The effect of Nafion film on the cathode catalyst layer performance in a low–Pt PEM fuel cell

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Abstract

A single–pore model for performance of the cathode catalyst layer (CCL) in a PEM fuel cell is developed. The model takes into account oxygen transport though the CCL depth and through the thin Nafion film, separating the pore from Pt/C species. Analytical solution to model equations reveals the limiting current density $j_N^{\text{lim}}$ due to oxygen transport through the Nafion film. Further, $j_N^{\text{lim}}$ linearly depends of the CCL thickness, i.e., the thinner the CCL, the lower $j_N^{\text{lim}}$. This result may explain unexpected lowering of low–Pt loaded catalyst layers performance, which has been widely discussing in literature.

Keywords: PEM fuel cell, low–Pt cathode, polarization curve, modeling

1. Introduction

High cost of platinum could potentially slow down development and marketing of low–temperature fuel cells. At present, standard oxygen reduction reaction (ORR) electrode contains 0.4 mg of Pt per square centimeter. This translates to nearly 100 g of precious metal in a 100–kW stack for automotive applications. High Pt cost stimulates worldwide interest in three to four–fold reduction of Pt loading.

As the cell current density $j_0$ is proportional to Pt surface, one would anticipate a linear decay of $j_0$ with the Pt loading. However, low–Pt cathodes exhibit unexpected overlinear performance loss (OPL) [1][2]. So far, the reason for this effect is not fully understood. Grezler et al. [1] attributed poor low–Pt cathode performance to oxygen transport through the Nafion film covering Pt/C agglomerates. However, to explain the observed transport resistance, their study has led to unrealistically high Nafion film thickness. Owejan et al. [3] developed a series of cathodes varying Pt loading and keeping the cathode thickness

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constant. This has been achieved by diluting Pt/C by “pure” carbon particles. Their results, however, did not allow to make a definite conclusion about the OPL nature. Weber and Kusoglu [4] discussed the nature of OPL and provided arguments in favor to the oxygen transport through the Nafion film. Choo et al. [5] have found that the OPL in the low–Pt cathode can partly be mitigated by proper water management of the cell. This work is another indirect evidence that the origin of the OPL is related to oxygen transport in Nafion. Kudo et al. [6] showed that the dominant part of the oxygen transport resistivity in the thin Nafion film is due to Pt/ionomer interface.

Yet, however, the question remains: why oxygen transport in the Nafion film does not affect the performance of standard electrodes with high Pt loading, and it has a strong effect on the performance of low–Pt electrodes? Recent modeling works [7–9] do not give indisputable answer to this question.

In this work, we report a single–pore model for the cathode catalyst layer (CCL) performance. The model includes oxygen transport in the void pore and in the Nafion film separating the pore from the Pt/C particles. Analytical solution to model equations shows that the polarization curve of this system exhibits limiting current density due to oxygen transport in the Nafion film. Moreover, this limiting current appears to be proportional to the CCL thickness. This effect may explain OPL of low–Pt electrodes, as these electrodes are typically three– to four times thinner, than the standard Pt/C systems.

2. Performance equations

Schematic of a single mesopore in the cathode catalyst layer (CCL) is shown in Figure 1a. SEM pictures show that in a real CCL, the pore walls are formed by numerous agglomerates of Pt/C particles, surrounded by a thin Nafion film [10]. It is assumed that the Pt/C clusters have electric contact between them for transport of electrons to the ORR sites.

To model this system, we consider a cylindrical pore depicted in Figure 1b. The system is formed by three coaxial tubes: void, Nafion film and Pt/C, as shown in Figure 1b. Let the void pore radius be \( R_p \) and the Pt/C radius be \( R_m \) (Figure 1).

To write down equations for the pore performance, we need an oxygen flux balance equation in the pore. Consider a cylindrical element of the pore volume of the radius \( R_m \) and the thickness \( dx \) (Figure 1b). The oxygen diffusive flux along the pore is \( D_p \frac{\partial c}{\partial x} \), where \( D_p \) is the oxygen diffusion coefficient in the pore volume, and \( c \) is the local oxygen concentration in the pore. As \( c(x) \) decays toward the membrane, the balance of fluxes in the volume element is

\[
- \pi R_p^2 D_p \frac{\partial c}{\partial x} \bigg|_{x+dx} + \pi R_p^2 D_p \frac{\partial c}{\partial x} \bigg|_{x} = (2\pi R_m dx) N_{N,m}
\]

(1)

where

\[
N_{N,m} = D_N \frac{\partial c_N}{\partial r} \bigg|_{r=R_m}
\]

(2)
is the radial oxygen flux at the metal/Nafion interface consumed in the ORR, \( c_N \) is the dissolved oxygen concentration in the Nafion film and \( D_N \) is the oxygen diffusion coefficient in the film. Note that \( D_N \) is the effective parameter, which includes interfacial Nafion resistance.

Dividing both sides of Eq. (1) by \( \pi R_p^2 \, dx \), we come to

\[
-D_p \frac{\partial^2 c}{\partial x^2} = \frac{2 R_m N_{N,m}}{R_p^2} \frac{\partial c}{\partial x} \bigg|_{x=0} = 0, \quad c(l_i) = c_1, \quad (3)
\]

where \( c_1 \) is the oxygen concentration at the CCL/gas diffusion layer (GDL) interface, and \( l_i \) is the CCL thickness.

Oxygen transport through the Nafion film along the radial direction is described by

\[
\frac{D_N}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_N}{\partial r} \right) = 0, \quad c_N(R_p) = K_H c(x),
\]

\[
D_N \frac{\partial c_N}{\partial r} \bigg|_{r=R_m} = -\frac{i_* R_p^2}{2 R_m (4F)} \left( \frac{c_{N,m}}{c_{ref}} \right) \exp \left( \frac{\eta}{b} \right) \quad (4)
\]

Here, \( K_H \) is the dimensionless Henry constant (mol/mol) for oxygen solubility in Nafion, \( c_{N,m} \equiv c_N(R_m) \), \( i_* \) is the ORR volumetric exchange current density,
and \( c_{\text{ref}} \) is the reference oxygen concentration. The first boundary condition in Eq. (4) is obvious, while the second means that the oxygen flux at the Nafion/Pt interface equals the flux consumed in the ORR at the Pt surface. This flux is given by the product of the Tafel ORR rate 
\[
\frac{i_\ast}{4F} \left( \frac{c_{N,m}}{c_{\text{ref}}} \right) \exp \left( \frac{\eta}{b} \right)
\]
by the characteristic length \( R_p^2/(2R_m) \). This relation provides correct transition to the limiting case of vanishing Nafion film. Indeed, setting \( K_H = 1 \), \( R_p = R_m \), we may omit Eq. (4), set \( c_N = c \) and substitute the flux on the right side of the second boundary condition in Eq. (4) instead of \( N_{N,m} \) into Eq. (3). This gives 
\[
- D_N \frac{\partial^2 c}{\partial x^2} = \frac{i_\ast}{4F} \left( \frac{c}{c_{\text{ref}}} \right) \exp \left( \frac{\eta}{b} \right),
\]
which is a standard macrohomogeneous model (MHM) equation for oxygen transport in the CCL. The system of equations (3), (4) is completed by the proton current conservation equation in the Nafion film:
\[
\frac{\partial j}{\partial x} = -i_\ast \left( \frac{c_{N,m}}{c_{\text{ref}}} \right) \exp \left( \frac{\eta}{b} \right)
\]
To simplify calculations we introduce dimensionless variables
\[
\tilde{x} = \frac{x}{l_t}, \quad \tilde{j} = \frac{j}{j_p}, \quad \tilde{\eta} = \frac{\eta}{b}, \quad \tilde{r} = \frac{r}{l_t}
\]
where
\[
j_p = \frac{\sigma_p b}{l_t}
\]
is the characteristic current density for proton transport, \( \sigma_p \) is the CCL proton conductivity, and \( b \) is the ORR tafel slope. With these variables Eqs. (3), (4) and (6) transform to
\[
- \varepsilon^2 \tilde{D}_{ox} \frac{\partial^2 \tilde{c}}{\partial \tilde{x}^2} = \varepsilon^2 \tilde{N}_{N,m}, \quad \frac{\partial \tilde{c}}{\partial \tilde{x}} \bigg|_{\tilde{x}=0} = 0, \quad \tilde{c}(1) = \tilde{c}_1,
\]
\[
\varepsilon^2 \tilde{D}_N \left( \frac{\partial \tilde{c}_N}{\partial \tilde{r}} \right) = 0, \quad \tilde{c}_N(\tilde{R}_p) = K_H \tilde{c}(\tilde{x}),
\]
\[
\varepsilon^2 \tilde{D}_N \frac{\partial \tilde{c}_N}{\partial \tilde{r}} \bigg|_{\tilde{r}=\tilde{R}_m} = -\tilde{c}_{N,m} \exp \tilde{\eta}
\]
\[
\varepsilon^2 \frac{\partial \tilde{j}}{\partial \tilde{x}} = -\tilde{c}_{N,m} \exp \tilde{\eta}
\]
Here, $\tilde{c}_{N,m}$ and $\tilde{\eta}$ depend parametrically of $\tilde{x}$ (see below).

In Eq. (9), the dimensionless flux $\tilde{N}_{N,m}$ is given by

$$\tilde{N}_{N,m} = \frac{4Fl_n N_{N,m}}{\sigma_p b} = \tilde{D}_N \frac{\partial \tilde{c}_N}{\partial \tilde{r}} \bigg|_{\tilde{r} = \tilde{R}_m},$$

(12)

the oxygen diffusion coefficients are normalized according to

$$\tilde{D} = \frac{4FDc_{ref}}{\sigma_p b}$$

(13)

and $\epsilon, \epsilon^*$ are the dimensionless parameters

$$\epsilon = \frac{2\tilde{R}_m}{R_p^2}, \quad \epsilon^* = \sqrt{\frac{\sigma_p b}{iR_t^2}}.$$  

(14)

To find $\tilde{c}_{N,m}$ in Eq. (11) we solve Eq. (10):

$$\tilde{c}_N = \left( \frac{\tilde{R}_m \ln (\tilde{R}_m/\tilde{r})}{\tilde{R}_m \ln (\tilde{R}_m/\tilde{R}_p)} \right) \exp \tilde{\eta} + \epsilon \epsilon^* \tilde{D}_N K_H \tilde{c}. $$

(15)

Setting $\tilde{r} = \tilde{R}_m$ in this solution, we obtain

$$\tilde{c}_{N,m} = \frac{K_H \tilde{c}}{1 + \alpha \exp \tilde{\eta}},$$

(16)

where $\alpha > 0$ is a constant parameter:

$$\alpha = \frac{\tilde{R}_m}{\epsilon \epsilon^* \tilde{D}_N} \ln \left( \frac{R_m}{R_p} \right).$$

(17)

With this, Eq. (11) takes the form

$$\epsilon \epsilon^* \frac{\partial \tilde{j}}{\partial \tilde{x}} = - \frac{K_H \tilde{c} \exp \tilde{\eta}}{1 + \alpha \exp \tilde{\eta}}.$$  

(18)

For further references we solve Eq. (18) for $\exp \tilde{\eta}$:

$$\exp \tilde{\eta} = - \frac{\epsilon \epsilon^* \frac{\partial \tilde{j}}{\partial \tilde{x}}}{K_H \tilde{c} + \alpha \epsilon \epsilon^* \frac{\partial \tilde{j}}{\partial \tilde{x}}}. $$

(19)

To eliminate $\tilde{\eta}$ from Eq. (18) we differentiate Eq. (18) over $\tilde{x}$, substitute $\exp \tilde{\eta}$ from Eq. (11) and use the Ohm’s law $\tilde{j} = -\partial \tilde{\eta}/\partial \tilde{x}$. After simple algebra we
come to
\[ \frac{\partial^2 \tilde{j}}{\partial x^2} - \left\{ \frac{\partial (\ln \tilde{c})}{\partial x} - \left( 1 + \frac{\alpha \varepsilon^2}{K_H \tilde{c}} \frac{\partial \tilde{j}}{\partial x} \right) \right\} \frac{\partial \tilde{j}}{\partial x} = 0, \]
\[ \tilde{j}(0) = \tilde{j}_0, \quad \tilde{j}(1) = 0 \]  \hspace{1cm} (20)

Eq. (15) allows us to calculate the flux \( \tilde{N}_{N,m} \), which appears in Eq. (9). Calculating derivative \( \frac{\partial \tilde{c}}{\partial \tilde{r}} \), multiplying the result by \( \tilde{D}_N \) and setting \( \tilde{r} = \tilde{R}_m \), we get
\[ \tilde{N}_{N,m} = -\frac{K_H \tilde{c} \exp \tilde{\eta}}{\varepsilon^2 \varepsilon^2 (1 + \alpha \exp \tilde{\eta})} \]

Using here Eq. (19), we come to
\[ \tilde{N}_{N,m} = \frac{1}{\varepsilon} \frac{\partial \tilde{j}}{\partial \tilde{x}} \]  \hspace{1cm} (21)

With this, Eq. (9) transforms to
\[ \tilde{D}_{ox} \frac{\partial^2 \tilde{c}}{\partial \tilde{x}^2} = -\frac{\partial \tilde{j}}{\partial \tilde{x}}, \quad \frac{\partial \tilde{c}}{\partial \tilde{x}} \bigg|_{\tilde{x}=0} = 0, \quad \tilde{c}(1) = \tilde{c}_1, \]  \hspace{1cm} (22)

Integrating this equation once, we find
\[ \tilde{D}_{ox} \frac{\partial \tilde{c}}{\partial \tilde{x}} = \tilde{j}_0 - \tilde{j}, \quad \tilde{c}(1) = \tilde{c}_1, \]  \hspace{1cm} (23)

which is a standard MHM equation for oxygen transport through the CCL depth.

Thus, the problem is reduced to the system of Eqs. (20), (23). With \( \tilde{j}(\tilde{x}) \) and \( \tilde{c}(\tilde{x}) \) at hand, the overpotential \( \tilde{\eta} \) is obtained from Eq. (19):
\[ \tilde{\eta} = \ln \left( -\frac{\varepsilon^2 \frac{\partial \tilde{j}}{\partial \tilde{x}}}{K_H \tilde{c} + \alpha \varepsilon^2 \frac{\partial \tilde{j}}{\partial \tilde{x}}} \right) \]  \hspace{1cm} (24)

and the radial shape of dissolved oxygen concentration \( \tilde{c}_N \) can be calculated from Eq. (15).

3. Results and discussion

Consider first the case of fast proton and oxygen transport along the pore. In that case, the static oxygen concentration \( \tilde{c} \) and overpotential \( \tilde{\eta} \) are nearly constant through the CCL depth. Integrating Eq. (18) over \( \tilde{x} \) from 0 to 1, we get
\[ \varepsilon_2^2 \tilde{j}_0 = \frac{K_H \tilde{c} \exp \tilde{\eta}_0}{1 + \alpha \exp \tilde{\eta}_0}, \]  \hspace{1cm} (25)
where the subscript 0 marks the values at the membrane/CCL interface. Solving Eq. (25) for \( \tilde{\eta}_0 \) we get polarization curve of the CCL:

\[
\tilde{\eta}_0 = \ln \left( \frac{\varepsilon^2 j_0^*}{K_H \tilde{c} - \alpha \varepsilon^2 j_0^*} \right) \tag{26}
\]

Figure 2 shows the polarization curves of the CCL of the thickness 10 \( \mu \)m and 3 \( \mu \)m. Solid lines are calculated using Eq. (26), while the dashed lines result from numerical solution of the system of Eqs. (20), (23). The solid lines thus correspond to the fast rate of proton and oxygen transport in the CCL, while the dashed lines take into account finite rate of these processes.

As can be seen, all the curves demonstrate limiting current density. Eq. (26) helps to understand the effect: it exhibits the limiting current density \( \tilde{j}_{N}^{\text{lim}} \) due to oxygen transport through the Nafion film. This current density makes the denominator in Eq. (26) equal to zero. With \( \alpha \) from Eq. (17) and \( \epsilon \) from Eq. (14), we find

\[
\tilde{j}_{N}^{\text{lim}} = \frac{2 \tilde{D}_N K_H \tilde{c}}{R_p^2 \ln \left( R_m/R_p \right)} \tag{27}
\]

In the dimension form this equation reads

\[
\tilde{j}_{N}^{\text{lim}} = \frac{8 F D_N l_t K_H \tilde{c}}{R_p^2 \ln \left( R_m/R_p \right)} \tag{28}
\]

In the context of this work, most important is that \( \tilde{j}_{N}^{\text{lim}} \) is proportional to \( l_t \), i.e., the limiting current density due to oxygen transport through the Nafion film linearly decreases with the decrease in the CCL thickness. This may explain unexpected poor performance of the low–Pt catalyst layers. Indeed, lower Pt loading means proportional decrease in the CCL thickness. For example, the standard CCL with the Pt loading of 0.4 mg cm\(^{-2}\) is four times thicker, than the CCL with the Pt loading of 0.1 mg cm\(^{-2}\). Note that all the other parameters appearing in Eq. (28) are the same for the thick and thin CCLs.

Suppose that the model above is completed with the oxygen transport in the GDL. This would lead to another limiting current density \( \tilde{j}_{GDL}^{\text{lim}} \) due to finite oxygen diffusivity of the GDL. Thus, we may face the situation when in the standard CCL, \( \tilde{j}_{N}^{\text{lim}} \) exceeds \( \tilde{j}_{GDL}^{\text{lim}} \), and the effect of oxygen transport through the Nafion film is not seen. However, in the low–Pt CCL, several times lower \( \tilde{j}_{N}^{\text{lim}} \) may limit the cell polarization curve.

Qualitatively, the oxygen transport path from the CCL/GDL interface to the Pt surface consists of two consecutive steps: the transport in the void pore followed by the transport through the Nafion film. The shorter the pore, the larger the weight of the transport in Nafion in the overall balance of oxygen fluxes. This explains proportionality \( \tilde{j}_{N}^{\text{lim}} \sim l_t \) in Eq. (25).

Finite through–plane oxygen diffusion coefficient \( D_p \) strongly affects the shape of the curve in the thick 10–\( \mu \)m CCL, while in the thin 3–\( \mu \)m CCL, the effect of \( D_p \) on the limiting current density is marginal (Figure 2). It is inter-
esting to note that finite $D_p$ improves the polarization curve of a thin (low–Pt) CCL in the range of currents below $j_{N}^{\text{lim}}$ (Figure 2). The effect is seemingly due to redistribution of oxygen concentration along the pore length, which lowers transport losses in the Nafion film.

To rationalize the dependence of $j_{N}^{\text{lim}}$ on the pore radius $R_p$ we will assume that $R_p$ is much larger than the Nafion film thickness. Thus, $\ln \left( \frac{R_m}{R_p} \right) = \ln \left( 1 + \frac{l_N}{R_p} \right) \approx \frac{l_N}{R_p}$, where $l_N$ is the Nafion film thickness. Substituting this relation into Eq.(28) we get

$$j_{N}^{\text{lim}} = \frac{8FD_Nl_tK_Hc}{R_pl_N} \quad (29)$$

Thus, another useful hint from Eq.(29) is that $j_{N}^{\text{lim}} \sim R^{-1}_p$, i.e., lowering of the mean pore radius in the CCL increases $j_{N}^{\text{lim}}$, making the cell polarization curve less sensitive to oxygen transport in the Nafion film. Physically, lowering of $R_p$ means reduction of the total proton current entering the pore, as another pore takes over part of the current for the conversion.

No attempts to fit the numerical polarization curve following from Eqs.(20), (23) to the experimental curves available in literature have been done. The problem is that the effective oxygen diffusion coefficient in the CCL $D_{ox}$, which is a composite containing $D_p$ and $D_N$ strongly depends on the cell current density [14]. A much better alternative to validate the model above is impedance spectroscopy. This, however, requires development of a transient analog of the model, which will be reported in a full–length paper.
Table 1: Parameters used for calculation of the curves in Figure 2. The ORR Tafel slope and the CCL proton conductivity are taken from impedance measurements [14].

| Parameter                                      | Value                      |
|------------------------------------------------|----------------------------|
| Pore radius $R_p$, cm, Ref. [11]               | $5 \times 10^{-6}$ (50 nm) |
| Nafion film thickness $l_N$, cm                | $10^{-6}$ (10 nm)          |
| Oxygen diffusion coefficient in the Nafion film, $D_N$, cm$^2$ s$^{-1}$, Ref. [12] | $10^{-6}$                  |
| Oxygen diffusion coefficient through the CCL depth, $D_p$, cm$^2$ s$^{-1}$, Ref. [13] | $10^{-3}$                  |
| Exchange current density $i_*$, A cm$^{-3}$ (assumed) | $10^{-3}$                  |
| ORR Tafel slope $b$, V                         | 0.03                       |
| CCL proton conductivity $\sigma_p$, Ω$^{-1}$ cm$^{-1}$ | 0.03                      |
| Henry constant (mol/mol)                       | $6.76 \times 10^{-3}$     |
| Cell temperature $T$, K                         | 273 + 80                   |

4. Conclusions

A single-pore model for the cathode catalyst layer performance in a PEM fuel cell is developed. The model takes into account oxygen transport through the CCL depth and through the Nafion film covering Pt/C agglomerates. In the limit of fast proton and through-plane oxygen transport in the CCL analytical solution for the CCL polarization curve is derived. This solution reveals a limiting current density due to proton transport through the Nafion film $j_N^{\text{lim}}$. Moreover, $j_N^{\text{lim}}$ is proportional to the CCL thickness $l_t$; thus, in the low-Pt CCL, due to its much lower thickness, the effect of oxygen transport through the Nafion film may limit the cell current density. Qualitatively, for a fixed current density $j_0$, the thinner the CCL, the larger the fraction of oxygen flux that must be transported through the Nafion film to support $j_0$. Another useful hint from the analytical result is inverse proportionality of $j_N^{\text{lim}}$ to the mean mesopore radius $R_p$, i.e., the CCL with lower $R_p$ is less sensitive to oxygen transport through the Nafion.
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Nomenclature

\( \text{\textsuperscript{~}} \) Marks dimensionless variables
\( b \) ORR Tafel slope, V
\( c \) Oxygen molar concentration in the pore, mol cm\(^{-3}\)
\( c_{\text{ref}} \) Reference oxygen concentration, mol cm\(^{-3}\)
\( D_p \) Oxygen diffusion coefficient in the pore, cm\(^2\) s\(^{-1}\)
\( D_N \) Oxygen diffusion coefficient in the Nafion film, cm\(^2\) s\(^{-1}\)
\( F \) Faraday constant, C mol\(^{-1}\)
\( j \) Local proton current density along the pore, A cm\(^{-2}\)
\( j_{\text{lim}} \) Limiting current density due to oxygen transport in Nafion film, A cm\(^{-2}\)
\( j_0 \) Cell current density, A cm\(^{-2}\)
\( i_* \) Volumetric exchange current density, A cm\(^{-3}\)
\( l_t \) Catalyst layer thickness, cm
\( l_N \) Nafion film thickness, cm
\( R_m \) Radius of a Pt/C tube, cm
\( R_p \) Pore radius, cm
\( r \) Radial coordinate, cm
\( x \) Coordinate through the CCL, cm

Subscripts:
0 Membrane/CCL interface
1 CCL/GDL interface
t Catalyst layer

Greek:
\( \alpha \) Dimensionless parameter, Eq. [17]
\( \varepsilon \) Dimensionless Newman’s reaction penetration depth, Eq. [14]
\( \epsilon \) = \( 2/R_m \)
\( \eta \) ORR overpotential, positive by convention, V
\( \sigma_p \) CCL proton conductivity, \( \Omega^{-1} \) cm\(^{-1}\)