method applied to analyze $R_{\text{gas}}$ for hydrogen will be discussed in this section using the data obtained at 20% RH. Transitions in the current density with and without inert gas flow are shown in Fig. 4.1.3. During the first few minutes, a large oxidation current due to Pt oxidation was observed in both cases. When the potential was stepped to 0.9, 0.8, 0.7 and 0.6 V vs. RHE, reduction current spikes occurred corresponding mainly to reduction of Pt oxides. The current density increased with decreasing potential and then it was saturated with inert gas flow. A similar tendency was reported in the literature for both a glass cell [9,10] and a solid-state cell [11]. It is said that Pt oxides form in a high potential region and suppress the kinetics of HOR presumably because of site blocking [9-11]. In this study, the current density was almost independent of the potential without inert gas flow. This result suggested that the decrease of the current density in the high potential region can be recovered by enhancing mass transport and it was not caused by the suppression of the inherent Pt activity for HOR. Presumably, this phenomenon is the same as that of the increase in $R_{\text{CL}}$ with lower Pt loading [12], which also results from a loss of effective sites. This result also does not deny the possibilities that the inherent Pt activity may be reduced by neighboring Pt oxides or HOR can occur on Pt oxide. However, the activity should be much lower than that of bare Pt and insignificant on this analysis.
Figure 4.1.3 shows the relation between the current density and the potential more clearly. The plots in the figure were obtained by averaging the last 20 values (or 20 values in the plateau region when the data fluctuated) at each potential. The results show that the current density was always lower with the inert gas flow than without it regardless of the potential. The value obtained without the inert gas flow was regarded as $N_{\text{total}}$ because crossover hydrogen could not exit the system. The gap corresponding to $N_{\text{GDL}}$ showed its minimum value at 0.3 V. The minimum gap was used to investigate the RH dependence of the current density because there should not be any influence of Pt oxides at that potential. The current density with inert gas flow at the minimum gap was used as $N_{\text{CL}}$. In this way, $N_{\text{total}}$, $N_{\text{CL}}$ and $N_{\text{GDL}}$ were obtained, respectively.
Fig. 4.1.4. Current density with and without inert gas flow at the working electrode and \( R_{\text{micro, Pt}} \) for HOR as a function of potential at 20% RH and 80°C.

In addition to the fluxes, the values of \( R_{\text{GDL}} \) and \( R_{\text{macro}} \) are necessary to obtain \( R_{\text{CL}} \). \( R_{\text{GDL}} \) was evaluated by the method explained in Ref. 7. In the evaluation, the same flow rate of 8 NL min\(^{-1}\) was used to avoid any effects on the analysis of \( R_{\text{CL}} \) due to an error in \( R_{\text{GDL}} \). \( R_{\text{GDL}} \) values for the H\(_2\)/N\(_2\) and O\(_2\)/N\(_2\) systems were 0.27 s m\(^{-1}\) kPa\(^{-1}\) and 0.86 s m\(^{-1}\) kPa\(^{-1}\). \( R_{\text{macro}} \) depends on the diffusion coefficient in the macropores of the catalyst layer and diffusion length. The diffusion coefficient in the macropores was calculated from the porosity of the catalyst layer and found to be ca. 4.07 x 10\(^{-6}\) m\(^2\) s\(^{-1}\) for hydrogen and 1.02 x 10\(^{-6}\) m\(^2\) s\(^{-1}\) for oxygen. The details of the calculation are given in Ref. 12. The relation between mass transport resistance and gas flux is explained below.

Gas flux is usually expressed as

\[
N = \frac{I}{nFA} \tag{4.1.2},
\]

where \( F \) and \( A \) express the Faraday constant and the geometric surface area for crossover, respectively. It is also expressed as

\[
N = D \frac{dC}{dx} \tag{4.1.3},
\]

where \( dx \) expresses the diffusion length. The diffusion length at a segment can be simply calculated from the number of segments (100) in the equivalent circuit model.
and the average thickness of the catalyst layer. To obtain the average thickness, a cross-sectional image of another catalyst layer was observed with an optical microscope. The observation was made over about half of the catalyst layer width (2.5 cm) and the thickness was measured along the length at 20 points. The average thickness was then estimated as 3.48 μm. Consequently, the diffusion length was obtained as 34.8 nm. In Eq. (4.1.3),

\[ \frac{D}{dx} = \frac{1}{R} \]

thus \( R_{macro} \) values were calculated at a segment for hydrogen and oxygen using the diffusion length and the diffusion coefficient. As a result, \( R_{macro} \) for hydrogen and oxygen were \( 8.55 \times 10^{-3} \) s m\(^{-1}\) and \( 3.42 \times 10^{-2} \) s m\(^{-1}\), respectively. From Eqs. (4.1.3) and (4.1.4),

\[ N = \frac{dC}{R} \]

Using Eq. (4.1.5) and the values obtained above, the total consumption and unconsumed amount of hydrogen were calculated while changing \( R_{micro} \) at each segment and the results were then compared with \( N_{CL} \) and \( N_{GDL} \), respectively. The same values of \( R_{macro} \) and \( R_{micro} \) were used for all the segments. This process was repeated until the deviation between the measured and calculated values fell below 0.01. After that, was kept constant and \( R_{CL} \) was calculated from \( R_{macro} \) and the fixed \( R_{micro} \). \( R_{CL} \) obtained with this new method was compared with the value calculated by the previous method [12], although the two values cannot be properly compared directly because the details of the catalyst layers were not exactly the same. It was found that \( R_{CL} \) obtained with the new method was slightly lower than that with the previous method. The reactant concentration was probably distributed more evenly when using the new method as the reactant passed through the membrane, resulting in the lower value. The results of the analyses will be discussed in the last subsection in connection with the RH dependence.

The potential dependence of \( R_{CL} \) was also calculated in the same manner. \( R_{micro} \) can be regarded as the only value that varied with the potential in this model because the other parameters, namely, \( R_{macro} \) and \( R_{GDL} \), had no relation to the Pt surface and were probably independent of the potential. As mentioned in Ref. 5, the gas transport resistance toward the Pt surface is a function of \( S^{ef} \). Therefore, the gas transport resistance per unit of Pt surface area in a segment, \( R_{micro,Pt} \), was calculated from \( R_{micro} \) and the volumetric Pt surface area. The volumetric Pt surface area was obtained from the ECA measured by cyclic voltammetry (Fig. 4.1.5.), the Pt loading and the average thickness of the catalyst layer. The ECA at 20% RH was 22.4 m\(^2\) g\(^{-1}\) as shown in Fig. 4.1.5. The calculated \( R_{micro,Pt} \) is also shown in Fig. 4.1.4. \( R_{micro,Pt} \) increased markedly in
the high potential region. As noted above, the loss of effective sites was probably the main cause of the increase. Therefore, assuming that the entire surface was effective at 0.3V vs. RHE, the fraction of the ineffective surface area, $\chi^{\text{ineff}}$, was calculated as

$$\chi^{\text{ineff}} = 1 - \frac{R_{\text{micro},V}}{R_{\text{micro},0.3V}}$$

(4.1.6).

As shown in Fig. 4.1.6, $\chi^{\text{ineff}}$ started to increase from 0.4 V and reached almost 1.0 at 0.9 V. It has been reported that Pt oxide formation generally occurs at a more positive potential such as 0.7 or 0.8 V [13,14].

Fig. 4.1.5. RH dependence of the electrochemical surface area of the catalyst layer obtained by cyclic voltammetry at 80°C.
As mentioned before, Pt oxides presumably block active sites and inhibit HOR. Therefore, for comparison, the amount of Pt oxides was investigated from linear sweep voltammograms (LSVs). LSVs with a different start potential are shown in Fig. 4.1.7. When the start potential was 0.5 V there were no distinguishable peaks originating from the reduction of Pt oxides. Therefore, this curve was used as the base line for the other curves. The quantity of electricity due to the reduction of Pt oxides, $Q_{\text{red}}$, was obtained from the difference between the LSV and the base curve. Pt oxide coverage was then calculated with $Q_{\text{red}}$ and the ECA using a charge-to-Pt surface area conversion factor of 420 $\mu$C cm$^{-2}$Pt, assuming that all of the Pt oxides were only PtO (Fig. 4.1.6). Although the experimental conditions such as the holding time and method of potential control were different, there was a huge gap between the two curves.

![Graph showing the fraction of the ineffective surface area for HOR at 20% RH and 80°C obtained from $R_{\text{gas}}$ measurement (solid symbols) and amount of Pt oxides (open symbols).]
There are several possible reasons for the difference. One significant possibility is that the assumption made about Pt oxides was inappropriate. If it is instead assumed that all Pt oxides were PtOH, the value should double as shown in Fig. 4.1.6. The mechanism of Pt oxidation is still not clear despite a long history of research [15,16], making it difficult to understand the relation between Pt oxides and $S_{\text{eff}}$. With the latter assumption, the gap in the high potential region became smaller, however, there was still a large gap in the low potential region. Another factor complicating the relation between Pt oxides and $S_{\text{eff}}$ is the number of sites affected by one oxide molecule. This also strongly influences the gap. Notwithstanding these factors, the gap in the low potential region still seemed large. It has been reported that adsorbates such as anion species [17] and the Nafion® ionomer [18] can suppress HOR. For example, the Nafion® ionomer might be adsorbed on the Pt surface and inhibit HOR. A second reason for the difference is that the gas permeability of the ionomer on Pt could be affected by the potential and be reduced with an increasing potential. Although there is room for further investigation to understand better the factors causing the decrease in $S_{\text{eff}}$, it is still possible to evaluate $S_{\text{eff}}$ on the basis of this analysis.
Gas transport resistance for oxygen

The method applied to analyze $R_{\text{gas}}$ for oxygen will be discussed in this section using the data obtained at 20% RH as well. LSVs for the oxygen reduction reaction (ORR) with and without inert gas flow are shown in Fig. 4.1.8. As mentioned in the experimental section, the counter electrode did not work as a reference electrode because pure oxygen was supplied to that side. Therefore, the cell voltage was swept from -0.2 to -1.8 V. The electrochemical reaction that occurred mainly at the working electrode during the scan was ORR. Water electrolysis occurred at the counter electrode to produce protons for ORR at the other side. As there was no carbon support at the counter electrode, morphological change in the catalyst layer resulting in a different level of oxygen transport from the counter electrode was probably negligible. The current density due to ORR increased with a lower cell voltage, and the limiting current density was observed at ca. -1.35 V when gas was fed to the working electrode. On the other hand, without any inert gas flow the curve showed a large peak around -0.85 V. At the beginning of the scan, crossover oxygen could not be fully consumed and was stored at the working electrode side because the overpotential on that side was still low and the valves were closed. When the overpotential was increased high enough, the stored oxygen was reduced quickly and produced the large peak around -0.85 V. The curve then reached the limiting current density and hydrogen evolution occurred below -1.5 V. A larger limiting current density occurred without the inert gas flow, similar to the result seen for HOR. The observed limiting current densities and the gap between the current densities with and without inert gas flow were used in the analysis. The analysis was carried out in the same way as that for hydrogen. A comparison with the results for HOR and a detailed analysis with different RH levels will be presented in the next section.
Fig. 4.1.8. Linear sweep voltammograms for oxygen reduction reaction with and without inert gas flow at the working electrode at 20% RH and 80°C.

**RH dependence of gas transport resistance**

The RH dependence of $R_{\text{gas}}$ for HOR and ORR was investigated in the same manner as described in the previous sections, respectively. As a result, $R_{\text{CL}}$ increased with a lower RH in both cases. These results, however, contain the influence of the RH dependence of the ECA because $R_{\text{CL}}$ is a function of the ECA as noted before. Therefore, a correction based on the ECA is necessary to investigate the physical properties of the ionomer. The RH dependence of the ECA was evaluated by cyclic voltammetry (Fig. 4.1.5). As seen in the figure, the ECA decreased with a lower RH. This is probably because the proton path consisting of condensed water under the high RH condition disappeared as the RH decreased [19]. $R_{\text{micro,Pt}}$ values for hydrogen and oxygen were then obtained from $R_{\text{micro}}$ and the ECA at each RH and summarized in Fig. 4.1.9.
Fig. 4.1.9. RH dependence of $R_{\text{micro, Pt}}$ for hydrogen (solid symbols) and oxygen (open symbols) at 80°C.

For a comparison with the gas permeability of the membrane, the RH dependence of the amount of gas crossover, in other words, the RH dependence of $N_{\text{total}}$, was investigated (Fig. 4.1.10). The solid symbols in the figure express $N_{\text{total}}$ obtained by the method noted in the previous sections. The amount of gas crossover increased with increasing RH for both hydrogen and oxygen. However, the influence of the water vapor pressure was still involved. The partial pressure of hydrogen or oxygen increases with decreasing water vapor pressure when the total pressure is constant. To focus on the physical properties of the ionomer, these plots were normalized by the differential partial pressure of the reactants (open symbols in Fig. 4.1.10). For a further direct comparison, the normalized $N_{\text{total}}$ was converted to the gas transport resistance of the membrane, $R_{\text{mem}}$, using the ideal gas law, namely,

$$PV = nRT$$ \hspace{1cm} (4.1.7).

Here, the concentration gradient, $dC$, can be expressed as

$$dC = \frac{dn}{V} = \frac{dP}{RT}$$ \hspace{1cm} (4.1.8).

Thereby, Eq. (4.1.5) and Eq. (4.1.8) yield

$$R = \frac{dP}{NRT}$$ \hspace{1cm} (4.1.9).
was calculated with Eq. (4.1.9) and the results are shown in Fig. 4.1.11 for hydrogen and in Fig. 4.1.12 for oxygen.

Fig. 4.1.10. RH dependence of the amount of gas crossover at 80°C (circles: hydrogen, squares: oxygen).

- 100 -
Fig. 4.1.11. RH dependence of $R_{\text{mem}}$ (solid symbols) and $R_{\text{micro,Pt}}$ (open symbols) for hydrogen at 80°C.

Fig. 4.1.12. RH dependence of $R_{\text{mem}}$ (solid symbols) and $R_{\text{micro,Pt}}$ (open symbols) for oxygen at 80°C.
As can be seen in Figs. 4.1.11 and 4.1.12, it was found that the general
tendency for the RH dependence of $R_{\text{micro,Pt}}$ and $R_{\text{mem}}$ was almost the same for both
hydrogen and oxygen. As the membrane (25 $\mu$m) was much thicker than the ionomer,
the value of $R_{\text{mem}}$ was much larger than that of $R_{\text{micro,Pt}}$. Moreover, $R_{\text{mem}}$ for both
hydrogen and oxygen increased with a lower RH and this tendency was more evident for
oxygen. These trends agree with the results obtained by gas chromatography [20].

However, the difference in gas species is not that simple. While the ratio of
$R_{\text{mem}}$ for hydrogen to that for oxygen was approximately double, the ratio of $R_{\text{micro,Pt}}$ was
over 10 times greater. The ratio of the permeability of the membrane mentioned in the
literature is at most three times [20,21]. This suggests that the oxygen transport
resistance of the ionomer was particularly high for some reason. It has been reported in
other studies that the interfacial resistance of a Nafion® thin film for oxygen dissolution
is markedly high [6,22]. However, it is not clear that such a high interfacial resistance is
an inherent property of the Nafion® thin film. Even if it is, the difference between
hydrogen and oxygen is still unclear. Pt electrodes and the Nafion® thin film (or the
ionomer) were used in the other works as they were used in this study. Altogether, the
results could also be interpreted as indicating that the interaction between the Nafion®
thin film and the electrodes produced the difference.

One possible mechanism is that the strong interaction between the ionomer
and Pt can exist in the case of the ionomer and vary the former’s physical properties,
resulting in lower permeability, especially for oxygen. The interaction between Pt and
side-chains of the Nafion was identified using Pt single crystals [23]. Apart from the Pt
catalyst layer on the electrodes, the possibility that the interaction between the ionomer
and functional groups on the carbon supports has a significant influence on ionomer
properties has been reported based on both experimental [24,25] and computational [26]
results. Recent studies based on molecular dynamics conducted by Borges et al. [27,28]
suggested that the structure of the ionomer strongly depends on the hydrophilicity of
the substrate. According to their calculation, the side-chains of the ionomer should
points towards Pt because Pt is hydrophilic. If so, the strong interaction could exist even
in the catalyst layer. To obtain further understanding, controlling the hydrophilicity of
the surface, for instance, changing Pt concentration in the catalyst or applying more
hydrophobic or hydrophilic supports could be useful. While not contradicting the
literature [6,22], the difference between hydrogen and oxygen is still not well explained.
Another possible mechanism is that the adsorption of the ionomer can reduce $S^{\text{ff}}$, and
this effect could be significant for oxygen. Although it is reported that the potential of
zero total charge (pztc) of Pt is around 0.25 - 0.3 V [29,30], a certain amount of the
ionomer could adsorb on Pt, considering the under potential deposition of protons. Therefore, this second mechanism possibly occurs even in the low potential region where the limiting current density was observed. Moreover, Nafion® adsorption reportedly suppresses both HOR [18] and ORR [23,31-33], though the impact on these reactions is not fully understood. Considering these points, the latter mechanism is more likely to occur. Further investigation is necessary to verify these hypotheses.

Aside from the interaction between the ionomer and Pt surface, the counter flux of water may cause the difference seen between the different gas species. In the case of oxygen, water produced by ORR has to go out from the interface, though that is not true for hydrogen. In the case of the membrane, this should not matter because ORR occurs in the catalyst layer. Additionally, the amount of product water is too small relative to the total system volume to produce counter flux in the system. Although it may complicate the analysis, this should be taken into account for a better understanding of gas transport phenomena in the catalyst layer, in particular transport through the ionomer.

4.1.4. Conclusions

A convenient method has been newly developed for evaluating gas transport resistance, using gas crossover. It is applicable to lower proton conductive samples and conditions because it involves extremely low limiting current density. $R_{C1}$ and $R_{\text{micro,Pt}}$ for hydrogen and oxygen were analyzed with the method and an equivalent circuit model. A comparison of the HOR limiting current density with and without inert gas flow suggested that the decrease in HOR current at a high potential was mainly due to mass transfer loss caused by the loss of $S^{\text{eff}}$ and not by the loss of inherent Pt activity. For hydrogen, this method makes it possible to evaluate the potential dependence of $S^{\text{eff}}$ for the electrochemical reactions rather than the ECA determined by proton adsorption in the low potential region.

The RH dependence of $R_{\text{micro,Pt}}$ was investigated for hydrogen and oxygen with the new method. $R_{\text{micro,Pt}}$ increased for both hydrogen and oxygen with a lower RH and the impact of RH was larger for oxygen. These trends correspond to the results obtained for the membrane by both electrochemical and non-electrochemical methods. $R_{\text{micro,Pt}}$ for oxygen was over 10 times larger than that of hydrogen, while the ratio of $R_{\text{mem}}$ was about 2-3 times greater. The interaction between the ionomer and Pt was probably the main cause of this difference. Though there is still room for further investigation, two hypotheses were suggested. One possible mechanism is that the strong interaction
between the ionomer and Pt can vary the physical properties of the former and result in lower oxygen permeability. Another possible mechanism is that Nafion® adsorption can reduce $S^e$ for electrochemical reactions, in particular for ORR. Aside from the interaction, the counter flux of water produced by ORR could also suppress mass transport through the ionomer.
References

[23] R. Subbaraman, D. Stremcik. A. P. Paulikas, V. R. Stamenkovic, N. M. Markovic,
4.2. Gas transport inside and outside carbon supports of catalyst layers for PEM fuel cells

4.2.1. Introduction

As mentioned in Chapter 1, according to a U.S. DOE report, Pt accounts for about a quarter of the total fuel system cost [1]. The most effective measure for this issue is to reduce the loading of the Pt noble metal and to use it more effectively.

In recent years, various core-shell catalysts have been researched to reduce Pt usage by replacing the core of a Pt particle, which does not directly contribute to electrochemical reactions, with other materials such as Au, Pd, and other metals or alloys [2,3]. Another expected benefit of replacing the core is the improvement of area-specific activity. This kind of approach is focused on the catalyst itself, while, on the other hand, the modification of catalyst supports also contributes to improving electrochemical reactions. Carbon supports with high surface areas (HSA carbon) usually have high electrochemical surface areas (ECA), resulting in high mass-specific activity [4,5], although they also result in poorer proton conductivity in the catalyst layer [6-8]. Moreover, they may also have poorer durability against both carbon corrosion [9,10] and Pt dissolution [11,12], due to the instability of carbon and high roughness and smaller Pt particle size.

Even though they may have negative repercussions with respect to proton conduction and durability, HSA carbon supports look promising because they are useful in designing the catalyst layer microstructure as well as in increasing the ECA. HSA carbon usually has numerous primary pores of several nm in diameter, and Pt can be deposited inside the pores, resulting in higher ECA. In the previous chapters, it was suggested that the ionomer cannot penetrate into the primary pores of the carbon support [6-7,13]. This is also substantiated by simulations based on coarse-grained molecular dynamics [14,15]. Since the ionomer is not present inside the primary pores, the ionomer coverage on Pt strongly depends on the presence of the primary pores, as indicated by an in-situ analysis of ionomer coverage on Pt [13]. Although Pt particles inside the primary pores are not in contact with the ionomer, they could be electrochemically active because water condensed in the primary pores could contribute to proton transport from the ionomer to the Pt particles.

A recent study indicated that the oxygen reduction activity of Pt located inside the primary pores is higher than that of Pt located outside the pores and covered with the ionomer [16]. However, it is still controversial whether the effectiveness of Pt in the
primary pores is as good as or better or worse than that located outside the pores. That is because since there are no effective methods of evaluating the transport property of reactants towards Pt inside and outside the primary pores separately. It is important to understand the transport property of reactants towards Pt inside and outside the carbon primary pores separately in order to use the precious Pt catalyst effectively.

Among various phenomena occurring in the catalyst layer, gas transport is an issue of concern because gas transport resistance, $R_{gas}$, increases with lower Pt loading [17]. I established a method for evaluating $R_{gas}$ in the catalyst layer using gas crossover and analyzed the phenomenon (see the previous section) [18]. As a result, gas transport resistance that takes place towards Pt on a micro scale was successfully identified from the overall resistance. The method, however, did not enable us to separate $R_{gas}$ for Pt inside the primary pores, $Pt_{in}$, from that for Pt on the outer surface of the support, $Pt_{out}$. I also established an in-situ technique for analyzing ionomer coverage (see Chapter 3) [13]. Under a certain condition in the analysis process, only Pt located outside the primary pores and covered with the ionomer was activated. In that condition, it is likely that the electrochemical and mass transport properties of $Pt_{in}$ and $Pt_{out}$ can be separately evaluated. In this section, I applied the evaluation method for $R_{gas}$ to the catalyst layer in which only $Pt_{in}$ was deactivated by CO adsorption. That made it possible to evaluate the gas transport resistance of the reactant towards Pt inside and outside the primary pores separately.

4.2.2. Experimental

*Preparation of MEA*

Table 4.2.1 shows the membrane electrode assembly (MEA) specifications used in this study. Two catalyst inks were prepared respectively by mixing Pt black (manufactured by TKK, Japan) with the Nafion® ionomer dispersion (D2020, EW1000, DuPont), and Pt/C based on a porous carbon support (catalyst: 45 wt. %) with the Nafion® ionomer dispersion so that the weight ratio of the ionomer content was 0.17 relative to the Pt black and 0.9 to the carbon support. In order to investigate $R_{gas}$ in the primary pores, a carbon support having numerous primary pores was used.
Table 4.2.1. Specifications of the MEA.

<table>
<thead>
<tr>
<th></th>
<th>Counter and reference electrodes</th>
<th>Working electrode (Pseudo catalyst layer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Pt black</td>
<td>Pt/C (45 wt. %)</td>
</tr>
<tr>
<td>Carbon support</td>
<td>-</td>
<td>Porous carbon black</td>
</tr>
<tr>
<td>Loading</td>
<td>0.6 mg·Pt cm⁻²</td>
<td>0.15 mg·C cm⁻²</td>
</tr>
<tr>
<td>Ionomer</td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
<td>Nafion® (D2020, EW1000, DuPont)</td>
</tr>
<tr>
<td>Ionomer/Carbon weight ratio</td>
<td>0.17 (I/Pt)</td>
<td>0.9 (I/C)</td>
</tr>
<tr>
<td>Electrode area / cm²</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>GDL</td>
<td>Carbon Paper with MPL (25BCH, SGL Carbon)</td>
<td>Carbon Paper without MPL (TGP H120, Toray)</td>
</tr>
</tbody>
</table>

The anode side consisting of Pt black was fabricated on perfluorosulfonic acid (PFSA) square (72 mm on one side) membranes (Nafion® NR211, thickness = 25 μm) by a spray coating method and then dried for 30 min at 80°C to remove the organic solvent. The cathode side consisting of Pt/C was then fabricated on the other side and dried again. The membrane was masked with polyethylene naphthalate (PEN) films (Q51, 25 μm, Teijin-DuPont) having 10 cm² (vertical direction: 2 cm, horizontal direction: 5 cm) of open area on both sides beforehand so as not to create any gaps between the film and the catalyst layer. This was done because gas crossover through such gaps could affect the analysis, although its effect would probably be small. The film also provided reinforcement. Pt loadings of the anode and the cathode were 0.6 and 0.15 mg cm⁻², respectively. The anode layer would have been very thin if the Pt loading had been almost the same as on the cathode side because it did not contain a carbon support. Therefore, a higher Pt loading was applied on the anode side in order to prevent the gas diffusion layer (GDL) from attacking the membrane directly. The thickness of the catalyst layer was observed with a scanning electron microscope (SEM) and found to be around 2 μm.

GDLs with a microporous layer (25BCH, SGL Carbon) and without a microporous layer (TGP-H120, Toray) were used for the anode and cathode side, respectively. A GDL without a microporous layer was desirable for the cathode side in order to avoid affecting the measured gas transport resistance. The MEA was formed by assembling the GDLs on both sides of the catalyst coated membrane (CCM). The MEA was assembled in a single cell between bipolar plates with a straight flow field.
consisting of graphite and gaskets made of silicone rubber. The compression pressure was kept uniform by measuring it with pressure-sensitive paper (Prescale, Fuji Film).

**Experimental conditions**

To deactivate Pt, 1% CO gas balanced with N₂ was used. All the measurements using CO were carried out at 30°C to enhance CO adsorption. As it is difficult to control RH just by heating a bubbler tank at such low temperature, it was controlled by mixing dry gas and the wet gas that goes through the bubbler. The flow system used in this study is illustrated in Fig. 4.2.1. The flow rates of the dry and wet gases were controlled with mass flow controllers to prepare the specified RH condition in Table 4.2.2 and then mixed in a mixer tube right before entering the cell. An HZ-3000 electrochemical measurement system (Hokuto Denko, Japan) was used to perform the electrochemical measurements.

![Fig. 4.2.1. A schematic diagram of the flow system used in this study.](image)

**Table 4.2.2. Test conditions for gas transport resistance measurements.**

<table>
<thead>
<tr>
<th>Anode gas</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode gas</td>
<td>N₂ (with or without flow) or 1% CO balanced with N₂ (for CO adsorption)</td>
</tr>
<tr>
<td>Back pressure</td>
<td>Ambient</td>
</tr>
<tr>
<td>Cell temperature / °C</td>
<td>30</td>
</tr>
<tr>
<td>Humidity for CO treatment / % RH</td>
<td>5, 20, 40, 70</td>
</tr>
<tr>
<td>Humidity for gas transport measurement / % RH</td>
<td>90</td>
</tr>
<tr>
<td>Anode flow rate / NL min⁻¹</td>
<td>1.0</td>
</tr>
<tr>
<td>Cathode flow rate / NL min⁻¹</td>
<td>1.0 (with flow)</td>
</tr>
</tbody>
</table>
The entire process for analyzing gas transport resistance in the primary pores will be explained in the following section. The whole experiment was conducted according to the procedure shown in Fig. 4.2.2.

|   | 1. Gas transport resistance measurement  |   |
|   | (w/o CO treatment, at 90% RH)          |   |
|   | 2. Purge H₂O from the system           |   |
|   | (dry H₂ and N₂ supply)                 |   |
|   | 3. CO supply to the cathode            |   |
|   | (at 5, 20, 40, 70% RH)                 |   |
|   | 4. Partial CO oxidation                |   |
|   | (at 5, 20, 40, 70% RH)                 |   |
|   | 5. Gas transport resistance measurement |   |
|   | (w/ CO treatment, at 90%RH)            |   |
|   | 6. Remaining CO oxidation              |   |
|   | (at 90%RH)                            |   |

Fig. 4.2.2. The experimental procedure for analyzing gas transport resistance in the primary pores of a carbon support.

**4.2.3. Method**

*Measurement of gas transport resistance*

Gas transport resistance in the catalyst layer, $R_{CL}$, for hydrogen was measured under the conditions shown in Table 4.2.2. $R_{CL}$ was obtained from the limiting current due to oxidation of hydrogen that leaked through the membrane from the anode side with and without cathode gas flow. Although the details of the gas transport resistance measurement were described in our previous study [18], the method is briefly explained here. Firstly, pure H₂ and N₂ were fed to the counter (and reference) and working sides respectively at 30°C. After a certain waiting period, the potential was held at 0.95 V vs. RHE for 10 minutes and then set at 0.9 V for 5 minutes. Potential step voltammetry was conducted from 0.9 V to 0.2 V in 0.1 V increments at intervals of 5 minutes. The
valves on the working side were then closed. Potential step voltammetry was conducted under a condition without inert gas flow to the working side in the same way as in the case with inert gas flow. The measured current density as a function of the potential is shown in Fig. 4.2.3. The plots were obtained by averaging the data of the last 20 seconds (or 20 seconds in a plateau region when the data fluctuated) at each holding potential.

![Graph showing current density with and without inert gas flow as a function of potential](image)

Fig. 4.2.3. Current density with and without inert gas flow on the cathode side as a function of potential at 90% RH and 30°C (without CO treatment).

With the inert gas flow, the current density increased with decreasing potential and then saturated, while it did not depend on the potential without the inert gas flow. The same tendency was seen in Ref. 18. It was concluded that the depression of the HOR current at a high potential is mainly caused by the lower mass transport stemming from the reduction of the effective Pt surface area due to Pt oxidation. A comparison of the two curves in Fig. 4.2.3 indicates that the current density without the inert gas flow was always higher than that with it regardless of the potential. The current density obtained without the inert gas flow can be regarded as the hydrogen crossover current since hydrogen does not escape from the system and all of the hydrogen is consumed on the working side.
The current density can be converted to the flux of hydrogen by the equation,

\[ N = \frac{I}{nFA} \tag{4.2.1} \]

where \( F \) and \( A \) express the Faraday constant and the geometric surface area for gas crossover, respectively. The total flux of crossover hydrogen, \( N_{\text{total}} \), was obtained from the current density without the inert gas flow. Under the condition with the inert gas flow to the working side, a certain amount of hydrogen exits the system through the GDL. Therefore, the difference between the current density with and without inert gas flow was derived as the flux through the GDL, \( N_{\text{GDL}} \), under the condition with the inert gas flow. \( N_{\text{GDL}} \) was calculated from the current densities at 0.3 V, as the minimum difference was observed at 0.3 V. Under the condition with the inert gas flow, the flux of hydrogen consumed in the catalyst layer, \( N_{\text{CL}} \), and that of hydrogen not consumed in the catalyst layer, \( N_{\text{GDL}} \), are determined by the gas transport resistance in the catalyst layer, \( R_{\text{CL}} \), and GDL, \( R_{\text{GDL}} \). Therefore, \( R_{\text{CL}} \) can be obtained from the equation below.

\[ \frac{N_{\text{CL}}}{N_{\text{GDL}}} = \frac{R_{\text{GDL}}}{R_{\text{CL}}} \tag{4.2.2} \]

\( R_{\text{GDL}} \) for hydrogen in a H\(_2\)/N\(_2\) system was evaluated as 0.28 s m\(^{-1}\) at 80°C by the method shown in Ref. 19. According to the Chapman-Enskog equation [20], binary diffusion coefficients are proportional to temperature to the 3/2nd power. Therefore, \( R_{\text{GDL}} \) should be proportional to temperature to the 2/3rd power and was calculated as 0.33 s m\(^{-1}\) kPa\(^{-1}\).

\( R_{\text{CL}} \) can be expressed as a parallel circuit consisting of gas transport resistance in the through-plane direction, which corresponds to gas transport resistance in the macro pores of the catalyst layer, \( R_{\text{macro}} \), and gas transport resistance towards Pt, \( R_{\text{micro}} \), as shown in Fig. 4.2.4. \( R_{\text{macro}} \) was calculated from the diffusion coefficient in the macropores, which was estimated from the macropore size and the length of the segments (divided into 100 in the through-plane direction) in the equivalent circuit model. The details of the calculation for \( R_{\text{macro}} \) are given in Ref. 18. \( R_{\text{macro}} \) at 30°C was calculated as \( 3.85 \times 10^{-2} \) s m\(^{-1}\). \( R_{\text{micro}} \) was obtained from \( R_{\text{CL}} \) and \( R_{\text{macro}} \) after solving the equivalent circuit model in Fig. 4.2.4.
Fig. 4.2.4. An equivalent circuit model for gas transport in the MEA and a schematic diagram of the flux for each component.

**CO adsorption**

After gas transport measurement, dry H₂ and pure N₂ were fed to the anode and the cathode until the cell resistance became saturated at a high level to purge water vapor from the MEA. The RH on both sides was then set at 5% and the gases continued to flow for some time. Then, 1% CO gas balanced with N₂ was supplied to the cathode side while holding the cathode potential at 0.05 V vs. RHE and monitoring the current. After the current reached almost zero, CO in the whole cathode system, aside from the cell, was purged with N₂ for at least 15 minutes with the cathode valves next to the cell closed. After that, N₂ was supplied to the cathode to purge the remaining CO in the cell. In this way, CO was adsorbed on and deactivated the entire Pt surface. This process is the same as that used in our previous study [18].

**Partial CO oxidation**

To deactivate only Ptₐₘᵢ, CO was partially oxidized under 5% RH. After CO adsorption, the cathode potential was held at 0.3 V for 3 minutes and then stepped to 1.0 V and kept for 12 minutes. In this way, CO adsorbed only on Ptₐₘᵢ was oxidized as described in Ref. 13. The Pt oxidation charge was estimated from the background voltammetry. The CO oxidation charge, $Q_{CO}$, was then obtained by subtracting the Pt oxidation charge and the hydrogen oxidation charge approximated from the current density observed in the last few minutes of the chronoamperogram. As a result, the ECA was determined to be 7.05 m² g⁻¹Pt (Fig. 4.2.5) using $Q_{CO}$ and a charge to the Pt surface area conversion factor of 420 μC cm²Pt. CO partial oxidation was conducted at 20, 40 and 70% RH in the same way as at 5% RH. At 40 and 70% RH, however, CO oxidation...
was performed by cyclic voltammetry instead of potential step voltammetry used for 5 and 20% RH. As shown in Fig. 4.2.5, the ECA significantly increased with increasing RH.

![Graph showing ECA as a function of RH](image)

**Fig. 4.2.5.** Electrochemical surface area obtained by CO stripping voltammetry at 30°C as a function of RH.

In order to investigate the contribution of water to the triple-phase boundary under the low RH condition, water adsorption isotherms for the catalyst and the carbon support were evaluated by means of a volumetric method using an automatic vapor adsorption apparatus (Belsorp 18 Plus-HT, Nihon Bell) at 30°C. As the atmosphere on the cathode side was H₂/N₂ because of crossover hydrogen, the Pt surface would have been reduced. Therefore, the samples were exposed to hydrogen at 100°C for 15 minutes before preconditioning (evacuation at 100°C for over an hour). After the preconditioning, the temperature was lowered to 30°C, and the water isotherm measurement was carried out. The obtained isotherms are shown in Fig. 4.2.6. As shown in the figure, the amount of water adsorbed at 5% RH was very small: less than 5.4 mg g⁻¹carbon for the catalyst and less than 2.4 mg g⁻¹carbon for the carbon support. The amount of adsorbed water was higher with Pt. This is probably due to the high wettability of Pt and indicates that water adsorbs around Pt well at 5% RH. However, the important point in the analysis is whether the water contributed to the triple-phase boundary. Though the
contribution of adsorbed water to the triple-phase boundary should depend not only on the amount of water but also on the structure of the boundary (thickness of water, whether the adsorbed water is involved in the proton network, etc.), such a small amount of water might not contribute to the triple-phase boundary. Consequently, it is safe to say that only the Pt particles deposited outside the primary pores, which were covered with the ionomer, contributed to the ECA obtained at 5% RH. Accordingly, $P_{an}$ was gradually activated with increasing RH resulting in an increase in ECA.

Fig. 4.2.6. Water adsorption isotherms for a catalyst and a carbon support at 30°C with hydrogen exposure.

Measurement of gas transport resistance after CO treatment

After partial CO oxidation, gas transport resistance was measured again at 90% RH. This time, however, the potential was stepped from 0.2 to 0.4 V in 0.05 V increments at intervals of 5 minutes so as not to oxidize the remaining CO. The relation between the potential and the current density is shown in Fig. 4.2.7. The current density with the inert gas flow was higher than that without it just as in the case without the CO treatment. In Fig. 4.2.7, it is clear that the difference between current densities with and without the inert gas flow was much larger than that without the CO treatment in Fig. 4.2.3. Despite this, almost the same current density was observed without the inert gas flow. This indicates that $R_{ct}$ increased due to the CO treatment.
$R_{CL}$ and $R_{micro}$ were calculated in the same manner as in the case without the CO treatment.

![Graph](image)

Fig. 4.2.7. Current density with and without inert gas flow on the cathode side as a function of potential at 90% RH and 30°C (with CO treatment).

**Oxidation of remaining CO**

To oxidize the remaining CO, CO stripping voltammetry was carried out under 90% RH. After the measurement of gas transport resistance, the cathode potential was scanned between 0.02 and 0.95 V vs. RHE at a scan rate of 5 mV s⁻¹ for five cycles. The quantity of electricity attributable to CO oxidation, $Q_{CO}$, was calculated from the difference in the voltammograms.

### 4.2.4. Results and discussion

**Gas transport resistance in primary pores**

The estimated $R_{CL}$ and $R_{micro}$ with and without the CO treatment are summarized in Table 4.2.3.
Table 4.2.3. Gas transport resistances and ECA for different CO treatment conditions.

<table>
<thead>
<tr>
<th>RH conditions for CO treatment / %</th>
<th>( R_{\text{CL}} / \text{s m}^{-1} )</th>
<th>( R_{\text{micro}} / \text{s m}^{-1} )</th>
<th>ECA / ( \text{m}^2 \text{g}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>29.6</td>
<td>2992</td>
<td>7.05</td>
</tr>
<tr>
<td>20</td>
<td>7.36</td>
<td>743</td>
<td>30.3</td>
</tr>
<tr>
<td>40</td>
<td>5.82</td>
<td>588</td>
<td>44.1</td>
</tr>
<tr>
<td>70</td>
<td>5.06</td>
<td>511</td>
<td>58.4</td>
</tr>
<tr>
<td>Without CO treatment</td>
<td>4.26</td>
<td>430</td>
<td>63.2</td>
</tr>
</tbody>
</table>

A comparison of \( R_{\text{CL}} \) and \( R_{\text{micro}} \) with and without the CO treatment shows that both values increased significantly with the CO treatment. This is because the surface of the Pt particles that were deposited inside the primary pores was deactivated by CO and resulted in an increase in gas transport resistance towards Pt. Based on the results obtained with and without the CO treatment, \( R_{\text{micro}} \) can be deconvoluted into two transport resistances (one corresponding to gas transport resistance towards Pt inside the primary pores, \( R_{\text{micro, in}} \), and the other corresponding to gas transport resistance towards Pt outside the pores, \( R_{\text{micro, out}} \)) as shown in Fig. 4.2.4, when a porous carbon support is used. The relationship of the three can be simply expressed as

\[
R_{\text{micro}} = \left( \frac{1}{R_{\text{micro, in}}} + \frac{1}{R_{\text{micro, out}}} \right)^{-1}
\]

As mentioned before, with the CO treatment at 5% RH, all Pt particles inside the primary pores would be rendered inactive by adsorbed CO, and only Pt particles outside the primary pores would be active. In other words, \( R_{\text{micro, in}} \) can be considered to be infinite after the CO treatment at 5% RH in Eq. (4.2.3). Therefore, \( R_{\text{micro, out}} \) is the same as \( R_{\text{micro}} \) after the CO treatment at 5% RH, and was estimated to be 2992 s m\(^{-1}\). On the other hand, both \( R_{\text{micro, in}} \) and \( R_{\text{micro, out}} \) are effective without the CO treatment. Therefore, can be calculated with \( R_{\text{micro}} \) without the CO treatment (430 s m\(^{-1}\)) and \( R_{\text{micro, out}} \) (2992 s m\(^{-1}\)). As a result, \( R_{\text{micro, in}} \) was found to be 502 s m\(^{-1}\).

Our previous study revealed that \( R_{\text{micro}} \) was inversely proportional to the total effective Pt surface area due to the increase in local gas flux near the Pt surface as the Pt surface area decreased [17,18]. In order to subtract the influence of ECA, the gas transport resistance per unit Pt surface area, \( r_{\text{micro}} \), was calculated from the volumetric Pt surface area. The volumetric Pt surface area was obtained from the ECA, the Pt loading, and the average thickness of the catalyst layer. \( r_{\text{micro}} \) for Pt outside the primary pores, \( r_{\text{micro, out}} \), was obtained from \( R_{\text{micro, out}} \) and the volumetric roughness factor for \( P_{\text{out}} \).
Likewise, $r_{\text{micro}}$ for Pt inside the primary pores, $r_{\text{micro,in}}$, was also obtained. A comparison of the two shows that $r_{\text{micro,in}}$ was slightly larger than $r_{\text{micro,out}}$ ($r_{\text{micro,in}}/r_{\text{micro,out}}$ was 1.34). This implies that Pt outside the primary pores was more effective than that deposited inside the pores in terms of mass transport.

Gas transport resistance with different CO treatments

To understand the trend described in the preceding section, permeability, $P$, of hydrogen through water and a Nafion® film was compared. Permeability is a function of flux and can be expressed as

$$N = P \frac{dC}{dx}$$

(4.2.4),

where $dx$ denotes the permeation length. As the flux of hydrogen through the Nafion® membrane was already obtained as $N_\text{total}$ in Subsec. 4.2.3, the permeability through the film can be calculated with Eq. (4.2.4) and $N_\text{total}$. In this case, $dx$ represents the thickness of the Nafion® membrane of the MEA (25 $\mu$m) and $dC$ is the differential partial pressure of hydrogen between the anode and the cathode. $dC$ can be simply obtained by subtracting the water vapor pressure from the total pressure (101.3 kPa). According to the Antoine equation, the saturated vapor pressure at 30°C is 4.22 kPa, therefore, the water vapor pressure at 90% RH is 3.80 kPa. As a result, $dC$ was estimated to be 97.5 kPa. With these values and Eq. (4.2.4), the permeability of hydrogen through the membrane was obtained as $1.31 \times 10^{-13}$ mol cm cm$^{-2}$ s$^{-1}$ kPa$^{-1}$. Verhallen et al. investigated the permeability of a variety of gases through water [21]. According to their results, hydrogen permeability through water at 30°C was $4.15 \times 10^{-13}$ mol cm cm$^{-2}$ s$^{-1}$ kPa$^{-1}$. This is larger than that of the Nafion® membrane ($P_\text{water}/P_\text{Nafion}$ was about 3.2). Although the permeability of hydrogen through a bulk Nafion® membrane may be different from that of the ionomer, it is probably smaller than that of water. Despite this, the transport resistance through the primary pores, in other words, that through the water, was larger than that through the ionomer. Presumably, the difference in the diffusion length caused this different trend.

To investigate the influence of the diffusion length further, gas transport resistance was measured for different ECA. As mentioned earlier, it is possible to control the ECA by changing the RH conditions for the CO treatment. The same series of experiments described in 4.2.3 was conducted with different RH conditions for the CO treatment. The values obtained for $R_{\text{CL}}$ and $R_{\text{micro}}$ are shown in Table 4.2.3. As seen in the table, $R_{\text{CL}}$ and $R_{\text{micro}}$ strongly depended on ECA. Although the effectiveness of Pt inside the primary pores was not as high as that of Pt outside the pores, increasing the
total ECA did improve overall gas transport in the catalyst layer.

Under a condition of RH less than 90% and greater than 5%, Pt particles inside the primary pores were partially active and all Pt particles outside the primary pores were active. Therefore, from the $R_{\text{micro}}$ measured at different RH levels, $R_{\text{micro, in}}$ can be deconvoluted further into $R_{\text{micro, in}}$ at the Pt surface that becomes active in different RH ranges of $20 \geq x > 5\%$, $40 \geq x > 20\%$, $70 \geq x > 40\%$, and $90 \geq x > 70\%$. Therefore, $R_{\text{micro, in}}$ in the equivalent circuit model in Fig. 4.2.4 was divided into five parts as shown in Fig. 4.2.8. Each part was defined as follows: $R_1$ that is covered with the ionomer and becomes active at 5% RH and below, $R_2$ that becomes active at $20 \geq x > 5\%$ RH, $R_3$ that becomes active at $40 \geq x > 20\%$ RH, $R_4$ that becomes active at $70 \geq x > 40\%$ RH, and $R_5$ that becomes active at $90 \geq x > 70\%$ RH.

In Fig. 4.2.8, $R_1$ corresponds to $R_{\text{micro, out}}$ mentioned above. $R_{\text{micro, in}}$ is the combination from $R_2$ to $R_5$. $R_{\text{micro}}$ with the CO treatment at RH of 20% can be expressed as a parallel circuit consisting of $R_1$ and $R_2$. Therefore, $R_2$ can be calculated from $R_1$ and $R_{\text{micro}}$ with the CO treatment at RH of 20%. When $R_3$ is obtained, $R_5$ becomes obtainable. $R_4$ and $R_5$ can be calculated in the same way. The calculated values are summarized in Table 4.2.4. ECA values for $R_1$ to $R_5$ were obtained from the difference between the plots in Fig. 4.2.5 and are shown in Table 4.2.4. Using these ECA values, $R_1$ to $R_5$ were standardized per unit of Pt surface area in each segment ($r_1$ to $r_5$). Transport resistances through the primary pores that were filled with water under different RH levels, $r_2$ to $r_5$, were compared with $r_1$, representing the transport resistance through the ionomer, and summarized as a ratio to $r_1$ in Table 4.2.4. From $r_2$ to $r_5$, the ratio increased with an increasing number. According to the capillary condensation theory, the smaller the pore size is, the lower the RH becomes at which capillary condensation takes place. Therefore, the increase in $r$ from $r_2$ to $r_1$ implies that the larger pores, which were filled with water at higher RH, could have a longer diffusion length, while the smaller pores, which were filled with water at lower RH, could have a shorter diffusion length.
Fig. 4.2.8. An equivalent circuit for $R_{\text{micro}}$ expressed as a parallel circuit consisting of five resistances which are active at different RH conditions. $R_1$ becomes active at 5% RH and below (equivalent to $R_{\text{micro, out}}$), $R_2$ becomes active at $20 ≥ x > 5$% RH, $R_3$ becomes active at $40 ≥ x > 20$% RH, $R_4$ becomes active at $70 ≥ x > 40$% RH and $R_5$ becomes active at $90 ≥ x > 70$% RH.

Table 4.2.4. Gas transport resistances towards Pt that is active under different RH conditions.

<table>
<thead>
<tr>
<th>Designated number of the resistance in Fig. 4.2.8 and RH at which Pt becomes active</th>
<th>$R$ / s m$^{-1}$</th>
<th>ECA / m$^2$ g$^{-1}$</th>
<th>$r$ / s m$^{-1}$</th>
<th>ratio to $r$ / *</th>
<th>Estimated diffusion length / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, any RH</td>
<td>2992</td>
<td>7.05</td>
<td>321</td>
<td>-</td>
<td>2*</td>
</tr>
<tr>
<td>2, &gt;5% RH</td>
<td>989</td>
<td>23.3</td>
<td>350</td>
<td>1.09</td>
<td>6.9</td>
</tr>
<tr>
<td>3, &gt;20% RH</td>
<td>2807</td>
<td>13.8</td>
<td>588</td>
<td>1.83</td>
<td>11.6</td>
</tr>
<tr>
<td>4, &gt;40% RH</td>
<td>3906</td>
<td>14.3</td>
<td>846</td>
<td>2.64</td>
<td>16.7</td>
</tr>
</tbody>
</table>

* Assumed to be the same as in Ref. [6].

As the relation between flux and transport resistance can be expressed as

$$N = \frac{dC}{R}$$ \hspace{1cm} (4.2.5),

Eqs. (4.2.4) and (4.2.5) yield

$$\frac{1}{R} = \frac{P}{dx}$$ \hspace{1cm} (4.2.6).

According to Eq. (4.2.6), it is possible to estimate the average diffusion lengths for Pt inside the primary pores from gas permeability through water and the ionomer and the gas transport resistances in Table 4.2.4. Since the actual transport property inside the primary pores would depend on the pore geometry, the simple estimation made with Eq. (4.2.6) would not provide precise values, though it might be useful for a qualitative analysis. For hydrogen, the difference between the transport resistance through the ionomer and that through the Nafion® membrane was not so large [18]. Therefore, $P_{\text{water}}$
and $R_{\text{ion}}$ obtained above might not be inappropriate. The thickness of the ionomer is also necessary for the estimation. The thickness was previously estimated at about 2 nm for a porous Ketjen black [6], although the carbon support was different from the one used in this study. The diffusion lengths were roughly estimated under the assumption that the diffusion length through the ionomer was the same as the ionomer thickness (Table 4.2.4). The results revealed that one of them reached over 15 nm. To take into account the size of the carbon support, the catalyst was observed with a scanning transmission electron microscope (HD-2700, Hitachi High-Technologies Corporation). STEM images are shown in Fig. 4.2.9. While many Pt particles were observed in the TEM image, the number of Pt particles in the SEM image was much less. The difference in these images shows that the majority of the Pt particles were deposited inside the primary pores. From these images, the size of the carbon primary particles was estimated to be around 30~40 nm. Considering that the paths in the primary pores would not be straight but tortuous to some extent, the diffusion lengths in Table 4 could be possible. However, a non-uniform Pt distribution would cause an error in the values in the table. For example, pores having many Pt particles would be filled with water from a lower RH level due to the high wettability of Pt compared with other pores even of the same size. In that case, the former pores would be identified as a lower number of $r$, resulting in a higher transport resistance of $r$. Likewise, pores having fewer Pt particles would be identified as a higher number of $r$, resulting in a lower transport resistance of $r$. Although the Pt distribution in Fig. 4.2.9 looked uniform, it was difficult to quantify it. To examine this effect, further investigation is necessary.

Fig. 4.2.9. (Left) scanning electron microscope and (right) transmission electron microscope images of Pt/C catalyst.
Only $r_5$ was smaller than $r_1$ and resulted in a shorter diffusion length than in the other cases. As mentioned before, pores that are filled with water at a high RH condition should have a larger diameter compared with those that are filled with water at a low RH condition [22]. Accordingly, Pt corresponding to $r_5$ could be located on the outer surface of the carbon support or in relatively shallow pores as illustrated in Fig. 4.2.10. In the previous chapters (Chapter 2 and 3), the influence of the ionomer content on the ionomer coverage on carbon supports was investigated. The results revealed that the ionomer coverage was constant regardless of the ionomer content as long as the ionomer/carbon weight ratio was over 0.9 [6, 7]. Accordingly, it is presumed that the entire outer surface was covered with the ionomer. However, the ionomer content might not have been sufficient to cover the entire outer surface of the carbon support in this study. If it was not, Pt corresponding to $r_5$ must have had a shorter diffusion length. The proton path to Pt located on the outer surface and not covered with the ionomer could have been formed by water condensation. As defined above, Pt corresponding to $r_5$ does not contribute to electrochemical reactions at 70% RH and less, but it does at 90% RH. According to Ref. 23, mesopores of activated carbons located on the outer surface of the carbon support are filled with water at around 90% RH due to capillary condensation. These two results correspond well. Further investigation with different ionomer contents should be useful in understanding $r_5$ in more detail. The present analysis implies that the effectiveness of Pt inside the primary pores of the carbon support strongly depends on the pore geometry. Therefore, controlling the pore geometry suitably is indispensable for making the most effective use of Pt.

Fig. 4.2.10. A schematic representation of different primary pores corresponding to those from $R_1$ to $R_6$. 
4.2.5. Conclusions

A new method of evaluating gas transport resistance inside the primary pores of a carbon support in a catalyst layer has been developed using a partial CO covering technique. After gas transport resistance in the catalyst layer, $R_{\text{CL}}$, and gas transport resistance towards the Pt surface, $R_{\text{micro}}$, for hydrogen were measured in the same way as in the previous section (Sec. 4.1.) [18], 1% CO gas balanced with $N_2$ was supplied to the working electrode to deactivate the whole Pt surface. To activate Pt particles outside the primary pores, CO was partially oxidized under a 5% RH condition at which only the Pt particles outside the primary pores and covered with the ionomer became active. After partial CO oxidation, Pt inside the primary particles was still inactive. The gas transport resistance was then measured and compared with that without partial CO oxidation. With partial CO covering, both $R_{\text{CL}}$ and $R_{\text{micro}}$ increased significantly. The main cause of the increase was the decrease of the effective surface area for the hydrogen oxidation reaction due to CO adsorption. The transport resistance towards Pt located inside and outside the primary pores was compared according to the unit Pt surface area ($r_{\text{micro}}$). It was found that $r_{\text{micro}}$ for Pt inside the primary pores was slightly larger than that for Pt outside the primary pores. This result indicates that Pt inside the primary pores is not as effective as Pt outside the pores. A comparison of hydrogen permeability through water and the Nafion® membrane showed that it was over three times more permeable through the former medium than through the latter. Despite that, transport resistance inside the primary pores was higher. This implies that the diffusion length through the primary pores was probably longer than the ionomer thickness.

Transport resistance inside the primary pores was investigated and evaluated in more detail for different ECA values that were controlled by changing the RH level for partial CO oxidation. Transport resistance was found for primary pores in which Pt became active at different RH levels. Pores that filled with water at higher RH showed higher transport resistance. This is probably because larger pores have a longer diffusion length. It suggests that the effectiveness of Pt inside the primary pores strongly depends on the pore geometry. Although increasing the total ECA by applying a porous support does improve overall gas transport, controlling the geometry of the primary pores of a carbon support suitably is indispensable for utilizing Pt more effectively.
References


Chapter 5 General conclusions
In this thesis, I developed the techniques for evaluating proton and gas transport resistances in catalyst layers and analyzed key parameters for the resistances with the techniques. In addition, I developed an in-situ technique for evaluating the microstructure of the catalyst layer such as ionomer coverage for Pt and carbon support. With the technique, I elucidated the relation between the microstructure and the key parameters for mass transport property.

The conclusions obtained in this study are summarized as follows:

1. From the study in Chapter 2, key parameters for proton transport in the catalyst layers were revealed. They are volume fraction, tortuosity and water adsorbability of the ionomer. Increasing the volume fraction of the ionomer would enhance proton transport in the catalyst layers. However, it would also suppress gas transport because the volume fraction of the pore in the catalyst layers, which works as gas transport path. The tortuosity of the ionomer was found to be a function of outer surface of the carbon support. In the case of pseudo catalyst layers consisting of a carbon support and the ionomer, the outer surface of the support can be estimated by evaluating the RH dependence of electric double layer capacitance ($C_{dl}$). In the case of actual catalyst layers which contain Pt, it can be estimated with the method developed in Chapter 3. Decreasing the outer surface of the support led lower tortuosity and yielded higher proton conductivity. Reducing the number of functional groups such as carboxyl groups on the carbon surface would also enhance proton transport because the interaction between the functional groups on the support and the ionomer brought about lower water adsorbability of the ionomer, resulting in lower bulk proton conductivity.

2. A noble in-situ technique for evaluating ionomer coverage was developed and explained in Chapter 3. The technique utilized $C_{dl}$ that is a function of the interfacial area between an electroconductor and an ionconductor. The validity of the technique was well examined by evaluating specific capacitance with different interfaces and investing water adsorption property of a porous carbon support and the electrocatalyst based on the carbon. With the new technique, estimating the ionomer coverage for Pt and carbon support became possible. As the result of the analysis, it was found that the ionomer cannot penetrate into primary pores of the porous carbon support although water can condense in the pore and work as electrolyte there. The technique can be used to validate the microstructure of optimized catalyst layers.
3. The study in *Chapter 4* revealed that increasing volumetric surface area of Pt in catalyst layers enhances gas transport. To achieve that, placing Pt particles in primary pores of a porous carbon support is preferable. However, the value of gas transport resistance inside the primary pores per Pt surface area was higher than that for Pt on the carbon outer surface. Considering the difference in the gas permeability through water and a bulk Nafton® membrane, it is inferred that the diffusion length in primary pores was remarkably longer than the average ionomer thickness. From these points of view, controlling the depth of the primary pores to be as shallow as possible is necessary for more effective use of Pt with increasing the primary pore volume in order to place Pt particles more in the pores.

From this study, I conclude that the optimized catalyst layer structure from the aspect of proton and gas transport is consisting of the electrocatalyst which meets the requirements i) with less (or no) functional groups at least on outer surface where the ionomer can contact with, ii) with numerous primary pores in which most of Pt locates and iii) the depth of the primary pores is as shallow as possible and the ionomer that does not fill the primary pores.
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List of publications

1. Analysis of proton transport in pseudo catalyst layers
   H. Iden, A. Ohma, K. Shinohara

2. Analysis of proton exchange membrane fuel cell catalyst layers for reduction of platinum loading at Nissan

3. Relationship among microstructure, ionomer property and proton transport in pseudo catalyst layers
   H. Iden, K. Sato, A. Ohma, K. Shinohara

4. An in situ technique for analyzing ionomer coverage in catalyst layers
   H. Iden, A. Ohma

5. Relationship between gas transport resistance in the catalyst layer and effective surface area of the catalyst
   H. Iden, S. Takaichi, Y. Furuya, T. Mashio, Y. Ono, A. Ohma

6. Gas transport inside and outside carbon supports of catalyst layers for PEM fuel cells
   H. Iden, T. Mashio, A. Ohma