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Inhomogeneous distribution of platinum and ionomer in the porous cathode to maximize the performance of a PEM fuel cell

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Abstract

A proton exchange membrane (PEM) fuel cell model, accounting for the combined water transport mechanism, ionomer swelling, water phase-transfer, two-phase flow and transport processes, is developed. The inhomogeneous distributions of Pt and ionomer inside the catalyst layer (CL) are numerically studied to achieve an optimal cell performance for two types of oxygen reduction reaction catalysts at different loadings. Results indicate that the optimal variation in loading through the thickness of the electrode (slopes) of Pt catalyst and ionomer vary with conditions of operation. An optimal platinum slope increases the agglomerate effectiveness factor and decreases the second Damköhler number near the CL-membrane interface. An optimal ionomer slope increases the CL porosity near the GDL-CL interface and decreases the mass transport resistance of reactant through the ionomer film. Their interaction shows that the optimal platinum slope is a tradeoff between the electrochemical active surface area and porosity at high current densities.

Keywords: PEM fuel cell, inhomogeneous distribution, graded catalyst layer, platinum and ionomer loading, mathematical modeling.

Introduction

Due to high efficiency and low environmental impact, proton exchange membrane fuel cells (PEMFCs) are one of the most promising energy conversion devices for portable power sources and alternative to combustion engines in vehicles^{1,2}. However, the high cost and insufficient utilization of platinum as the sluggish oxygen reduction reaction (ORR) catalysts at the cathode hamper the widespread use of PEMFCs³. It is reported that the acceptable cost for the application of the automotive fuel cell system should be below \$30/kW⁴. Since platinum is dispersed within a complex porous carbon matrix and combines with ionomer (typically Nafion[®]) and void space to build up triple-phase-boundaries (TSBs) for effective electrochemical reaction in an operating condition⁵, the architectural design and size of the catalyst layer (CL), especially the rational distributions of platinum and ionomer inside the CL, is critically important to reduce the cost and improve the cell performance⁶⁻⁹. Moreover, a good water removal ability is another vital consideration for improved cell performance at high current densities, as the liquid water inside the cathode CL and the GDL strongly influence the cell performance and durability¹⁰⁻¹⁴.

Prior research has experimentally improved the cell performance using the electrode design with a graded distribution of platinum, ionomer and pores through the electrode thickness¹⁵⁻¹⁷. However, experimental studies are very expensive and time-consuming in which the trial-and-error procedures only allow a small portion of design parameters being explored. Computational modelling therefore provides an alternative to address this issue. A few modelling activities are available in the open literature on CL optimization considering the inhomogeneous spatial distributions of CL compositions. Wang et al.¹⁸ investigated the non-uniform Nafion[®] distribution across the entire thickness of a three-sublayer structure and found that significant enhancement of cell performance was achieved with higher Nafion[®] content on the membrane side. Song et al.¹⁹ numerically studied the optimal distributions of both platinum and ionomer loadings and concluded that Nafion[®] distribution is a more important parameter than the platinum distribution of cathode catalyst layer (CCL) design. Jain et al.²⁰ adopted an agglomerate model to minimize the platinum usage at different operating voltages. It was indicated that significant

improvement in current density can be obtained by placing higher amounts of platinum adjacent to the CL-membrane interface and following a non-linear decrease to the CL-GDL interface. However, these three studies did not account for the dependency of liquid water content on current density and the dynamic influence of liquid water on mass transport. Srinivasarao et al.²¹ developed a multi-layer model in which the weight fraction of platinum to carbon (Pt/C), platinum loading and ionomer loading were optimized. Although dynamic liquid water generation and spherical agglomerate CL microstructure were taken into account, Nafion[®] membrane/ionomer swelling was omitted in this study. In fact, the ionomer is capable of expanding its volume for approximately 20% when fully hydrated^{22,23}. Ionomer swelling on one hand reinforces the crosslinking of adjacent agglomerates thus increases the diffusivity of dissolved water, oxygen and proton, on the other hand, it reduces the porosity of CL, leading to an increase in gas transport resistance through the CL void space^{24,25}.

ORR activity, specific area, proton conductivity and porosity are vital important parameters of the CL. However, it is impossible to simultaneously improve those parameters through optimization. Typically, the improvement of one parameter in the CL will worsen another one. Therefore, the objective of optimization is to maximize the synergistic effect of all important parameters at a certain operating condition. It is commonly accepted that the CL adjacent to the gas diffusion layer (GDL) should be more porous than that near the membrane as the concentration of oxygen decreases within the CL; from the GDL-CL interface towards the CL-membrane interface. In addition, the CL adjacent to the membrane should contain more ionomer to guarantee a good proton conductivity. For the precious platinum, increasing its effectiveness by placing more amounts in specific regions is essential to reduce its loading. To achieve the maximum cell performance at various load conditions, the optimal parameters, e. g. platinum loading, ionomer loading, are typically various according to the operational requirement of a PEM fuel cell. Unfortunately, such studies are limited in the previously published literature. Secanell et al.^{26,27} developed a multi-variable optimization model to obtain the optimal composition of the cathode catalyst layer (CCL), represented according to an agglomerate assumption. It was found that the optimal design parameters depend on current density, e. g. the optimal platinum loading decreases from 1.0 to

0.35 mg cm⁻² and the optimal porosity increases from 10% to 32%, corresponding to low and high current densities, respectively. In addition to the above-mentioned findings, our previous work found that the proton conductivity is of importance to the cell performance at low current densities²⁸.

In this work, we numerically examined the linear variations in platinum and ionomer loadings through the thickness of the cathode of a PEM fuel cell. For this purpose, we developed a comprehensive model for a single PEM fuel cell, accounting for water-gas two-phase flow, the combinational water transport mechanism through the membrane, ionomer swelling, water phase-transfer and most of the physical and chemical transport processes. Platinum loading is assumed to linearly decrease through the CL from the GDL toward the membrane, while ionomer loading decreases in the opposite direction. The optimal slopes of platinum and ionomer are suggested at various cell voltages, corresponding to a range of current densities, for two types of ORR catalysts with low and high activities. The capillary diffusion coefficients for liquid water at a variety of platinum and ionomer slopes are studied. The Damköhler number is used to represent the competitive relation between reaction and diffusion of reactant gas inside the CL. The interactive effect of platinum and ionomer loading are studied. The optimal slopes for both platinum and ionomer loadings are obtained for a maximum current density at various cell voltages.

Development of a functional graded CL is a challenge in practical activities due to the very limited thickness and complexity of the CL. The multi-layer design is used in most of previous experimental studies^{16,17,21}. However, the optimized platinum and ionomer slopes and the associated mechanisms for the reinforced species and mass transport can be used as guidance in the commercial and industrial multi-layer CL preparation.

Mathematical model

Model description and assumption

As shown in Figure 1, the fuel cell unit geometry consists of flow channels, GDLs, CLs for the anode and cathode, respectively, and a Nafion[®] membrane sandwiched in between. The CLs are assumed to be

comprised of a large number of spherical catalyst agglomerates according to the agglomerate assumption as shown in Figure 2. In addition to the assumptions of the agglomerate morphology, reactant transport, water phase-transfer and membrane/ionomer swelling in the previous publications^{24,25,29,30}, the proton conductivity and the gradients of platinum and ionomer loading are assumed in detail as follow:

(1) *Proton conductivity*. It is assumed that the agglomerate is coated with a uniformly thick ionomer film. As shown in Figure 2, the contact area between agglomerates increases as the ionomer film thickness increases, leading to an increase in proton conductivity.

(2) *Gradients of platinum and ionomer loadings*. Platinum loading is assumed to be linearly decreased from the CL-GDL interface to the CL-membrane interface at a fixed slope, while ionomer loading decreases in the opposite direction. The maximum decreasing slope (abbreviated as slope below) of ionomer loading should guarantee an interactive ionomer network; that means all agglomerates are contacted by ionomer films with different ionomer loading dependent, contact area. Only the through-plane platinum and ionomer distribution are studied.

Governing equations

Conservation equations

The most important equations in a general form was summarized as follows. Detailed conservation equations for the transport of gas, water, heat and charge were developed in our previous publications^{24,29-32}.

By substituting the expression of the gas velocity according to Darcy's law^{29,30} into a general convection-diffusion equation³³, the conservation of mass, momentum, species, charge and energy at a steady state is given as the follow form:

$$-\nabla \cdot \left(\frac{k_p \tilde{\rho} \phi}{\mu} \nabla p \right) = \nabla \cdot (\Gamma_\phi \nabla \phi) + S_\phi \quad (1)$$

where ϕ is the general variable to be solved, $\tilde{\rho}$ is the nominal density, Γ_ϕ is the generalized diffusion coefficient of ϕ . k_p (m^2) is the permeability of the porous media, μ (Pa s) is the viscosity of the variable, p (Pa) is the pressure. The expressions of ϕ , $\tilde{\rho}$ and Γ_ϕ for different equations were listed in Table 1. S_ϕ is the source term of ϕ in different modelling domain, which was given in detail elsewhere²⁹.

For the transport of dissolved water through the membrane and liquid water within the porous electrode, the following equations were applied³⁰:

$$\nabla \cdot (n_d \frac{i_M}{F}) - \nabla \cdot (D_{w-M} \nabla c_w^d) - \nabla \cdot (\frac{k_{p,M} c_w^d}{\mu_w} \nabla p) = S_w^d \quad (2)$$

$$\nabla \cdot (\rho_w^l D_c \nabla s - \frac{\rho_w^l k_r^l \mu_w^g}{k_r^g \mu_w^l} \mathbf{u}^g) = M_w S_w^l \quad (3)$$

Equation 2 was developed by combining the diffusive approach and the conservation equation of dissolved water, while Eq. 3 was obtained by applying the volume average approach to the continuity equation and using Darcy's law for both the liquid and gas phases.

The liquid water transport through GDLs, CLs and channel, D_c ($\text{m}^2 \text{s}^{-1}$), was calculated using the capillary diffusion coefficient as follow³⁴:

$$D_c = -\frac{k_r^l}{\mu_w^l} \sigma \cos(\theta_c) (\varepsilon_i k_{p,i})^{1/2} \frac{dJ(s)}{ds} \quad (4)$$

where k_r^l is the relative permeability, μ_w^l (Pa s) is the dynamic viscosity, σ (N m^{-1}) is the surface tension, θ_c ($^\circ$) is the contact angle, $J(s)$ is the Leverett-J function, ε is the porosity of the electrode, s is the liquid water saturation, defining as the volume fraction of the pores occupied by liquid water. The subscript i represents different computational domains, including CLs, GDLs and channels of the anode and cathode.

Although the capillary diffusion through a porous layer and related wetting properties (such are breakthrough pressure and adhesion force) are also a function of pore size, pore structure and the thickness of the layer^{35,36}, the Leverett-J function has been widely used for fuel cell models and it provides a reasonable estimation of capillary diffusion for any arbitrary porous transport layers with a known contact angle^{11,37}.

The membrane/ionomer water content was described as^{34,38}:

$$\lambda = 0.043 + 17.81\alpha_w - 39.85\alpha_w^2 + 36.0\alpha_w^3 \quad \alpha_w \leq 1 \quad (5)$$

where α_w is the water activity. The equilibrium membrane/ionomer water content, determined based on water uptake measurement, was given as³⁵:

$$\lambda^{eq} = 16.8s + 14.0(1-s) \quad s > 0 \quad (6)$$

Reaction kinetics

Electrochemical reactions occur when reactant gas reaches the catalyst active site. In the conservation equation of charge, the volumetric current density inside the CLs according to agglomerate assumption³⁹⁻⁴¹ can be written as below:

$$i_{agg,i} = n_i F \left(\frac{p_i}{c_i^{ref} H_i} \right)^\gamma \left[\frac{1}{E_{agg,i} k_{agg,i}} + \frac{r_{agg} + \delta_M + \delta_{w,i}}{r_{agg}} \left(\frac{\delta_M}{a_{agg,i}^M D_{i-M}} + \frac{\delta_{w,i}}{a_{agg,i}^w D_{i-w}} \right) \right] \quad (7)$$

where the first term in the square bracket represents the reaction kinetics and the second term includes the mass transport resistance of species through the ionomer and liquid water films. Here $k_{agg,i}$ (s^{-1}) is the reaction rate coefficient of species i , which is defined as

$$k_{agg,i} = \frac{a_{agg,i}^M i_{0,i}^{ref}}{n_i F} \left[\exp\left(\frac{-\alpha_{Rd,i} F \eta_i}{RT}\right) - \exp\left(\frac{\alpha_{Ox,i} F \eta_i}{RT}\right) \right] \quad (8)$$

where p_i (Pa) is the partial pressure, $E_{agg,i}$ is the effectiveness factor of the agglomerate, $\delta_{w,i}$ (m) is the liquid water film thickness, $a_{agg,i}^M$ (m^{-1}) presents the electrochemical active surface area (EASA) available for the reaction, r_{agg} (m) is the radius of the agglomerate, and $\alpha_{Rd,i}$ and $\alpha_{Ox,i}$ is the charge transfer coefficient for reduction and oxidation reactions, respectively.

The agglomerate effectiveness factor, $E_{agg,i}$, and the Thiele's modulus for spherical agglomerate, $M_{T,i}$ are defined as:

$$E_{agg,i} = \frac{1}{M_{T,i}} \left[\frac{1}{\tanh(3M_{T,i})} - \frac{1}{3M_{T,i}} \right] \quad (9)$$

$$M_{T,i} = \frac{r_{agg}}{3} \sqrt{\frac{k_{agg,i}}{D_{i,agg}^{eff}}} \quad (10)$$

It is worth of noting that, the current density mainly depends on the EASA, charge transfer coefficient, the thickness of ionomer and liquid water films, the partial pressure of reactant gas at the outer boundary of liquid water film, and reactant diffusivity through the films. One can also find other electrochemical and physical parameters elsewhere^{24,25,28,31}.

Reactant gas transport in porous electrode

In the conservation equation of species, the equivalent coefficient for gas diffusing within electrode void space is given as follows:

$$\frac{1}{D_{i-P}} = \frac{1}{D_{i-g}} + \frac{1}{D_{Kn,i}} \quad (11)$$

where D_{i-P} ($\text{m}^2 \text{s}^{-1}$) is the equivalent diffusion coefficient of gas species through the porous media, D_{i-g} ($\text{m}^2 \text{s}^{-1}$) is the intrinsic diffusion coefficient of gas species in the gas mixture, and $D_{Kn,i}$ ($\text{m}^2 \text{s}^{-1}$) is the

Knudsen diffusion coefficient accounting for the gas diffusion in nano-size pores. The Knudsen diffusion coefficient ($D_{Kn,i}$), the average pore diameter of the agglomerate (d_{avg}), and the intrinsic diffusion coefficient (D_{i-p}) are defined as:

$$D_{Kn,i} = \frac{d_{avg}}{3} \sqrt{\frac{8R_g T}{\pi M_i}} \quad (12)$$

$$d_{avg} = \frac{4\epsilon_{agg,p}}{3(1-\epsilon_{agg,p})} r_{agg} \quad (13)$$

$$D_{i-p} = \frac{1-x_i}{\sum_{i \neq j} (x_j / D_{i-j})} \quad (14)$$

It is worth noting that the secondary pores of the CL can be partially filled by the liquid water due to the formation of liquid water in the CLs, which leads to a loss of the void space for gas diffusion. For the CL, the effective diffusion coefficient for reactant gas diffusing, therefore, is corrected by the water saturation as follows:

$$D_{i,s}^{eff} = [\epsilon_s (1-s')]^{1.5} D_{i-p} \quad (15)$$

where ϵ_s is the secondary pores volume fraction, s' is the corrected liquid water saturation, representing the secondary pores volume fraction occupied by liquid water. Since the primary pores are also partially filled, in this case with an ionomer, gas species diffusion inside the agglomerate was estimated by:

$$D_{i,p}^{eff} = (\%M \epsilon_p)^{1.5} D_{i-M} + [(1-\%M) \epsilon_p]^{1.5} D_{i-p} \quad (16)$$

where ϵ_p is the volume fraction of the primary pores, $\%M$ is the volume fraction of the primary pores occupied by ionomer.

Porous catalyst layer properties

The properties of CL are mainly determined by the platinum loading (m_{Pt}), platinum to carbon ratio (f), ionomer loading (m_M), CL thickness (l_{CL}) and the agglomerate size (r_{agg}). The CL properties, such as catalyst layer porosity (ε_{CL}), ionomer film thickness (δ_M) and liquid water film thickness (δ_w) are briefly shown as follow. Other parameters are available elsewhere^{24,25,28,31}.

$$\varepsilon_{CL} = 1 - \frac{m_{Pt}}{l_{CL}} \left(\frac{1}{\rho_{Pt}} + \frac{1-f}{f} \frac{1}{\rho_C} \right) - \frac{m_M}{\rho_M l_{CL}} (1 + k_s \lambda) - L_{GDL} (1 - \varepsilon_{GDL}) \quad (17)$$

$$\delta_M = r_{agg} \left(\sqrt[3]{\frac{(1 - \varepsilon_{CL}) [1 - \varepsilon_{CL} - L_S] + L_{Pt/C} \varepsilon_{CL} (1 - \%M)}{L_{Pt/C}}} - 1 \right) \quad (18)$$

$$\delta_w = \sqrt[3]{\left(r_{agg} + \delta_M \right)^3 + \frac{3s\varepsilon_{CL}}{4\pi N_{agg}}} - (r_{agg} + \delta_M) \quad (19)$$

where m_{Pt} and m_M (kg m^{-2}) are the platinum and ionomer loadings, ρ_{Pt} and ρ_M (kg m^{-3}) are the densities of platinum and ionomer, ε_{CL} and ε_{GDL} are the porosity of CL and GDL, respectively. f is the mass ratio of platinum to Pt/C, L_{GDL} is the volume fraction of GDL penetrating into CL, l_{CL} (m) is the catalyst layer thickness, k_s is the swelling coefficient of ionomer, λ is the ionomer water content. $L_{Pt/C}$ and L_S are the volume fraction of Pt/C and solid penetration, N_{agg} (m^{-3}) is the agglomerate density.

On the right side of Eq. 17, the second term is the volume fraction of Pt/C catalyst, the third term represents the volume fraction of ionomer with consideration of swelling, the last term accounts for the volume fraction of solid penetration into the CL. It is clear ε_{CL} and l_{CL} are the two variables to be solved. In this study, l_{CL} was set as a constant, ε_{CL} varies with CL composition, e. g. platinum and ionomer loadings, ionomer water content.

Proton conductivity

In the conservation equation of charge, the effective electronic conductivity was obtained by the Bruggeman correction. In order to rationally account for the effect to contacting area between agglomerates, the effective electronic and proton conductivities were calculated using the following expressions⁴⁰:

$$\sigma_s^{eff} = (L_{Pt/C})^{1.5} \sigma_s \quad (20)$$

$$\sigma_M^{eff} = (1 - \varepsilon_{CL}) \left[1 + \frac{(\%M\varepsilon_{CL} - 1)}{(1 + \delta_M/r_{agg} + a_0)^3} \right] \sigma_M \quad (21)$$

where σ_s^{eff} and σ_M^{eff} are the effective electronic and protonic conductivity of the catalyst layer, respectively. The intrinsic membrane conductivity is expressed as^{42,43}:

$$\sigma_M = \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right] (0.5139\lambda - 0.326) \quad (22)$$

The details of the properties of the catalyst layer, gas transport through the porous electrode, the formula of the conservation equations, and numerous key parameters and fundamental equations can be found in the literature^{24,25,28-32}.

The effective proton conductivity of the CL at various initial dry-ionomer loadings and average ionomer water contents is shown in Fig. 3. It can be found that the proton conductivity almost linearly increases as the ionomer loading increases and higher ionomer water content leads to a higher proton conductivity. The increase in ionomer water content is due to water uptake during cell operation, which leads to an increase in proton conductivity by reinforcing the contact between the adjacent agglomerates due to ionomer swelling.

Gradient of platinum and ionomer decreasing

$$m_{Pt}(X) = m_{Pt}^0 - k_{Pt}(1 - X) \quad (23)$$

$$m_M(X) = m_M^0 - k_M X \quad (24)$$

m_{Pt}^0 (kg m⁻²) is the platinum loading at the CL-GDL interface ($X = 1$), m_M^0 (kg m⁻²) is the ionomer loading at the CL-membrane interface ($X = 0$), X is the dimensionless distance, $X = 0$ represents the CL-membrane interface and $X = 1$ represents the CL-GDL interface.

The effect of platinum loadings at the GDL-CL interface with the initial values of 2×10^{-3} , 4×10^{-3} , 6×10^{-3} and 8×10^{-3} kg m⁻², corresponding to 0.2, 0.4, 0.6 and 0.8 mg cm⁻², are numerically studied, while the initial ionomer loadings at the CL-membrane interface are 6×10^{-3} , 9×10^{-3} , 1.2×10^{-2} , 1.5×10^{-2} and 1.65×10^{-2} kg m⁻², corresponding to 0.6, 0.9, 1.2, 1.5 and 1.65 mg cm⁻², respectively. The slopes for platinum and ionomer loadings are also varied. For the platinum loading slope (k_{Pt}), it increases from zero at a step of $20 \text{ kg m}^{-2} \text{ m}^{-1}$ ($2.0 \times 10^{-3} \text{ mg cm}^{-2} \mu\text{m}^{-1}$) to the minimum platinum loading at the CL-membrane interface. For the ionomer loading slope (k_M), the increasing step is $30 \text{ kg m}^{-2} \text{ m}^{-1}$ ($3.0 \times 10^{-3} \text{ mg cm}^{-2} \mu\text{m}^{-1}$) and in the opposite direction to the change of platinum loading. Table 2 shows the range of the slope of platinum and ionomer loadings with various initial values.

Figure 4 shows the distribution of dimensionless platinum and dry-ionomer loadings through the thickness of CL, respectively. It is clear that the platinum loading decreases to zero at the maximum slope. However, the ionomer loading cannot be lower than a critical value to guarantee the interactive network of each agglomerate. For a catalyst layer with an agglomerate density of $7.5 \times 10^{17} \text{ m}^{-3}$ and agglomerate size of $5 \times 10^{-7} \text{ m}$, the critical thickness of the ionomer film is $2 \times 10^{-9} \text{ m}$, corresponding to the dry-ionomer loading of $4 \times 10^{-3} \text{ kg m}^{-2}$ when taking the ionomer swelling into account. This means that $4 \times 10^{-3} \text{ kg m}^{-2}$ is the minimum required dry-ionomer loading for a well-interconnected network of ionomer crosslink.

Competitive relation between reaction and diffusion

Reactant gases undergo a diffusion-reaction process inside the porous CL as shown in Figure 2. Taking the sluggish ORR in the cathode CL, for example, oxygen transport through the CL from CL-GDL interface to CL-membrane interface via the secondary pores between agglomerates. Meanwhile, oxygen diffuses through the ionomer and liquid water films surrounding the agglomerate and transport via the primary pores inside the agglomerates, where the electrochemical reaction occurs. It is important to know the competitive relationship between oxygen diffusion and ORR, that is of benefit to optimize the CL thickness by avoiding the low utilization of a portion of CL. For this purpose, the second Damköhler number (Da_{II}) is used to relate the electrochemical reaction rate to the diffusive mass transport rate occurring in the porous electrode, which is defined as:

$$Da_{II} = \frac{R_{reaction}}{R_{diffusion}} = \frac{k_{agg} c_{O_2}}{a_{agg} D_{O_2,p}^{eff} \nabla c_{O_2}} \quad (25)$$

$$c_{O_2} = \frac{p_{O_2}}{c_{O_2}^{ref} H_{O_2}} \quad (26)$$

Da_{II} represents a competitive relation between reaction and diffusion. Larger Da_{II} means a faster reaction rate than the diffusion rate when larger than 1.

Boundary conditions

At the cathode inlet (A-B) and anode inlet (G'-H') as shown in Figure 1, the temperature, mole fractions of reactant gases in the gas mixture, reactant gas pressure, liquid water saturation, and gas velocities at the inlets of both electrodes as a function stoichiometric ratio are given as below:

$$T = T_a^0, x_{w,a}^0 = \frac{p_{sat} RH_a}{p_a}, x_{H_2}^0 = 1 - x_{w,a}^0, p_a = p_a^0, s_a = 0 \quad (27)$$

$$T = T_c^0, x_{w,c}^0 = \frac{p_{sat} RH_c}{p_c}, x_{O_2}^0 = 0.21(1 - x_{w,c}^0), x_{N_2}^0 = 0.79(1 - x_{w,c}^0), p_c = p_c^0, s_c = 0 \quad (28)$$

$$\mathbf{u}_a^{g,0} = \frac{\xi_a RT_i^{ref} A_M}{2F p_a x_{H_2} A_{ch}}, \mathbf{u}_c^{g,0} = \frac{\xi_c RT_i^{ref} A_M}{4F p_c x_{O_2} A_{ch}} \quad (29)$$

where i^{ref} ($A\ m^{-2}$) is the reference current density, ξ_a and ξ_c are the anode and cathode stoichiometric flow ratios, and A_M (m^2) and A_{ch} (m^2) are the effective area of the electrode and the cross-sectional area of the channel, respectively. The water content on the GDL-CL interfaces of an anode (F-F') and cathode (C-C') are defined by the values according to Eq. 6.

Numerical solution

The finite element method (FEM) is used to solve the fully coupled equations. Prior to the solution, we developed a mesh over the computational domains. At every node of the mesh, the governing equations are computed by an iterative process with the boundary conditions and initial values, until reliable results are obtained with a certain residual value (10^{-5} in this study). The stationary solver of COMSOL Multiphysics 4.4 is used to implement the equations on a laptop with Intel Core i7 2.00 GHz CPU and 8.00 GB RAM. For each case, the computational period is about 20 minutes.

Model validation

The modeling results were compared with the experimental data in Figure 5, where the experimental data were obtained in-house and from literature⁴⁴, respectively. The MEA properties and operating conditions were listed in Table 3. The cathode charge transfer coefficients were carefully selected to fit the experimental data well at low current density, because in this current density range the cell performance is mainly determined by the intrinsic kinetics rather than mass transport and ohmic loss. It is clear that the model can be well validated by the experiments for both cases at low and media current densities. At high current density, the modeling results depart from the experimental data, especially for large area MEA with long flow channel. For the relative short parallel channel used in the in-house case, the discrepancy between the modeling and experimental results is small, which is caused by the increased mass transport resistance due to water formation and accumulation. However, in the larger size cell of Wang et al.⁴⁴, longer serpentine channel was used. Due to the severe water accumulation along the

serpentine channels, the amount of liquid water is higher than the parallel channel. Such significant increase in mass transport resistance cannot be captured by the 2D model developed in this paper.

Results and discussions

Effect of platinum loading

The current densities obtained at various platinum slopes are shown in Fig. 6. For relatively low activity ORR catalyst ($\alpha_c = 0.7$) with four levels of initial platinum loadings, the predicted current densities at 0.8 V decrease as the platinum slope increases. This is primarily due to low platinum loading near the CL-membrane, which leads to a small electrochemical active surface area (EASA) and results in low current densities at high cell voltages. At high cell voltages, the concentration polarization is not significant due to the slow reaction rate. The overall reaction rate is therefore mainly determined by the intrinsic kinetics rather than the reactant gas transport.

The situations at low cell voltages, corresponding to high current densities, are very different. For the initial platinum loading of 2×10^{-3} and 4×10^{-3} kg m⁻², the predicted current densities at 0.6 V decreases as the platinum slope decreases, as shown in Fig. 6b. A similar profile is also observed for 2×10^{-3} kg m⁻² platinum loading at 0.1 V. This is due to the decrease in the through-plane EASA. In this situation, ORR intrinsic kinetics, rather than reactant gas transport, is the rate control process. When the initial platinum loading increases to higher than 6×10^{-3} kg m⁻² for 0.6 V and 4×10^{-3} kg m⁻² for 0.1 V, the predicted current densities firstly increase then decrease as the platinum slopes increase. This is because the EASA associated with platinum loading is still high enough to support the ORR reaction when the inner platinum loading decreases to a certain critical value. For example, according to the maximum current densities in Fig. 6c, the critical platinum loading at the CL-membrane interface is 1.6×10^{-3} and 1.2×10^{-3} kg m⁻² for the initial platinum loadings of 4×10^{-3} and 6×10^{-3} kg m⁻² at the CL-GDL interface. However, with a further increase in platinum loading slope, less platinum remains near the CL-membrane interface. The significant decrease in EASA is insufficient to support the ORR, leading to a decrease in current

densities. This can be further confirmed in the case of a platinum loading of $8 \times 10^{-3} \text{ kg m}^{-2}$. It is clear that the predicted current density at 0.1 V increases in the full range of platinum loading slopes investigated, which indicates that the EASA is sufficient to catalyze the ORR in full domain of the CCL. The increase in platinum loading slope also increases the CCL porosity. For example, as the platinum loading slope increases from 20 to $500 \text{ kg m}^{-2} \text{ m}^{-1}$ for an initial platinum loading of $8 \times 10^{-3} \text{ kg m}^{-2}$, the EASA decreases from 3.5×10^7 to $2.3 \times 10^6 \text{ m}^{-1}$ and the porosity increases from 0.13 to 0.55 at the CL-membrane interface.

Overall, except for very low initial platinum loading at the CL-GDL interface, e. g. $2 \times 10^{-3} \text{ kg m}^{-2}$, decreasing the through-plane platinum loading at an optimal slope is of benefit to the cell performance at medium and high current densities. At low current densities, the obtained current density is proportional to the platinum loading. At medium and high current densities, the optimal platinum slope is a tradeoff of the EASA related ORR kinetics and porosity related effective oxygen diffusivity in the porous CCL.

Compared to the low activity ORR catalyst, the initial platinum loading from 2×10^{-3} to $6 \times 10^{-3} \text{ kg m}^{-2}$ for high ORR activity catalyst ($\alpha_c=1.0$) lead to a similar profile to that of the low activity at high cell voltage. As seen in Fig. 7, only the loading of $8 \times 10^{-3} \text{ kg m}^{-2}$ creates a different variation in performance, in which the predicted current density initially goes through a maximum value as the platinum loading slope increases. This is primarily due to the relatively high current density achieved for highly active ORR catalyst and the larger electrochemical active surface area. The inner area near the CL-membrane becomes less important to the overall ORR rate. At this condition, oxygen, determined by CCL porosity plays a more important role. However, with the further increase in platinum loading slope, the predicted current density decreases, because the ORR kinetics rather than the oxygen diffusivity becomes the rate controlling process.

For low cell voltages, the predicted current densities for the high ORR activity catalyst change in a similar manner in comparison with that for the low activity catalyst. However, the optimal slope of platinum loading is different. The optimal slopes of platinum loading for two ORR activity catalysts, at a variety of cell voltages, are summarized in Table 4. It is found that, for high initial platinum loading, e. g. $8 \times 10^{-3} \text{ kg m}^{-2}$, the maximum current densities are achieved at the highest platinum loading slopes for both

low and high active catalysts. However, for a lower initial platinum loading, e. g. $6 \times 10^{-3} \text{ kg m}^{-2}$ for low activity and $4 \times 10^{-3} \text{ kg m}^{-2}$ for high activity catalyst, the optimal platinum loading slope firstly increases then decreases as the cell voltage decreases from 0.9 to 0.1 V. This is due to the fact that when low platinum loading is applied, the increase in the slope may lead to insufficient platinum inside the catalyst layer. As the cell voltages decrease from high to medium, the decrease in platinum loading could offer sufficient platinum loading for the ORR, even at a very large slope. However, when the cell voltage further decreases from medium to low, the increase in current density requires a larger amount of platinum particles to catalyze the ORR. In addition, the higher ORR activity catalyst requires lower platinum loading within the CL, corresponding to larger platinum slopes. The percentages of the saved platinum for two ORR activity catalysts at various cell voltages at the optimal platinum loading slopes are shown in Table 5. It is clear as an increase in the initial platinum loading at the CL-GDL interface, more platinum is saved for an optimal cell performance. Up to 37.5 wt%, 47.5 wt% and 46.9 wt% of platinum is saved for 4×10^{-3} , 6×10^{-3} and $8 \times 10^{-3} \text{ kg m}^{-2}$ initial platinum loadings, respectively.

The effectiveness factor indicates how sufficient the catalyst in the catalyst layer is utilized. Fig. 8 shows that as the platinum loading increases, the CCL effectiveness factor decreases along two directions: reactant flowing along the channel and diffusion through the catalyst layer. The maximum effectiveness factor is observed at the CCL-GDL boundary near the cathode.

Figure 9 shows the variation in CCL effectiveness factor with various platinum loading slopes. It is shown that the effectiveness factor does not improve significantly near the CL-GDL interface. In contrast, it improves near the CL-membrane interface. Surprisingly, the effectiveness factor is larger in the inner area than that in the outer area inside the CCL. This indicates that diffusion inside the pores of the agglomerate accelerates due to the increase in porosity as the platinum loading decreases. Generally, reactant diffusion and reaction kinetics are competing processes, the overall rate is determined by the slower one. At high current densities, reactant diffusion plays a vital role in determining the overall reaction rate. Diffusivity is proportional to the porosity according to Bruggeman correlation. Thus the reactant diffusion through the primary pores inside the agglomerate before reaching the active site is more

important than that through the secondary pores between the agglomerates. The increase in the platinum slope is helpful for enlarging the CCL porosity, which consequently increases the reactant mass transport rate and improves the effectiveness factor.

For high active ORR cathode catalyst, the effectiveness factor along the through-plane direction sharply decreases at 0.1 V, indicating a very fast ORR kinetics near the CL-GDL interface. As an increase in ORR activity, the effect of reactant diffusion through the primary pores of the agglomerate on overall reaction rate is more significant. The increase in ORR activity accelerates the oxygen consumption rate, with the majority of reactant consumed near the CL-GDL interface; the reactant diffusion driving force through the entire CCL is thus reduced. In this situation, only a small amount of reactant can reach the catalyst located near the CL-membrane interface, resulting in a very low effectiveness factor.

Da_{II} represents a competitive relation between the ORR reaction and the reactant gas diffusion through the secondary pores inside the CL. Larger Da_{II} means a faster reaction rate than the diffusion rate if it is larger than 1. Figure 10 shows that for all platinum loadings the second Damköhler number firstly slowly increase along the through-plane direction, then undergoes a sharp increase after a certain distance along the diffusion direction of reactant gas. There is also an increase in Da_{II} along the gas flow direction, especially near the CL-membrane interface. The effect of platinum loading on Da_{II} along the through-plane distance from CL-GDL to CL-membrane interfaces is shown in detail in Figure 11. It is clear for low platinum loadings, e.g. 2×10^{-3} and 4×10^{-3} kg m⁻², the reactant diffusive transport rate is faster than the electrochemical reaction rate within 90% of the CCL area along the reactant diffusion direction. With an increase in platinum loading, this area becomes smaller. For platinum loading of 8×10^{-3} kg m⁻², the reaction rate is faster than the diffusion rate in about 40% of the CCL area near the CL-membrane interface. The dashed lines show the effect of platinum loading slopes on the second Damköhler number, with an initial platinum loading of 8×10^{-3} kg m⁻² on the GDL-CL interface. The slope increases from 100 to 400 kg m⁻² m⁻¹. It is clear the increase in platinum slope decreases the second Damköhler number, especially near the CL-membrane interface. At a fixed reaction rate, the decrease in the second

Damköhler number is due to the increase in the reactant mass transport rate, which is helpful in improving the utilization of platinum catalyst near the CL-membrane interface.

Effect of ionomer loading

Nafion[®] ionomer provides a pathway for proton migration from the anode to the Pt/C active site of the cathode by crosslinking all agglomerates inside the porous CLs. The rational design of the spatial distribution of ionomer inside the CLs can reduce the reactant gas mass transport resistance while maintaining a sufficient proton conductivity.

The current densities obtained at relatively low active ORR catalyst for various ionomer loading slopes are shown in Fig. 12. The predicted current densities at 0.8 V almost linearly decrease as the ionomer slope increases, indicating a significant impact of proton conductivity on cell performance at low current densities. At medium current densities corresponding to 0.6 V, the increase in ionomer slope for initial dry-ionomer loading lower than $1.2 \times 10^{-2} \text{ kg m}^{-2}$ leads to a decrease in cell performance. However, for ionomer loading higher than $1.5 \times 10^{-2} \text{ kg m}^{-2}$, the increase in the slope leads to a volcano-curve like profile. On the contrary, the increase in ionomer slope leads to a monotonically increasing of the cell performance at 0.1 V. Especially for high ionomer loading, the linear increase in ionomer slope results in a nonlinear increase in current density. This is due to the apparent decrease in the mass transport resistance of reactant gas through the thinned ionomer film. For example, the thickness of the ionomer film at the GDL-CL interface decreases from 2.26×10^{-7} to $1.45 \times 10^{-8} \text{ m}$ when the ionomer slope increases from 30 to $720 \text{ kg m}^{-2} \text{ m}^{-1}$ for an initial ionomer loading of $1.5 \times 10^{-2} \text{ kg m}^{-2}$ in the CL-membrane interface.

Comparing Figure 12 and Figure 13 indicates that for a highly active ORR cathode catalyst, the increase in ionomer loading slope results in a similar trend in changing the current density at the dry-ionomer loading lower than $1.2 \times 10^{-2} \text{ kg m}^{-2}$ to that of low ORR activity. However, at high dry-ionomer loadings, e. g. higher than $1.2 \times 10^{-2} \text{ kg m}^{-2}$, the current density initially increases then decreases as a consequence of the increase in ionomer loading slope. In other words, the optimal slopes exist up to the maximum current densities at high dry-ionomer loading. The optimal slopes of ionomer loading for two

ORR activity catalysts at a variety of cell voltages are summarized in Table 6. It is found that for initial ionomer loading larger than $9 \times 10^{-3} \text{ kg m}^{-2}$, the increase in ionomer loading slope results in an improvement of the cell performance in the full range of cell voltage, for both low and high ORR activity catalysts. At high voltages, the optimal ionomer slopes are at their minimum values, indicating that proton conductivity is vital when the fuel cell is operated at high cell voltages. It is clearly in Fig. 14 that when ionomer loading decreases along the through-plane direction inside the CCL, the proton conductivity decreases. The larger the ionomer loading slopes, the smaller is the proton conductivity away from the CL-membrane interface.

On the contrary, the optimal ionomer slopes are at their maximum values at low cell voltages, which is explained by the increase in porosity initiated by the decrease in ionomer loading. As can be seen in Fig. 15, the profiles of CCL porosity are diametrically opposed to that of proton conductivity. Due to the decrease in ionomer content from the CL-membrane interface to the GDL-CL interface, the CCL porosity linearly increases along the through-plane direction and reaches the maximum at the GDL-CL interface. The increase in porosity improves the reactant gas transport rate through the CCL, resulting in a higher current density compared to the traditional CCL.

At medium cell voltages, both proton conductivity and reactant gas diffusivity are important to the cell performance. Thus, an appropriate “optimal” ionomer loading slope is capable of balancing the proton and gas transport. For example, as shown in Figure 16, the optimal slope for $9 \times 10^{-3} \text{ kg m}^{-2}$ dry-ionomer loading is $210 \text{ kg m}^{-2} \text{ m}^{-1}$ at 0.4 V and for $1.5 \times 10^{-2} \text{ kg m}^{-2}$ dry-ionomer loading is $450 \text{ kg m}^{-2} \text{ m}^{-1}$ at 0.6 V, respectively.

The non-uniform distribution of CL porosity also leads to a change of the capillary diffusion coefficient for liquid water transport. As shown in Figure 17, as the ionomer slope increases, for both initial ionomer loadings of 9×10^{-3} and $1.5 \times 10^{-2} \text{ mg cm}^{-2}$, the increase in ionomer slope results in an increase in the capillary diffusion coefficient. We can, in fact, explain this by the increase in porosity from the CL-membrane interface to the GDL-CL interface. According to Eq. 4, the capillary diffusion coefficient is

proportional to the electrode porosity. The increase in capillary diffusion coefficient accelerates the diffusive transport rate of liquid water, which improves the cell performance at high current densities.

Interactive effects of platinum and ionomer loadings

The interactive effects of the slopes of platinum and ionomer loadings on current densities at 0.6, 0.4, 0.3 and 0.1 V are shown in Figure 18. At cell voltages higher than 0.6 V, the maximum cell performance is achieved with a uniformly distributed platinum and ionomer, due to the required highest electrochemical active surface area and proton conductivity when ORR kinetics govern the overall reaction rate. As a decrease in cell voltage, corresponding to an increase in current density, the ionomer slope increases to $330 \text{ kg m}^{-2} \text{ m}^{-1}$ and the platinum slope firstly increases to $200 \text{ kg m}^{-2} \text{ m}^{-1}$ at 0.3 V then decreases to $160 \text{ kg m}^{-2} \text{ m}^{-1}$ at 0.1 V. Given the previous discussion, the increase in ionomer slope decreases the ionomer content in the CL away from the CL-membrane interface. When an effective ionomer network is guaranteed, the lower ionomer contents the higher porosity and thinner ionomer film surrounding the agglomerates. Thus, the maximum ionomer slope is of benefit to the cell performance at high current densities. The decrease in cell voltages triggers a faster ORR and a more apparent impact of gas transport. Therefore, the optimal platinum slope has to balance the rate of ORR kinetics and gas diffusion inside the porous CL. The increase in platinum slope, on one hand, decreases the EASA, and on the other hand, increases the CL porosity. The optimal platinum slope is a tradeoff of the EASA and CL porosity. The optimal slopes of platinum and ionomer loadings at various cell voltages are shown in Table 7.

Conclusions

A comprehensive numerical model for a single PEM fuel cell unit is developed to investigate the inhomogeneous spatial distributions of platinum and ionomer inside the catalyst layer, in order to maximize the fuel cell performance at various operating load conditions. This model accounts for water-gas two-phase flow, the combined water transport mechanism through the membrane, ionomer swelling,

water phase-transfer and majority of physical and chemical processes. Within the catalyst layer, the platinum is assumed to linearly decrease along the through-plane direction of reactant gas diffusion from the GDL toward the membrane. On the contrary, the ionomer loading decreases in the opposite direction.

The proton conductivity of the CL is higher when larger ionomer loading is applied due to the reinforced contact between the agglomerates. The optimal slopes of platinum and ionomer are respectively obtained for two types of ORR catalysts with relatively low and high activity at various cell voltages from 0.9 to 0.1 V, corresponding to a full range of current density. Results show that the optimal slopes depend on the current densities. At low current densities, high electrochemical active surface area and proton conductivity are of benefit to the improvement of cell performance. Thus, the maximum cell performance is achieved when platinum and ionomer uniformly distributed inside the CL without gradients.

At medium and high current densities, the optimal ionomer slope is at the maximum value as long as all agglomerates are interlinked. In this situation, low ionomer towards the GDL-CL interface increases the CL porosity in this region and decreases the mass transport resistance of reactant through the thinned ionomer film. In contrast, the optimal platinum slope depends on the initial platinum loading at the GDL-CL interface. For high platinum loading, e. g. larger than $8 \times 10^{-3} \text{ kg m}^{-2}$, the maximum current densities are achieved at the maximum platinum loading slopes for both low and high active ORR catalysts. However, for a lower initial platinum loading, e. g. lower than $6 \times 10^{-3} \text{ kg m}^{-2}$, the optimal platinum slope firstly increases then decreases as the current density increases. The optimal platinum slope is a tradeoff of the electrochemical active surface area and CL porosity. At such optimal slope, the remained platinum has to be sufficient to provide reaction sites for the ORR.

The interactive effect of platinum and ionomer loading indicates that the optimal slopes of both platinum and ionomer are various at different cell loads. For a catalyst layer with relative low ORR activity, if the initial platinum loading of $4 \times 10^{-3} \text{ kg m}^{-2}$ at the GDL-CL interface and dry-ionomer loading of $9 \times 10^{-3} \text{ kg m}^{-2}$ at the CL-membrane interface are applied, the optimal slopes of platinum and ionomer are 160 and $330 \text{ kg m}^{-2} \text{ m}^{-1}$ near the limiting current density at 0.1 V, respectively.

Although the complexity of preparing a functional graded CL is a challenge in commercial MEA fabrication process, the linear variation in platinum and ionomer at optimal slopes can improve the cell performance up to 16.3 % and significantly reduce the platinum usage up to 46.9 wt% at medium current density in comparison with conventional electrode with uniform distribution of platinum and ionomer.

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Notation

A_M	effective area of electrode, m^2
A_{ch}	cross-sectional area of channel, m^2
a	specific area, m^{-1}
c	concentration, mol m^{-3}
d	diameter, m
D	diffusivity, $\text{m}^2 \text{s}^{-1}$
D_c	capillary diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
Da_{II}	second Damköhler number
E_{agg}	effectiveness factor

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E^{cell}

cell voltage, V

F

Farady's constant, 96485 C mol⁻¹

f

platinum mass ratio to Pt/C

H

Henry's constant, Pa m³ mol⁻¹

i

current density, A m⁻²

i_0

exchange current density, A m⁻²

$J(s)$

Leverett function

k_{Pt}, k_M

slope of platinum and ionomer, kg m⁻² m⁻¹

k_{agg}

rate coefficient, s⁻¹

k_s

swelling coefficient

k_r

relative permeability

k_p

hydraulic permeability, m²

L

volume fraction

l

thickness, m

M_j

molecular weight for specie j, kg mol⁻¹

M_T

Thieles's modulus

m

loading, kg m⁻²

n

number

p

pressure, Pa

R

ideal gas constant, 8.314 J mol⁻¹ K⁻¹

r

radius of agglomerate

RH

relative humidity

S

source term

 s

liquid water saturation

 T

temperature, K

 $\mathbf{u}$

velocity vector, m s^{-1}
 X

normalized distance (x/l)

 x

mole fraction

 $\%M$

volume fraction of primary pores occupied by ionomer

Greek

 α

charge transfer coefficient

 α_w

water activity

 λ

water content

 μ

viscosity, Pa s

 ρ

density, kg m^{-3}
 ε

porosity

 δ

thickness/depth, m

 η

overpotential, V

 σ

surface tension, N m^{-1}
 ξ

Stoichiometric flow ratio

 θ_c

contact angel, $^\circ$
 σ_s

electronic conductivity, S m^{-1}
 σ_M

ionic conductivity, S m^{-1}
 ϕ

general variable to be solved

Γ	generalized diffusion coefficient
<i>Superscripts</i>	
0	initial value
d	dissolved phase
eff	effective
ref	reference
eq	equilibrium
l	liquid phase
g	gas phase
<i>Subscripts</i>	
agg	agglomerate
CL	catalyst layer
GDL	gas diffusion layer
i	species i
M	membrane/ionomer
r	relative
w	liquid water

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Figure 1. Sketch and computation domain of a PEM fuel cell.

Figure 2. Schematic representation and reactant gas transport pathway within porous catalyst layer.

Figure 3. Effective proton conductivity with various initial ionomer loadings at different ionomer water contents.

Figure 4. Distribution of dimensionless (a) platinum and (b) dry ionomer loadings through the thickness of catalyst layer. $X=0$ - CL-membrane interface, $X=1$ - CL-GDL interface; (a) initial platinum loading of $4 \times 10^{-3} \text{ kg m}^{-2}$ at GDL-CL interface and (b) initial dry ionomer loading of $9 \times 10^{-3} \text{ kg m}^{-2}$ at CL-membrane interface.

Figure 5. Model validation: $\circ$ – in-house experimental data; $\square$ – experimental data from literature; solid line - modeling results for in-house case; dash line - modeling results for literature case.

Figure 6. Predicted current densities at various platinum slopes at the cell voltage of (a) 0.8, (b) 0.6 and (c) 0.1 V in base-case condition. $\alpha_c = 0.7$ represents low ORR activity cathode catalyst.

Figure 7. Predicted current densities at various platinum slopes at the cell voltage of (a) 0.8, (b) 0.6 and (c) 0.1 V in base-case condition. $\alpha_c = 1.0$ represents high ORR activity cathode catalyst.

Figure 8. CCL effectiveness factor with various platinum loadings at 0.1 V in base-case condition: $\alpha_c=0.7$: $m_{Pt}=2 \times 10^{-3}$, 4×10^{-3} , 6×10^{-3} and $8 \times 10^{-3} \text{ kg m}^{-2}$ from up down. X and Y are the dimensionless through-plane and in-plane directions. Boundaries $X=0$ - cathode membrane-CL interface; $X=1$ - cathode GDL-CL interface; $Y=0$ - cathode gas outlet; $Y=1$ - cathode gas inlet.

Figure 9. CCL effectiveness factor with various platinum loading slopes at 0.1 V with (a) $\alpha_c=0.7$ and (b) $\alpha_c=1.0$ in base-case condition: $m_{Pt}=6 \times 10^{-3} \text{ kg m}^{-2}$, $k_{Pt}=0$, 100, 200 and $300 \text{ kg m}^{-2} \text{ m}^{-1}$ from down up. X and Y are the dimensionless through-plane and in-plane directions. Boundaries $X=0$ - cathode membrane-CL interface; $X=1$ - cathode GDL-CL interface; $Y=0$ - cathode gas outlet; $Y=1$ - cathode gas inlet.

Figure 10. The second Damköhler number in CCL with various platinum loadings at 0.1 V in base-case condition: $\alpha_c=0.7$, $m_{Pt}=2 \times 10^{-3}$, 4×10^{-3} , 6×10^{-3} and $8 \times 10^{-3} \text{ kg m}^{-2}$ from down up. X and Y are the dimensionless

through-plane and in-plane directions. Boundaries $X=0$ - cathode membrane-CL interface; $X=1$ - cathode GDL-CL interface; $Y=0$ - cathode gas outlet; $Y=1$ - cathode gas inlet.

Figure 11. The second Damköhler number along the through-plane distance at $Y=0$ with various platinum loadings at 0.1 V in base-case condition: $\alpha_c=0.7$, Solid lines: $m_{Pt}=2\times10^{-3}$, 4×10^{-3} , 6×10^{-3} and 8×10^{-3} kg m⁻² from down to up, $k_{Pt}=0$; Dash lines: $m_{Pt}=8\times10^{-3}$ kg m⁻², $k_{Pt}=100$, 200, 300 and 400 kg m⁻² m⁻¹ from up down; Dot line: $Da_{\square}=1.0$. Boundaries $X=0$ - cathode membrane-CL interface; $X=1$ - cathode GDL-CL interface.

Figure 12. Predicted current densities at various ionomer loading slopes at the cell voltage of (a) 0.8, (b) 0.6 and (c) 0.1 V in base-case condition. $\alpha_c = 0.7$ represents high ORR activity cathode catalyst.

Figure 13. Predicted current densities at various ionomer loading slopes at the cell voltage of (a) 0.8, (b) 0.6 and (b) 0.1 V in base-case condition. $\alpha_c = 1.0$ represents high ORR activity cathode catalyst.

Figure 14. CCL effective proton conductivity at initial ionomer loading of 9×10^{-3} kg m⁻² with various ionomer loading slopes at 0.1 V in base-case condition: $k_M = 0$, 90, 180 and 270 kg m⁻² m⁻¹ from up down.

Figure 15. CCL porosity at initial ionomer loading of 9×10^{-3} kg m⁻² with various ionomer loading slopes at 0.1 V in base-case condition: $k_M = 0$, 90, 180 and 270 kg m⁻² m⁻¹ from down to up.

Figure 16. Maximum current densities achieved at optimal ionomer loading slopes in base-case condition. $\alpha_c = 1.0$ represents high ORR activity cathode catalyst.

Figure 17. Liquid water capillary diffusion coefficient with various ionomer loading slopes through the CCL in base-case condition. Solid line: initial ionomer loading 1.5×10^{-2} kg m⁻², ionomer slope from 0 to 7.2×10^4 kg m⁻² m⁻¹ at a step of 9×10^2 kg m⁻² m⁻¹; Dash line: : initial ionomer loading 9×10^{-3} kg m⁻², ionomer slope from 0 to 2.7×10^4 kg m⁻² m⁻¹ at a step of 9×10^2 kg m⁻² m⁻¹.

Figure 18. Interactive effect of platinum and ionomer loading slopes on the predicted current densities at (a) 0.6 V; (b) 0.4 V; (c) 0.3 V and (d) 0.1 V in base-case condition: $\alpha_c=0.7$, initial platinum loading of 4×10^{-3} kg m⁻² at GDL-CL interface and dry ionomer loading of 9×10^{-3} kg m⁻² at CL-membrane interface.

Figure 1 Sketch and computation domain of a PEM fuel cell

162x133mm (150 x 150 DPI)

Figure 2 Schematic representation and reactant gas transport pathway within porous catalyst layer

166x182mm (150 x 150 DPI)

Figure 3 Effective proton conductivity with various initial ionomer loadings at different ionomer water contents

296x209mm (300 x 300 DPI)

Figure 4a Distribution of dimensionless (a) platinum loading through the thickness of catalyst layer
259x203mm (300 x 300 DPI)

Figure 4b Distribution of dimensionless (b) dry ionomer loading through the thickness of catalyst layer

296x209mm (300 x 300 DPI)

Figure 5 Model validation

291x204mm (300 x 300 DPI)

Figure 6a Predicted current densities at various platinum slopes at the cell voltage of (a) 0.8 V in base-case condition, low ORR activity cathode catalyst: $\alpha_c=0.7$

259x203mm (300 x 300 DPI)

Figure 6b Predicted current densities at various platinum slopes at the cell voltage of (b) 0.6 V in base-case condition, low ORR activity cathode catalyst: $\alpha_{\text{c}}=0.7$

259x203mm (300 x 300 DPI)

Accep

Figure 6c Predicted current densities at various platinum slopes at the cell voltage of (c) 0.1 V in base-case condition, low ORR activity cathode catalyst: $\alpha_c=0.7$

259x203mm (300 x 300 DPI)

Figure 7a Predicted current densities at various platinum slopes at the cell voltage of (a) 0.8 V in base-case condition, high ORR activity cathode catalyst: $\alpha_c=1.0$

259x203mm (300 x 300 DPI)

Accep

Figure 7b Predicted current densities at various platinum slopes at the cell voltage of (b) 0.6 V in base-case condition, high ORR activity cathode catalyst: $\alpha_c=1.0$

259x203mm (300 x 300 DPI)

Figure 7c Predicted current densities at various platinum slopes at the cell voltage of (c) 0.1 V in base-case condition, high ORR activity cathode catalyst: $\alpha_{\text{c}}=1.0$

259x203mm (300 x 300 DPI)

Accep

Figure 8 CCL effectiveness factor with various platinum loadings at 0.1 V in base-case condition

259x203mm (300 x 300 DPI)

Figure 9a CCL effectiveness factor with various platinum loading slopes at 0.1 V in base-case condition (a)
 $\alpha_c=0.7$

259x203mm (300 x 300 DPI)

Accep

Figure 9b CCL effectiveness factor with various platinum loading slopes at 0.1 V in base-case condition (b)

$$\alpha_C = 1.0$$

259x203mm (300 x 300 DPI)

Figure 10 The second Damköhler number in CCL with various platinum loadings at 0.1 V in base-case condition

259x203mm (300 x 300 DPI)

Accep

Figure 11 The second Damköhler number along the through-plane distance at $Y=0$ with various platinum loadings at 0.1 V in base-case condition

259x203mm (300 x 300 DPI)

Figure 12a Predicted current densities at various ionomer loading slopes at the cell voltage of (a) 0.8 V in base-case condition, low ORR activity cathode catalyst: $\alpha_c=0.7$

296x209mm (300 x 300 DPI)

Accept

Figure 12b Predicted current densities at various ionomer loading slopes at the cell voltage of (b) 0.6 V in base-case condition, low ORR activity cathode catalyst: $\alpha_c=0.7$

296x209mm (300 x 300 DPI)

Accept

Figure 12c Predicted current densities at various ionomer loading slopes at the cell voltage of (c) 0.1 V in base-case condition, low ORR activity cathode catalyst: $\alpha_c=0.7$

296x209mm (300 x 300 DPI)

Accept

Figure 13a Predicted current densities at various ionomer loading slopes at the cell voltage of (a) 0.8 V in base-case condition, high ORR activity cathode catalyst: $\alpha_c=1.0$

296x209mm (300 x 300 DPI)

Figure 13b Predicted current densities at various ionomer loading slopes at the cell voltage of (b) 0.6 V in base-case condition, high ORR activity cathode catalyst: $\alpha_c=1.0$

296x209mm (300 x 300 DPI)

Figure 13c Predicted current densities at various ionomer loading slopes at the cell voltage of (c) 0.1 V in base-case condition, high ORR activity cathode catalyst: $\alpha_c=1.0$

296x209mm (300 x 300 DPI)

Figure 14 CCL effective proton conductivity at initial ionomer loading of $9 \times 10^{-3} \text{ kg m}^{-2}$ with various ionomer loading slopes at 0.1 V in base-case condition

259x203mm (300 x 300 DPI)

Accep

Figure 15 CCL porosity at initial ionomer loading of $9 \times 10^{-3} \text{ kg m}^{-2}$ with various ionomer loading slopes at 0.1 V in base-case condition

259x203mm (300 x 300 DPI)

Figure 16 Maximum current densities achieved at optimal ionomer loading slopes in base-case condition, high ORR activity cathode catalyst: $\alpha_c=1.0$

296x209mm (300 x 300 DPI)

Accept

Figure 17 Liquid water capillary diffusion coefficient with various ionomer loading slopes through the CCL in base-case condition

259x203mm (300 x 300 DPI)

Figure 18a Interactive effect of platinum and ionomer loadings slopes on the predicted current densities at (a) 0.6 V in base-case condition

296x209mm (300 x 300 DPI)

Accept

Figure 18b Interactive effect of platinum and ionomer loadings slopes on the predicted current densities at (b) 0.4 V in base-case condition

296x209mm (300 x 300 DPI)

Figure 18c Interactive effect of platinum and ionomer loadings slopes on the predicted current densities at (c) 0.3 V in base-case condition

296x209mm (300 x 300 DPI)

Accept

Figure 18d Interactive effect of platinum and ionomer loadings slopes on the predicted current densities at (d) 0.1 V in base-case condition

296x209mm (300 x 300 DPI)

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Table 1. Specific Expressions in the general Convection-Diffusion Equation

	Mass	Momentum	Species	Energy	Charges
Computational domain	Channels, GDLs and CLs			All domains	CLs and membrane
ϕ	1	$k_p \nabla p / \mu$	x_i	T	φ_s, φ_M
$\tilde{\rho}$	ρ^g	ρ^g / ε^2	ρ^g	ρ^g	0
Γ_ϕ	0	μ^g / ε	$\rho^g D_i^{eff}$	k^{eff} / c_p^{eff}	σ_s, σ_M

Table 2. The Range of Slopes of Platinum and Ionomer Loadings with various Initial Values

	Initial value at GDL-CL interface (kg m ⁻²)	Range of slope (kg m ⁻² m ⁻¹)	Slope increasing step (kg m ⁻² m ⁻¹)	Final value at CL-membrane interface (kg m ⁻²)
Platinum loading	2×10 ⁻³	0 - 120	20	2×10 ⁻⁴
	4×10 ⁻³	0 - 260	20	1×10 ⁻⁴
	6×10 ⁻³	0 - 380	20	3×10 ⁻⁴
	8×10 ⁻³	0 - 520	20	2×10 ⁻⁴
	Initial value at CL-membrane interface (kg m ⁻²)	Range of slope (kg m ⁻² m ⁻¹)	Slope increasing step (kg m ⁻² m ⁻¹)	Final value at GDL-CL interface (mg cm ⁻²)
Ionomer loading	6×10 ⁻³	0 - 120	30	4.2×10 ⁻³
	9×10 ⁻³	0 - 330	30	4.05×10 ⁻³
	1.2×10 ⁻²	0 - 510	30	4.2×10 ⁻³
	1.5×10 ⁻²	0 - 720	30	4.2×10 ⁻³
	1.65×10 ⁻²	0 - 810	30	4.35×10 ⁻³

Table 3. Parameters used in Model Validation and Base-Case Condition

Symbol	Description (unit)	Validation in-house	Validation Literature ⁴⁴	Base-case
l_{Ch}	Channel depth (m)	1×10^{-3}	1×10^{-3}	1×10^{-3}
L_{Ch}	Channel length (m)	1×10^{-2}	7×10^{-2}	1×10^{-2}
l_{GDL}	GDL thickness (m)	3×10^{-4}	3×10^{-4}	3.8×10^{-4}
l_{CL}	CL thickness (m)	1.5×10^{-5}	1.29×10^{-5}	1.5×10^{-5}
l_M	Membrane thickness (m)	5.5×10^{-5}	1.08×10^{-4}	1.2×10^{-4}
ε_{GDL}	GDL porosity	0.4	0.4	0.4
m_{Pt}^0	Platinum loading (kg m ⁻²)	4×10^{-3}	4×10^{-3}	$(2 \sim 8) \times 10^{-3}$
f	Platinum mass ratio	20%	40%	40%
ECSA	Electrochemical active surface area (m ⁻¹)	4.88×10^7	4.61×10^7	$(3.69 \sim 8.35) \times 10^7$
m_M^0	Ionomer loading (kg m ⁻²)	4×10^{-3}	1×10^{-2}	$(9 \sim 16.5) \times 10^{-3}$
α_c	Cathode charge transfer coefficient	0.85	2.0	0.7, 1.0
T	Operating temperature (K)	333	343	343
p	Back pressure (Pa)	1.0×10^5	1.0×10^5	1.0×10^5
RH	Relative humidity	100%	100%	100%
ξ_a	Anode stoichiometric flow ratio	11.8 ^a	1.8 ^b	1.0
ξ_c	Cathode stoichiometric flow ratio	12.4 ^a	1.4 ^b	2.0

a Calculated at the volumetric flow ratio of 200 and 500 sccm using Eq. (29) for anode and cathode, respectively, at in-house operation conditions.

b Calculated at the volumetric flow ratio of 1200 and 2200 sccm using Eq. (29) for anode and cathode, respectively, at given operation conditions in Wang et al⁴⁴.

Table 4. Optimal Platinum Slopes for Two ORR Activity Catalysts at various Cell Voltages

Charge transfer coefficient $\alpha_c = 0.7$									
Platinum loading m_{Pt}	0.9 V	0.8V	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V	0.2 V	0.1 V
2×10^{-3}	0	0	0	0	0	0	0	0	0
4×10^{-3}	0	0	0	0	60	200	200	180	160
6×10^{-3}	0	0	0	80	280	360	360	340	320
8×10^{-3}	0	0	80	300	500	500	500	500	500
Charge transfer coefficient $\alpha_c = 1.0$									
Platinum loading m_{Pt}	0.9 V	0.8V	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V	0.2 V	0.1 V
2×10^{-3}	0	0	0	20	40	0	0	0	0
4×10^{-3}	0	0	20	200	200	180	140	140	120
6×10^{-3}	0	0	220	360	380	380	380	380	380
8×10^{-3}	0	180	440	500	500	500	500	500	500

Note: the units of platinum loadings and slopes are kg m^{-2} and $\text{kg m}^{-2} \text{m}^{-1}$, respectively.

Table 5. Percentages of the Saved Platinum for Two ORR Activity Catalysts at Various Cell Voltages at the Optimal Platinum Loading Slopes

$\alpha_c = 0.7$	Platinum loading m_{Pt} (kg m ⁻²)	0.8V	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V	0.2 V	0.1 V
	4×10^{-3}	0	0	0	11.3%	37.5%	37.5%	33.8%	30%
	6×10^{-3}	0	0	10%	35%	45%	45%	42.5%	40%
	8×10^{-3}	0	7.5%	28.1%	46.9%	46.9%	46.9%	46.9%	46.9%
$\alpha_c = 1.0$	Platinum loading m_{Pt} (kg m ⁻²)	0.8V	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V	0.2 V	0.1 V
	4×10^{-3}	0	3.8%	37.5%	37.5%	33.8%	26.3%	26.3%	22.5%
	6×10^{-3}	0	27.5%	45%	47.5%	47.5%	47.5%	47.5%	47.5%
	8×10^{-3}	16.9%	41.3%	46.9%	46.9%	46.9%	46.9%	46.9%	46.9%

Table 6. Optimal Ionomer Slopes for Two ORR Activity Catalysts at various Cell Voltages

Charge transfer coefficient $\alpha_c = 0.7$									
Platinum loading m_M	0.9 V	0.8V	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V	0.2 V	0.1 V
9×10^{-3}	0	0	0	0	30	210	300	330	330
1.2×10^{-2}	0	0	0	120	360	510	540	540	540
1.5×10^{-2}	0	0	120	450	720	720	720	720	720
1.65×10^{-2}	0	60	330	660	810	810	810	810	810
Charge transfer coefficient $\alpha_c = 1.0$									
Platinum loading m_M	0.9 V	0.8V	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V	0.2 V	0.1 V
0.9×10^{-3}	0	0	0	150	270	300	330	330	330
1.2×10^{-2}	0	0	270	480	510	510	510	510	510
1.5×10^{-2}	0	270	630	720	720	720	720	720	720
1.65×10^{-2}	90	480	810	810	810	810	810	810	810

Note: the units of ionomer loadings and slopes are kg m^{-2} and $\text{kg m}^{-2} \text{m}^{-1}$, respectively.

Table 7. Optimal Slopes of Platinum and Ionomer Loadings at various Cell Voltages

	≥ 0.6 V	0.5 V	0.4 V	0.3 V	0.2 V	0.1 V
k_{Pt} (kg m ⁻² m ⁻¹)	0	60	180	200	180	160
k_{M} (kg m ⁻² m ⁻¹)	0	0	120	240	300	330