A low platinum loading model, considering both the platinum loading and platinum particle distribution on carbon support, is developed. This model takes into account the interfacial transport resistances at ionomer, water film and Pt particle surfaces in order to capture the effects of Pt loading and electrode composition on fuel cell performance. After coupling this electrode model into a comprehensive PEM fuel cell model, i.e. M2 model, experimental validation is performed for a wide range of Pt loading from 0.2 to 0.025 mg/cm² for two electrode compositions with and without carbon dilution. Good agreement between the predicted and measured polarization curves is achieved under wide-ranging operating conditions. The agglomerate size effect is also examined, and it is shown that the agglomerates have virtually no effect on cell performance for agglomerate radius smaller than 150 nm. Since in realistic fuel cell catalyst layers, agglomerates may not exist, or may only exist with sizes no larger than 150 nm based on SEM observations, the present work suggests that the standard homogeneous electrode model is suitable and sufficient for analyses of transport losses in PEM fuel cell electrodes where interfacial transport resistances exist.

Performance, durability, and especially cost are still the main challenges for commercialization of PEM fuel cell vehicles. Per the US Department of Energy (DOE) technical target, loading of the platinum group metal must be reduced to 0.125 mg/cm² or less in a fuel cell vehicle before 2017.1 Although dramatic reduction of Pt loading has been achieved in the past decade, the current level of Pt loading still approaches or exceeds 0.25 mg/cm², which is twice the DOE short-term target. Advanced nanotechnology is used to create new electrode architectures for low Pt loading, such as the 3 M nanotructured thin-film (NSTF) electrode.2–4 While the mass activity of this novel electrode can be 10 times that of the commercial dispersed structured thin-film (NSTF) electrode,2–4 the predicted I-V curves overestimated the experimental results without considering the local resistance, especially at lower Pt loading, indicating that the oxygen transport loss caused by local resistance is marked at low Pt loading. Generally, modeling has been an effective tool to understand transport phenomena in the very thin catalyst layer that are difficult to probe through experimental methods.

The agglomerate model has been commonly used to study the Pt loading effect in the PEM fuel cell electrode. By modeling the agglomerate particles consisting of a mixture of ionomer, carbon particles and carbon-supported platinum particles, the oxygen transport resistance at the micro-scale was introduced in the agglomerates. Such a model introduces additional parameters relating to the electrode structure, such as the agglomerate size and the ionomer film thickness surrounding an agglomerate. The oxygen transport resistance in the agglomerate is a function of these parameters.5 However, a wide range of agglomerate sizes from 100 nm to 2000 nm, and ionomer thicknesses from 10 nm to 100 nm, had to be assumed in the literature5–8 as fitting parameters in order to match their experimental data. Such large and random agglomerate size and thick ionomer film were not supported by microscopy observations.21,22 For a Pt/C electrode, Suzuki et al. found interconnecting particles with diameters from 10 to 50 nm, which is nearly the same as the size of Pt/C particles. Even if regarding the loosely-packed rod-like region as the agglomerate, its diameter is still smaller than 300 nm. Similar electrode morphology was also observed in Greszler’s work.8 Therefore, the agglomerates probably do not exist in reality. Even if non-uniform agglomerates may exist with a size distribution as discussed by Epting and Lister,23 the diameter of the largest agglomerates may not exceed 300 nm, and these agglomerates occupy only a small percentage of the total catalyst particles.

The thick ionomer film assumed in agglomerate models may not be physical either. Assuming the ionomer is uniformly distributed on the Pt/C particles or surface of small agglomerates, this ionomer film thickness only allows several nanometers given an actual electrode’s ionomer to carbon ratio (I/C).5,21 It is questionable that thick ionomer film (tens to one hundred nanometers) is required to capture the measured local transport resistance. Some research argued a much smaller oxygen diffusivity in the thin ionomer film than that in the bulk membrane in order to obtain a relatively reasonable ionomer thickness.5,24 Indeed, oxygen diffusivity has not been measured in-situ in very thin film in the catalyst layer. Although a decreased ion conductivity in thin ionomer film was suggested in some studies,25–27 probably due to the decrease of water uptake with decreasing film thickness, extending this conclusion to oxygen diffusivity remains an open question. Other works, however, showed ion conductivity in the catalyst layer similar to that in the bulk membrane.28,29 In ex-situ measurements,
Kudo et al.\textsuperscript{30,31} measured the oxygen dissolution and transport resistance through ionomer films on a Pt substrate. The results showed that the oxygen transport resistance does not deviate from the linear relationship from film thickness of 800 nm to 25 nm, indicating a similar oxygen diffusivity in this large thickness range. They introduced an interfacial resistance at the ionomer surface by assuming an oxygen dissolution resistance there and fitted a reasonable, small agglomerate size for their model. The most recent study,\textsuperscript{32} however, demonstrated that the dissolution resistance has little impact on the cell performance, using Kudo et al.’s experimental data.\textsuperscript{30,31} Much controversy remains as to exact physical origins of the local micro-scale oxygen transport resistance at low Pt loading.

The local transport resistance in the catalyst layer depends not only on the Pt loading but also on the electrode composition. Owejan et al.\textsuperscript{33} recently reported several sets of experiments by diluting various wt\% Pt catalyst material with bare carbon support, while keeping constant Pt loading with same electrode thickness. The measured data showed that performance loss increases with increased carbon dilution fraction at a given Pt loading, especially at Pt loading lower than 0.1 mg/cm\textsuperscript{2}. This work stresses that the electrode structure is more complicated than only considering the Pt loading effect. The distribution of the catalyst particles, i.e. Pt particles, may have significant impact on fuel cell performance as well. However, both the experimental and modeling studies on this issue are still limited.

In this work, a comprehensive electrode model is proposed taking both the Pt loading and electrode composition into consideration, and coupled into a macro-scale PEM fuel cell model. The effect of Pt loading and electrode compositions with and without carbon dilution on PEM fuel cell performance is examined and validated with extensive experimental data under different operating conditions from Owejan et al.\textsuperscript{33} The present electrode model does not consider the agglomerates for the reasons discussed earlier; however, in the final part of this work, this assumption is examined by further extending the present model into an agglomerate model to study the agglomerate size effect.

**Electrode Model**

The catalyst layer is composed of gas pores, carbon particles, Pt catalyst particles and the ionomer network. We further assume solid carbon particles as validation shall be performed against the experiments of Owejan et al.\textsuperscript{33} that used Vulcan carbon support. Fig. 1 schematically illustrates the catalyst layer structure including both the activated Pt/C particles and the bare carbon particles as the diluent. Pt particles disperse on the carbon particle surface. The ionomer in the catalyst layer forms a film covering the Pt/C or bare carbon particles and connects them together to form an ionic network. The catalyst layer possibly has a few small agglomerates or none. For the latter case, we develop a homogeneous porous electrode model, and for the former case we shall justify the assumption of neglecting agglomerates in a later section.

**Transport resistance near Pt/C particles.** — As shown in Fig. 1, the catalyst layer is assumed to consist of independent particles covered by an ionomer film with the thickness $\delta_c$. For a single Pt/C particle, we depict the oxygen concentration profile in Fig. 2. Reactant oxygen in the gas phase will first dissolve into the ionomer. According to Henry’s law, the equilibrium concentration of oxygen $C_{o_2}^1$ in the ionomer is,

$$C_{o_2}^1 = \frac{RT}{H_{o_2,e}} C_{o_2}^g,$$  \[1\]

where $H_{o_2,e}$ is the Henry constant of oxygen at the ionomer surface. Because the oxygen dissolution rate in ionomer is not unlimited, a dissolution resistance at the interface exists.\textsuperscript{30,31} The oxygen flux $N_{o_2}$...
across the ionomer surface is given by,
\[
N_{o_2} = \frac{1}{R_{e,dissol}} \left( C_{o_2}^1 - C_{o_2}^2 \right)
\]  
[2]
where \( R_{e,dissol} \) is the non-equilibrium dissolution resistance and depends on the dissolution rate for oxygen in the ionomer.

Through the thin ionomer film, the oxygen flux is described by one dimensional Fick’s equation (this is a reasonable approximation for an ionomer film of several nanometers thick as compared to ~25 nm of carbon particle radius),
\[
N_{o_2} = \frac{D_{o_2,ion}}{\delta_e} \left( C_{o_2}^1 - C_{o_2}^3 \right)
\]  
[3]
where \( D_{o_2,ion} \) is the oxygen diffusivity in the ionomer film and \( C_{o_2}^3 \) is the oxygen concentration near the carbon particle surface.

In addition, an interfacial resistance may also exist at the Pt surface due to the modification of the Pt atoms and ionomer structure at Pt/ionomer interface by sulfonate ion absorption, which leads to the decrease of the effective Pt surface area and decrease of the oxygen permeability.\[22\] It follows that the oxygen flux near the Pt surface can be written as
\[
N_{o_2} = \frac{1}{R_{pt,int}} \left( C_{o_2}^1 - C_{o_2}^{pt} \right)
\]  
[4]
where \( C_{o_2}^{pt} \) is the oxygen concentration at the Pt surface and \( R_{pt,int} \) is the interfacial transport resistance near the Pt surface.

The above expressions of the transport resistances near the Pt/C particle assume a perfect and uniform coverage of the ionomer. However, actual ionomer distribution appears to be heterogeneous, from relatively thick coverage to non-coverage.\[22\] It is more convenient to combine Equation 1 and 2 into a single interfacial resistance if assuming a uniform ionomer coverage, which is,
\[
N_{o_2} = \frac{1}{R_{e,int}} \left( C_{o_2}^1 - C_{o_2}^3 \right)
\]  
[5]
where \( R_{e,int} \) is the integrated interfacial transport resistance at the pore/ionomer interface.

From Equation 3 through Equation 5, we get the relationship between the oxygen concentration in gas phase and on the Pt surface,
\[
\left( R_{e,int} + \frac{\delta_e}{D_{o_2,ion}} + R_{pt,int} \right) N_{o_2} = C_{o_2}^3 - C_{o_2}^{pt}
\]  
[6]

It should be noted that Equation 6 reflects the ionomer film effect on oxygen transport resistance. On the other hand, if liquid water exists in the catalyst layer, the liquid water would prefer to cover the ionomer surface because of its hydrophilic characteristic.\[22\] A similar equation can be written to describe the oxygen transport resistance through a water film, as was done for that in ionomer film, and the total transport equation through both water and ionomer films is,
\[
\left( R_{w,int} + \frac{\delta_w}{D_{o_2,w}} + R_{e,int} + \frac{\delta_e}{D_{o_2,ion}} + R_{pt,int} \right) N_{o_2} = C_{o_2}^3 - C_{o_2}^{pt}
\]  
[7]
where \( R_{w,int} \) is the transport resistance at the water film surface, \( \delta_w \) is the water film thickness and \( D_{o_2,w} \) is the oxygen diffusivity in water film.

The oxygen flux across the water and ionomer films is related to the local reaction rate. Based on Subramanian et al.’s work,\[35\] the Pt-oxide-coverage-dependent kinetics equation for oxygen reduction reaction (ORR) is given by,
\[
j_c = -i_{0,c} \alpha_{pt}(1 - \theta_{po}) \left( \frac{C_{o_2}^{pt}}{C_{o_2,ref}} \right)^\gamma \exp \left( -\frac{\alpha_c}{RT} F \eta_e - \frac{\alpha_0 \theta_{po}}{RT} \right)
\]  
[8]
\[
i_{0,c} = i_{0,c}^{ref} \exp \left( -\frac{E_c}{RT} \left( 1 - \frac{1}{1.353} \right) \right)
\]  
[9]
where \( \omega \) is the energy parameter for the Temkin isotherm, \( \gamma \) is the reaction order in ORR, \( \alpha_{pt} \) is the active volumetric surface area of Pt which is related to the Pt loading \( \rho_{pt} \) and electrochemical specific area (ECSA) of Pt particles \( \alpha_{ECSA} \), by,
\[
\alpha_{pt} = \frac{\alpha_{ECSA} \rho_{pt}}{\delta_{CL}}
\]  
[10]
Here \( \delta_{CL} \) is the thickness of the catalyst layer.

The Pt-oxide coverage \( \theta_{po} \) is fitted from the experimental data in Ref. 35 and can be expressed by,
\[
\theta_{po} = 1 / \left( 1 + c^{22.40.818-E} \right)
\]  
[11]
where \( E \) is the cathode potential vs. RHE.

As mentioned before, the catalyst layer may have both Pt/C catalyst particles and bare carbon particles, as shown in Fig. 1. The bare carbon is inactive for ORR, so the effective specific surface area of the ionomer on Pt/C particles is given by,
\[
a_{eff} = a_c X = n_c A_c x
\]  
[12]
where \( a_c = n_c A_c \) is the volumetric surface area of ionomer, \( n_c \) is the number of Pt/C particles and bare carbon particles per volume, \( A_c \) is the ionomer surface area for one particle and \( x \) is the number fraction of the Pt/C particles. Equation 12 assumes that the Pt/C particle and the bare carbon particle have the same size because the much smaller Pt particles dispersed on carbon support almost do not change the carbon size. If further assuming spherical shape of these particles, we have,
\[
n_c = \frac{\epsilon_c}{\frac{4}{3} \pi r_e^3}
\]  
[13]
\[
A_c = 4 \pi (r_c + \delta_e)^2
\]  
[14]
\[
a_c = \frac{3 \delta_e}{r_e} (r_c + \delta_e)^2
\]  
[15]
where \( \epsilon_c \) is the volume fraction of the carbon particle in the catalyst layer and \( r_e \) is the carbon particle radius.

For a Pt/C catalyst particle, the oxygen flux around it is given by,
\[
j_c = -i_{0,pt/C} \frac{RT}{4F} = -\frac{j_c}{4F a_c x}
\]  
[16]
Substitute the oxygen flux Equation 16 into Equation 7, we have,
\[
\left( R_{w,int} + \delta_w D_{o_2,w} + R_{e,int} + \delta_e D_{o_2,ion} + R_{pt,int} \right) j_c 4Fa_c x = C_{o_2}^3 - C_{o_2}^{pt}
\]  
[17]
If we define the following parameters,
\[
A = R_{w,int} + \delta_w D_{o_2,w} + R_{e,int} + \delta_e D_{o_2,ion} + R_{pt,int}
\]
\[
D = i_{0,c} \alpha_{pt}(1 - \theta_{po}) \left( \frac{C_{o_2}^{pt}}{C_{o_2,ref}} \right)^\gamma \exp \left( -\frac{\alpha_c}{RT} F \eta_e - \frac{\alpha_0 \theta_{po}}{RT} \right)
\]  
[18]
Then Equation 17 can be rewritten by,
\[
D(C_{o_2}^{pt})^\gamma + \frac{4F}{A/\langle a_c \rangle} C_{o_2}^{pt} - \frac{4F}{A/\langle a_c \rangle} C_{o_2}^3 = 0
\]  
[19]
For the first order reaction, where \( \gamma = 1 \), Equation 18 can be solved analytically. However, a numerical method is needed for Equation 18 if the reaction order \( \gamma \) is smaller than 1.

The above model assumes that the Pt particles completely cover the carbon particle surface, as used in prior homogeneous and agglomerate models in literature. This should be valid for high wt% Pt catalyst materials. However, for the low wt% Pt catalyst material, the Pt particles are distributed in a more dispersed manner on the carbon particle, resulting in a longer oxygen diffusion path than the ionomer film thickness. As indicated in a 2D simplified particle model conducted by Yoon and Weber,\[12\] the oxygen diffusion path increases as the number of active sites or Pt particles on carbon support decreases.

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Assuming Pt particles having the spherical shape with the same size, the Pt particle number on a Pt/C carbon particle can be estimated by:

\[ n_{pt} = \frac{\rho_c}{\rho_{pt}} \left( \frac{r_c}{r_{pt}} \right)^3 \left( \frac{\text{wt}\%}{1 - \text{wt}\%} \right) \]  

[19]

where wt% is the Pt weight percentage of the Pt/C catalyst material (not the overall weight percentage of the catalyst layer). \( \rho_c \) and \( \rho_{pt} \) are carbon and Pt densities, respectively. The Pt particle radius \( r_{pt} \) can be expressed by:

\[ r_{pt} = \frac{3}{\rho_{pt} \cdot a_{ECSA}} \]  

[20]

If the Pt particles are uniformly distributed on the carbon particle surface, as shown in Fig. 3, the effective surface area of a Pt particle \( A_{pt,eff} \) and the effective ionomer surface area available for one Pt particle \( A_{film,eff} \) are calculated by:

\[ A_{pt,eff} = 4\pi r_{pt}^2 (1 - \theta_{PtO}) \]  

[21]

\[ A_{film,eff} = \frac{4\pi (r_c + \delta_t)^2}{n_{pt}} \]  

[22]

Obviously, the effective diffusion length of oxygen from the ionomer surface to the Pt particle is longer than the ionomer film thickness when \( A_{film,eff} \) is larger than \( A_{pt,eff} \) for a sparse Pt particle distribution. In Equation 21, the Pt-oxide coverage is excluded because of no activation there.

If we consider that the oxygen flux in Equation 3–5 is based on the flux scaling to the ionomer surface, the effective diffusion length can be approximately obtained by:

\[ \delta_{eff} = \frac{A_{film,eff}}{A_{pt,eff}} \delta_t = \frac{(r_c + \delta_t)^2/n_{pt}}{r_{pt}^2 (1 - \theta_{PtO})} \delta_t \]  

[23]

In addition, the interfacial transport resistance near the Pt surface \( R_{pt,int} \) should also be revised when scaling the flux to the ionomer surface, which is:

\[ R_{pt,int,eff} = \frac{A_{film,eff}}{A_{pt,eff}} R_{pt,int} = \frac{(r_c + \delta_t)^2}{r_{pt}^2 (1 - \theta_{PtO})} R_{pt,int} \]  

[24]

Substitute Equation 19 into 23 and 24, we have,

\[ \delta_{eff} = \frac{(r_c + \delta_t)^2}{r_{pt}^2 (1 - \theta_{PtO})} \frac{\rho_{pt}}{\rho_c} \left( \frac{r_c}{r_{pt}} \right)^3 \left( \frac{1 - \text{wt}\%}{\text{wt}\%} \right) \delta_t \]  

[25]

\[ R_{pt,int,eff} = \frac{(r_c + \delta_t)^2}{r_{pt}^2 (1 - \theta_{PtO})} \frac{\rho_{pt}}{\rho_c} \left( \frac{r_c}{r_{pt}} \right)^3 \left( \frac{1 - \text{wt}\%}{\text{wt}\%} \right) R_{pt,int} \]  

[26]

Notice that Equation 26 applies only to a Pt/C catalyst particle. In this case, a lower wt% means less Pt loading, and thus a higher interfacial transport resistance.

Using the effective diffusion length \( \delta_{eff} \) and the scaled interfacial transport resistance \( R_{pt,int,eff} \) instead of \( \delta_t \) and \( R_{pt,int} \) in Equation 17, the Pt weight percentage effect of the Pt/C material on oxygen transport resistance is taken into account. Finally, the oxygen concentration difference between \( C_{O_2}^e \) and \( C_{O_2}^{pt} \) is obtained as:

\[ C_{O_2}^e - C_{O_2}^{pt} = - \left[ R_{wt,int} + \frac{\delta_t}{D_{o_2,w}} + R_{ECSA} + \frac{(r_c + \delta_t)^2}{r_{pt}^2 (1 - \theta_{PtO})} \frac{\rho_{pt}}{\rho_c} \left( \frac{r_c}{r_{pt}} \right)^3 \right] \times \left( \frac{1 - \text{wt}\%}{\text{wt}\%} \right) \left( \frac{R_{pt,int} + \delta_t}{D_{o_2,ion}} \right) \frac{j_e}{4F \alpha_{x,ion}} \]  

[27]

The three interfacial resistances in the above equation are unknown. If we estimate them by the following simple formulas,

\[ R_{ECSA} = k_1 \frac{\delta_t}{D_{o_2,ion}} \quad R_{pt,int} = k_2 \frac{\delta_t}{D_{o_2,ion}} \quad R_{wt,int} = k_3 \frac{\delta_t}{D_{o_2,w}} \]  

[28]

then, Equation 27 becomes,

\[ C_{O_2}^e - C_{O_2}^{pt} = - \left[ (k_1 + 1) \frac{\delta_t}{D_{o_2,w}} + \frac{(k_2 + 1) (r_c + \delta_t)^2}{r_{pt}^2 (1 - \theta_{PtO})} \frac{\rho_{pt}}{\rho_c} \left( \frac{r_c}{r_{pt}} \right)^3 \right] \times \left( \frac{1 - \text{wt}\%}{\text{wt}\%} \right) \left( k_2 + 1 \right) \frac{\delta_t}{D_{o_2,ion}} \frac{j_e}{4F \alpha_{x,ion}} \]  

[29]

Substituting Equation 15 and 20 into Equation 29, we get the total transport resistance near a Pt/C particle,

\[ R_T = \frac{4F (C_{O_2}^e - C_{O_2}^{pt})}{j_e \cdot \delta_{CL}} = \left[ (k_1 + 1) \frac{\delta_t}{D_{o_2,w}} \frac{a_{ECSA}}{\alpha_{x,ion}} + \left( k_2 + 1 \right) \frac{1 - \theta_{PtO}}{1 - \theta_{PtO}} \left( \frac{1 - \text{wt}\%}{\text{wt}\%} \right) \frac{\delta_t}{D_{o_2,ion}} \frac{1}{a_{ECSA} \delta_{CL} x} \right] \frac{j_e}{\alpha_{x,ion}} \]  

[30]

Here, \( f_t = 1/(\delta_t \cdot r_{pt}) \) is the factor of catalyst layer thickness from carbon loading and this value is about 28 (nm/mg/cm^2) for the electrode with ionomer/carbon (IC) weight ratios smaller than 3.39

In addition, the Pt loading can be calculated by,

\[ L_{pt} = x \cdot n_{pt} \cdot \delta_{CL} \cdot n_{pt} \cdot \frac{4\pi r_{pt}^3}{3} \rho_{pt} = \frac{x \cdot \delta_{CL}}{f_t} \frac{1}{1 - \text{wt}\%} \]  

[31]

Combining Equation 30 and 31, we have,

\[ R_T = \left( k_2 + 1 \right) \frac{\delta_t}{D_{o_2,ion}} \left( 1 - \theta_{PtO} \right) a_{ECSA} L_{pt} + \left[ k_1 \delta_t D_{o_2,ion} + (k_2 + 1) \frac{\delta_t}{D_{o_2,w}} \right] \frac{1}{a_{ECSA} \delta_{CL} x} \]  

[32]

Note that Equation 32 takes into account the Pt loading effect and catalyst particles fraction effect, respectively, and that the transport resistance \( R_T \) increases with the decrease of Pt loading \( L_{pt} \) and Pt/C catalysts fraction \( x \) in the electrode. Therefore, this new catalyst layer model captures the role of the catalyst composition on oxygen transport resistance in addition to the Pt loading.

In the above analysis, a single catalyst material with uniform Pt weight percentage is assumed. However, blended Pt/C materials with differing wt% may be used in actual catalyst layer fabrications. For such a blended catalyst layer, Equation 32 is also valid (see detail in Appendix A) with \( x \) being the total catalyst particle number fraction,
which can be expressed by,
\[ x = \frac{(1 - w_{tav\%})(1 - y_{bare})}{1 - w_{tav\%}(1 - y_{bare})} \]  \[ [33] \]
where \( w_{tav\%} \) is the average Pt weight percentage of the Pt/C catalyst and is given by,
\[ w_{tav\%} = \frac{\sum_{i} n_{i} w_{i,\%}}{\sum_{i} n_{i}} \]  \[ [34] \]

In Equation 33 and 34, \( y_{i} \) and \( y_{bare} \) are the weight fraction of the catalyst type \( i \) and bare carbon, respectively, and \( N \) is the number of the catalyst types.

**Structural parameters of catalyst layer.**— Structural parameters of the catalyst layer, such as carbon particle fraction, ionomer film thickness, carbon particle size, and ionomer volumetric surface area are incorporated as inputs in the above transport resistance analysis. Moreover, other parameters, such as porosity, pore size and ionomer fraction, are needed to evaluate the effective transport properties in the porous electrode. These parameters should not be arbitrarily specified but depend upon the catalyst layer design and fabrication.

The size of the commonly used Vulcan XC-72 carbon support is ~25 nm. Given the carbon loading \( L_{c} \), the volume fraction of carbon particles can be estimated by,
\[ \varepsilon_{c} = \frac{1}{(I/C)} \frac{L_{c}}{\rho_{c} \delta_{CL}} \]  \[ [35] \]

As mentioned above, the effective electrode thickness \( \delta_{CL}/L_{e} \) is about 28 \( \mu \text{m}/(\text{mg/cm}^{2}) \) for I/C ratios smaller than 3. From this value, the thickness of a catalyst layer with Pt loading of 0.4 mg/cm\(^2\) is about 11.2 \( \mu \text{m} \) when using pure 50\% wt Pt/Vulcan catalyst.

Using Equation 35, the volume fraction of ionomer in the catalyst layer is,
\[ \varepsilon_{e} = (1/C) \varepsilon_{c} \rho_{c} \frac{\rho_{c}}{\rho_{e}} (1 + \frac{M_{w} \rho_{c}}{\rho_{e} \rho_{w} C_{p} w}) \]  \[ [36] \]
where \( \rho_{c} \) is the density of ionomer. The volume of ionomer expands with water uptake, so the above equation should be revised by an expansion factor in wet conditions, which is,
\[ \varepsilon_{e} = (1/C) \varepsilon_{c} \rho_{c} \frac{\rho_{c}}{\rho_{e}} (1 + \frac{M_{w} \rho_{c} \delta_{CL}}{\rho_{e} \rho_{w} C_{p} w}) \]  \[ [37] \]

where \( \rho_{w} \) is the water density, \( EW \) is the ionomer equivalent weight and \( \lambda \) is the water content in ionomer.

The porosity of the catalyst layer is,
\[ \varepsilon_{CL} = 1 - \varepsilon_{c} - \varepsilon_{e} \]  \[ [38] \]

From geometry analysis, the ionomer volume fraction can also be expressed by,
\[ \varepsilon_{e} = \frac{4}{3} \pi (r_{c} + \delta_{c})^{3} - r_{c}^{3} \]  \[ [39] \]

Substitute Equation 13 of \( n_{c} \) into Equation 39, the ionomer thickness surrounding the carbon particles is estimated by,
\[ \delta_{c} = \left( \frac{\rho_{e}}{\varepsilon_{c}} + 1 \right)^{1/3} - 1 \]  \[ [40] \]

The pore size in catalyst layer \( r_{p} \) can be estimated according to the same specific surface area of ionomer from the particle side and pore side, which is,
\[ a_{c} = \frac{3(1 - \varepsilon_{CL})}{r_{c} + \delta_{c}} = \frac{3\varepsilon_{CL}}{r_{p}} \]  \[ [41] \]

From Equation 41, we have
\[ r_{p} = \frac{\varepsilon_{CL}}{1 - \varepsilon_{CL}} (r_{c} + \delta_{c}) \]  \[ [42] \]

**Table I. Input parameters for catalyst layer structure parameters estimation.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_{c} )</td>
<td>1.95</td>
<td>g/cm(^{3})</td>
</tr>
<tr>
<td>( \rho_{w} )</td>
<td>21.45</td>
<td>g/cm(^{3})</td>
</tr>
<tr>
<td>( \rho_{e} )</td>
<td>1.0</td>
<td>g/cm(^{3})</td>
</tr>
<tr>
<td>( \rho_{i} )</td>
<td>1.9</td>
<td>g/cm(^{3})</td>
</tr>
<tr>
<td>( M_{w} )</td>
<td>18.0</td>
<td>g/mol</td>
</tr>
<tr>
<td>( EW )</td>
<td>950.0</td>
<td>g/mol</td>
</tr>
<tr>
<td>( a_{ECSA} )</td>
<td>70</td>
<td>m(^{2})/gPt</td>
</tr>
<tr>
<td>( r_{c} )</td>
<td>25</td>
<td>nm</td>
</tr>
<tr>
<td>( I/C )</td>
<td>0.6 (anode) / 0.95 (cathode)</td>
<td>-</td>
</tr>
</tbody>
</table>

Therefore, the estimated pore radius in the catalyst layer has the same order as the carbon particle.

The inputs for catalyst layer structural parameters estimated from the above equations are listed in Table I.

**PEM Fuel Cell Model**

The present electrode model described above is integrated into a full-cell PEM fuel cell model, i.e. M2 model. This model simulates mass, momentum, energy, species and charge transport processes, under either single- or two-phase conditions, throughout a PEM fuel cell. The governing equations can be summarized as follows:

**Continuity equation**
\[ \nabla \cdot (\rho \vec{u}) = 0 \]  \[ [43] \]

**Momentum conservation**
\[ \nabla \cdot \left( \frac{\rho_{a} \vec{u}}{e_{a}} \right) = - \nabla P + \nabla \cdot (\mu \nabla \vec{u}) + S_{u} \]  \[ [44] \]

**Energy conservation**
\[ \nabla \cdot \left( \frac{\gamma_{T} \rho_{a} \vec{u} T}{e_{a}} \right) = \nabla \cdot \left( k^{eff} \nabla T \right) + S_{T} \]  \[ [45] \]

**Species conservation**
\[ \nabla \cdot \left( \frac{\gamma_{C} \vec{u} C_{i}}{e_{a}} \right) = \nabla \cdot \left( D_{i}^{eff} \nabla C_{i} \right) - \nabla \cdot \left( \left( \frac{m_{f} j_{i}}{M_{i}} - \frac{C_{i}}{\rho_{g}} \right) j_{i} \right) + S_{i}^{C} \]  \[ [46] \]

**Electron conservation**
\[ 0 = \nabla \cdot \left( \sigma^{eff} \nabla \Phi_{e} \right) - j \]  \[ [47] \]

**Proton conservation**
\[ 0 = \nabla \cdot \left( \kappa^{eff} \nabla \Phi_{p} \right) + j \]  \[ [48] \]

where, \( \rho, \vec{u}, P, T, C_{i}, \Phi_{e}, \Phi_{p} \) are the density, superficial fluid velocity vector, pressure, temperature, molar concentration of species \( i \), electronic phase potential, and electrolyte phase potential, respectively. For more detail about this model, refer to reference 37. in Equation 47 and 48 is the reaction current. The oxygen reduction reaction current in the cathode catalyst layer is given by Equation 8 and 9, and the hydrogen oxidation reaction current in anode side is,
\[ j_{a} = \alpha_{a} j_{a}^{ref} \exp \left( - \frac{E_{a}}{R} \left( \frac{1}{T} - \frac{1}{353.15} \right) \right) \left( \frac{C_{H_{2}}^{ref}}{C_{H_{2},ref}} \right)^{y} a_{a} T \eta \]  \[ [49] \]

The parameters for electrode kinetics are listed in Table II.

**Transport parameters.**— The effective transport coefficients in various porous components of a PEM fuel cell are functions of their structural parameters. In GDL, the effective diffusivities of the species are assumed following the Bruggeman approximation, which are,
\[ D_{i}^{eff} = \frac{e_{k}}{\varepsilon_{k}} D_{i}^{g} \]  \[ [50] \]

where \( e_{k} \) and \( \tau_{a} \) are the porosity and tortuosity of the porous material, \( D_{i}^{g} \) is the molecular diffusion coefficient of the species \( i \).
The proton conductivity of ionomer in the catalyst layer is fitted from the measured data in Ref. 36 and given by,

\[ \sigma_{\text{wet}} = \sigma_{\text{dry}} \times \left( 1 + \frac{E_{\text{w}}}{{\lambda}_{\text{w}}} \right) \]

where \( \sigma_{\text{wet}} \) and \( \sigma_{\text{dry}} \) are the proton conductivities of ionomer in wet and dry phases, and \( E_{\text{w}} \) and \( {\lambda}_{\text{w}} \) are the activation energy for oxygen transport in wet and dry phases, respectively.

The water uptake in ionomer is described by Mittlesteadt et al.’s formula:39

\[ \lambda = \left( 1 + 0.2325a^2 \left( \frac{T - 303}{30} \right) \right) \left[ 14.22a^3 - 18.92a^2 + 13.41a \right] \]

\[ \times \left( 8.71 \left( 1 + 0.2325 \left( \frac{T - 303}{30} \right) \right) (1 - s) + (9.22 + 0.181 (T - 273.15)) s \right) \]

where \( \lambda \) is the water activity and \( a \) is the water activity at the in-situ measured range in Greszler et al.’s8 limiting current experiments under a similar RH of 62%. Therefore, it is expected that the present electrode transport model predicts the local transport resistance in good agreement with the experimental data in the literature.

**Table II. Parameters for electrochemical kinetics.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode side</td>
<td>( i_{0,\text{ref}} )</td>
<td>0.3 A/cm(^2)-Pt</td>
</tr>
<tr>
<td></td>
<td>( E_{\text{a}} )</td>
<td>10.0 kJ/mol</td>
</tr>
<tr>
<td></td>
<td>( C_{\text{O}_2,\text{ref}} )</td>
<td>4.0e-5 mol/cm(^3)</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>( a_{\text{a}} )</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>Cathode side</td>
<td>( i_{0,\text{c}} )</td>
<td>3.0e-5 A/cm(^2)-Pt</td>
</tr>
<tr>
<td></td>
<td>( E_{\text{c}} )</td>
<td>67.0 kJ/mol</td>
</tr>
<tr>
<td></td>
<td>( C_{\text{O}_2,\text{ref}} )</td>
<td>4.0e-5 mol/cm(^3)</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>( a_{\text{c}} )</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>( \omega )</td>
<td>3.0</td>
<td>kJ/mol</td>
</tr>
</tbody>
</table>

In the catalyst layer, where the pore size is smaller than 100 nm, the Knudsen diffusion is important and the species diffusivity can be calculated by the following equation,

\[ D' = \left( 1/D_{\text{Knud}} + 1/D'_{\text{Knud}} \right)^{-1} \]

with the Knudsen diffusion coefficient evaluated as,

\[ D'_{\text{Knud}} = \frac{2\pi p}{3(8 RT/M_1)^{1/2}} \]

Here, \( p \) is the radius of the pore size and \( M_1 \) is the molar mass of the species \( i \).

The proton conductivity of ionomer in the catalyst layer is fitted from the measured data in Ref. 36 and given by,

\[ \kappa = \frac{22.0 \exp \left( -\frac{E_{\text{a}}}{R} \left( \frac{1}{T} - \frac{1}{353.15} \right) \right)}{a^{2.24}} \]

where \( a \) is the water activity and \( E_{\text{a}} \) is the activation energy with the value of 12 kJ/mol. In addition, the measured tortuosity of the ionomer phase in the catalyst layer in Ref. 36 is given by,

\[ \tau_\varepsilon = \begin{cases} 0.0845(\varepsilon_{\varepsilon} - 0.04)^{-1.17} \quad & \varepsilon_{\varepsilon} < 0.16 \\ 1.0 \quad & \varepsilon_{\varepsilon} \geq 0.16 \end{cases} \]

The water uptake in ionomer is described by Mittlesteadt et al.’s formula:39

\[ p_w = 3.2 \times 10^{-11} \exp \left( \frac{E_{\text{w}}}{R} \left( \frac{1}{T} - \frac{1}{363} \right) \right) \exp(3.4a) \]

where the activation energy \( E_{\text{w}} = 22k\text{kJ/mol} \).
In this work, \( k_1 = 8.5 \) and \( k_2 = 5.4 \) are used in all of the following simulations. Using Equation 32, the electrode transport resistance with Pt loading and catalyst particle number fraction are plotted in Fig. 5a and 5b, respectively. As reported in some experimental works, Fig. 5a shows that the electrode transport resistance increases significantly with Pt loading lower than 0.1 mg/cm\(^2\). Moreover, higher transport resistance is also observed for higher carbon dilution at a given Pt loading, as shown in Fig. 5b. These figures quantify the effects of not only the Pt loading but also electrode compositions.

A series of simulation studies are subsequently conducted to compare the predicted and measured polarization curves for a wide range of Pt loadings and electrode compositions. In the experiments of Owejan et al., two electrode compositions were used for the cathode catalyst layers: (1) without bare carbon dilution; (2) with bare carbon dilution. All these catalyst layers were designed to have the same thickness, i.e. \( \sim 11 \) \( \mu \)m, by controlling the fraction of the electrode components. In addition, all samples used Pt/Vulcan catalyst and Vulcan XC-72 carbon as the diluent. The anode catalyst layer has the same Pt loading of 0.05 mg/cm\(^2\) and the I/C ratio was maintained to be 0.6 and 0.95 in anode and cathode catalyst layer, respectively. Table III lists the Pt loading and the corresponding components of the catalyst layer samples examined in the present work. Owejan et al. used a small MEA of 5 cm\(^2\) in their experiments and used very high stoichiometry of hydrogen and oxygen, so it is appropriate to use a differential cell (i.e. 2D cell with negligible variation along the gas flow direction) to perform the full cell simulations. Fig. 6 shows the geometry and mesh of this differential cell, whose geometrical parameters are given in Table IV. The operating temperature and pressure in all of the following simulations are set at 80 \( ^\circ \)C and 150 kPa.

![Figure 6. Geometry and computational mesh.](image)

### Table IV. Geometry parameters of the differential cell.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane thickness</td>
<td>18</td>
<td>( \mu )m</td>
</tr>
<tr>
<td>CCL thickness</td>
<td>11</td>
<td>( \mu )m</td>
</tr>
<tr>
<td>ACL thickness</td>
<td>6</td>
<td>( \mu )m</td>
</tr>
<tr>
<td>MPL thickness</td>
<td>30</td>
<td>( \mu )m</td>
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<tr>
<td>GDL thickness</td>
<td>160</td>
<td>( \mu )m</td>
</tr>
<tr>
<td>Channel width</td>
<td>0.5</td>
<td>mm</td>
</tr>
<tr>
<td>Channel height</td>
<td>0.7</td>
<td>mm</td>
</tr>
<tr>
<td>Land width</td>
<td>0.5</td>
<td>mm</td>
</tr>
</tbody>
</table>

No carbon dilution.— Fig. 7 shows the comparison of the predicted and experimental polarization curves for the non-diluted electrodes.

![Figure 5.](image)

### Table III. Cathode catalyst layer Pt loading and components.

<table>
<thead>
<tr>
<th>Case</th>
<th>Pt Loading mg/cm(^2)</th>
<th>Carbon dilution</th>
<th>Bare carbon mass fraction</th>
<th>Catalyst Type</th>
<th>Catalyst mass fraction</th>
<th>Catalyst particles number fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>N</td>
<td>-</td>
<td>50%\text{wt}/0%\text{wt}</td>
<td>0.56/0.44</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>N</td>
<td>-</td>
<td>30%\text{wt}/15%\text{wt}</td>
<td>0.29/0.71</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>N</td>
<td>3</td>
<td>10%\text{wt}</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>0.025</td>
<td>N</td>
<td>-</td>
<td>5%\text{wt}</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>Y</td>
<td>0.58</td>
<td>50%\text{wt}</td>
<td>0.42</td>
<td>0.265</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>Y</td>
<td>0.78</td>
<td>50%\text{wt}</td>
<td>0.22</td>
<td>0.123</td>
</tr>
<tr>
<td>7</td>
<td>0.025</td>
<td>Y</td>
<td>0.89</td>
<td>50%\text{wt}</td>
<td>0.11</td>
<td>0.055</td>
</tr>
</tbody>
</table>

\( ^a \)Vulcan XC-72 carbon; \( ^b \)Pt/Vulcan (TKK) catalyst.

Anode catalyst layer Pt loading 0.05 mg/cm\(^2\); anode I/C ratio 0.6; cathode I/C ratio 0.95 for all cases.
Figure 7. Comparison of polarization curves between experiments and simulations for non-diluted catalyst under pure oxygen, 100% RH, 80 °C and 150 kPa operating condition.

with pure oxygen in the cathode side. There is good agreement from high (0.2 mg/cm²) to low (0.025 mg/cm²) Pt loading. Because of the high oxygen concentration with pure oxygen feed, the cells operate in the ohmic region until current density of 2.0 A/cm². Lower cell performance with decreasing Pt loading results from the kinetic loss. The distribution of oxygen concentration in catalyst layer pores and on the Pt surface, as well as the distributions of oxygen concentration drop around the Pt particle and oxygen reduction reaction (ORR) current density are plotted in Figs. 8a and 8b for Pt loading of 0.2 mg/cm² and 0.025 mg/cm², respectively. It should be noted that the catalyst layers have the same thickness of ~11 μm for the two different Pt loadings as mentioned earlier. Evidently, Pt loading has negligible effect on the pore concentration, but has significant influence on the concentration at the Pt surface. However, due to pure oxygen condition, oxygen concentration at the Pt surface is still so high that the mass transfer is not a limitation for ORR.

The predicted polarization curves and HFR for non-diluted electrodes also show good agreement with the experimental data for air feed, as shown in Figs. 9a and 9b. Under the same operating conditions, air feed instead of pure oxygen feed gives rise to an increased transport loss with decreasing Pt loading. As seen in Fig. 10, the oxygen concentration on the Pt surface for Pt loading of 0.025 mg/cm²

Figure 8. Oxygen concentration in the pore, on the Pt particle surface, concentration drop near the Pt particle and reaction current density distributions in CCL at current density of 2.0 A/cm² under pure oxygen, 100% RH, 80 °C and 150 kPa operating condition for Pt loading of 0.2 mg/cm² (a) and 0.025 mg/cm² (b).
is much smaller than that for 0.2 mg/cm² loading, although their concentrations in the macro pores are close to each other. The oxygen concentration drop in the cathode catalyst layer is mostly caused by the transport resistance near the Pt particle rather than the macro diffusion resistance through the layer at low Pt loading. This suggests that the cells with low Pt loading still have significant oxygen available in the catalyst layer pores but cannot reach the reaction sites under high current density. In addition, the reaction current density distribution with air and pure oxygen appears different. For pure oxygen, the reaction current density under the rib is a little higher than under the channel due to smaller ionomer conductivity with higher RH there. Under air condition, however, the reaction current density under the channel is higher, especially at the loading of 0.025 mg/cm². This difference indicates that the mass transfer begins to dominate in ORR at higher current density for low Pt loading with air feed. On the other hand, the reaction near the catalyst layer/membrane interface cannot further increase once the mass transfer limitation occurs there, although there is higher overpotential. The reaction therefore spreads to the regions with higher oxygen concentration near the MPL/CL interface, as shown in Fig. 10b for low Pt loading case.

The model validation under a drier condition with 65% inlet RH is also performed and the results are plotted in Fig. 11. Again, the predicted results match the measured polarization curves and the HFR values very well. Cells under a drier condition have lower ionomer conductivity and higher electrode resistance because of lower oxygen diffusivity in ionomer, thus leading to higher HFR and worse performance.

**With carbon dilution.**— The cell polarization curves and HFR for carbon diluted electrode with air feed are shown in Fig. 12 and Fig. 13 for inlet RH of 100% and 65%, respectively. Evidently, the model captures the dilution effect on cell performance and there is

Figure 10. Oxygen concentration in the pore, on the Pt particle surface, concentration drop near the Pt particle and reaction current density distributions in CCL at current density of 2.0 A/cm² under air, 100% RH, 80 °C and 150 kPa operating condition for Pt loading of 0.2 mg/cm² (a) and 0.025 mg/cm² (b).
Comparison of polarization curves (a) and HFR (b) between experiments and simulations for non-diluted catalyst under air, 65% RH, 80°C and 150 kPa operating condition. Non-diluted polarization curves are also plotted in (a) for comparison.

Figures 11 and 12. Predicted and measured polarization curves (a) and HFR (b) for carbon diluted catalyst under air, 100% inlet RH, 80°C and 150 kPa operating condition. Non-diluted polarization curves are also plotted in (a) for comparison.

still good agreement between the predictions and experiments. The mixture of bare carbon into a catalyst layer indeed reduces the cell performance for a given Pt loading. As shown in Fig. 5b, the transport resistance begins to have obvious increase after the number fraction of catalyst particles is lower than 0.25 and dramatically increases if the fraction is lower than 0.1. For case 5 of 0.1 mg/cm² loading listed in Table III, the catalyst particles fraction is about 0.265, so the dilution has negligible influence on the cell performance, as shown in Fig. 12 and 13. However, for case 7 of 0.025 mg/cm² loading, the catalyst particles fraction is as low as 0.055, and significant performance loss is observed in both RH conditions compared with the non-diluted case. These results indicate the very important role of the electrode composition besides Pt loading.

Agglomeration effect.— In the preceding sections, we have used a homogeneous electrode model based on the recent SEM observations that the agglomerates probably do not exist. However, some literature argued that agglomerates may exist. As mentioned in the introduction, even though the agglomerates exist, their size is not very large. In this section, we will examine whether these small agglomerates have significant impacts on the homogeneous model.

Most of agglomerate models assume ionomer filled agglomerates. However, there is still a debate about this assumption. Actually, because the ionomer has a chain structure with the diameter of 3 to 5...
Figure 14. Agglomerate size effect on polarization curve prediction for Pt loading of 0.2 mg/cm² at 65% (a) and 100% (b) inlet RH.

Figure 15. Agglomerate size effect on polarization curve prediction for Pt loading of 0.025 mg/cm² at 65% (a) and 100% (b) inlet RH.

Figure 16. Effective factor with and without the interfacial resistance.
is more than one order of magnitude larger than in ionomer. Second, we introduce the interfacial transport resistances at ionomer film and Pt particle surfaces. These resistances make the oxygen concentration in the agglomerate more uniform, thus a higher effective factor of the agglomerate is obtained. Fig. 16 shows the agglomerate effective factor with and without the interfacial resistances. The presence of the interfacial resistances results in a higher effective factor so that the reaction in the agglomerate is more uniform because the oxygen transport is controlled by the interfacial resistances rather than the diffusion resistance inside the agglomerate.

Conclusions

In this work, a homogeneous electrode model is developed based on the assumption of no agglomerate or sufficiently small agglomerates (<150 nm). By introducing the interfacial transport resistances at ionomer and Pt particle surfaces, Pt loading and catalyst material fraction are taken into consideration in the present electrode model. The electrode transport resistance is found to dramatically increase not only for Pt loading lower than 0.1 mg/cm² but also for catalyst material fraction lower than 0.2. We have implemented this electrode model into a full PEM fuel cell model and studied the effect of Pt loading and electrode composition, with and without carbon dilution, on cell performance. The predicted polarization curves and HFR are in very good agreement with the extensive experimental data of Owejan et al. under different operating conditions. The agglomerate is also found to have negligible effect on the cell performance prediction if the agglomerate radius is smaller than 150 nm. For a practical electrode design, this agglomerate size is believed to be the upper limit, if agglomerates indeed exist in a real catalyst layer, suggesting that the homogeneous electrode assumption is sufficient to predict cell performance.

List of Symbols

- \( A \) Area (m²)
- \( a \) Water activity
- \( a_{pt} \) Active volumetric surface area of Pt (m²/m³)
- \( a_{ECSA} \) Electrochemical specific area of Pt (m²/gpt)
- \( a_c \) Volumetric area of ionomer (m²/m³)
- \( C_{O2} \) Oxygen concentration (mol/m³)
- \( D_{O2} \) Oxygen diffusivity (m²/s)
- \( E \) Cathode potential vs. RHE (V)
- \( E_c \) Activation energy in oxygen reduction reaction (J/mol)
- \( F \) Faraday’s Constant
- \( H_{O2,c} \) Henry’s constant of oxygen at ionomer surface
- \( i_{O2,c} \) Exchange current density of oxygen reduction reaction (A/m²)
- \( j_c \) Volumetric current density of oxygen reduction reaction (A/m³)
- \( k_1 \) Transport resistance coefficient at ionomer film surface
- \( k_2 \) Transport resistance coefficient at Pt particle surface
- \( k_3 \) Transport resistance coefficient at water film surface
- \( L_{pt} \) Pt loading (mg/cm²)
- \( n_c \) Number density of carbon particles (m⁻³)
- \( n_{pt} \) Number of Pt particles on a Pt/C particle
- \( N_{O2} \) Oxygen flux (mol/m² s)
- \( R \) Ideal-gas constant
- \( R_{int} \) Interfacial transport resistance at ionomer film surface (s/m)
- \( R_{int}^{pt} \) Interfacial transport resistance at Pt surface (s/m)
- \( r_{agg} \) Radius of agglomerate (m)
- \( r_c \) Radius of carbon particle (m)
- \( r_{pt} \) Radius of Pt particle (m)
- \( s \) Water saturation
- \( T \) Temperature (K)
- \( x \) Number fraction of Pt/C particles
- \( wt \) Weight percentage (%)

Greek Symbols
- \( \alpha_c \) Transfer coefficient of oxygen reduction reaction
- \( \gamma \) Reaction order
- \( \delta_{CL} \) Catalyst layer thickness (m)
- \( \varepsilon \) Porosity
- \( \eta \) Over potential (V)
- \( \eta_{PtO} \) Pt-oxide coverage
- \( \kappa \) Ionomer proton conductivity (s/m)
- \( \lambda \) Water content in ionomer
- \( \rho \) Density (kg/m³)
- \( \tau \) Tortuosity
- \( \omega \) Energy parameter for Temkin isotherm (J/mol)

Subscripts
- \( a \) Anode
- \( c \) Carbon; cathode
- \( CL \) Catalyst layer
- \( e \) Ionomer
- \( int \) Interface
- \( w \) Water

Superscripts
- \( agg \) Agglomerate
- \( eff \) Effective value
- \( g \) Gas
- \( pt \) Platinum

Appendix A

Catalyst layers may have several types of Pt/C materials with different Pt weight percentage. Here, we consider a blended catalyst layer with two catalyst types, and with bare carbon as the diluent. For simplification, number 1 and 2 indicate catalyst material 1 and 2, respectively, and number 0 indicates the bare carbon. Assuming the carbon support of the catalyst has the same size as the bare carbon, we can obtain the volume fraction (or number fraction) of catalyst type 1, type 2 and bare carbon 0 as follows,

\[
x_1 = \frac{(1 - w_1 \% y_1)}{(1 - w_1 \%) y_1 + (1 - w_2 \%) y_2 + y_0}
\]

\[
x_2 = \frac{(1 - w_2 \%) y_2}{(1 - w_1 \%) y_1 + (1 - w_2 \%) y_2 + y_0}
\]

\[
x_0 = \frac{y_0}{(1 - w_1 \%) y_1 + (1 - w_2 \%) y_2 + y_0}
\]

where \( y_1 \), \( y_2 \) and \( y_0 \) are the weight fraction of the catalyst type 1, 2 and bare carbon, respectively.

The contribution of the current density for each catalyst type depends on its Pt particle number density, so we have

\[
j_1 + j_2 = j_c
\]

\[
\frac{j_1}{j_c} = \frac{n_{pt1} x_1}{n_{pt1} x_1 + n_{pt2} x_2}
\]

\[
\frac{j_2}{j_c} = \frac{n_{pt2} x_2}{n_{pt1} x_1 + n_{pt2} x_2}
\]

From Equation 29, the oxygen concentration difference between \( C_{O2}^{pt} \) and \( C_{O2}^{CL} \) for catalyst type 1 and 2 are:

\[
\Delta C_{O2-1} = - \left[ (k_1 + 1) \frac{b_o}{D_{O2}} \right] \left[ (k_1 + 1) \left( \frac{r_c + b_c}{r_c} \right)^2 \frac{r_c}{r_{pt}^3} \right] \times \left[ (1 - w_1 \%) (k_2 + 1) \frac{b_o}{D_{O2}} \right] \frac{j_1}{4T\alpha_s x_1}
\]
\[
\Delta C_{O_2,avg} = - \left[ (k_1 + 1) \frac{h_0}{D_{agg}} + \left( k_1 + \frac{(r_c + b_c)^2}{r_c (1 - \theta_{Pt})} \rho_{Pt} \left( \frac{r_c}{r'} \right)^3 \right) \frac{b_0}{D_{agg,ion}} \right] \frac{j_f}{4 F a \delta (x_1 + x_2)} \]  
\]

The average oxygen concentration difference is assumed as,
\[
\Delta C_{O_2,avg} = \Delta C_{O_2,1} x_1 + \Delta C_{O_2,2} x_2
\]

Equation A10 defines the average oxygen concentration difference by a volume averaged method. Substitute A6–A9 and Equation 19 into A10, we get,
\[
\Delta C_{O_2,avg} = - \left[ (k_1 + 1) \frac{h_0}{D_{agg}} + \left( k_1 + \frac{(r_c + b_c)^2}{r_c (1 - \theta_{Pt})} \rho_{Pt} \left( \frac{r_c}{r'} \right)^3 \right) \frac{b_0}{D_{agg,ion}} \right] \frac{j_f}{4 F a \delta (x_1 + x_2)} \]  
\]

If we define the average Pt weight percentage of the mixed catalyst material by,
\[
wt_{avg} = \frac{\sum_i y_i w_i\%}{\sum_i y_i \frac{w_i\%}{y_i + y_{bare}}}
\]

From Equation A12 and A1–A2, one has,
\[
wt_{avg} = \frac{x_1}{x_1 + x_2} \frac{1 - wt_{avg}}{1 - wt_{avg}} + \frac{x_2}{x_1 + x_2} \frac{wt_{avg}}{1 - wt_{avg}}
\]

Finally, Equation A11 becomes,
\[
\Delta C_{O_2,avg} = - \left[ (k_1 + 1) \frac{h_0}{D_{agg}} + \left( k_1 + \frac{(r_c + b_c)^2}{r_c (1 - \theta_{Pt})} \rho_{Pt} \left( \frac{r_c}{r'} \right)^3 \right) \frac{b_0}{D_{agg,ion}} \right] \frac{j_f}{4 F a \delta (x_1 + x_2)} \]  
\]

and the total transport resistance near the Pt/C particles is expressed as,
\[
R_f = \left( k_1 + 1 \right) \frac{h_0}{D_{agg,ion}} \frac{\alpha_{CELL}}{\alpha_f} + \left( k_1 \frac{\alpha_{CELL}}{\alpha_f} + \frac{k_1 + 1}{1 - \theta_{Pt}} \left( 1 - \frac{wt_{avg}}{y_{bare}} \right) \frac{b_0}{D_{agg,ion}} \right) \frac{\alpha_{CELL} h_{CELL} L_{CELL}}{\alpha_f}
\]

Equation A15 is the same as Equation 30 when using the average Pt weight percentage A12. Although Equation A15 is derived from two types of catalyst, it can be used for any mixed catalyst formulation if the carbon support has the same size, where the average Pt weight percentage and total number fraction of the Pt/C particles are given by,
\[
wt_{avg} = \frac{\sum_i y_i w_i\%}{\sum_i y_i \frac{w_i\%}{y_i + y_{bare}}}
\]

where \( N \) is the number of the catalyst type and \( y_{bare} \) is the bare carbon weight percentage. Using A16, A17 is reduced to,
\[
x = \sum_i y_i (1 - w_i\%) \left( \frac{y_i - y_{bare}}{\sum_j y_j (1 - w_j\%) + y_{bare}} \right)
\]

Additionally, the total Pt loading in the catalyst layer of the mixed catalysts is,
\[
L_{pt} = \sum_i \frac{y_i \cdot \rho_{Pt} \cdot \gamma_{CL} \cdot n_{Pt} \cdot \xi}{1 - \theta_{Pt}} \frac{4}{\pi r'^3} \rho_{Pt} = \sum_i \frac{h_0}{D_{agg}} \frac{y_i w_i\%}{f_i} \frac{w_i\%}{1 - w_i\%}
\]

Using A16 and A17, Equation A19 can be rewritten by,
\[
L_{pt} = \frac{h_0}{D_{agg}} \frac{w_{avg}}{f_{avg}} \frac{w_{avg}}{1 - w_{avg}}
\]

As a result, Equation A15 becomes Equation 32.

Appendix B

Consider an agglomerate shown in Fig. B1. The agglomerate may include both Pt/C particles and bare carbon particles. In addition, the agglomerate is probably not filled by the ionomer, as discussed in the main text. Assuming that the electronic and ionomer potentials in the agglomerate are constant, the diffusion equation of oxygen in the agglomerate is described by:
\[
\frac{1}{r} \frac{d}{dr} \left( r^2 D_{eff} \frac{dC_{O_2}}{dr} \right) + j _{O_2} = 0
\]

where
\[
j _{O_2} = \frac{j_f}{4 F} - \frac{\alpha_c}{2 RT} \frac{\rho_{Pt} (1 - \theta_{Pt})}{\rho_{O_2} (1 - \theta_{Pt})} \frac{C_{O_2}^p}{C_{O_2,ref}} \exp \left( - \frac{\alpha_c}{RT} \frac{F \eta_{Pt} - \omega_{Pt} \rho_{Pt}}{RT} \right)
\]

If we use \( D = \frac{i_{O_2}}{\eta_{O_2} (1 - \theta_{Pt})} \frac{4}{\pi} \frac{1}{r_{agg}^2} \) \exp \left( - \frac{\alpha_c}{RT} \frac{F \eta_{Pt} - \omega_{Pt} \rho_{Pt}}{RT} \right) \), Equation B2 is reduced to,
\[
j _{O_2} = - \frac{D}{4 F} \left( C_{O_2}^p \right)^2
\]

For each Pt/C particle in the agglomerate, the relationship between the \( O_2 \) concentration near the Pt/C particle and the \( O_2 \) concentration in the pores of the agglomerate \( C_{O_2}^p \) is given by Equation 18, which is,
\[
D \left( C_{O_2}^p \right)^2 + 4 F \frac{C_{O_2}^p}{\rho_{Pt} (1 - \theta_{Pt})} C_{O_2}^p - 4 F \frac{C_{O_2}^p}{\rho_{Pt} (1 - \theta_{Pt})} C_{O_2} = 0
\]

From B4, the \( O_2 \) concentration near Pt/C particle can be solved. For a general case, the oxygen reduction flux \( B3 \) can be expressed as a function of \( C_{O_2}^p \) instead of \( C_{O_2}^p \), which is,
\[
j _{O_2} = - f(A, D) D C_{O_2} \frac{\gamma}{2}
\]

where \( f(A, D) \) is a function solved from B4. If ignoring the interfacial transport resistances inside the agglomerate, \( f(A, D) = 1 \). Using the effectiveness-factor method to indicate the agglomerate effect on \( O_2 \) transfer phenomena and kinetics, the analytic solution of the effective factor can be obtained for first-order reaction,
\[
E_r = \frac{3}{\xi (\xi \cos \theta - 1)}
\]

where \( \xi \) is the Thiele modulus. Though B6 is from the first-order reaction, it also can be used in non-first-order reaction 32 if the Thiele modulus uses the following expression,
\[
\xi = \frac{f(D C_{O_2})^{\gamma - 1}}{4 F D_{eff}^{\gamma - 1}}
\]

where \( r_{agg} \) is the radius of the agglomerate, \( D_{eff}^{\gamma - 1} \) is the effective diffusivity of \( O_2 \) in the agglomerate, \( C_{O_2,ref} \) is the \( O_2 \) concentration on the agglomerate surface.

If the agglomerate is covered by ionomer or liquid water, the oxygen reduction flux satisfies the following equation,
\[
4 F E_r j_2 = \frac{C_{O_2}^p + j_2 B_{Swell}\eta_{ion}}{a_{eff}} \frac{\gamma}{2}
\]

where \( B_{Swell} \) is the transport resistance by the ionomer or water film covering the agglomerate, which includes the interfacial resistance and bulk film transport resistance; \( a_{eff} \) is the agglomerate surface area per volume. For first order reaction where \( \gamma = 1 \), the solution of Equation B8 gives,
\[
j _{O_2} = - C_{O_2} \left( \frac{4 F E_r}{r_{agg}^2} + \frac{B_{Swell}\eta_{ion}}{a_{eff}} \right)^{-1}
\]

For reaction order different from the unity, a numerical method is used.
References


