X-ray Imaging and Numerical Simulation for Optimization of PEFCs with Advanced Materials

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ABSTRACT: Materials used for polymer electrolyte fuel cells (PEFCs) can affect transport phenomena in the PEFCs and resultant cell performance. The objective of this study is to clarify the relationship between advanced materials and transport phenomena. In this study, X-ray radiography of a PEFC under operating conditions was performed using the advanced materials used for a catalyst layer and a gas diffusion layer, respectively. Furthermore, a novel PEFC model considering electrochemical reaction and transport phenomena, which can reflect the effects of materials, was developed and a numerical simulation was performed for the optimization of PEFC design and performance. Parameter optimization based on the developed model was demonstrated.

KEY WORDS: polymer electrolyte fuel cells, catalyst layer, gas diffusion layer, transport phenomena, x-ray radiography, numerical simulation, parameter optimization

1. INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) are prospective energy devices for automotive use and distributed power supply. The PEFC is assembled by putting a membrane electrode assembly (MEA), which consists of the polymer electrolyte membrane (PEM) with the catalyst layers (CL) and the gas diffusion layers (GDL) on both sides, between separators as shown in Figure 1(a). Most of the typical materials today had been developed before the early 2000s and have been used. However, materials used for PEFCs still have several challenges. Recently, novel advanced materials for GDLs and CLs have been developed, respectively, to achieve higher cell performance and durability.

GDLs are fibrous porous layers, which are basically made from carbon fibers. This layer is a key component for the water management of PEFCs and one of the causes of high cost. Conventional GDLs are flat layers and separators with flow channels are placed outside them for gas supply. Recently, a novel GDL with flow channels (GDLFC^{+}), which contains flow channels and porous ribs inside itself, have been developed.[1-3] GDLFC^{+} is fabricated from relatively low-cost carbon material and can use flat separators without flow channels. Therefore, this advanced material has the potential for significant cost reduction. Furthermore, this material can provide superior performance. However, the mechanism that how GDLFC+ show higher cell performance is not clear. A fundamental understanding of

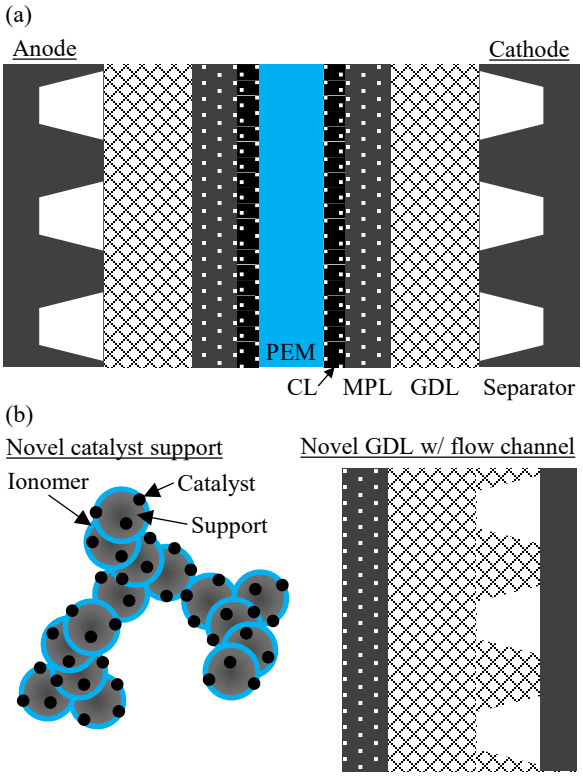

Fig. 1. Schematic diagrams of (a) PEFC and (b) advanced materials.

transport phenomena, especially focusing on water transport is required.

Pt nanoparticle catalysts supported on carbon black (Pt/C) are usually used in the CLs. However, there is a problem that the CLs deteriorate due to oxidative corrosion of the carbon supports. Pt loss simultaneously occurs with this corrosion and severe performance degradation is shown as the result. Pt supported on tin oxide (Pt/Nb-SnO_2) has been developed as an alternative material for the CLs.[4,5] This ceramic support shows not only high durability but also other superior characteristics such as high activity and characteristic ionomer adsorption properties. However, this ceramic support is more hydrophilic than carbon supports, and it is not clear how this characteristic affects the liquid water behavior during power generation. There is a concern that the hydrophilicity of the material may cause excessive liquid water accumulation (flooding), inhibiting gas supply and degrading the performance of the cell. Clarifying the liquid water transport phenomena in the PEFC is essential in order to realize high current density operation.

Understanding water transport mechanism is a common challenge for the advanced materials. X-ray radiography is a key technique to visualize liquid water in the PEFC.[6] X-ray system and optimum cell materials and structure can realize visualization of the inside of the PEFC including a membrane electrode assembly (MEA), flow channels and liquid water under operating conditions as shown in Figure 2. In this study, imaging of liquid water behavior in PEFCs with the advanced materials under operating conditions was performed and was compared with that in a conventional PEFC to clarify the effects of advanced materials on transport phenomena in the PEFCs.

A numerical simulation is an important tool for the PEFC development. A macroscale model of PEFCs has been developed

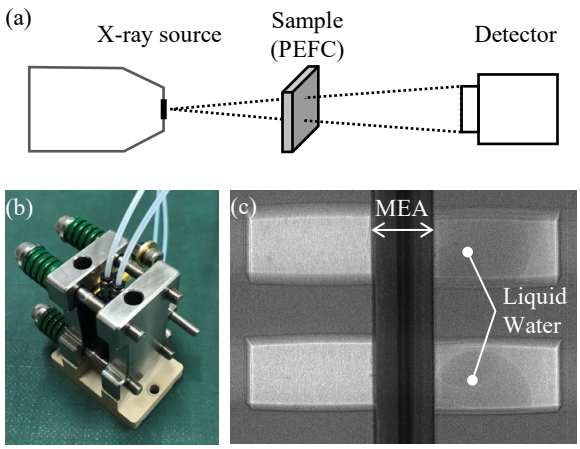

Fig. 2. (a) A schematic diagram of X-ray radiography, (b) a PEFC cell for X-ray radiography, and (c) an X-ray radiography image of the PEFC.

including electrochemical reaction and transport phenomena. Liquid water transport in the porous media is also implemented as a two-phase flow model. Recent models can quantitatively simulate the cell performance variation by changes in flow conditions and geometries. However, the effects of materials have been rarely mentioned in the fuel cell models. Although materials used in the PEFC and/or their composition significantly affect cell performance as a number of experimental studies have been presented, existing PEFC models cannot show such a significant difference. Therefore, macroscale modeling that can express performance variation caused by materials is required. One of the ultimate goals of numerical simulation of the PEFCs is to show optimum structure, material composition and material distribution. Recently, parameter optimization[7] and topology optimization[8] have been performed in the field of electrochemical energy devices. In this study, a novel macroscale model which has realistic sensitivity of cell performance by material composition was developed and parameter optimization of the catalyst layer was performed.

2. EXPERIMENTAL AND NUMERICAL SIMULATION METHODS

2.1. Materials

GDLFC$^+$ was fabricated by Enomoto Co., Ltd. Detail of material information can be referred to previous papers.[1,2] SIGRACET®24BC (SGL Carbon) was used as a conventional GDL for the comparison.

Catalyst inks were prepared by dispersing platinum-supported substrate and Nafion solution into an alcohol-based dispersion media. The carbon support CL was fabricated by applying the catalytic ink on the substrate using the doctor blade method. Catalyst-coated membrane (CCM) using the carbon supports was made by transferring the CL onto the PEM (NR212, Chemours) by hot pressing. This conventional CCM was used in the performance test of GDL materials and was used as a reference sample in the performance test of CL support materials. The SnO_2 supports CCM was made by the pulse swirl spray (PSS) method. Two types of PEFCs with a reaction area of 5×8 mm^2 were composed by layering each CCM, GDL with microporous layer (MPL), gaskets, and separators, respectively.

2.2. Experimental methods

X-ray radiography of the PEFC cell was performed under operating conditions. Separators in the cell were made of carbon material. Polypropylene with a low attenuation coefficient was

used as the gasket material, and the X-ray transmission length of the MEA was 5 mm.

Humidified hydrogen and humidified air were supplied to the anode and the cathode, respectively. The humidity and cell temperature were controlled on demand for each experiment.

X-ray radiography of the cell operated at constant current density was performed. The PEFCs were observed in the through-plane direction, which can visualize the thickness direction of materials. Time-lapse imaging was conducted to analyze time-dependent water transport behavior.

2.3. Numerical simulation methods

A numerical simulation of the macroscale fuel cell model[9] including electrochemical reaction and transport phenomena was performed. The two-phase flow was implemented. In this study, a novel approach based on percolation theory was applied to express notable variations in cell performance by material components. In conventional models, gas and ionic transport in porous media have been expressed using the Bruggeman correlation equation as follows,

$$\sigma_i^{eff} = \varepsilon_i^{1.5}\sigma_i^{bulk}, \quad (1)$$

where ε_i is the volume fraction of ionomer, σ_i^{eff} and σ_i^{bulk} are effective and bulk ionic conductivity, respectively. Gas diffusivity is also expressed in the same way. Although the exponent of ε_i is often modified, this equation is not enough to express variation of conductivity by materials, especially in the case of CLs. When the volume fraction of conductive materials or pores is extremely low, the conductivity was degraded not only by the decrease in volume fraction but also by broken paths as shown in Figure 3. To express this effect, percolation theory was referred to in this study. Conductivity is expressed as follows,

$$\sigma_i^{eff} = \chi(\varepsilon_i - \varepsilon_{i,c})^{\xi}, \quad (2)$$

where $\varepsilon_{i,c}$ is a critical level. This equation by itself does not meet in the high volume fraction range of conductive materials. Therefore, the Boltzmann function, f_B was applied instead of Eq. (2) and combined with Eq. (1). Finally, the effective conductivity is expressed as follows,

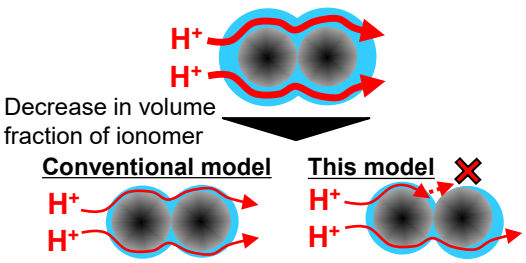

Fig. 3. The concept of the developed model.

$$\sigma_i^{eff} = f_B\varepsilon_i^{1.5}\sigma_i^{bulk}. \quad (3)$$

This equation converges to Eq. (1) when the volume fraction of the conductive material is sufficiently high. Gas diffusivity was treated in the same way.

Parameter optimization of the structure of CLs in the novel model was demonstrated by using the bound optimization by quadratic approximation algorithm.[7] The results are not shown in this manuscript and will be presented at the conference.

3. RESULTS AND DISCUSSION

3.1. Water behavior in the advanced materials for GDLs

Performance tests and X-ray radiography were performed at room temperature. 150 mL/min of hydrogen and 800 mL/min of air were supplied. The relative humidity of both anode and cathode was around 85%. Two types of cells, which differ in cathode composition, were tested and compared. One was a combination of the conventional GDL and a separator with parallel straight channels. The other was a combination of interdigitated GDLFC$^+$ and a flat separator. The performance test was conducted at 0.6 A/cm^2 in the case of the conventional GDL and 0.7 A/cm^2 in the case of GDLFC$^+$, respectively. The current density applied to the two types of cells was different because GDLFC$^+$ showed higher cell performance and the conventional GDL could not show stable performance at 0.7 A/cm^2. X-ray radiography was conducted every 15 s during the performance test. Fig. 4 shows water content distribution in each cell at 1200 s from the start of the test. The distribution of liquid water in the cathode GDL of these two cases showed a significant difference. In the case of the conventional GDL, most of water was under the rib and near the channel side, while little water was observed in the GDL of MPL side. On the other hand, GDLFC$^+$ contained most of water under the outflow channels and near MPL. Although GDLFC$^+$ was

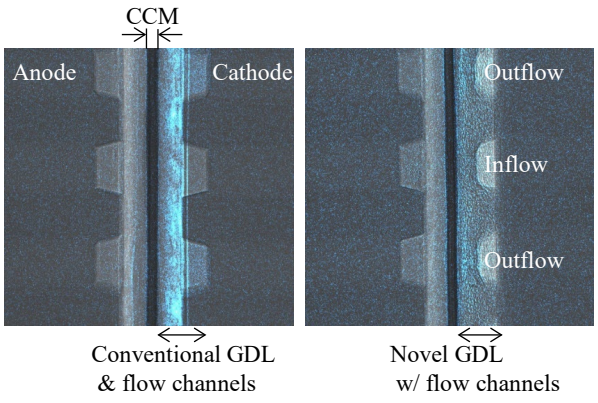

Fig. 4. X-ray radiography images of the conventional GDL (left) and GDLFC$^+$ (right), respectively. Liquid water is indicated by a cyan color.

operated at a higher current density, it showed a smaller amount of water in the cathode GDL. Liquid water distribution was changed and concentration overpotential was reduced in the case of GDLFC$^+$ because of a combination of porous rib structure and interdigitated flow field.

3.2. Effects of the advance materials for CLs

Carbon support and Nb-SnO_2 support were used in the cathode catalyst layer, respectively. Performance tests and X-ray radiography were performed at room temperature and compared to these two materials. The cell was operated at 0.8 A/cm^2 for 1200 s. An important finding is that water content distribution in GDL was different in these two cases although GDL structure was completely the same. The water distribution of the cell with carbon support was almost the same as the left figure in Fig. 4. On the other hand, the cell with Nb-SnO_2 support contained a larger amount of water in the GDL of MPL side. All the difference in the two cases was the support material of the cathode catalyst layer. The wettability of the support materials can affect water content distribution even in the GDLs. Experimental results will be presented at the conference.

3.3. Numerical simulation and parameter optimization

Materials and structure of CL and GDL significantly affect cell performance as shown in 3.1 and 3.2. The numerical simulation of the cell performance was conducted as a preliminary approach for the optimization of PEFCs. Fig. 5 shows simulated cell performance with various ionomer to carbon ratios (I/C) of the cathode catalyst layer. The suggested model could express the trend of performance variation by I/C, which has been presented by experimental approaches.[10,11] When ionomer content is too low as well as when it is too high, the cell performance is degraded.

Parameter optimization of the structure of CLs including Pt loading, I/C, porosity and thickness was performed. The results are not shown in this manuscript and will be presented at the conference.

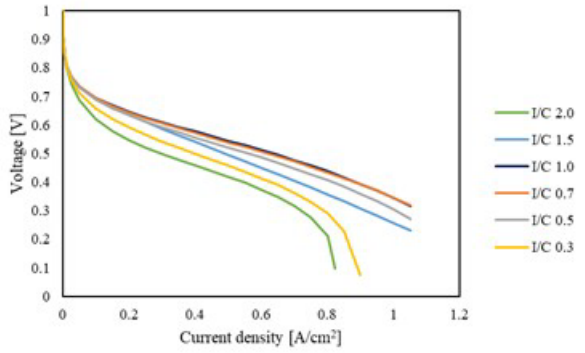

Fig. 5. Simulated polarization curves with variation of I/C in the cathode catalyst layer.

4. CONCLUSION

X-ray radiography of the PEFCs using the advanced materials was performed under operating conditions. A combination of GDL materials, structure and flow field has the potential to enhance cell performance by improving mass transport properties. The materials of catalyst support in the CLs affect water transport properties in the cell. Control of wettability and the porous structure is important to enhance water transport and resultant cell performance. A modified model based on percolation theory could successfully show cell performance variation by I/C in the cathode catalyst layer in the numerical simulation. Based on the numerical simulation that includes the effects of materials sufficiently, practical optimization of PEFCs can be realized.

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