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Abstract: This paper presents a numerical study of the inhomogeneous platinum loading within the catalyst layer (CL) and porosity inside the gas diffusion layer (GDL) at the cathode of a proton exchange membrane fuel cell. Their distributions along the in-plane (longitudinal) direction and the effect of their interactions on the cell performance and current density uniformity are investigated. A strong interaction of platinum loading and GDL porosity on performance is revealed, and a significant impact of GDL porosity on the optimal platinum gradients exists, due to the correlations between the electrochemical reaction rate and species transport rate. When the initial platinum loading and GDL porosity are high at the cathode inlet, individually increasing the platinum loading near the outlet cannot improve the cell performance and current density uniformity. Systematically controlling the gradients of platinum loading and GDL porosity achieves a more uniform distribution of current density within the membrane electrode assembly.

Graphical abstract

Highlights

- Graded Pt loading and GDL porosity were experimentally and numerically studied.
- Their longitudinal distributions strongly affect the uniformity of current density.
- Solely increasing Pt loading at the cathode outlet cannot improve the uniformity.
- Systematical design of the gradients Pt loading and GDL porosity is essential.

Homogenization of current density of PEM fuel cells by in-plane graded distributions of platinum loading and GDL porosity

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Abstract

This paper presents a numerical study of the inhomogeneous platinum loading within the catalyst layer (CL) and porosity inside the gas diffusion layer (GDL) at the cathode of a proton exchange membrane fuel cell. Their distributions along the in-plane (longitudinal) direction and the effect of their interactions on the cell performance and current density uniformity are investigated. A strong interaction of platinum loading and GDL porosity on performance is revealed, and a significant impact of GDL porosity on the optimal platinum gradients exists, due to the correlations between the electrochemical reaction rate and species transport rate. When the initial platinum loading and GDL porosity are high at the cathode inlet, individually increasing the platinum loading near the outlet cannot improve the cell performance and current density uniformity. Systematically controlling the gradients of platinum loading and GDL porosity achieves a more uniform distribution of current density within the membrane electrode assembly.

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Introduction

Membrane electrode assembly (MEA) is considered as the core of proton exchange membrane (PEM) fuel cells, which is typically fabricated by hot pressing the gas diffusion layer (GDL), catalyst layer (CL) and micro-porous layer (MPL) on both sides of the PEM. Electricity is generated via the complicate coupled physical and chemical processes inside the MEA. However, the use of precious metals, e. g. platinum and platinum-based alloys, inside the CL as reaction catalysts results in a high cost and a low durability for the application of PEM fuel cells. Typically, the uniform distribution of platinum-based catalysts inside the CLs of a traditional electrode (without graded design) exacerbates the cost because high catalysts loadings are used in the regions of CL where low electrochemical activity is required. In addition, the non-uniform distribution of current density within the MEA accelerates the degradations of membrane, catalyst and carbon, which shortens the life span of PEM fuel cells [St-Pierre and Wilkinson, 2001; Wang et al., 2011; Holdcroft, 2013; Wang, 2015]. For PEM fuel cells operated at different power levels/loads, the reaction activity and mass transport rates vary spatially in the CLs, due to the non-uniform distribution of reactant gases and change in void space for gas transport, initiated by the formation of liquid water. Therefore, a rational design of the spatial distribution of functional components inside the MEA is considered a promising strategy to reduce the amount of catalysts and achieve a more uniform distribution of current density.

Numerous experimental and numerical studies with respect to the functional graded design of the MEA, along with both the through-plane and in-plane directions, have been reported over the last three decades. The graded distributions of functional components and factors that have received attention include platinum [Antoine et al. 2000; Santis et al. 2006; Prasanna et al. 2007; Lee et al. 2007; Taylor et al. 2007; Srinivasarao et al. 2012; Roshandel and Ahmadi 2013; Su et al. 2014; Xing et al. 2017], ionomer [Wang et al. 2004; Xie et al. 2005; Song et al. 2005; Kim et al. 2008; Su et al. 2010; Xing et al. 2017] and void space (pore) [Chu et al. 2003; Roshandel et al. 2005; Zhan et al. 2006; Sinha et al. 2007; Chen et al. 2008; Huang et al. 2010; Zhang et al. 2016], associated with electrochemical reaction, proton migration and

reactant gas transport inside the CLs, respectively. In addition, due to the significant impact of water flooding at high current densities, the graded design of hydrophobicity is of benefit to the more efficient water removal through the electrodes [Weng et al. 2011; Kang et al. 2012; Ito et al. 2014, 2015, 2016]. The mass transport process through porous electrodes is also closely correlated to the pore morphology. The irregular and anisotropic pores inside the sub-micro/nanoscale porous electrodes affect the Knudsen diffusion of reactant gases [Niu et al. 2017]. Moreover, the electrode performance is strongly affected by the pore size, porosity, tortuosity and thickness of the electrode [Niu et al. 2018].

Ideally in PEM fuel cells, platinum particles must be well dispersed and rationally distributed inside the CL to provide the high electrochemical active surface area (EASA). The optimal distribution of platinum depends on the current density and the amount of the generated liquid water. Without considering the influence of liquid water, Antoine et al. (2000) and Roshandel et al. (2013) indicated that placing more platinum near the membrane-CL interface yields the improved cell performance, especially in the low current density range. Taking the impact of liquid water into account, Srinivasarao et al. (2012) and Xing et al. (2017) concluded that higher loadings of platinum close to the CL-GDL interface are preferred for better cell performance at medium and high current densities. Prasanna et al. (2007) prepared a catalyst-gradient electrode, in which the catalyst loading was increased from the gas inlet to the outlet, aiming to counteract the depletion of reactant gases in the gas stream. The maximum power density increases by 17% in comparison with the traditional electrode.

Within the CLs, the cross-linked ionomer network is required for effective proton migration. An “optimal” Nafion ionomer content should minimize the species transport resistance while maintaining good ionic conductivity of the CL. A graded CL with higher content of ionomer near the membrane and low content near the GDL has been investigated to improve the cell performance at medium and large current densities [Wang et al. 2004; Xie et al. 2005; Kim et al. 2008]. Moreover, it is believed that the region of the CL adjacent to the GDL should be more porous than that near the membrane, as the oxygen concentration decreases within the CL from the GDL-CL interface towards the CL-membrane interface

[Song et al. 2005]. Sinha et al. (2007) investigated a functionally graded diffusion media, along with the in-plane direction in the cathode flow channel, composed of fine (high tortuosity) and coarse (low tortuosity) structures. They concluded that the cell performance was improved by a proper selection of gradual transition length changing from a fine to coarse structure. Recently, Zhang et al. (2016) explored the porosity-graded GDL along the gas flow direction using a computational model together with experimental study and showed that using an optimally graded porosity distribution improved the uniformity in current density and maximized the power density of the cell.

In a variety of studies of the functional graded electrode design, in-plane distributions of platinum in the CL and porosity in the GDL have been separately studied in most of the published literature. However, their interactions are equally important because better cell performance and more uniform current density distribution can be achieved by rationally matching the rates of electrochemical reactions and species transport. In this work, we numerically investigate the linear variations of platinum loading and GDL porosity along the air flow direction in the cathode. The effects of the gradients of platinum and porosity, as well as their interaction, on cell performance and current density uniformity at a given operating condition, are examined for the first time to the best knowledge of the authors. Results indicate that the current density uniformity is hard to achieve by applying the graded design individually considered platinum and GDL porosity, especially with high initial platinum loading and GDL porosity at the cathode inlet. In order to achieve more uniform current density distributions inside the MEA, it is much more effective when both the gradients of platinum loading and GDL porosity are simultaneously and systematically designed.

Model development

The mathematical equations, accounting for conservation of mass, species, momentum and heat, as well as species transport in porous electrode, water migration through membrane, catalyst layer properties, boundary conditions, and computational solution, et al., used in this paper are as same as those in the

recently published one [Xing et al. 2017]. Only selected equations for the most important physical and chemical processes are summarized below to avoid repetition. More details of governing equations can be found elsewhere [Xing et al. 2014, 2015].

For the transport of gas mixture in porous media and channel, the equation for the conservation of momentum is shown as follow:

$$\frac{\rho^g}{\varepsilon} \left[(\mathbf{u}^g \cdot \nabla) \frac{\mathbf{u}^g}{\varepsilon} \right] = -\nabla \cdot \left[pI + \frac{\mu^g}{\varepsilon} (\nabla \mathbf{u}^g + (\nabla \mathbf{u}^g)^T) - \frac{2\mu^g}{3\varepsilon} (\nabla \cdot \mathbf{u}^g) I \right] - \left(\frac{\mu^g}{k_p} \right) \mathbf{u}^g \quad (1)$$

The conservation of mass of the multi-component gas mixture is described as Maxwell-Stefan equation:

$$\rho^g \mathbf{u}^g \cdot \nabla w_i^g - \nabla \cdot \left[\rho^g \sum_{j=1}^N (1-s') D_{ij} (\nabla x_j^g - w_j^g) \frac{\nabla p}{p} + D_i^T \frac{\nabla T}{T} \right] = M_i S_i^g \quad (2)$$

The distribution of temperature within the cell unit is studied using the theory of conservation of energy:

$$\nabla \cdot \left[\sum_{i=g,l} (\varepsilon \rho c_p \mathbf{u}^g)_i T \right] - \nabla \cdot \left(\sum_{i=g,l,s} k_i \nabla T \right) = S_T \quad (3)$$

The conservation of charge within the CLs of the anode and cathode obeys the following equation:

$$-\sigma_s^{eff} \nabla \cdot \nabla \phi_s = i_{agg} \quad (4)$$

$$\sigma_l^{eff} \nabla \cdot \nabla \phi_l = i_{agg} \quad (5)$$

where i_{agg} (A m^{-3}) is the volumetric current density obtained based on agglomerate model, which is expressed as:

$$i_{agg} = -4F \frac{p_i}{H_i} \left[\frac{1}{E_{agg} k_{agg}} + \frac{r_{agg} + \delta_l + \delta_w}{r_{agg}} \left(\frac{\delta_l}{a_{agg} D_{i-l}} + \frac{\delta_w}{a_{agg} D_{i-w}} \right) \right]^{-1} \quad (6)$$

where p_i (Pa), H_i ($\text{Pa m}^3 \text{ mol}^{-1}$), D_{i-l} ($\text{m}^2 \text{ s}^{-1}$) and D_{i-w} ($\text{m}^2 \text{ s}^{-1}$) are the partial pressure, Henry's constant of reactant gas i and its diffusion coefficient through ionomer and water film, respectively. r_{agg}

(m) is agglomerate radius, a_{agg} (m^{-1}) is agglomerate specific area, δ_l and δ_w (m) are the thicknesses of ionomer and liquid water films surrounding agglomerates, respectively. E_{agg} is effectiveness factor, k_{agg} (s^{-1}) is reaction rate coefficient, given as the following formula:

$$k_{agg} = \frac{a_{agg} i_{0,i}^{ref}}{4F C_i^{ref}} \left[\exp\left(\frac{-\alpha_i F \eta_i}{RT}\right) - \exp\left(\frac{(1-\alpha_i) F \eta_i}{RT}\right) \right] \quad (7)$$

where $i_{0,i}^{ref}$ (A m^{-2}) and α_i are the reference exchange current density and charge transfer coefficient of the anode and cathode, respectively. The overpotential at the anode and cathode, η_i (V) is defined as the difference between the potential of the solid phase (ϕ_s), electrolyte phase (ϕ_l) and equilibrium potential (ϕ_i^{eq}):

$$\eta_i = \phi_s - \phi_l - \phi_i^{eq} \quad (8)$$

In above equations, $\mathbf{u}^g$ (velocity of gas mixture), p (pressure of gas mixture), x_j^g (molar fraction of species j in gas mixture), T (temperature), ϕ_s (potential of solid phase), and ϕ_M (potential of electrolyte phase), are the variables to solve. ρ and μ are the density and viscosity of gas mixture, respectively. D_{ij} is the binary diffusion coefficient of species i and j . M is the molecular weight. ε , k_p , σ , k are the porosity, permeability, electron/ion conductivity and thermal conductivity of the electrode, respectively. The superscript g , T and eff represent gas, thermal and effective. The subscript i , g , l , s , M and T stand for species, gas, liquid, solid, electrolyte and temperature, respectively.

The two-phase flow of gas and water through the porous electrode and channel is described by the following equation:

$$\nabla \cdot (\rho_w^l D_c \nabla S - \frac{\rho_w^l k_r^l \mu_w^g}{k_r^g \mu_w^l} \mathbf{u}^g) = M_w S_w^l \quad (9)$$

Considering the electro-osmotic drag (EOD), back diffusion and hydraulic permeation, the conservation of dissolved water within the PEM follows:

$$\nabla \cdot (n_d \frac{i_M}{F}) - \nabla \cdot (D_{w-M} \nabla c_w^d) - \nabla \cdot (\frac{k_{p,M} c_w^d}{\mu_w} \nabla p) = S_w^d \quad (10)$$

In Eqns. (5) and (6), s (water saturation) and c_w^d (concentration of dissolved water) the variables to solve.

D_c and D_{w-M} are the diffusion coefficients for liquid water transport through the porous media under capillary force and dissolved water transport through the membrane, respectively. k_r is relative permeability of vapor and liquid water, ϕ_i^{eq} is the permeability of PEM. n_d is the EOD coefficient and S is the source term. Detailed expressions for source terms and key parameters in the model, e. g. diffusion coefficient, effectiveness factor and electrode properties, can be found elsewhere [Xing et al. 2016a, 2016b]. Key parameters used in this model are listed in Table 1 and source terms of thermal and electrochemical processes are given in Table 2.

The volume fraction of each component (L_i) within the CLs can be expressed as the function of their loadings as follow:

$$L_i = \frac{m_i}{l_{CL} \rho_i} \quad (11)$$

The Pt/C ratio was defined as the mass ratio of platinum to the total mass of platinum and carbon:

$$f = \frac{m_{Pt}}{m_{Pt} + m_C} \quad (12)$$

The porosity of CLs is defined as the volume fraction of void space to the total volume of CL.

Considering the penetration of GDL into CL, it can be expressed as follow:

$$\varepsilon_{CL} = 1 - \sum_i L_i - L_{GDL} (1 - \varepsilon_{GDL}) \quad (13)$$

where subscript i represents platinum, carbon and ionomer, respectively. L_{GDL} is the volume fraction of GDL penetrated into CL, defined as 10% in this work, ε_{GDL} is the GDL porosity.

Note that Nafion ionomer swells in contact with water, it's volume fraction (L_I) is a function of membrane/ionomer water content (λ):

$$L_I = (1 + k_s \lambda) L_I^0 \quad (14)$$

where k_s is the swelling coefficient, and L_I^0 is the volume fraction of dry ionomer.

The membrane/ionomer water content can be calculated based on the relation shown as follow:

$$c_w^d = \frac{\rho_I}{EW} \frac{\lambda}{1 + k_s \lambda} \quad (15)$$

The concentration of dissolved water (c_w^d) can be known by solving Eq. (10).

As shown in Fig. 1, the platinum loading inside cathode CL increases at a fixed gradient from the E-F interface at the cathode inlet to the E'-F' interface at the cathode outlet, while the GDL porosity increases at a fixed gradient from the F-G interface at the cathode inlet to the F'-G' interface at the cathode outlet. The platinum loading and GDL porosity, m_{Pt} and ε_{GDL} , as a function of spatial distance along the gas flow in the cathode channel are shown in the following expression:

$$m_{Pt} = m_{Pt}^0 + k_{Pt}(1 - Y) \quad (16)$$

$$\varepsilon_{GDL} = \varepsilon_{GDL}^0 + k_{GDL}(1 - Y) \quad (17)$$

where m_{Pt}^0 (mg cm⁻²) is the initial platinum loading at the cathode inlet, k_{Pt} (mg cm⁻² m⁻¹) is the gradient of the increasing platinum loading, ε_{GDL}^0 is the initial GDL porosity at the cathode inlet, k_{GDL} (cm⁻¹) is the gradient of the increasing porosity, Y is the dimensionless distance from the cathode inlet ($Y = 1$) to the outlet ($Y = 0$) along the cathode channel.

The initial platinum loading of 0.1, 0.2 and 0.4 and the platinum loading gradient from 0 to 50 mg cm⁻² m⁻¹ at a step of 5 mg cm⁻² m⁻¹, while the initial GDL porosity of 0.2, 0.4 and 0.6 and the porosity gradient of 0 to 0.3 cm⁻¹ at a step of 0.025 cm⁻¹ are studied. These platinum loadings and GDL porosities were commonly used in the published literature. The current density distribution along the cathode CL-GDL interface (F-F') is investigated. There are 3 levels of initial platinum loading, 3 levels of initial GDL porosity, thus 9 levels of a combination of initial variables. For each level of combination, there are 11 levels of platinum gradient and 13 levels of porosity gradient. To find out the optimal porosity gradient in the range of 0 to 0.05 cm⁻¹ at fixed initial platinum loading and platinum gradient, we add 0.02, 0.03 and 0.04 cm⁻¹ as 3 new levels of porosity gradient. To summarize, the whole numerical study requires 1296 simulations in this study (9 levels of combination × 11 levels of platinum gradient × 13 levels of porosity gradient + 3 levels of initial GDL porosity × 3 levels of porosity gradient).

As shown in Fig. 2 and Fig. 3, the platinum loading and GDL porosity linearly increase along the gas flow direction. Larger gradients of platinum and porosity lead to higher platinum loading inside the cathode CL and GDL porosity in the region near the cathode outlet. The initial platinum loadings of 0.1, 0.4 and 0.6 mg cm⁻² show similar profiles to that of 0.2 mg cm⁻² in Fig. 2, while the initial GDL porosities of 0.2 and 0.6 show similar profiles to that of 0.4 in Fig. 3. The maximum platinum loading and GDL porosity near the cathode outlet at various initial values and gradients of platinum and porosity are given in Table 3.

In order to quantitatively investigate the current density distribution along the cathode GDL-CL interface with the aid of graded design, the standard variance between the non-uniform spatial current density along the GDL-CL interface and the current density at the cathode inlet is defined as follow:

$$sv = \sqrt{\frac{\sum (i_x - i_L)^2}{n-1}} \quad (18)$$

where i_x (A cm⁻³) is the volumetric current density along the GDL-CL interface, i_L (A cm⁻³) is the volumetric current density at the cathode inlet, n is the number of the node at the GDL-CL interface along the y direction (500 in this study). Dividing sv by i_L , the normalized variation is obtained as follow:

$$S = \frac{sv}{i_L} \quad (19)$$

Larger S means a more significant departure of current density from the inlet value, indicating a less uniform distribution of current density along the GDL-CL interface. An example is given in Fig. 4, in which the volumetric current density obtained at various GDL porosity gradients at 0.7 V is shown. The dashed line is the current density at the cathode inlet. It is clear the normalized variance is larger when less uniform current density is achieved.

Model features and assumptions

The developed 2D, along-the-channel, non-isothermal, two-phase flow model treats the catalyst layer as a domain consisted of numerous carbon agglomerates. Reactant gases must diffuse through the void space inside the agglomerates and react on the surface of Pt catalyst. Effectiveness factor is used to quantitatively describe the effect of species transport on the overall reaction rate, which is defined as the ratio of practical reaction rate (under the effect of species transport) over the intrinsic reaction rate (without the effect of species transport). When the graded design of Pt loading and GDL porosity is applied, both the reaction rate and species transport rate are altered. The most uniform current density is achieved when the desired reaction and species transport rates are carefully controlled. Effectiveness factor is used to investigate whether the utilization efficiency of Pt catalyst is reduced when the graded design is applied. In addition to the assumptions in previous work [Xing et al. 2016a, 2016b, 2017], there are two extra assumptions in this work shown as follow:

1. The CL porosity decreases as an increase in Pt loading while the CL thickness is maintained as a constant [Owejan et al. 2013].

2. The extra losses for low Pt loading of 0.1 mg cm^{-2} are not taken into account, although such unexplained losses ($m_{\text{Pt}} \leq 0.1 \text{ mg cm}^{-2}$) were observed in published papers [Weber and Kusoglu, 2014; Kongkanand and Mathias, 2016].

Experimental study

Experiments were conducted to measure the polarization curves of the as-prepared single fuel cell unit with various platinum loading and GDL porosity, with the objective of validating the developed numerical model. Prior to the fabrication of fuel cell unit, a certain amount of de-ionized water was added into Nafion[®] and well mixed in a glass beaker under stirring, followed by ultra-sonication for 15 mins. The required amount of Pt/C (Vulcan XC-72) and isopropanol were added into the above solution to prepare a catalyst ink, which was then placed in the ultrasonic bath for a further 30 mins at room temperature. The ink was sprayed evenly onto the surface of GDL using a spray gun (Badger Model 100TM) fed by N₂ as carrying gas.

The GDL is made of carbon paper with various porosities. In this study a discrete GDL at the cathode was designed by patching commercial carbon papers TGP-H-090 (Toray) with various porosities as illustrated in Fig. 1(b). The porosity-graded GDL was made of pristine and polytetrafluoroethylene (PTFE) treated TGP-H-090 carbon papers. The PTFE suspension was prepared by adding a certain amount of PTFE into di-ionized water, followed by an intensive ultra-sonication then sprayed on to the surface of the plain TGP-H-090. After the evaporation of solvent and a thermal treatment, a thin layer PTFE remained on the internal surface within the carbon paper, leading to a decrease in GDL porosity. The porosity of pristine TGP-H-090 is 67% [El-kharouf et al. 2012]. PTFE loading of 25 mg cm^{-2} is applied. Based on a theoretical calculation, the porosity decreased to 26% after PTFE treatment. A porosity-graded GDL with two piecewise constant porosities was finally prepared along the air flow direction. The carbon paper was heated on a hot plate to maintain the temperature at 80-100 °C for good liquid evaporation. Nafion[®] solution in di-ionized water was used as a binder. The variation of Pt loading was controlled by

spaying same volumes of two different catalyst inks onto the abovementioned two types of TGP-H-090 carbon papers with fixed ionomer ratio, which was defined as the mass of ionomer to the total mass of Pt, carbon and ionomer. One ink was prepared from 20% Pt/C at I/C ratio of 0.54, and the other one was prepared from 40% Pt/C at I/C ratio of 0.72. The ionomer ratios for two inks were fixed at 0.3. The Pt loading of 0.2 and 0.4 mg cm⁻² were achieved for two types of CLs, respectively. A 10 × 10 cm² electrode was repaired and cut into several 1.0 × 10 cm² small pieces for MEA fabrication.

For model validation, Pt loading and GDL porosity obey the following piecewise functions:

$$m_{Pt} = \begin{cases} m_{Pt}(1) & 0 \leq Y \leq 0.5 \\ m_{Pt}(2) & 0.5 \leq Y \leq 1 \end{cases} \quad (18)$$

$$\varepsilon_{GDL} = \begin{cases} \varepsilon_{GDL}(1) & 0 \leq Y \leq 0.5 \\ \varepsilon_{GDL}(2) & 0.5 \leq Y \leq 1 \end{cases} \quad (19)$$

where 1 and 2 inside the blanket represent different regions of the CL and GDL as shown in Fig. 1(b). The detailed Pt loading and GDL porosity for studying cases A to D were listed in Table 4. Note that the average Pt loading and porosity over the CL and GDL are equivalent for different cases.

The Nafion[®] 112 membrane (DuPont) was sandwiched between the cathode and the anode, and then hot pressed for 3 min at a pressure of 500 kg and temperature of 100 °C. The single cell body was made of titanium with the active areas of 1.0 cm² surrounded by an O-ring seal for both the anode and cathode. Parallel channels with the depth and width of 1.0 mm were grooved on the fluid flow plate (FFP). The cell was thermostatically controlled by cartridge heaters. Pure hydrogen and air were supplied as the reactants which are humidified by passing through an external humidifier. The operating conditions were fuel cell and gas inlet temperatures of 60 °C, gas pressure of 1.0 atm, anode and cathode gas humidity of 100%, hydrogen stoichiometry of 1.5 and air stoichiometry of 3.0. Polarization curves were recorded during at a scan rate of 10 mV s⁻¹ by employing Autolab (PGSTAR 30, Eco Chemie), subject to several cycles until the steady performance was reached.

Results and discussions

Model validation

The developed models for cases A to D were validated against experimental data, as shown in Fig. 5, with respect to polarization curves. As an increase in current density, there is a typical fall in cell voltage. The polarization curves are therefore divided into three regimes, named as activation polarization regime, Ohmic polarization regime and concentration polarization regime, corresponding to low, medium and high current densities. The cathode charge transfer coefficient was regressed from experimental data in the activation polarization regime, in which the effect of mass transfer is limited, and the reaction rate is very close to the intrinsic rate.

It is clear that the modeling results of all cases show good inconsistency with experimental data at high cell voltages due to the weak impact of mass transport. The cell voltages typically drop as an increase in current density due to a variety of losses, which drop more rapidly as an increase in mass transport loss. Among all studying cases, Case A and Case C show the worst and best cell performance, respectively. The effect of GDL porosity can be seen by comparing Case A, C and B, D. With the same distribution of Pt loading, it is demonstrated that more porous GDL near the cathode outlet is of benefit to the cell performance due to the more efficient removal of the generated water. Greater porosity in this region facilitates the oxygen transport from the channel to the CL, so that higher current density is obtained. However, the porosity-graded GDL has virtually very limited influence on the level of polarization when the current density is medium or low, which agrees well with the conclusion of [Chu et al. \(2003\)](#). Comparing Case A and B indicates that the cell performance is not improved by placing more Pt near the cathode inlet region when the GDL porosity in this region is low. The increase in Pt loading also reduces the CL porosity, leading to a further increment of gas transport resistance and low utilization of Pt catalysts near the cathode inlet. This finding is in consistent with that of [Antoine et al. \(2000\)](#), who confirmed that the effect of catalyst gradient strongly depends on porosity. Comparing Case C and D

confirms this finding since it is observed that the cell performance improves by placing more Pt near the cathode inlet when GDL porosity is high. The better cell performance can be explained by the reduced volume fraction of void space occupied by liquid water as an increase in GDL porosity, that facilitates the gas transport through the GDL. The best cell performance is achieved by placing more Pt near the cathode inlet while maintaining high GDL porosity near the outlet. However, such design causes a more inhomogeneous distribution of current density along the air flow direction. It is well known that the reaction rate is highest near the cathode inlet due to the low degree of water flooding. Placing more Pt near the inlet leads to more generated water flowing to the outlet with the air, which deteriorates the gas transport rate and eventually reduces the current density near the outlet. It is assumed that the uniformity of current density can either be achieved by placing more Pt near the cathode outlet or reducing the GDL porosity near the cathode inlet. The increase in Pt near the outlet is to increase the local reaction rate for the ORR as indicated by Prasanna et al. (2007), while the decrease in GDL porosity near the inlet is to sacrifice the original overall rate by increasing the oxygen transport resistance. Once the ORR rate and oxygen transport rate are spatially matched along the channel, the uniform distribution of current density is obtained. The following work is to vary our hypothesis and find out the optimal gradients of Pt loading and GDL porosity.

Effect of the gradient of platinum loading

The predicted cell performance (polarization curves) for two sets of initial platinum loading and GDL porosity with various platinum gradients is shown in Fig. 6. It is shown that with low initial platinum loading and high GDL porosity, e. g. 0.2 mg cm^{-2} and 0.6, a very limited improvement of cell performance is obtained as the platinum gradient increases to $30 \text{ mg cm}^{-2} \text{ m}^{-1}$. With relative high initial platinum loading of 0.4 mg cm^{-2} and low GDL porosity of 0.4, the cell performance is not improved as expected by placing more platinum near the cathode outlet. The current density profiles for lower platinum loading, e. g. 0.1 and 0.2 mg cm^{-2} , are similar (not shown here). The difference is that the cell performance is slightly improved at lower platinum gradients. As indicated by Shukla et al. (2016), the

increase in platinum loading only led to an increase in cell performance up to an optimal loading value, and the optimal loading might not only be a function of the type of catalyst, but also the manufacturing method. The worse performance can be explained by the increased mass transport resistance inside the CL due to the reduced void space at high platinum loadings. The improved electrode performance at higher Pt loading can be explained by the increase in ECSA with Pt loading. It is known that the apparent reaction rate is a function of ECSA and the intrinsic reaction rate. Thus, the apparent reaction rate is proportional to the ECSA. However, the intrinsic reaction rate depends on the concentration of reactant on the surface of catalysts. The increase in Pt loading decreases the CL porosity according to Eq. (13), leading to a reduced local concentration of reactant with a decreased effective diffusion coefficient decreases at low CL porosity. At the cathode, the apparent reaction rate of ORR is accelerated at higher Pt loading. More generated water blocks more void space inside the CL. Consequently, the local concentration of reactant gas within the CL is reduced, especially near the membrane. Briefly, the increase in Pt loading, on one hand, accelerates the ORR by enlarging the ECSA, on the other hand, decreases the local concentration of reactant gas by reducing the CL porosity. It is implied that the initial increase in Pt loading is of benefit to the cell performance. However, the improved ORR rate is off-traded by the decreased oxygen transport rate with the further increase in Pt loading beyond the optimal value. As indicated previously [Xing et al. 2016a, 2016b], the increase in platinum loading leads to a decrease in CL porosity when the CL thickness is set as a constant, which results in a lower transport rate of reactant gas within the CL. In high current density range, the cell performance is mainly determined by the species transport rate rather than the electrochemical kinetics. Thus, the cell performance is declined when the higher platinum gradient is used.

The effect of platinum gradient on the current density along the cathode CL-GDL interface (F-F' in Fig. 1b) at 0.7 V is shown in Fig. 7. The electrochemical behavior at this voltage is believed to be under a mixing control of activation and Ohmic polarizations due to the relatively low current density. Two initial platinum loadings, 0.1 and 0.4 mg cm⁻², are compared. It is found that with the increase in platinum

gradient, the current density increases for the case of low platinum loading. It is due to the increase in active sites and specific area. However, when the initial platinum loading increases to 0.4 mg cm^{-2} , the current density initially increases then sharply decreases as the platinum gradient increases. The reason is that the increase in platinum loading leads to a decrease in CL porosity and an increase in the amount of produced water. A significant decrease in gas transport rate occurs when more liquid water fills in the reduced void space of CL. With the help of inhomogeneous distribution of platinum, the current density becomes more uniform. However, it is achieved at the cost of sacrificing the cell performance because the overall current density is reduced. This finding agrees well with the conclusions of Santis et al. (2006), in which no increase in cell performance was observed by homogenization of current density.

Fig. 8 shows the current density along the cathode CL-GDL interface with various platinum loading gradients and initial platinum loading and GDL porosity at 0.4 V, under a mixing control of Ohmic and concentration polarizations at a relatively high current density. The initial GDL porosity is fixed at 0.4 in Fig. 8a and 8b. It is indicated that the increase in platinum gradient, rather than improves the current density, decreases the current density along the gas flow direction. The decrease is more significant when higher initial platinum loading at the cathode inlet is applied. It can be explained by the decrease in CL porosity, especially for higher initial platinum loadings. In this condition, although the electrochemical reaction rate is accelerated by the increased platinum loading, the reactant transport through the porous electrode, including CL and GDL, becomes the rate control process. For example, the CL porosity at the cathode outlet decreases from 0.32 to 0.06 as the platinum gradient increases from 5 to $50 \text{ mg cm}^{-2} \text{ m}^{-1}$ when the initial platinum loading is fixed at 0.4 mg cm^{-2} . The remarkable decrease in CL porosity significantly decreases the gas transport rate through the CL, leading to a decrease in current density along the CL-GDL interface. Comparing Fig. 8a and 8c also shows the significance of initial platinum loading on the current density distribution. When the initial platinum loading is low, e. g. 0.1 mg cm^{-2} , the platinum gradient smaller than $20 \text{ mg cm}^{-2} \text{ m}^{-1}$ to a certain extent improves the current density uniformity.

However, when the initial platinum loading is higher than 0.1 mg cm^{-2} , the platinum-graded design worsens the current density uniformity.

In Fig. 8c and 8d, the initial platinum loading is fixed at 0.1 mg cm^{-2} and the effects of the platinum gradient with different initial GDL porosities of 0.4 and 0.6 are compared. It is shown that the current density is firstly improved then declined as the platinum gradient increases. The increase in current density is caused by the increase in reaction rate with higher platinum loading and the decrease in current density is due to the larger amount of generated water in the GDL. It is clear that the increase in GDL porosity expands the range of platinum gradients, which increase the current density near the cathode outlet. The maximum platinum gradient for an increased current density near the cathode outlet is $20 \text{ mg cm}^{-2} \text{ m}^{-1}$ for the initial GDL porosity of 0.4, which is expanded to $40 \text{ mg cm}^{-2} \text{ m}^{-1}$ for the initial GDL porosity of 0.6. The cases for cell voltage of 0.1 V show similar profiles to that of 0.4 V. In other words, the GDL porosity is vitally important to the distribution of current density. The increase in platinum loading inside the CL alone without considering the porosity-graded GDL design is insufficient to the uniformity of cathode current density with various electrode compositions at different operating conditions.

With various initial platinum loadings, platinum gradients and cell voltages, the normalized variance regarding the uniformity of current density distribution are summarized in Table 5. To improve the uniformity of the current density along the cathode CL-GDL interface, the optimal platinum gradient at 0.7 V for all studied initial platinum loadings is zero, indicating that the platinum-graded CL is not helpful. At 0.4 V, the optimal platinum gradient decreases from $20 \text{ mg cm}^{-2} \text{ m}^{-1}$ to zero as the initial platinum loading increases from 0.1 to 0.4 mg cm^{-2} . The decrease in this gradient is due to the increase in mass transport resistance with higher platinum loading near the outlet. The increase in platinum gradient leads to an increase in electrochemical reaction rate and results in a decrease in gas transport rate through the GDL due to the greater loss of void space by the larger amount of generated liquid water. Therefore,

the optimal platinum gradient in the middle current density range (0.4 V) is a tradeoff of reaction rate and mass transport rate.

It is difficult to fully fill the GDL with liquid water due to its hydrophobic property. When more liquid water is generated, the water removal rate is also accelerated, as described by the Leverett-J function [Das et al., 2010, 2012; Santamaria et al., 2014]. At 0.1 V, once the generation rate and removal rate of liquid water reach a balance, the water saturation in the porous electrode, defined as the volume fraction of void space occupied by liquid water, is close to a constant. As shown in Fig. 9, the water saturation in the cathode GDL changes slightly as the platinum gradient increases from 0 to $40 \text{ mg cm}^{-2} \text{ m}^{-1}$, the maximum water saturation only increases from 0.221 to 0.238. The average water saturation inside the cathode GDL with various platinum gradients as a function of current density is shown in Fig. 10. As the platinum gradient increases from 0 to $40 \text{ mg cm}^{-2} \text{ m}^{-1}$, the average water saturation near the limiting current density only increases by 0.01. In this condition, the average oxygen transport coefficient through the GDL slightly decreases from 8.82×10^{-6} to $8.71 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, only changes about 1.25%. The profiles of water saturation inside the CLs are similar to those within the GDLs. Since water is generated via ORR inside the CLs, the water saturation is slightly higher in this region. Moreover, the water saturation is relatively higher in the outlet area [Xing et al. 2016c]. The increase in platinum loading increases the current density near the outlet and leads to a more uniform distribution of current density along the CL-GDL interface. The optimal platinum gradient is therefore at the maximum value.

Effect of the gradient of GDL porosity

The GDL porosity plays an important role in determining the cell performance and the uniformity of current density. The predicted cell performance with various initial GDL porosities and porosity gradients are shown in Fig. 11. It is indicated that better cell performance is achieved as a consequence of the increased initial GDL porosity and gradient. For the initial GDL porosity of 0.2, the current density at 0.1 V increases from 0.9 to 1.7 A cm^{-2} as the porosity gradient increases from 0 to 0.3 cm^{-1} . On the contrary,

it only increases from 2.4 to 2.6 A cm⁻² for the initial porosity of 0.6. Therefore, the porosity-graded GDL cannot significantly improve the performance of fuel cells with high initial GDL porosity.

Fig. 12 shows the current density distribution along the CL-GDL interface at the cathode, obtained at 0.4 V with various initial GDL porosities and porosity gradients. The current density profiles for 0.7 and 0.1 V are similar to that of 0.4 V. Without the porosity-graded GDL design, higher current density is observed near the cathode inlet and it decreases along the gas flow direction. Once the porosity-graded GDL is applied, the current density near the cathode outlet is improved, which shows good agreement to the experimental and numerical studies of Zhang et al. (2016). The channel length is 7.0 cm in their work, and a segmented current collector (6 parts with equal area) was used to measure the local current density along the flow length of a single channel fuel cell. It was pointed out that the optimal porosity distribution of the cathode GDL followed a power law expression, in which the porosity slowly increased in the near inlet region then steeply increased near the outlet. It was found that the local current density near the cathode outlet was improved with the optimal graded GDL porosity distribution so that the average current density distribution became more uniform in comparison with the uniform porosity distribution.

Larger GDL porosity gradient results in greater improvement in current density. It is clear in Fig. 12a that, for the initial GDL porosity of 0.4, when the porosity gradient is larger than 0.1 cm⁻¹, the current density near the outlet is higher than that near the inlet, leading to a negative effect on the uniformity of current density. When the initial GDL porosity increases to 0.6, it is clear in Fig. 12b that, the uniform distribution of current density cannot be achieved, even with the maximum GDL porosity gradient. It is because, once the initial GDL porosity increases to a certain value, due to the faster reactant gas transport through the more porous GDL near the cathode inlet, more liquid water is generated and built up in the void space of the GDL toward to cathode outlet. Such decreased porosity is hard to be compensated by the increased porosity initiated by the porosity-graded GDL design, resulting in a lower current density near the outlet in comparison with that near the inlet. With various GDL initial porosities, porosity

gradients and cell voltages, the normalized variance regarding the uniformity of current density distribution are summarized in Table 6.

A smaller normalized variance means more uniform current densities distribution along the CL-GDL interface. It is clear the optimal porosity gradients for GDL initial porosity of 0.2, 0.4 and 0.6 at 0.7 V are 0.03, 0.15 and 0.3 m^{-1} , respectively. Similarly, the optimal gradients at 0.4 V are 0.05, 0.2 and 0.3 m^{-1} , while at 0.1 V are 0.04, 0.2 and 0.3 m^{-1} . It is found that the optimal gradient is lower at high cell voltages and higher with larger GDL initial porosities. It can be explained by the higher gas transport rate with larger GDL porosity. It is known that the purpose of the porosity-graded GDL is to control the transport rate of reactant gas and produced water through the GDL along the gas flow direction. In order to improve the current density near the outlet, greater porosity gradient must be applied for GDL with larger initial porosity.

Effectiveness factor represents the competitive relationship between reaction rate and species diffusion rate. Higher effectiveness factor indicates a weaker influence of oxygen diffusion through the CL on the overall reaction rate. Due to the loss of void space for oxygen diffusion as a result of the increase in platinum loading, the CL effectiveness factor may decrease as the platinum gradient increases toward the cathode outlet. Fig. 13 shows the CL effectiveness factor with various gradients of GDL porosity and platinum loading at 0.4 V. It is clear the effectiveness factor decreases along two directions: from the inlet to the outlet (from $Y = 1$ to $Y = 0$) and from the CL-GDL interface to the membrane-CL interface (from $X = 1$ to $X = 0$). The increase in GDL porosity gradient monotonically increases the effectiveness factor toward the cathode outlet. On the contrary, at a fixed GDL porosity, the effectiveness factor decreases as the platinum gradient increases. The change of effectiveness factor can be explained by the change of oxygen transport rate through the porous media. The increase in the gradient of GDL porosity enhances the oxygen transport rate, whereas the increase in platinum gradient weakens the transport rate, through the porous media.

Interaction of the gradients of platinum and GDL porosity

The interaction of the gradients of platinum loading and GDL porosity on current density uniformity along the cathode CL-GDL interface at 0.4 V is shown in Fig. 14. The initial GDL porosity is fixed at 0.4 in Fig. 14a and Fig. 14b, while fixed at 0.6 in Fig. 14c and Fig. 14d. Comparing the normalized variances at different initial GDL porosity implies the significant influence of GDL porosity on the optimal platinum gradient and the further impact on current density uniformity. In Fig. 14a and Fig. 14b, two optimal regions are respectively found for the most uniform distribution of current density. In Fig. 14a, one is the GDL gradient around 0.2 cm^{-1} with platinum gradient between 0 to $30 \text{ mg cm}^{-2} \text{ m}^{-1}$. The other one is the GDL gradient larger than 0.25 cm^{-1} with a platinum gradient between 40 to $45 \text{ mg cm}^{-2} \text{ m}^{-1}$. On the contrary, in Fig. 14b, the GDL gradient between 0.15 to 0.25 cm^{-1} with platinum gradient between 0 to $10 \text{ mg cm}^{-2} \text{ m}^{-1}$, and the GDL gradient between 0.25 to 0.3 cm^{-1} with platinum gradient between 15 to $25 \text{ mg cm}^{-2} \text{ m}^{-1}$, result in the most uniform current density distribution. In Fig. 14c and Fig. 14d, the optimal GDL porosity gradient near its maximum value of 0.3 cm^{-1} , while the optimal platinum gradient for lower initial platinum loading, e. g. 0.1 mg cm^{-2} , is between 25 to $40 \text{ mg cm}^{-2} \text{ m}^{-1}$, and for higher initial platinum loading, e. g. 0.2 mg cm^{-2} , is between 20 to $30 \text{ mg cm}^{-2} \text{ m}^{-1}$. It indicates that, at a fixed initial GDL porosity, the optimal platinum gradient is larger with the lower initial platinum loadings at the cathode inlet. Comparing Fig. 14a and Fig. 14d illustrates that, at the maximum gradient of GDL porosity, the optimal platinum gradient is larger with lower initial GDL porosity.

The interaction of the gradients of platinum loading and GDL porosity on current density uniformity along the cathode CL-GDL interface at 0.1 V is shown in Fig. 15. It is observed that the optimal GDL porosity gradient is at its maximum value when the initial GDL porosity is higher than 0.6. However, the optimal GDL porosity gradient is between 0.2 to 0.25 cm^{-1} when the initial GDL porosity is lower than 0.4. Moreover, at lower initial GDL porosity, as the platinum gradient increases from 0 to $50 \text{ mg cm}^{-2} \text{ m}^{-1}$, the current density becomes more uniform when the GDL porosity gradient is smaller than 0.15 cm^{-1} . The GDL porosity gradient larger than 0.15 cm^{-1} leads to a less uniform distribution of current density. For a fixed initial GDL porosity in Fig. 15a and Fig. 15b, the range of optimal platinum loading is broader with

lower initial platinum loadings. For example, the optimal platinum gradient is between 0 to 40 mg cm⁻² m⁻¹ for the initial platinum loading of 0.2 mg cm⁻². The range shrinks to 0 to 20 mg cm⁻² m⁻¹ as the initial platinum loading increases to 0.4 mg cm⁻². In the conditions of high GDL porosity and low platinum loading, the optimal gradients for both porosity and platinum loading can be their maximum values, e. g. the case in Fig. 15c. As the initial platinum loading increases to a certain value, e. g. 0.4 mg cm⁻² in Fig. 15d, the platinum gradient at the maximum level results in a less uniform distribution of current density. The gradients of platinum and GDL porosity are strongly interacted.

Conclusions

The numerical modeling study of the effect of gradients of platinum loading and GDL porosity on the cell performance and current density uniformity has been achieved and indicates the potential for such a strategy to reduce the use of platinum and possibly prolong the cell lifespan by a more uniform current density. Results reveal that individually increasing the platinum loading near the cathode outlet is insufficient to achieve a more uniform distribution of current density along the channel, so that both the platinum loading and GDL porosity have to be systematically designed.

The effect of platinum gradient on the current density distribution strongly depends on the GDL porosity. With an increase in platinum gradient, with high GDL porosity, e. g. 0.4, the current density near the cathode outlet is improved and a more uniform current density along the cathode CL-GDL interface is achieved. On the contrary, with low GDL porosity, the current density along the CL-GDL initially increases then sharply declines as the platinum gradient increases. The increase in GDL porosity accelerates the oxygen transport rate through the porous media, which is helpful to the uniformity of current density at middle and high current density ranges. The optimal platinum gradient for the most uniform current density distribution increases as the GDL porosity increases. In other words, a more porous GDL is capable of expanding the range of the optimal platinum gradient.

It is also found that, at low current density, the platinum- and porosity-graded design can increase the current density toward the cathode outlet. However, the current density uniformity becomes worse in comparison with the conventional electrode.

The optimal platinum gradient and GDL porosity gradient is determined by the competitive relationship between the intrinsic reaction rate and reactant gas transport rate. The intrinsic reaction rate is improved by higher platinum loading whereas the gas transport rate through the GDL is close to a constant near the limiting current density. When the intrinsic reaction rate is slower than the gas transport rate, the increase in platinum gradient is of benefit to current density uniformity. Otherwise, the reaction rate near the cathode inlet must be sacrificed by the reduced gas transport rate to achieve the more uniform distribution of current density toward the outlet. For this purpose, the GDL with a lower porosity near the inlet is a practical option.

The interaction of the gradients of platinum and GDL porosity, at middle and high current densities, demonstrates that the optimal platinum gradient is larger with lower initial platinum loading and GDL porosity at the cathode inlet. The optimal GDL porosity gradient is at its maximum when the initial GDL porosity is high, e. g. 0.6, although it is not the maximum value at low initial GDL porosity, e. g. 0.4. The range of optimal platinum loading is broader with lower initial platinum loadings. The optimal gradients of platinum and porosity are determined by the strong interaction of platinum loading and GDL porosity in various operating conditions.

It is worthwhile to note that some unexplained losses, e. g. extra proton transport resistance through the ionomer, were observed with ultra-low platinum loading, e. g. lower than 0.1 mg cm^{-2} [Weber and Kusoglu, 2014; Kongkanand and Mathias, 2016]. Novel and smart devices are required to experimentally determine the spatial distribution of reactant gases and current density along flow channels [He et al. 2013, 2014]. Additional mathematic models for the unexplained losses and more delicate measurement of spatial distributions of reactant gases and current density are of great significance and interest as future work.

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Fig. 1 (a) 3D sketch of a PEM fuel cell unit for the graded CL and GDL design; (b) Detailed 2D representation of the graded Pt and porosity design in the cathode CL and GDL.

Fig. 2 Platinum loading as a function of dimensionless distance from the cathode inlet to the outlet with an initial platinum loading of 0.2 mg cm^{-2} .

Fig. 3 GDL porosity as a function of dimensionless distance from the cathode inlet to the outlet with an initial porosity of 0.4.

Fig. 4 Current density uniformity along the GDL-CL interface with various GDL porosity gradients.

Fig. 5 Validation of modeling results against experimental data for various cases at the operation condition of 60 °C, 1.0 atm, 100% relative humidity, anode stoichiometry of 1.5 and cathode stoichiometry of 3.0. symbols – experimental data, lines – modeling results, $\square$ and solid line – Case A, $\circ$ and dash line – Case B, $\triangle$ and dot line – Case C, $\star$ and dash dot line – Case D.

Fig. 6 Predicted polarization curves with various platinum loading gradients: (a) $m_{\text{Pt}}^0 = 0.2 \text{ mg cm}^{-2}$, $\varepsilon_{\text{GDL}}^0 = 0.6$; (b) $m_{\text{Pt}}^0 = 0.4 \text{ mg cm}^{-2}$, $\varepsilon_{\text{GDL}}^0 = 0.4$.

Fig. 7 Current density along the cathode CL-GDL interface with various platinum loading gradients at 0.7

V : $\varepsilon_{GDL}^0 = 0.4$, (a) $m_{Pt}^0 = 0.1 \text{ mg cm}^{-2}$; (b) $m_{Pt}^0 = 0.4 \text{ mg cm}^{-2}$.

Fig. 8 Current density along the cathode CL-GDL interface with various platinum loading gradients at 0.4

V: (a) $\varepsilon_{GDL}^0 = 0.4$, $m_{Pt}^0 = 0.2 \text{ mg cm}^{-2}$; (b) $\varepsilon_{GDL}^0 = 0.4$, $m_{Pt}^0 = 0.4 \text{ mg cm}^{-2}$; (c) $m_{Pt}^0 = 0.1 \text{ mg cm}^{-2}$, $\varepsilon_{GDL}^0 = 0.4$;

(d) $m_{Pt}^0 = 0.1 \text{ mg cm}^{-2}$, $\varepsilon_{GDL}^0 = 0.6$.

Fig. 9 Water saturation in the cathode GDL with various platinum gradients at 0.1 V: $\varepsilon_{GDL}^0 = 0.4$, $m_{Pt}^0 = 0.4 \text{ mg cm}^{-2}$, $k_{Pt} = 0, 20 \text{ and } 40 \text{ mg cm}^{-2} \text{ m}^{-1}$ from down to up.

Fig. 10 Average water saturation in the cathode GDL with various platinum gradients as a function of current density: $\varepsilon_{\text{GDL}}^0 = 0.4$, $m_{\text{Pt}}^0 = 0.4 \text{ mg cm}^{-2}$.

Fig. 11 Predicted polarization curves with various GDL porosity gradients: $m_{Pt}^0 = 0.4 \text{ mg cm}^{-2}$, solid line - $\epsilon_{GDL}^0 = 0.2$; dash line - $\epsilon_{GDL}^0 = 0.6$.

Fig. 12 Current density along the cathode CL-GDL interface with various GDL porosity gradients at 0.4

V: $m_{\text{Pt}}^0 = 0.4 \text{ mg cm}^{-2}$, (a) $\varepsilon_{\text{GDL}}^0 = 0.4$; (b) $\varepsilon_{\text{GDL}}^0 = 0.6$.

Fig. 13 Effectiveness factor with various (a) gradients of GDL porosity and (b) platinum loading at 0.4 V: $\varepsilon_{GDL}^0 = 0.4$, $m_{pt}^0 = 0.4 \text{ mg cm}^{-2}$, $X = 0$ - membrane-CL interface, $X = 1$ - CL-GDL interface, $Y = 0$ - cathode outlet, $Y = 1$ - cathode inlet.

Fig. 14 Interactive effect of the gradients of platinum and GDL porosity on current density uniformity at 0.4 V: (a) $\varepsilon_{GDL}^0 = 0.4$, $m_{Pt}^0 = 0.2 \text{ mg cm}^{-2}$; (b) $\varepsilon_{GDL}^0 = 0.4$, $m_{Pt}^0 = 0.4 \text{ mg cm}^{-2}$; (c) $\varepsilon_{GDL}^0 = 0.6$, $m_{Pt}^0 = 0.1 \text{ mg cm}^{-2}$; (d) $\varepsilon_{GDL}^0 = 0.6$, $m_{Pt}^0 = 0.2 \text{ mg cm}^{-2}$.

Fig. 15 Interactive effect of the gradients of platinum and GDL porosity on current density uniformity at 0.4 V (a) $\varepsilon_{GDL}^0 = 0.4$, $m_{Pt}^0 = 0.2 \text{ mg cm}^{-2}$; (b) $\varepsilon_{GDL}^0 = 0.4$, $m_{Pt}^0 = 0.4 \text{ mg cm}^{-2}$; (c) $\varepsilon_{GDL}^0 = 0.6$, $m_{Pt}^0 = 0.2 \text{ mg cm}^{-2}$; (d) $\varepsilon_{GDL}^0 = 0.6$, $m_{Pt}^0 = 0.4 \text{ mg cm}^{-2}$.

Table 1 Key physical and electrochemical parameters used in the model

Symbol	Description (unit)	Value
ρ_{Pt}	Platinum density (kg m ⁻³)	2.145×10^4
ρ_C	Carbon density (kg m ⁻³)	1.8×10^3
ρ_I	Dry Nafion ionomer density (kg m ⁻³)	2.0×10^3
EW	Membrane/ionomer equivalent weight (kg mol ⁻¹)	1.10
k_s	Ionomer swelling coefficient	1.26×10^{-2}
σ	Liquid water surface tension (N m ⁻¹)	6.25×10^{-2}
θ	Contacting angle (°)	120
k_{con}	Vapor condensation rate (s ⁻¹)	100
k_{eva}	Water evaporation rate (atm ⁻¹ s ⁻¹)	100
∇S_a	Entropy of HOR (J mol ⁻¹ K ⁻¹)	161.2
∇S_c	Entropy of ORR (J mol ⁻¹ K ⁻¹)	-324.0
h_w^{vd}, h_w^{dl}	Latent heat of membrane adoption/desorption (J kg ⁻¹)	3.462×10^6
h_w^{vl}	Latent heat of condensation/evaporation (J kg ⁻¹)	2.308×10^6
L_{Ch}	Channel length (m)	1×10^{-2}
l_{Ch}	Channel depth (m)	1×10^{-3}
W_{Ch}	Channel width (m)	1×10^{-3}
l_{GDL}	GDL thickness (m)	2.8×10^{-4}
l_{CL}	CL thickness (m)	1.5×10^{-5}
l_M	Membrane thickness (m)	1.2×10^{-4}
ε_{GDL}^0	GDL porosity at cathode inlet	0.2, 0.4, 0.6
m_{Pt}^0	Pt loading at cathode inlet (mg cm ⁻²)	0.1, 0.2, 0.4
f	Platinum mass ratio to Pt/C	40 %
I/C	Ionomer/carbon mass ratio	70 %
r_{agg}	Agglomerate radius (m)	1.0×10^{-7}
α_c	Cathode charge transfer coefficient	0.7
T	Operating temperature (K)	333.15
p	Back pressure (Pa)	1.0×10^5
RH	Relative humidity	100 %
ξ_a	Anode stoichiometric flow ratio	1.0
ξ_c	Cathode stoichiometric flow ratio	2.0

Table 2 Source terms of thermal and electrochemical processes

Source terms	Expression	Unit
Hydrogen consumption	$S_{H_2}^g = -\frac{i_a}{2F}$	$\text{mol m}^{-3} \text{ s}^{-1}$
Oxygen consumption	$S_{O_2}^g = -\frac{i_c}{4F}$	$\text{mol m}^{-3} \text{ s}^{-1}$
Water generation	$S_w^{rc} = \frac{i_c}{2F}$	$\text{mol m}^{-3} \text{ s}^{-1}$
Vapor to dissolved water (mass)	$S_w^{vd} = k_{ads}(c_w^{eq} - c_w^d) \quad c_w^d < c_w^{eq}$	$\text{mol m}^{-3} \text{ s}^{-1}$
Dissolved water to liquid water (mass)	$S_w^{dl} = k_{des}(c_w^d - c_w^{eq}) \quad c_w^d \geq c_w^{eq}$	$\text{mol m}^{-3} \text{ s}^{-1}$
Vapor to liquid water (mass)	$S_w^{vl} = \begin{cases} k_{con} \frac{\varepsilon(1-s)x_w^g}{R_g T} (x_w^g p^g - p_{sat}) & x_w^g p^g \geq p_{sat} \\ k_{eva} \frac{\varepsilon s \rho_w^l}{M_w} (p_{sat} - x_w^g p^g) & x_w^g p^g < p_{sat} \end{cases}$	$\text{mol m}^{-3} \text{ s}^{-1}$
Joule heating at anode	$S_T^{sa} = \frac{i_a^2}{\sigma_{GDL,a}^{eff}}$	W m^{-3}
Joule heating at cathode	$S_T^{sc} = \frac{i_c^2}{\sigma_{GDL,c}^{eff}}$	W m^{-3}
Joule heating in membrane	$S_T^M = \frac{i_M^2}{\sigma_M^{eff}}$	W m^{-3}
Heat absorbed by HOR	$S_T^{ra} = - i_a \left[\frac{T \nabla S_a}{2F} \right]$	W m^{-3}
Heat released by ORR	$S_T^{rc} = i_c \left[\eta_c - \frac{T \nabla S_c}{4F} \right]$	W m^{-3}
Vapor to dissolved water (heat)	$S_T^{vd} = M_w S_w^{vd} \nabla h_w^{vd}$	W m^{-3}
Dissolved water to liquid water (heat)	$S_T^{dl} = M_w S_w^{dl} \nabla h_w^{dl}$	W m^{-3}
Vapor to liquid water (mass)	$S_T^{vl} = M_w S_w^{vl} \nabla h_w^{vl}$	W m^{-3}

Table 3 Maximum platinum loading and GDL porosity with various initial values and gradients

	Initial value at E-F interface (mg cm ⁻²)	Platinum loading gradient (mg cm ⁻² m ⁻¹)	Maximum value at E'-F' interface (mg cm ⁻²)
Pt loading	0.1	5 – 50	0.15 – 0.6
	0.2	5 – 50	0.25 – 0.7
	0.4	5 – 50	0.45 – 0.9
	0.6	5 – 50	0.65 – 1.1
	Initial value at F-G interface (mg cm ⁻²)	GDL porosity gradient (cm ⁻¹)	Maximum value at F'-G' interface
GDL porosity	0.2	0.02 – 0.3	0.22 – 0.5
	0.4	0.02 – 0.3	0.42 – 0.7
	0.6	0.02 – 0.3	0.62 – 0.9

Table 4 Variation of Pt loading and GDL porosity in different regions of CL and GDL for model validation

	$m_{Pt} (1)$	$m_{Pt} (2)$	$\varepsilon_{GDL} (1)$	$\varepsilon_{GDL} (2)$
Case A	0.2 mg cm ⁻²	0.4 mg cm ⁻²	0.26	0.67
Case B	0.4 mg cm ⁻²	0.2 mg cm ⁻²	0.26	0.67
Case C	0.2 mg cm ⁻²	0.4 mg cm ⁻²	0.67	0.26
Case D	0.4 mg cm ⁻²	0.2 mg cm ⁻²	0.67	0.26

Table 5 Normalized variance of current density with various initial Pt loading, gradients and cell voltages

Initial Pt loading (mg cm ⁻²)	Cell voltage (V)	Pt loading gradient k_{Pt} (mg cm ⁻² m ⁻¹)								
		0	5	10	15	20	25	30	35	40
0.1	0.7	0.0034	0.0175	0.0376	0.0568	0.0753	0.0930	0.1100	0.1262	0.1416
	0.4	0.0403	0.0388	0.0378	0.0371	0.0368	0.0369	0.0373	0.0383	0.0398
	0.1	0.1252	0.1209	0.1179	0.1153	0.1128	0.1100	0.1070	0.1037	0.1000
0.2	0.7	0.0036	0.0139	0.0307	0.0468	0.0621	0.0768	0.0907	0.1037	0.1159
	0.4	0.0410	0.0407	0.0406	0.0409	0.0417	0.0431	0.0450	0.0477	0.0512
	0.1	0.1159	0.1136	0.1111	0.1085	0.1055	0.1021	0.0983	0.0940	0.0891
0.4	0.7	0.0040	0.0084	0.0199	0.0306	0.0404	0.0491	0.0565	0.0620	0.0651
	0.4	0.0436	0.0458	0.0486	0.0523	0.0569	0.0625	0.0695	0.0781	0.0887
	0.1	0.1024	0.0984	0.0939	0.0886	0.0826	0.0755	0.0674	0.0585	0.0505

Note: initial GDL porosity is fixed at 0.4.

Table 6 Normalized variance of current density with various GDL initial porosities, gradients and cell voltages

Initial GDL porosity	Cell voltage (V)	GDL porosity gradient k_{GDL} (cm ⁻¹)								
		0	0.02	0.03	0.04	0.05	0.1	0.15	0.2	0.3
0.2	0.7	0.0051	0.0017	0.0008	0.0016	0.0029	0.0084	0.0125	0.0157	0.0203
	0.4	0.086	0.047	0.030	0.018	0.014	0.072	0.123	0.162	0.218
	0.1	0.102	0.055	0.034	0.020	0.025	0.120	0.207	0.284	0.407
0.4	0.7	0.0040	0.0033	0.0030	0.0027	0.0025	0.0013	0.0005	0.0008	0.0020
	0.4	0.0436	0.0372	0.0343	0.0315	0.0288	0.0173	0.0084	0.0045	0.0138
	0.1	0.1024	0.0894	0.0832	0.0773	0.0715	0.0450	0.0238	0.0109	0.0294
0.6	0.7	0.0036	0.0034	0.0033	0.0032	0.0031	0.0026	0.0021	0.0017	0.0011
	0.4	0.0315	0.0294	0.0284	0.0274	0.0265	0.0222	0.0184	0.0152	0.0097
	0.1	0.0692	0.0645	0.0623	0.0602	0.0584	0.0493	0.0416	0.0351	0.0244

Note: initial platinum loading is fixed at 0.4 mg cm⁻².