

Development of Multi-scale Simulation Methods for Polymer Electrolyte Membrane Fuel Cell

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ABSTRACT

It is expected that polymer electrolyte membrane fuel cells (PEMFC) will be increasingly used as the power plants of automobiles in the future due to their high thermodynamic efficiency utilizing electrochemical reaction. PEMFC have a detailed internal structure including electrode catalysts, and various phenomena interact in a complex manner across a wide range of scales within this structure. Particularly important phenomena are thought to be (1) the interaction between the elementary reactions and the adsorbates on the electrode catalysts, (2) proton hopping within the polymer electrolyte, and (3) condensation of water droplets within the micro-porous electrolyte. However, these phenomena are rooted in nano-scale mechanisms, so they have not been investigated in sufficient detail in past studies. This paper focused on these issues from a computational science perspective, created appropriate models of the PEMFC internal environment, and applied the dynamic Monte Carlo method to phenomenon (1), a quantum molecular dynamics method based on tight binding approximation to phenomenon (2), and a molecular dynamics with constant chemical potential method to phenomenon (3). The results confirmed that each computational approach effectively simulates the respective issue. In addition, the various effects were calculated in a coupled manner as a multi-scale model to enable these nano-scale phenomena to be reflected when calculating the PEMFC unit cell performance. The results showed that the above phenomena interact and influence the unit cell current-voltage characteristics.

1. Introduction

Interest in energy issues and reducing environmental loads is increasing, and efforts are being made around the world to develop and popularize fuel cell vehicles as a solution to addressing these issues. Further enhancement of performance is desired in terms of cost and durability to help realize mass popularization of fuel cell vehicles in the future⁽¹⁾. Increasing PEMFC efficiency is an effective means of achieving this, which requires clarification of internal phenomena. PEMFC have a detailed internal structure including electrode catalysts, and various phenomena interact in a complex manner within this structure; therefore, it was thought that a computational approach would be effective. This paper reports the construction of numerical computation methods that accurately describe essential mechanisms, which have not been addressed thus far among the various PEMFC internal phenomena.

2. Development Goals

While issues facing the popularization of automobiles that use PEMFC span a wide range, the most important are

reducing cost and enhancing durability, and increasing the fuel cell efficiency is essential for addressing these issues. This study aimed to predict generating performance via the detailed phenomena occurring within the unit cell, which is the minimum generating unit inside the PEMFC stack. **Figure 1** shows a simplified schematic of the PEMFC unit cell structure. The structure consists of the cathode and anode electrodes, a polymer electrolyte membrane located between the cathode and anode, and conductive gas diffusion layers, gas channels and conductive current collectors outside the cathode and anode. The dimensions of the various components are generally on the order of approximately 10 μm thick for each of the electrodes and the electrolyte membrane, 100 μm thick for the gas diffusion layer, and 1 mm deep and 10 cm long for the gas channels.

The typical format for each electrode, which is called the electrocatalytic layer, consists of a precious metal catalyst powder coated onto a conductive support and impregnated with an electrolyte. As shown in Fig. 1, the hydrogen dissociated at the anode migrates inside the polymer electrolyte as protons, passes through the external circuit as electrons, and reacts with the oxygen at the cathode to

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form water. The hydrogen and oxygen pass through the gas diffusion layers on the outsides of the respective electrodes, and are transferred via the gas channels. The physical quantities that express these phenomena are thought to be, at the locations indicated in the figure, the respective molecule concentrations (C), the fluid density and velocity (ρ , $\mathbf{u}$), and the electrolyte and electron potentials (Φ). This study aimed to develop techniques for predicting these physical quantities by retracing the mechanisms by which the phenomena manifest.

The electrocatalytic layer is an important location where the actual generation is performed, and Fig. 2 shows an enlarged image of the actual catalyst layer made for

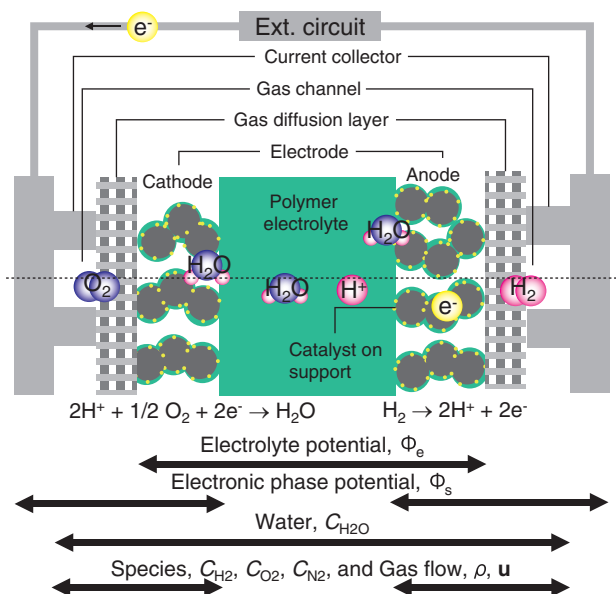


Fig. 1 Typical structure with transported species of unit cell of PEMFC. Related transport phenomena are also indicated.

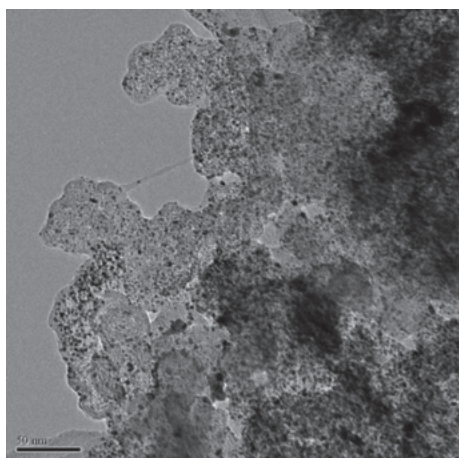


Fig. 2 TEM image of a catalyst layer of polymer electrolyte fuel cell. Grey objects are carbon support and polymer electrolyte. Black dots are platinum particles.

this study. The carbon and the electrolyte appear as gray. Platinum particles appear as black dots, and are supported on carbon (Ketjen Black) with a diameter of several 10 nm. This catalyst layer was made by spraying a liquid mixture of the polymer electrolyte and the catalyst onto the gas diffusion layer. The coating amounts were 0.5 mg/cm^2 for both the platinum and the carbon, and Nafion[®] was coated at 0.4 mg/cm^2 as the polymer electrolyte.

The important issues for enhancing the current-voltage characteristics are to reduce (1) the activation overpotential that derives from the activation energy needed to initiate the reaction at the electrocatalyst, (2) the resistance overpotential that mainly originates in the proton and other ion transfer resistance, and (3) the concentration overpotential produced by a lack of reactive matter at the reaction surface. Respectively, (1) the activation overpotential can be reduced by constructing a cathode electrocatalytic layer that facilitates the electrochemical reaction, (2) the resistance overpotential can be reduced by developing an electrolyte membrane with high proton conductivity, and (3) the concentration overpotential can be reduced by increasing the diffusivity of the reaction gas transfer paths that lead from the gas channels to the electrode catalysts, and by reducing obstruction of transfer by liquid water, particularly at high-current density operation.

Since the mechanisms that produce these phenomena need to be investigated down to the nano scale, they had not been sufficiently clarified thus far. Therefore, this paper attempted a computational science approach using a multi-scale model (a model that links phenomena of differing scales) that enables reflection of nano-scale mechanisms to the unit cell scale (several cm). The main goals when developing and applying the computational techniques were to take into account the following three effects:

- (1) Influence of proton hopping on proton conductivity;
- (2) Adsorbate status on the catalyst surface depending on electrode potential; and
- (3) Blocking of nano-pores in the catalyst layer by water droplets.

These correspond respectively to the three overpotentials (1) to (3) described above. Appropriate simplified models based on many assumptions need to be made in order to simulate these complex phenomena using computational science. Therefore, the validity of the various models was also verified.

In addition, techniques were also developed to calculate the various effects in a coupled manner to understand how individual phenomena manifest as fuel cell performance.

3. Computational Methods

3.1. Calculation of Surface Electrochemical Reaction Using the Dynamic Monte Carlo Method

In the electrode catalyst surface reactions, various elementary reactions involving adsorption and desorption

of chemical species occur in succession. For this reason, electrode potential should be taken into account when calculating adsorption, reaction and desorption on the reaction surface and the interaction between the adsorbates. The vector that represents the state of all sites in the adsorption site lattice on the catalyst surface is labeled $\mathbf{c}$. The equation that expresses the change over time of the probability $P_{\mathbf{c}}(t)$ that the status $\mathbf{c}$ will manifest at time t can generally be expressed as follows.

$$dP_{\mathbf{c}}(t)/dt = \sum_{\mathbf{c}' \neq \mathbf{c}} [k_{\mathbf{c}\mathbf{c}'} P_{\mathbf{c}'}(t) - k_{\mathbf{c}'\mathbf{c}} P_{\mathbf{c}}(t)] \quad (1)$$

Here, $k_{\mathbf{c}\mathbf{c}'}$ is the rate constant of the elementary reaction in which the state $\mathbf{c}'$ changes to $\mathbf{c}$. Since this equation is a challenge to solve analytically, this study used the dynamic Monte Carlo method (DMC)⁽²⁾, which is a probabilistic method. The DMC method first investigates the states of adjacent sites around all the reaction sites in status $\mathbf{c}$, and extracts the sites where the elementary reaction i can occur. Next, the probability of reaction i occurring is determined from the number of sites n_i where this reaction can occur and the reaction rate k_i , and this result is used to probabilistically determine which reaction will occur and initiate the reaction. In addition, the time required for a single reaction is determined probabilistically from the sum total of the times for all possible reactions to occur in this state. The reaction progress can be clarified by repeating this process.

The types of oxygen-reduction elementary reactions taken into account in this paper are described in the following chapter. Each elementary reaction rate is given by the Arrhenius equation expressed by Eq. (2).

$$k = A \exp(-E_{\text{act}} / (k_B T)) \quad (2)$$

Here, k_B is the Boltzmann constant, T is the absolute temperature, A is the frequency factor, and E_{act} is the activation energy. When quantifying the elementary reaction rates, they are considered as divided into reactions that include electron transfer and normal chemical reactions. In case of electron transfer reactions of adsorbed chemical species on platinum atoms, E_{act} is thought to depend on the electrode potential V , which uses the equilibrium electrode potential V_{rev} as the reference, in the manner of $E_{\text{act}} = f(V - V_{\text{rev}})$. Therefore, this was formulated as a conditional minimization problem of the energy obtained by first-principles calculation, and E_{act} was obtained by the method of Lagrange multipliers⁽³⁾. This condition is based on the assumption that the electron affinity in the reaction transition state is equal to the work function of the electrode at that potential and the Born-Oppenheimer (BO) approximation, which assumes that the motion of the atomic nucleus during electron exchange is sufficiently slow relative to the change in the electron

state. The equilibrium electrode potential V_{rev} can be calculated thermodynamically using the Nernst equation⁽⁴⁾. The frequency factor A is calculated based on a model that adds the protons in the electrolyte to the adsorbed oxygen atoms as described in the following chapter. In the case of normal chemical reactions, each factor in Eq. (2) is determined according to transient state theory⁽⁵⁾. In this case, the activation energy is the constant for each elementary reaction.

3.2. Tight Binding Molecular Dynamics (TBMD)

The proton transfer phenomena within the electrolyte are said to be due to two competing mechanisms; the vehicular mechanism and the Grotthuss mechanism⁽⁶⁾. Therefore, both mechanisms should be taken into account to predict the transfer rate. Of the two, the vehicular mechanism transfer phenomenon can be simulated by classical molecular dynamics calculations⁽⁷⁾. However, the Grotthuss mechanism is also known as proton hopping, which is the phenomenon where the water molecule adjacent to a hydronium ion (H_3O^+) changes to H_3O^+ as if a proton in the H_3O^+ is transported as shown in Fig. 3, which results in high-speed charge transfer. The Grotthuss mechanism involves reconfiguration of the chemical bonds, therefore the electronic state cannot be simulated using molecular dynamics calculation based on classical dynamics, and needs to be handled using quantum dynamics. The first-principles molecular dynamics approach supports this; however, an extremely large calculation cost is required to handle polymers. Therefore, in this study we developed a new computational code using the tight-binding molecular dynamics⁽⁸⁾ (TBMD) method that takes into account quantum chemistry. This method calculates the system energy and the electronic state of the molecules by solving a Schrödinger equation based on linear combination of atomic orbitals (LCAO) approximation. In this method, the calculation speed is increased by omitting the electron repulsion integral (ERI) calculations that have a high calculation cost. The equation of motion for the atomic nucleus A assumes the BO approximation described above, and is expressed as follows.

$$\mathbf{F}_A = \frac{\partial E}{\partial \mathbf{R}_A} = - \sum_{B \neq A} \sum_i^{\text{atoms MO}} n_i \sum_{rs}^{\text{AO}} C_{ir}^T \left(\frac{\partial H_{rs}}{\partial \mathbf{R}_A} - \frac{\partial S_{rs}}{\partial \mathbf{R}_A} \right) C_{is} - \sum_{B \neq A}^{\text{atoms}} \frac{\partial E_{\text{rep}}(\mathbf{R}_{AB})}{\partial \mathbf{R}_A} \quad (3)$$

Here, C_{ir} is a coefficient indicating the contribution of the basis function of the r th atomic orbital relative to the i th

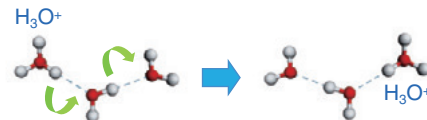


Fig. 3 Proton transfer by Grotthuss mechanism

molecular orbital, n is the number of electrons present in the i th molecular orbital, H is the Hamiltonian, S is the overlap integral, $\mathbf{R}$ is the position of the atomic nucleus, and the subscripts A and B indicate the atoms. To correct the short-range forces, this study enhanced the quantitativity by adding a term for the repulsion energy between the nuclei and the electrons to the second item on the right side of the equation. By omitting the ERI calculations as described above, the Hamiltonian matrix elements become adjustment parameters, and are determined in a manner to reproduce the results of separate first-principles calculation. In these calculations, the relationship between the change in energy and the O-H bond length in the H_3O^+ ions that affects the proton hopping frequency was adjusted to reproduce the results of accurate first-principles calculation using the MP2 method⁽⁹⁾. This method enabled performance of the quantum molecular dynamics calculations for approximately 1000 atoms using a single 8-core workstation.

3.3. Molecular Dynamics with Constant Chemical Potential

The gas-liquid phase transition point is known to change inside nm-order pores due to the phenomenon known as capillary condensation. Recently it has been confirmed that some phenomena cannot be adequately expressed by the Kelvin equation conventionally used to predict this phenomenon⁽¹⁰⁾. An effective means of accurately predicting the above phenomena within the PEMFC electrocatalytic layer is to perform direct calculations using the molecular dynamics method, taking into account the characteristics of the electrocatalytic layer wall surfaces. In the state where both the gas and liquid phases coexist within the pores, the temperatures and chemical potentials (Gibbs free energy per molecule) of both phases are equal, although the pressures differ. Although the molecular dynamics method generally performs calculations with the temperature and pressure fixed, this study used the Grand Molecular Dynamics (GMD) method⁽¹¹⁾ to perform calculations with the chemical potentials of both phases fixed to be equal. This method handles the issue of particle transfer into and out of the system by solving the equation of particle motion of a virtual particle that takes the value of 0 to 1 as the number of the particle in addition to the normal particles handled by molecular dynamics. This enables control of the chemical potential of the system to be calculated. Isochoric calculations that control the chemical potential and temperature were performed by introducing the Nose-Hoover method⁽⁷⁾ as the temperature control method to this equation of motion that takes into account virtual particles.

4. Modeling of PEMFC and Calculation Results

A target system was modeled to apply the methods described in the previous chapter to PEMFC, and the various calculation results were verified. The method used

to couple these results and calculate the current-voltage characteristics is described below.

4.1. Calculation of Electrochemical Reaction Rates

4.1.1. Modeling

The PEMFC cathode normally uses platinum catalyst particles, which have high oxygen reduction activity, coated on a carbon support and then covered by the electrolyte component. For the oxygen reduction reaction it was hypothesized that the oxygen dissolved in the water that exists together with the electrolyte is adsorbed to the platinum surface and reacts with the protons in the water. This reflects the fact that the diffusion coefficient of oxygen is larger in water than in Nafion[®], and that positively charged protons do not easily adsorb to the oxygen reduction electrode, which has a high potential.

The elementary reactions calculated in this study were narrowed down to the following reactions based on reference (12).

Adsorption and desorption of oxygen molecules and liquid water



Reduction of adsorbed oxygen molecules (Because the dissociation reaction after proton addition occurs easily, it is included in this reaction.)



Reduction of adsorbed oxygen atoms



Reduction of adsorbed hydroxyl groups



Desorption of adsorbed water



The asterisks (*) in the equations represent the adsorbed state to the metal surface. Here, the reaction activation energy in the electrochemical reactions expressed by Eq.

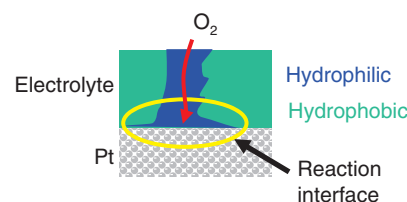


Fig. 4 Image of reaction interface

(6), (7) and (8) depends on the potential as described in the previous chapter. Assuming BO approximation, the energy in each adsorbed state in the reaction equations is calculated by first-principles calculations using DFT, and the equilibrium electrode potential is converted to the potential difference using the Nernst equation, based on this energy.

The platinum catalyst particles are assumed to consist of (111) facets and (100) facets with low surface energy and to exist in the stable state. The typical particle shapes are cubes and truncated octahedrons. In addition, all platinum surfaces are assumed to be electrochemically effective.

Two types of adsorbed states were confirmed for the water molecules on the platinum surface. One has two O-H bonds oriented parallel to the platinum surface and exists near the surface, and the other has a single O-H bond oriented perpendicular to the platinum surface and exists farther away from the surface. In addition, it has also been reported that an ordered structure results due to the hydrogen bonding that occurs between these states⁽¹³⁾. In consideration of these findings, this study calculated the state of the water adsorbed with an ordered structure on the platinum surface using DMC calculations beforehand, and used these results as the initial state to calculate the surface reaction. At this time the parallel-oriented water molecules described above have high adsorption energy; therefore, they are considered to be a substance not included in the oxygen reduction reaction system taken into account in these calculations, and it is hypothesized that only the perpendicular-oriented water molecules react.

In addition, the frequency factor based on transient state theory was corrected according to the proton concentration per unit volume in order to reproduce the water electrolysis tests using platinum electrodes⁽¹⁴⁾.

4.1.2. Calculation results

Figure 5 shows the activity of Pt(111) and Pt(100). The higher activity of Pt(111) was also exhibited in tests⁽¹⁵⁾, and matches qualitatively with the results of these calculations.

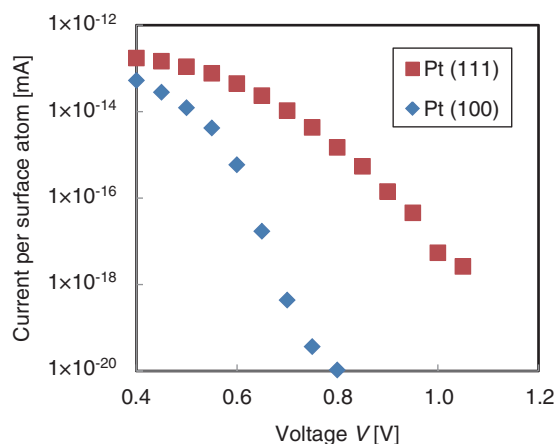


Fig. 5 Current per surface atom against cell voltage

Table 1 Change of Gibbs free energy ΔG , in eV

Reaction	Pt (111)	Pt (100)
OO $\rightarrow$ OOH	-0.82	-0.79
O $\rightarrow$ OH	-0.94	-1.27
OH $\rightarrow$ H ₂ O	-1.17	-0.53

Figure 6 shows snapshots of the adsorbed species states on the platinum surfaces at a voltage of 0.8 V. The Pt(100) is covered by OH groups and water molecules adsorbed parallel to the surface that do not easily contribute to the reaction as described previously, indicating that the OH-to-water reaction expressed by Eq. (9) is stagnating.

To help consider the reasons for this, Table 1 shows the change in the Gibbs free energy obtained by DFT calculation in the electrochemical reactions in the rightward directions of Eq. (6), (7) and (8). Here, the reaction equation (8) for Pt(100) suggests that the reaction does not proceed easily compared to Pt(111).

Next, the dependency of the activity on particle size was calculated for the typical shapes. The particle current density was estimated by adding the respective activity levels shown in Fig. 5 corresponding to the area of each particle surface orientation. Here, the adsorption energy of separate chemical species was calculated for the joints between surfaces (edges and apexes). Because the joints were found to have extremely high adsorption energy, they were considered to have low electrochemical activity, and were excluded from the reaction calculations. Figure 7 shows these results. This shows that the catalyst particle size has an optimum value in terms of activity, and that a regular octahedron is better as the shape.

4.2. Calculation of Proton Transfer within the Electrolyte

4.2.1. Modeling

This study targeted Nafion[®], which is generally used as the PEMFC electrolyte. Nafion[®] consists of a main chain made of carbon and fluorine, and a side chain with a sulfone group at the tip. Since the molecular weight

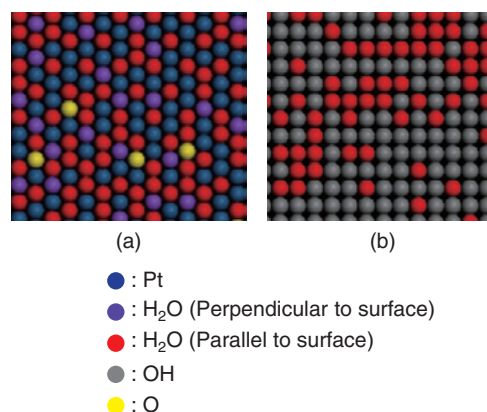


Fig. 6 Adsorption of species at 0.8V on Pt (111) ((a)) and Pt (100) ((b))

exceeds 10000 - 100000, it cannot be handled as is by the developed TBMD code in this study. Therefore, this study performed calculations with the degree of main chain polymerization, which is actually between 100 and 1000, set to 4, and the side chain simplified as shown in Fig. 8. TBMD calculations were performed for a sufficient time in the equilibrium state with a time increment of $\Delta t = 0.05$ fs, while controlling to a constant volume and a constant temperature of 300 K, and the results were used to calculate the H_3O^+ ion migration distance. The lengths of all O-H bonds were recorded during the calculations in order to track the H_3O^+ ion reconfiguration due to proton hopping. In this calculation, the ion exchange capacity (*IEC*, mmol/g) was used as the side chain density parameter, and the water content λ (number of water molecules per sulfone group) was used as the water concentration parameter. Figure 9 shows the calculated state when $\lambda = 12$ and *IEC* = 0.87 mmol/g.

During PEMFC operation, a nonequilibrium state called potential gradient occurs within the electrolyte, resulting in macro transport of the charge (H^+) accompanied by the electro-osmosis phenomenon whereby the water molecules also migrate. However, in these calculations the proton conductivity is calculated from the proton diffusion coefficient in the equilibrium state. Water transfer due to electro-osmosis is described separately in Sub-section 4.4.2.

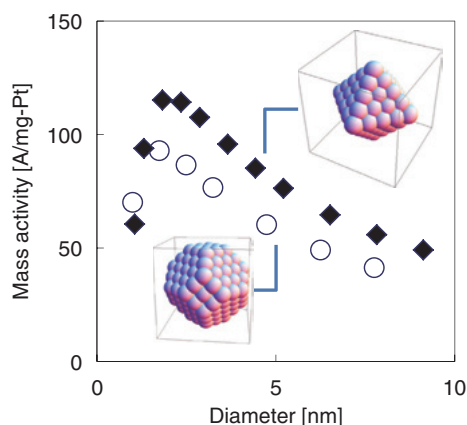


Fig. 7 Effect of catalyst particle size and shape on electrochemical activity

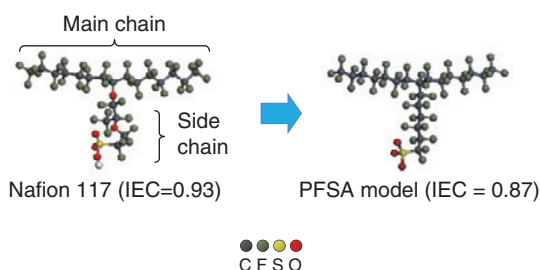


Fig. 8 Simplification of chemical structure

4.2.2. Calculation results

Figure 10 shows the calculated proton conductivity. The proton conductivity was calculated as follows. Each self-diffusion coefficient is calculated based on the mean-square displacement of the H_3O^+ , and this is then converted to the proton conductivity according to the Nernst-Einstein relation. Because the TBMD method is unable to take into account long-distance interactions, the hydrogen bonding energy cannot be quantitatively calculated. Therefore, this computational method evaluates the ratio (calculated value/measured value) of the water self-diffusion coefficient separately, and uses this to correct the proton conductivity. Figure 10 shows the change in proton conductivity due to the change in the side chain density obtained by this calculation, converted to the ion exchange capacity (*IEC*). The tendency of the proton conductivity to rise together with the change in water content closely matched the Nafion[®] proton conductivity measurement results reported by Zawodzinski et al.⁽¹⁷⁾. Since this tendency cannot be adequately reproduced by classical molecular dynamics calculations⁽¹⁷⁾, it is thought that this method enables understanding of the dependency on the water content by using quantum dynamics to solve proton hopping. In addition, based on these calculation results, increasing the *IEC* is predicted to greatly increase the proton conductivity, especially in the low-water-content range where $\lambda < 6$.

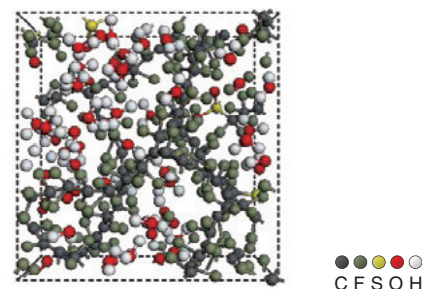


Fig. 9 Snapshot of TBMD calculation ($\lambda = 12$, *IEC* = 0.87 mmol/g)

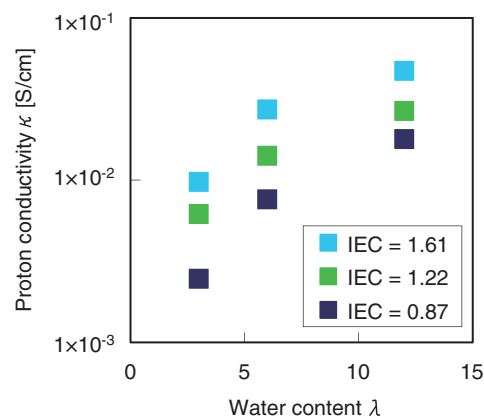


Fig. 10 Predicted conductivity

4.3. Calculation of Water Blockage inside Nano-pores

4.3.1. Modeling

Normally the PEMFC electrode catalyst consists of precious metal particles having a diameter of several nm coated onto carbon support having a diameter on the order of several tens of nm, and impregnated with electrolyte components. The remaining areas become gaps on the order of several nm as shown in Fig. 2. This study focused on the capillary condensation of water in these gaps.

Although the PEMFC is operated at a nonequilibrium state where water generation occurs continuously in the catalyst layer, this computational method assumed that this could be expressed by equilibrium state calculations. The calculations neglected the potential field within the catalyst layer, and focused on only the carbon wall surface, modeling it as follows. The gap was modeled as the space between two infinitely wide parallel flat plates, and the behavior of the water molecules inside this space was calculated using the chemical potential and the temperature as parameters. The calculations assumed a fixed interatomic distance within the water molecules, and the atoms comprising the wall surfaces were also fixed. The gap size is represented by the distance between the flat plates, and the wall surfaces are represented by graphite (graphene sheets). Figure 11 shows these parallel flat plates and the initial state for the calculations. The interaction between the atoms in the water is expressed by the SPC/E potential, the interaction between the graphite and the water is expressed by the LJ potential in which the parameters are set to reproduce the angle of contact between the flat plate surfaces and the water droplets of 86° , which is weakly hydrophilic⁽¹⁸⁾.

The change in the boiling point of the water inside the nano-pores was calculated to investigate the validity of the molecular dynamics calculations with constant chemical potential developed by this study. Since the catalyst layer surface was represented by a graphene sheet, the carbon potential was applied. In the case of a hydrophilic surface such as carbon, the boiling point inside the pores rises. The developed computational method calculated a rise in the boiling point of 5.8 K for an equivalent pore radius of 4 nm. In contrast, the rise in the boiling point for mesoporous carbon, which has the same modal pore diameter in the gas adsorption method, was 8.7 K measured by the DSC method. On the other hand, the Kelvin equation that has generally been used to predict the phase-change temperature inside the pores produced a value of 1.5 K. Based on these

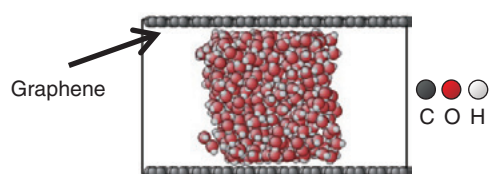


Fig. 11 Computational model of pore and initial state

results, it is thought that the developed computational method, which takes into account the behavior of the water molecules relative to the wall surface potential, is able to more accurately predict the actual phenomena.

4.3.2. Calculation results

The developed computation method was used to calculate the pressure at which the liquid phase evaporates at a certain temperature relative to the distance between the flat plates. The pressure at which the phase change occurs was obtained by performing GMD calculations multiple times with different chemical potentials, searching for the point at which the number of molecules decreases rapidly, and using the pressure value at that point. The temperature-pressure-pore diameter (distance between the flat plates) characteristics for the gas-liquid phase change can be obtained from this result. Next, the pore diameter distribution of an electrocatalytic layer created by the method described in Fig. 2 was measured using the gas adsorption method. The results were applied to the gas-liquid phase change characteristics described above, and the degree to which the electrocatalytic layer was blocked by liquid water according to the temperature and relative humidity was calculated. The pressure used was the water vapor pressure at the relative humidity. Figure 12 shows these results. For example, in the case of the created catalyst layer, when the temperature is 75°C and the relative humidity is 70%, it is predicted that approximately 10% of the pore volume will be blocked by water.

4.4. Coupled Computation of Multi-physics

4.4.1. Computational method

It is necessary to calculate the various phenomena described thus far simultaneously in a coupled manner to confirm the influence of the various phenomena on device performance. The relationship between the PEMFC current and voltage is determined from the governing equations for each chemical species, the behavior of the mixed gas consisting of these chemical species, the electrolyte phase potential, and the solid phase potential. As shown in Fig. 1, the dependent variables in these

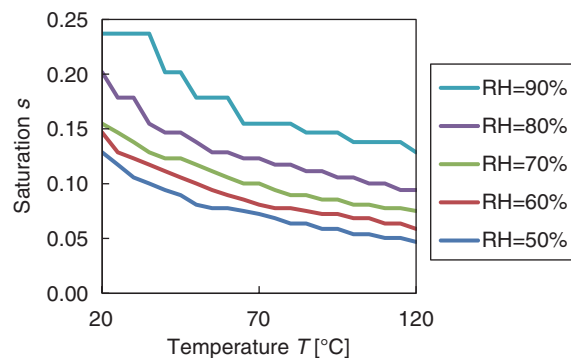


Fig. 12 Estimated pore volume fraction occupied by liquid water at various relative humidities

equations are the oxygen concentration C_{O_2} , hydrogen concentration C_{H_2} , water concentration C_{H_2O} , mixed gas velocity vector $\mathbf{u}$, electrolyte phase potential Φ_e , and solid phase potential Φ_s . The mixed gas density ρ is determined from the concentration of each chemical species and the state equation of the ideal gas. The electrocatalytic layer is considered to be a homogenous porous medium consisting of the three phases of the electrolyte phase that diffuses the protons, the gaseous phase inside the pores, and the support phase that transfers the electrons. The electrolyte phase and the gaseous phase water are assumed to be in the equilibrium state. The electric current generation per unit volume was calculated using a constitutive equation and given as a source term. Labeling the variable to be solved for all of these governing equations as ϕ , this can be expressed in the steady state in the form of the following convective diffusion equation⁽¹⁹⁾.

$$\rho \mathbf{u} \phi = \nabla \cdot (\Gamma \nabla \phi) + S \quad (10)$$

Here, ρ is the density, Γ is the diffusion coefficient, and S is the source term. The various governing equations can be expressed by replacing ϕ with the respective variables described above, and replacement with “1” results in an equation of continuity. Therefore, all governing equations can be solved by applying computational fluid dynamics techniques⁽²⁰⁾. The boundary conditions are the flow rate and composition of the gas flowing into the gas channels, and the current collector potential of both electrodes.

4.4.2. Multi-scale model

Based on the results obtained in the previous section, the various nano-scale phenomena were expressed as a multi-scale model (a model linking phenomena of differing scales) to enable incorporation into unit cell-scale (several cm) computations.

The reaction rate at the cathode was obtained as follows. The current value per platinum atom according to the potential, oxygen concentration and temperature was calculated by DMC calculations, and this current value was then converted to the reaction rate per unit volume $j = j_{MS}(V, T, C_{O_2})$ in accordance with the platinum coated mass per unit area, the area per unit platinum mass, and the catalyst layer thickness. Here, the catalyst effective utilization rate was set at 0.8 as suggested by the reference (21). The oxygen concentration of the catalyst surface used in the DMC calculations was calculated from the gas phase oxygen concentration C_{O_2} using Henry's constant. The effects of the oxygen concentration and the temperature appear via frequency factor A of the reaction rate in the reaction formula (Eq. (2)).

Based on the results in Fig. 12, the degree of catalyst layer pore blockage due to the influence of nano-pores was determined to be a function of the temperature and water concentration, and defined as $s = s_{MS}(T, C_{H_2O})$. Due to this effect, the catalyst surface area was thought to decrease,

Table 2 Models incorporated into the governing equation, Eq. (10). Listed modifications are applied to polymer electrolyte part including electrodes indicated in Fig. 1.

Variable, ϕ	Modified terms
Species, C_m	$\Gamma = D_m^{\text{eff}}$, only to electrodes.
	$S = S_d = \nabla \cdot [(n_d/F)\mathbf{i}_e]$ if $m = H_2O$
	$S = -j^{\text{eff}}/(2F) + S_d$, only to cathode if $m = H_2O$
	$S = j^{\text{eff}}/(4F)$, only to cathode if $m = O_2$ $S = -j^{\text{eff}}/(2F)$, only to anode if $m = H_2$
Electrolyte potential, Φ_e	$\Gamma = \kappa^{\text{eff}}(\lambda)$. $S = j^{\text{eff}}$, only to electrodes.
Electronic phase potential, Φ_s	$S = -j^{\text{eff}}$, only to electrodes.

and the reaction rate j was corrected to $j^{\text{eff}} = (1-s)j$. In addition, the diffusion coefficients for water, oxygen and hydrogen were also corrected to $D_m^{\text{eff}} = (1-s)^\tau D_m$ ($m = H_2O, H_2, O_2$). Here, τ is the tortuosity of the porous medium. The calculations assumed that the degree of blockage s did not increase further at a relative humidity of 99% or more.

In the electrocatalytic layer, the transfer rate of each conserved quantity with respect to the electrolyte phase water and potential, the gaseous phase chemical species in the pores, and the support phase electron potential is thought to be equivalent to the transfer rate multiplied by the volume fraction of the respective phases taken to the tortuosity power.

Based on the IEC dependency obtained by the TBMD calculations, the proton conductivity of the electrolyte membrane was corrected from the reference document value⁽¹⁹⁾ to $\kappa^{\text{eff}}(IEC, \lambda) = f(IEC, \lambda) \kappa_{\text{ref}}(\lambda)$. Various models have been proposed for the number of water molecules that migrate (electro-osmotic coefficient n_d) incidental to the current vector $\mathbf{i}_e$ due to H_3O^+ transfer within the membrane. However, from the MRI measurement results of the proton concentration inside the electrolyte membrane during operation, a water content dependent model was thought to be appropriate⁽²²⁾, and the model given in reference (23) was used.

Arbitrary models used the models given in reference (19), and arbitrary physical property values used generally known values. The diffusion coefficient Γ and source item S in Eq. (10) were modified as shown in Table 2, and calculations were performed with the above models applied to the locations indicated in Fig. 1. F in the table is the Faraday constant. Although the transfer of liquid phase water in the gas diffusion layers and gas channels is also an important issue, this study focused in particular on phenomena in the electrocatalytic layer. Therefore, only blockage of nano-scale pores inside the catalyst layer due to the liquid phase was taken into account. The calculation subject cell used 112 Nafion® as the electrolyte

membrane, simulated the electrocatalytic layer described in Chapter 1, and used three-dimensional shapes that simulate the JARI standard cell for other parts. Since appropriate thermophysical properties were not available, the calculations assumed that there was no temperature distribution and the temperature was fixed to 75°C. The dew point temperature of the inflow gas to the gas channels was set to 75°C at the anode and 55°C at the cathode, and the stoichiometry was set to 4 at the anode and 3 at the cathode. The inlet pressure was set to two times atmospheric pressure. The anode and cathode gas channels flow in parallel to each other on the respective sides of the membrane.

4.4.3. Calculation results

Figure 13 shows the calculated current density-voltage characteristics per unit electrode coated area. These results show a rapid drop in voltage in the low-current range and a drop in voltage in the high-current range, which are well known from experiments. Of particular note is the fact that this computational method calculates the reaction rate at the cathode from only the elementary reaction rate based on first-principles calculations and the measured characteristics. That is to say, arbitrary parameter fitting is not performed.

Next, Fig. 14 shows the calculated internal physical quantities at the cell voltage $V = 0.5$ V. This shows the distributions passing through the membrane in the direction from the cathode to the anode in the channel center section (cross-section along the dashed line shown in Fig. 1) near the inlet, center and outlet of the gas channels. This figure shows that the proton conductivity is widely distributed. This is due to the internal water content λ distribution. The current density per unit volume at the cathode is lower on the electrolyte membrane side at the inlet; however, this relationship reverses at the outlet. The reason is explained as follows: On the inlet side, the water content is low and the proton conductivity is also low accordingly. The electrolyte potential difference increases within the catalytic layer, causing the current density to increase near the electrolyte membrane. On the contrary, on the outlet side, the potential

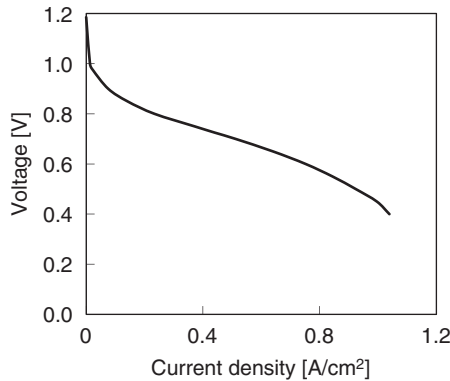


Fig. 13 Predicted voltage-current density curve with multi-scale models

difference is equalized and the oxygen concentration near the membrane drops, so the current density near the membrane drops. In addition, since the relative humidity exceeds 100% partway through the gas channels of both electrodes, the degree of catalytic layer blockage becomes saturated at this time. The fact that the computational model assumed that the degree of blockage s does not rise further at a relative humidity of 99% or more as mentioned previously is thought to have some influence. However, the degree of blockage reached nearly 30%, which is thought to contribute to the drop in oxygen concentration inside the catalyst layer near the outlet. Thus, the phenomena targeted by this study were found to interact and influence performance.

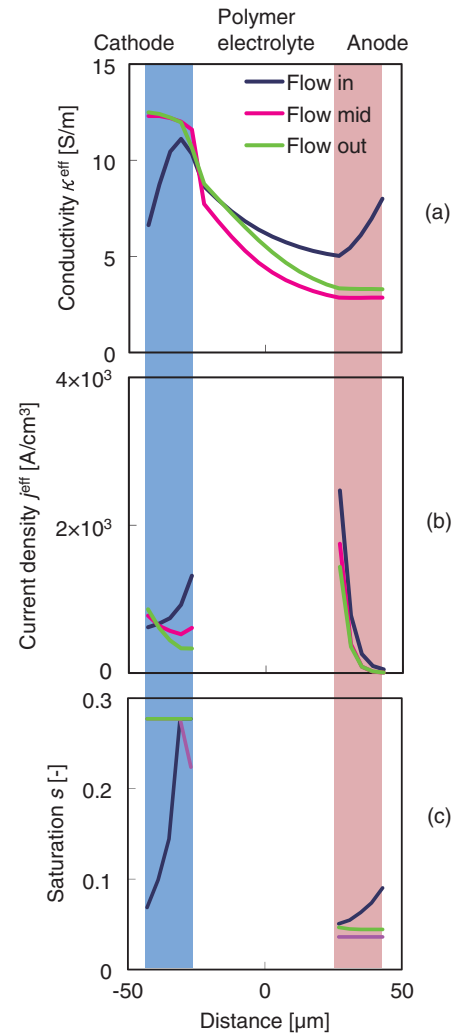


Fig. 14 Predicted distribution of physical quantities through polymer electrolyte membrane, (a) proton conductivity, (b) current density, (c) liquid saturation. The curves indicate values on the plane cut in the middle of the gas channel: Dashed line in Fig. 1. Anode and cathode are shaded with red and blue respectively.

5. Conclusion

Computational techniques that take into account nano-scale mechanisms were constructed for phenomena that had not been given sufficient consideration thus far in predictions of PEMFC performance, and the following knowledge was gained.

- (1) Calculations were performed that take into account the influence of proton hopping on proton conductivity, and clarified that there is a relationship between the ion exchange capacity and the conductivity.
- (2) Calculations were performed that take into account the states of the adsorbates on the catalyst surface in consideration of the potential, and clarified that the catalyst particle size influences the activity per unit catalyst mass.
- (3) Drop-wise condensation was calculated taking into account the influence of nm-order pores, and it was shown that capillary condensation inside the catalyst layer pores cannot be ignored.
- (4) A computational technique was also developed that calculates the effects of individual phenomena in a coupled manner as a multi-scale model that can be reflected to PEMFC unit cell performance. The results showed that the interaction between the above phenomena appears in the performance.

References

- (1) Wang, Y., Chen, K. S., Mishler, J., Cho, S. C., Adroher, X. C.: A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research, *Applied Energy*, Vol. 88, p. 981–1007 (2011)
- (2) Rai, V., Pitsch, H.: First-principles analysis of oxygen-containing adsorbates formed from the electrochemical discharge of water on Pt(111), *Journal of Physical Chemistry C*, Vol. 112, p. 9760–9768 (2008)
- (3) Aryanpour, M. M., Rai, V., Pitsch, H.: Convergent iterative constrained variation algorithm for calculation of electron-transfer transition states, *Journal of the Electrochemical Society*, Vol. 153 (3), p. E52–E57 (2006)
- (4) Rossmeisl, J., Nørskov, J. K.: Calculated Phase Diagrams for the Electrochemical Oxidation and Reduction of Water over Pt(111), *Journal of Physical Chemistry B*, Vol. 110, p. 21833–21839 (2006)
- (5) Glasstone, S., Laidler, K., Eyring, H.: *The theory of rate processes*, McGraw-hill (1941)
- (6) Agmon, N.: The Grotthuss Mechanism, *Chemical Physics Letter*, Vol. 244, p. 456 (1995)
- (7) Ueda, A.: *Molecular simulation, - From classical to quantum methods -*, Shokabo, Tokyo, 446 p. (2003) (in Japanese)
- (8) Laasonen, K., Nieminen, R. M.: Molecular dynamics using the tight-binding approximation, *Journal of Physics: Condens. Matter.*, Vol. 2, p. 1509–1520 (1990)
- (9) Pople, J. A., J. Binkley, J. S., Seeger, R.: Theoretical models incorporating electron correlation, *International Journal of Quantum Chemistry*, Vol. 10, S10, p. 1–19 (1976)
- (10) Klein, J., Kumacheva, E.: Confinement-Induced Phase Transitions in Simple Liquids, *Science*, Vol. 269, No. 5225, p. 816–819 (1995)
- (11) Çağın, T., Pettitt, B. M.: Grand molecular dynamics: A method for open systems, *Molecular Simulation*, Vol. 6, No. 1, p. 5–26 (1991)
- (12) Kim, S. H., Rai, V., Pitsch, H.: Multi-Scale Modeling of Catalyst Layers in PEM Fuel Cells Based on Dynamic Monte Carlo Method for Surface Reactions, 212th ECS Meeting, Abstract #512 (2007)
- (13) Meng, S., Wang, E. G., Gao, S.: Water adsorption on metal surfaces: A general picture from density functional theory studies, *Phys. Rev. B*, Vol. 69, p. 195404 (2004)
- (14) Wang, J. X., Markovic, N. M., Adzic, R. R.: Kinetic Analysis of Oxygen Reduction on Pt(111) in Acid Solutions: Intrinsic Kinetic Parameters and Anion Adsorption Effects, *Journal of Physical Chemistry B*, Vol. 108, p. 4127–4133 (2004)
- (15) Markovic, N. M., Adzic, R. R., Cahan, B. D., Yeager, E. B.: Structural effects in electrocatalysis: oxygen reduction on platinum low index single-crystal surfaces in perchloric acid solutions, *Journal of Electroanalytical Chemistry*, Vol. 377, p. 249–259 (1994)
- (16) Zawodzinski, T. A., Neeman, M., Sillerud, L. O., Gottesfeld, S.: Determination of water diffusion coefficients in perfluorosulfonate ionomeric membranes, *Journal of Physical Chemistry*, Vol. 95, p. 6040–6044 (1991)
- (17) Zhou, X., Chen, Z., Delgado, F., Brenner, D., Srivastava, R.: Atomistic Simulation of Conduction and Diffusion Processes in Nafion Polymer Electrolyte and Experimental Validation, *Journal of the Electrochemical Society*, Vol. 154, p. B82–B87 (2007)
- (18) Werder, T., Walther, J. H., Jaffe, R. L., Halicioglu, T., Koumoutsakos, P.: On the Water- Carbon Interaction for Use in Molecular Dynamics Simulations of Graphite and Carbon Nanotubes, *J. Phys. Chem. B*, Vol. 107, p. 1345–1352 (2003)
- (19) Wang, C. Y.: Fundamental Models for Fuel Cell Engineering, *Chemical Reviews*, Vol. 104, p. 4727–4766 (2004)
- (20) Ferziger, J. H., Peric, M.: *Computational Methods for Fluid Dynamics*, Springer (1997)
- (21) Gasteiger, H. A., Kocha, S. S., Sompalli, B., Wagner, F. T.: Activity benchmarks and requirements for Pt-Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, *Applied Catalysis B: Environmental*, Vol. 56, p. 9–35 (2005)
- (22) Tsushima, S., Ikeda, T., Koido, T., Hirai, S.:

Investigation of Water Distribution in a Membrane in an Operating PEMFC by Environmental MRI, Journal of the Electrochemical Society, Vol. 157, Iss. 12, p. B1814-B1818 (2010)

- (23) Springer, T. E., Zawodzinski, T. A., Gottesfeld, S.: Polymer Electrolyte Fuel Cell Model, J. Electrochem. Soc., Vol. 138, No. 8, p. 2334-2342 (1991)

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