Molecular dynamics study of the effect of wettability of the carbon support on proton transport in Nafion ionomer thin films

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Abstract
Molecular dynamics simulations were carried out to elucidate the effect of the wettability of the carbon support used for Nafion ionomer thin films on proton transport in the ionomer, which is related to the power density of polymer electrolyte fuel cells. The Lennard-Jones wall model was used as the support model for the ionomer to generate two different hydrophobic walls: the high hydrophobic wall (H-wall) and the low hydrophobic wall (L-wall). The proton transport model, including the Grotthuss mechanism, was used to express real proton transport phenomena (In early work, we confirmed that it well reproduces the experimentally measured proton self-diffusion coefficient in a Nafion membrane.) The obtained proton self-diffusion coefficient ($D_{H+}$) indicated that the $D_{H+}$ for the H-wall case is larger than for the L-wall case. This is related to the morphology of the films. For the H-wall case, the sulfonic groups that form part of the hydrophilic Nafion side chains were confirmed to be oriented in the direction to the wall in the upper side of the film and opposite from the wall in the lower side of the film, which can lead to the alignment of Nafion molecules and also create lamellar water structures in the film. It was also confirmed that such water structures have better cluster connectivity and larger cluster size, meaning that they serve as better proton transport pathways.

Key words : Polymer electrolyte fuel cell, Thin film, Wettability, Molecular dynamics, Transport property

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are promising for automotive and small-scale stationary applications due to their high power density and low operating temperature compared to other fuel cells (Peighambardoust et al., 2010). However, enhancement of durability and power density, as well as reduction of the amount of platinum catalyst required, remains hurdles to widely-distributed PEFC systems. To solve these problems, further understanding of power generation and the degradation mechanisms of PEFCs is required (Weber et al., 2014). Specifically, phenomena occurring in the catalyst layers (CLs) of PEFCs are not well understood because of their complicated and heterogeneous nanostructure, which makes it difficult to deal with unknown resistances, voltage loss, and degradation in CLs (Weber et al., 2014). It is therefore considered important to elucidate the nanoscale properties of CLs and to be better able to take measures to solve problems, as required. Basically, voltage loss arises from kinetic, ohmic, and diffusion losses. Furthermore, the latter two losses are attributed to mass transport losses, which account for a large part of the voltage loss, meaning that a reduction in mass transport loss is important to enhance performance. Oxygen and
proton transport resistances are considered as the main transport losses in CLs and therefore, investigating their determining factors and the mechanisms underlying these losses is considered essential in efforts to reduce them.

Conventional CLs consist of C/Pt aggregates covered with ionomer thin films. Protons and oxygen are transported inside the ionomer. Nafion, developed by DuPont, is widely employed as the membrane and ionomer thin film material in PEFCs. Membrane properties of Nafion have been well studied both experimentally and in numerical studies such as molecular dynamics (MD) with focus on nanoscale properties. However, the thin film properties are still not well understood. Moreover, only a few studies have focused on the proton transport property, which is related to the power density of PEFCs, as mentioned above. In one study, Paul et al. (2014) studied the film thickness, relative humidity, and temperature dependence on proton conductivity by generating films on silicon substrates. The film thickness ranged from 4 to 300 nm, which included the observed thickness range in CLs (4–10 nm) (Lopez-Haro et al., 2014). They derived the proton conductivity by assuming the films to be homogeneous and continuous films. However, generating such ideal films on silicon substrates experimentally may be difficult, particularly in the real thickness range in CLs. Therefore, their results may be doubtful, in some aspects. Paul et al. (2013) also reported that the film morphology differs depending on the substrate material: the film morphology on carbon supports differs from that on silicon substrates. It is therefore considered that the proton transport property on a carbon support will also differ from that on a silicon substrate. Focusing on nanoscale properties, Borges et al. (2015) and Mashio et al. (2010) studied proton transport properties in Nafion ionomer thin films using MD simulations. In their simulations, Mashio et al. generated ionomer films on graphite sheets. Borges et al., on the other hand, employed mean-field-like Lennard-Jones (LJ) walls as supports of ionomer films, to focus not on the effect of detailed solid wall structures but the effect of wettability of supports, as attributed to the physical and chemical properties of those surfaces. However, they did not consider the Grotthuss proton transport mechanism in their proton transport models, although the Grotthuss diffusion is reported to largely contribute, especially at high relative humidity (Zawodzinski et al., 1995). It is actually critical to consider the Grotthuss mechanism when analyzing the proton transport property.

In this study, proton transport in Nafion ionomer thin films in the CLs of PEFCs was simulated by MD methods to investigate the effect of the wettability of the carbon support on the proton transport property. The Grotthuss mechanism was modeled using the anharmonic two-state empirical valence bond (aTS-EVB) method (Mabuchi et al., 2015), and the films in the CLs were simplified as films on the LJ wall. The paper is organized as follows. Section 2 describes the simulation models. Section 3 describes the proton transport property in Nafion ionomer thin films and the morphological properties. Section 4 presents our conclusion.

Nomenclature

\[ D : \text{Self-diffusion coefficient, cm}^2/\text{s} \]
\[ e : \text{Unit vector} \]
\[ r : \text{Position vector} \]
\[ t : \text{Simulation time, s} \]
\[ V : \text{Potential, cal/mol} \]
\[ x, y, z : \text{Position coordinates} \]

Greek letters

\[ \varepsilon : \text{LJ parameter, cal/mol} \]
\[ \lambda : \text{Water content} \]
\[ \sigma : \text{LJ parameter, nm} \]

2. Simulation Models

An ionomer molecule was modeled by a Nafion molecule with an equivalent weight of ~1100. We generated a Nafion chain by linking the polar monomeric unit (P) to the end of the nonpolar monomeric unit N\textsubscript{7}, and repeated the procedure ten times to obtain (N\textsubscript{7}P)\textsubscript{10} (see Fig. 1), which corresponds to an equivalent weight of 1146. The Nafion model is represented by a combination of a united-atom site for CF\textsubscript{n} and atomistic sites for the remaining atoms. The potential model was referred to Cui et al. (2008). The aSPC/Fw model (Park et al., 2012) for H\textsubscript{2}O molecules and H\textsubscript{3}O+...
ions was employed. The aTS-EVB method (Mabuchi et al., 2015) for the Grotthuss proton transport mechanism was employed. The support model for the films is represented by a 9-3 LJ potential (Borges et al., 2015), as follows:

\[
V^a = \varepsilon^a \left( \frac{2}{15} \left( \frac{\sigma}{\alpha} \right)^9 - \left( \frac{\sigma}{\alpha} \right)^{12} \right),
\]

where \( \alpha \) is the normal distance from the wall, the cutoff distance is 1.5 nm, and \( \sigma \) is 0.32 nm in all cases. \( \varepsilon \) is the character identifying the hydrophobic (\( \alpha = \text{phob} \)) or hydrophilic (\( \alpha = \text{phyl} \)) molecules. \( \alpha = \text{phob} \) identifies the Nafion atoms except SO\(_3^-\), \( \varepsilon_{\text{phob}} \) is set at 0.5 kcal mol\(^{-1}\), corresponding to the typical strength of interaction of polymer units with a carbon sheet. \( \alpha = \text{phyl} \) identifies the polar molecules (H\(_2\)O, H\(_3\)O\(^+\), and SO\(_3^-\)). \( \varepsilon_{\text{phyl}} \) is a parameter to represent the wettability of the wall. \( \varepsilon_{\text{phyl}} \) is defined in Borges’s study (Borges et al., 2015) from the contact angle of the water droplet on the walls. We simply chose the two parameters used in their study, \( \varepsilon_{\text{phyl}} = 1.0 \) kcal mol\(^{-1}\) and 0.125 kcal mol\(^{-1}\), corresponding to the contact angles 100.9° and 163.0°, respectively, to generate the low hydrophobic wall (L-wall) and the high hydrophobic wall (H-wall).

On the LJ wall (size 5.1 nm \( \times \) 4.4 nm), Nafion molecules, H\(_2\)O\(^+\) ions, and H\(_2\)O molecules were placed in the box with two-dimensional periodic boundary conditions, parallel to the wall (see Fig. 2). The number of Nafion molecules was set at 6, the number of H\(_2\)O\(^+\) ions was set at 60, and the number of H\(_2\)O molecules was set according to the water content (\( \lambda \)), defined as the number of H\(_2\)O molecules and H\(_2\)O\(^+\) ions per SO\(_3^-\) of 3, 6, and 12, respectively. The resulting thickness of Nafion ionomer thin films was 3–4 nm which is in accordance with the minimum observed thickness of Nafion ionomer thin films in the CL (Lopez-Haro et al., 2014). The calculation procedure was as follows. Nafion molecules, H\(_2\)O\(^+\) ions, and H\(_2\)O molecules were randomly placed in a box (size 10 nm \( \times \) 10 nm \( \times \) 10 nm). The box had the 12 LJ wall represented as \( V = \varepsilon(\sigma/\alpha)^{12} \) on the bottom and top of the box to press and relax the films, where \( \varepsilon \) is 0.01 kcal mol\(^{-1}\), \( \sigma \) is 0.3 nm, and \( \alpha \) is the normal distance from the bottom of the box. The top wall was movable and the bottom wall was fixed. After all the molecules were set, the annealing procedure was carried out to establish the equilibrium state. First, MD calculation was done for 100 ps with 800 K to compress the box size parallel to the wall to 5.1 nm \( \times \) 4.4 nm, which is the same size as the 9-3 LJ wall inserted in the simulation box, and to compress the films to a density of 2.0 g cm\(^{-3}\) by moving the top wall. Next, MD calculation was done for 50 ps with the NVT ensemble, gradually changing the temperature from 800 K to 300 K. Then, the following procedures (1)–(4) were carried out three times: (1) MD calculation for 100 ps with the NPT ensemble at a temperature of 300 K and pressure of 1 atm (2) MD calculation for 50 ps with the NVT ensemble, with gradual temperature change from 300 K to 800 K (3) MD calculation for 50 ps with the NVT ensemble at a temperature of 800 K (4) MD calculation for 50 ps with the NVT ensemble, with a gradual temperature change from 800 K to 300 K. Note that the bottom wall was changed from the 12 LJ wall to the 9-3 LJ wall from the commencement of the second time procedures. Thereafter, the top wall was fixed at \( \alpha = 10 \) nm to prevent the molecules from evaporating. Another MD calculation for 500 ps with the NVT ensemble was done using the aTS-EVB method. This final structure was considered as the equilibrium state, and then MD calculation for 5 ns with the NVT ensemble was done to sample the data every 1 ps for the analyses of the mass density distributions, orientation of sulfonic groups (SO\(_3^-\)), water cluster structures, and proton self-diffusion coefficient. The temperature was held by the Nose–Hoover method (Hoover, 1986). A smooth particle mesh Ewald method (Essmann et al., 1995) was used to calculate electrostatic interactions. The cutoff distance for LJ potential and Coulomb potential was set at 1.5 nm.

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**Fig. 1** Chemical structure of a Nafion molecule employed in this study.

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**Fig. 2** Nafion ionomer thin film model used for simulating proton transport phenomena. Green, orange, and blue spheres indicate Nafion molecules, sulfur atoms that are a part of hydrophilic Nafion side chains, and water and hydronium molecules, respectively.
3. Results and discussions

The proton self-diffusion coefficients in the films parallel to the wall were calculated using the Einstein equation as follows:

\[
D_{H^+} = \lim_{t \to \infty} \frac{1}{4t} \langle (r_{H_3O^+}(t) - r_{H_3O^+}(0))^2 \rangle
\]

\((2)\)

\(D_{H^+}\) was estimated from the slope of the mean square displacement for oxygen atoms of \(H_3O^+\) ions from 1 to 2.5 ns in the sample time \((t)\). In this study, the vector, \(r\), is restricted to \(x-y\) components, to calculate \(D_{H^+}\) parallel to the wall. Fig. 3 summarizes the obtained \(D_{H^+}\) for each hydrophobic wall and the \(D_{H^+}\) in the bulk membrane referred to Aochi et al., (2016) as a function of \(\lambda\). According to Fig. 3, it was confirmed that the obtained \(D_{H^+}\) has different values from that in the bulk membrane, suggesting that the different proton transport property compared to the bulk membrane was found. Moreover, The obtained \(D_{H^+}\) indicates that the \(D_{H^+}\) increases with increasing \(\lambda\), regardless of the hydrophobicity of the wall, and also that the \(D_{H^+}\) for the H-wall is larger than the \(D_{H^+}\) for the L-wall at any water content.

![Fig. 3 Proton self-diffusion coefficient \(D_{H^+}\) in a Nafion ionomer thin film summarized as a function of water content for each wall. The black and blue lines indicate \(D_{H^+}\) for the low and high wall case, respectively. The red line indicates \(D_{H^+}\) for the bulk membrane calculated by Aochi et al., (2016). Also, the direction of the proton transport is explained schematically in the attached images. The left one represents carbon aggregates covered with ionomer thin films found in CL.](image)

The mass density distributions of Nafion molecules, solvent molecules, and sulfur atoms were next calculated to elucidate the effect of the hydrophobicity of the wall on the morphology of Nafion ionomer thin films. The films were divided into slabs with a width of 0.1 nm normal to the wall. Fig. 4 summarizes the averaged density in each slab. The first observation from Fig. 4 is that, with focus on the morphology near the wall, i.e., around \(z = 0\), the peaks of Nafion molecules can be confirmed regardless of the hydrophobicity of the wall and \(\lambda\) (described by green lines). Furthermore, for the H-wall case, the peaks of solvent molecules and sulfur atoms cannot be confirmed (see blue and orange lines in Fig. 4 (a)(b)(c)), whereas for the L-wall case, those peaks can be confirmed (see Fig. 4 (d)(e)(f)). Based on these observations, it can be predicted that the hydrophobic Nafion backbones are mainly adsorbed on the H-wall, while, on the other hand, the hydrophilic Nafion side chains and solvent molecules are adsorbed on the L-wall. Mashio et al. (2010) similarly reported that hydrophobic Nafion backbones are mainly adsorbed on the hydrophobic graphite sheets and water molecules are hardly adsorbed on the sheet, while water molecules are adsorbed on the low hydrophobic \(\text{COO}^-\)-terminated graphite sheets. The second observation from Fig. 4 is that, regarding the morphology around the film surface (\(z = 3 \sim 4\) nm), for all cases, it can be confirmed that the presence of Nafion molecules is dominant, while sulfur atoms hardly exist. Based on these observations, it can be predicted that the film surfaces are coated with the hydrophobic Nafion backbones regardless of the hydrophobicity of the wall and \(\lambda\). After using experimental approach, Bass et al. (2011) similarly reported that Nafion molecules are aligned at the film surface and the surface shows hydrophobicity even though the film thickness is 100 nm, which is about 25 times larger than the thickness employed.
in this study. The third observation from Fig. 4 is that, with focus on the global morphology of the films, distinguishable morphological differences attributed to the hydrophobicity of the wall cannot be confirmed except for the distribution of sulfur atoms and solvent molecules. It is therefore assumed that the different $D_{Hc}$ values attributed to the hydrophobicity of the wall as shown in Fig. 3 are likely to be caused by the different distributions of hydrophilic Nafion side chains and solvent molecules. To investigate this possibility, analysis of the orientation of the $SO_3^-$ groups and water cluster structures was carried out.

Fig. 4 Mass density distributions summarized as a function of the normal distance from the wall. (a), (b), and (c) indicate the case of the high hydrophobic wall at $\lambda = 3$, 6, and 12. (d), (e), and (f) indicate the case of the lower hydrophobic wall at $\lambda = 3$, 6, and 12. Green, blue, and orange lines indicate the distribution of Nafion molecules, solvent molecules, and sulfur atoms, respectively. Spheres in the figures are the same as in Fig. 2.

The orientation of $SO_3^-$ is defined as the inner product of the two vectors, $\cos \theta = e_z \cdot e_{so3}$, where $e_z$ represents the unit vector normal to the wall and $e_{so3}$ represents the unit vector normal to the plane formed by the three oxygen atoms and points toward the sulfur atom, as described schematically in Fig. 5. To investigate the local configurations, the films were divided into two slabs parallel to the wall at the position of $z = 1.6$ nm (see Fig. 4). Fig. 6 summarizes the normalized orientation at both the upper and lower sides of the films. First, for the H-wall case, Fig. 6(a) indicates that, in the upper side of the film, the $SO_3^-$ groups are oriented in the direction of $\cos \theta = 1$, i.e., the direction to the wall, and that this trend can be more pronounced with increasing $\lambda$. Fig. 6(b) indicates that, in the lower side of the film, the $SO_3^-$ groups are gradually oriented in the direction of $\cos \theta = -1$, i.e., the direction opposite to the wall, at $\lambda = 3$. However, it is also indicated that the $SO_3^-$ groups are gradually oriented in the direction of $\cos \theta = -1$, i.e., the direction
opposite from the wall, with increasing $\lambda$. Next, for the L-wall case, Fig. 6(c) and (d) indicate that the SO$_3^-$ groups in both the upper and lower sides of the film are oriented in the direction of $\cos \theta = \pm 1$, i.e., the direction to the wall and opposite from the wall, in each slab, respectively. It is also indicated that the SO$_3^-$ groups are not oriented in a specific direction even though $\lambda$ increases. Andersen et al. (2014) reported a similar trend, after using adsorption isotherm studies. They reported that the adsorption force between Nafion molecules and substrates decreases and then increases with decreasing hydrophobicity of substrates. According to them, the following mechanism applies: hydrophobic Nafion molecules are strongly adsorbed when the hydrophobicity of substrates is high, but, as the hydrophobicity gradually decreases, the hydrophobic adsorption force decreases and the backbones become detached, and then, with a further decrease in the hydrophobicity, hydrophilic Nafion side chains become adsorbed. The hydrophobicity of the L-wall is considered to be the hydrophobicity that corresponds to the case of the transition from the hydrophobic adsorption to the hydrophilic adsorption because the SO$_3^-$ groups in the lower side of the film are oriented in two directions, i.e., the directions to the wall and opposite from the wall.

The water cluster structures in the films were then evaluated in terms of the water cluster connectivity and size. A water cluster is defined as a group of solvent molecules whose intermolecular distances of oxygen atoms are within 6 Å.

![Fig. 5 Schematic representation of the definition of the orientation of the sulfonic groups](image)

![Fig. 6 (a) and (b) indicate the orientation of sulfonic groups in the upper and lower sides of the film on the high hydrophobic wall, and (c) and (d) indicate the orientation of sulfonic groups in the upper and lower sides of the film on the low hydrophobic wall. Black, red, and blue lines indicate the cases of $\lambda = 3, 6,$ and $12$, respectively.](image)
0.33 nm, corresponding to the distance of the first peak of the radial distribution function between oxygen atoms of H$_2$O in bulk water calculated in a previous MD simulation (Kawai et al., 2015). The connectivity was evaluated in terms of the number of water clusters in the film: the lower the cluster number is, the better the connectivity is in case where $\lambda$ is the same. The size of a cluster was evaluated by simply counting the number of solvent molecules in each cluster and then averaging the numbers. Fig. 7 summarizes the average cluster number and size as a function of $\lambda$ for each wall. Fig. 7(a) indicates that the decreased ratio of the cluster number from $\lambda = 3$ to 6 is larger than that from $\lambda = 6$ to 12, regardless of the hydrophobicity of the wall. This means that the clusters are actively connected to each other from $\lambda = 3$ to 6. Fig. 7(a) also indicates that, when comparing the number of the clusters for each wall, the number in the H-wall case is the same or lower than in the L-wall case at any $\lambda$. This suggests that the connectivity is better in the H-wall case. Fig. 7(b) indicates that the cluster size is always larger in the H-wall case. Furthermore, the increased ratio of the size from $\lambda = 6$ to 12 is larger than from $\lambda = 3$ to 6 in the H-wall case. This suggests that, after they connected to each other, the clusters easily grow up to a certain degree.

![Fig. 7 Water cluster structures summarized in terms of (a) the average cluster number and (b) average cluster size as a function of water content ($\lambda$). Black lines indicate the case of the low hydrophobic wall, and blue lines indicate the case of the high hydrophobic wall. Error bars are derived from standard deviation.](image)

Fig. 7 Water cluster structures summarized in terms of (a) the average cluster number and (b) average cluster size as a function of water content ($\lambda$). Black lines indicate the case of the low hydrophobic wall, and blue lines indicate the case of the high hydrophobic wall. Error bars are derived from standard deviation.

![Fig. 8 Schematic representation of the orientation of sulfonic groups and water cluster structures: (a) the case of a high hydrophobic wall and (b) the case of a low hydrophobic wall.](image)

Fig. 8 Schematic representation of the orientation of sulfonic groups and water cluster structures: (a) the case of a high hydrophobic wall and (b) the case of a low hydrophobic wall.

These morphological analyses suggest an important correlation between the orientation of SO$_3^-$ groups and the water cluster structures, i.e., the good orientational order of SO$_3^-$ groups in a specific direction in a slab can result in better cluster connectivity and larger cluster size, probably due to the aligned Nafion molecules parallel to the wall. For
the H-wall case, the SO$_3^-$ groups in the upper side of the film are oriented in the direction to the wall, and the SO$_3^-$ groups in the lower side of the film are oriented in the direction opposite from the wall. This can result in a lamellar water structure with better connectivity and larger size in the film, as described schematically in Fig. 8(a) and indicated in Fig. 4(c). This water structure model is also proposed by Paul et al. (2013) and Haubold et al. (2001). On the other hand, for the L-wall case, the SO$_3^-$ in a slab is not oriented in a specific direction, making it difficult for water clusters to connect or grow in a specific direction, as described schematically in Fig. 8(b). These different morphologies are also related to the proton transport property. At $\lambda = 3$, the different orientational order of SO$_3^-$ groups between the two walls is observed only in the upper side of the films (see black lines in Fig. 6), and, for only the H-wall case, the SO$_3^-$ groups in the upper side of the film are oriented in the direction to the wall. This results in local lamellar water structures with better cluster connectivity and larger cluster size, as indicated in Fig. 7. Therefore, at $\lambda = 3$, the $D_{H}$ for the H-wall is considered to be larger than that for the L-wall, as shown in Fig. 3. At $\lambda = 6$ and 12, for the H-wall case, the SO$_3^-$ groups in the upper side of the film are oriented in the direction to the wall, and the SO$_3^-$ groups in the lower side of the film are oriented in the direction opposite from the wall. This can also result in lamellar water structures in the film. On the other hand, for the L-wall case, the SO$_3^-$ groups in both the sides do not orient in a specific direction in each slab. Therefore, at $\lambda = 6$ and 12, the $D_{H}$ for the H-wall is considered to be greater than that for the L-wall, as shown in Fig. 3.

4. Conclusions

Proton transport in Nafion ionomer thin films on two different types of hydrophobic LJ walls, the H-wall and the L-wall, was simulated using MD simulations to investigate the effect of the wettability of carbon supports on the proton transport property. The proton transport property was evaluated in terms of the proton self-diffusion coefficient ($D_{H^{-}}$), and the morphology of Nafion ionomer thin films was evaluated in terms of the mass density distributions, the orientation of SO$_3^-$ groups, and water cluster structures. The obtained $D_{H^{-}}$ indicated that the $D_{H^{-}}$ for the H-wall was larger than that for the L-wall at any $\lambda$. Analysis of mass density distributions indicated different film morphology between the two walls, in terms of the distribution of sulfur atoms and solvent molecule. This suggests that the different $D_{H^{-}}$, values are caused by the orientation of SO$_3^-$ groups and water cluster structures. Analysis of the orientation of SO$_3^-$ groups indicated that, for the H-wall case, the SO$_3^-$ groups in the upper side of the films become oriented in the direction to the wall with increasing $\lambda$, whereas the SO$_3^-$ groups in the lower side of the films become oriented in the direction opposite from the wall with increasing $\lambda$. On the other hand, for the L-wall case, the orientational trend as observed in the H-wall case was not confirmed. Analysis of the water cluster structures indicated that, for the H-wall case, clusters with better connectivity and larger size are formed in the film. The different $D_{H^{-}}$, values can be related to morphological differences, i.e., for the H-wall case, Nafion molecules are aligned parallel to the wall because of the good orientational order of SO$_3^-$ groups, which results in lamellar water structures with better connectivity and size parallel to the wall. It was therefore concluded that, for the H-wall case, the proton transport parallel to the wall is enhanced. Finally, note that increasing in $\lambda$ is considered to enhance water cluster connectivity and size and, therefore, proton transport. However, it has been recently observed by Shim et al. (2015) and Kusoglu et al. (2012) that much lower water uptake in Nafion ionomer thin films compared to bulk Nafion membranes. It is therefore important to find out some other ways to enhance proton transport except increasing in $\lambda$. In this study, one of them, wettability of carbon support dependence, was discussed. It was indicated that high hydrophobic carbon supports enhance proton transport in Nafion ionomer thin films.

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