Can We Quantify Oxygen Transport in the Nafion Film Covering an Agglomerate of Pt/C Particles?  
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We report a model of the cathode catalyst layer (CCL) impedance, which includes impedances due to oxygen transport in the Nafion film covering Pt/C agglomerates, and due to oxygen transport through the CCL depth. In the case of small cell current density, analytical solutions for the CCL impedance $Z_{\text{ccl}}$ are derived; for larger currents, we analyze numerical solution for $Z_{\text{ccl}}$. The characteristic frequencies of the oxygen transport through the Nafion film and through the CCL depth are close to each other, and the contribution of the Nafion film impedance $Z_N$ to $Z_{\text{ccl}}$ is small up to the current densities $\approx 100 \text{ mA cm}^{-2}$. This makes it difficult to reliably determine $Z_N$ from experimental spectra of a standard 10 $\mu$m-thick CCL. However, with the decrease in the CCL thickness, the relative contribution of $Z_N$ to $Z_{\text{ccl}}$ increases. It gives us a chance to determine $Z_N$ by fitting the models of this work to measured spectra of a low-~load MEA with a thin CCL. An example of fitting the model to a synthetic numerical impedance is given.  

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Polymer electrolyte membrane fuel cells are ready to take their place in the spectrum of electrochemical sources powering the future society. Still, however, a lot needs to be done to improve stability and reduce the cost of these cells. Development of simple and robust ex situ characterization techniques for the fuel cell research and applications (cars, home appliances etc.) is an urgent task.

It is generally accepted that the impedance technique gives much more information on a PEM fuel cell, than the DC methods. One of the key problems in understanding impedance spectra is development of physics-based impedance models, which are fast enough to be used in numerical algorithms for fitting experimental spectra. In spite of numerous efforts in this field, some important questions remain unresolved.

PEMFC impedance is determined mainly by the cathode catalyst layer (CCL). The kinetics of oxygen reduction reaction (ORR) are sluggish and the oxygen transport through the catalyst layer is slow; thus, the CCL gives the major contribution to the cell impedance. SEM pictures show that a typical CCL is a porous structure formed by numerous spherical agglomerates of Pt/C particles covered by Nafion film. Recent experiments of Singh et al. have shown that the addition of Nafion significantly changes the catalyst layer impedance. At medium and large overpotentials, the presence of Nafion leads to formation of the second, low-frequency arc in the impedance spectrum of the electrode, which is associated by the authors with the oxygen transport in Nafion film covering Pt/C agglomerates.

The nature of the oxygen transport loss in the CCL is still controversial. Basically, this loss can be associated with the oxygen transport in agglomerates, and with the oxygen transport through the CCL depth. What is the contribution of each mechanism into the total transport loss in the CCL, and how can we separate and quantify each mechanism? Answering these questions is a challenge for the fuel cell modeling community.

Numerous papers have been devoted to static polarization curve modeling, taking into account Nafion-covered Pt/C agglomerates; references can be found in a recent work. One of the first physics-based models for PEMFC cathode impedance has been developed by Springer et al. The underlying transient model for the CCL performance was based on standard macro-homogeneous equations for the charge and oxygen mass conservation; no explicit account of the oxygen transport in agglomerates was done. A first attempt to incorporate the effect of oxygen transport in Pt/C agglomerates has seemingly been done by Raitstrick. He considered a planar agglomerate at the surface of a pore having a form of a slit. An equation for the perturbed oxygen concentration in the agglomerate has been derived; the solution for the pore impedance was obtained numerically. Recent SEM pictures show, however, that the agglomerates are spherical rather than the planar structures. Jaouen and Lindbergh considered oxygen transport in spherical agglomerates in their impedance model of the CCL; however, they neglected oxygen transport through the electrode depth. The electrode impedance was calculated numerically in their work. Similar numerical impedance model with neglect of the oxygen transport through the CCL depth has been developed by Gerteisen et al. It is worth noting that Gerteisen et al. assumed that the agglomerates are fully filled with Nafion. In a recent paper, Gerteisen developed a numerical impedance model of the CCL, which includes oxygen transport through the CCL depth and through the Nafion film covering agglomerate. However, the transport in the Nafion film/agglomerate was assumed to be infinitely fast, and hence this transport contributes to the real component of impedance only, i.e., it merely shifts the impedance spectrum as a whole along the real axis.

In this work, we report a model of the CCL impedance, which includes transient oxygen transport equations in the spherical Pt/C agglomerates and through the CCL depth. The agglomerate is assumed to be covered by a thin spherical Nafion film, while the agglomerate interior volume is filled with water. First, we construct a system of transient equations for the CCL performance; this system is then linearized and Fourier-transformed to yield a system of equations for the AC perturbation amplitudes. In the case of small cell current density, this system is solved and the analytical expression for the CCL impedance is derived. For larger currents (see below), we analyze numerical solution for the CCL impedance.

Impedance Model

A conceptual picture of the CCL structure suggested by Liu et al. is depicted in Figure 1. Spherical agglomerates of Pt/C particles coated by Nafion film form a contiguous cluster, which provides proton transport to the catalyst sites. The void space between agglomerates serves as a pathway for oxygen transport through the CCL depth. To reach Pt particles, oxygen must be dissolved and transported through the Nafion film.

Transient equations.—An elementary unit of the structure in Figure 1 providing electrochemical conversion is a single agglomerate. Below, we will consider a spherical agglomerate of Pt/C particles, covered by a thin Nafion film. Let the agglomerate radius, including

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Nafion film be \( R_a \), and the thickness of the Nafion film be \( d_N \) (Figure 2).

To derive a model for the CCL impedance, we need transient conservation equations for oxygen in agglomerate and a transient performance model for the whole CCL. The oxygen transport equations in the Nafion film and in the agglomerate read

\[
\frac{\partial c_N}{\partial t} = -\frac{D_N}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_N}{\partial r} \right) \exp \left( \frac{\eta}{b} \right)
\]

[1]

\[
\frac{\partial c_a}{\partial t} = -\frac{D_a}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_a}{\partial r} \right) \exp \left( \frac{\eta}{b} \right)
\]

[2]

where \( t \) is time, \( r \) is the radial coordinate, \( D_N \) and \( D_a \) are the oxygen diffusion coefficients in the Nafion film and in the agglomerate, respectively, \( c_N, c_a \) are the oxygen concentrations in the Nafion and agglomerate, respectively, \( c_{ref} \) is the reference oxygen concentration, \( i_s \) is the electrode volumetric exchange current density (A cm\(^{-2}\)), \( \eta \) is the ORR overpotential, positive by convention, and \( b \) is the ORR Tafel slope. Note that Eq. 1 contains the ORR rate on the right side, which means that the reaction runs also in the Nafion film (see discussion below).

To link the CCL and agglomerate models, consider a cylindrical pore of the radius \( R_a \) in the catalyst layer, with the pore walls formed by agglomerates (Figure 3). The oxygen mass transport equation along the pore reads

\[
\frac{\partial c_{ox}}{\partial t} - D_{ox} \frac{\partial^2 c_{ox}}{\partial x^2} = -\frac{D_{ox}}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial c_{ox}}{\partial \rho} \right) \bigg|_{\rho=R_p}
\]

[3]

where \( x \) is directed along the pore axis, and \( \rho \) is the radial position in cylindrical coordinates (\( \rho, x \)). The right side of Eq. 3 is the divergence of the oxygen flux through the unit surface of the pore cylinder.

The meaning of the divergence operator in Eq. 3 needs to be specified. This operator represents a divergence of the oxygen flux through the side wall of the cylindrical pore formed by agglomerates partly penetrating into the pore volume (Figure 3). To calculate this divergence we note, that in the limit of \( D_a = D_N = \infty \), the right side of Eq. 3 must transform to the standard macro–homogeneous ORR rate. \([2]\) This requirement leads to the following relation

\[
\frac{D_{ox}}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial c_{ox}}{\partial \rho} \right) \bigg|_{\rho=R_p} = \frac{3N_N}{R_a}
\]

[4]

where

\[
N_N = D_N \frac{\partial c_N}{\partial r} \bigg|_{r=R_p}
\]

[5]

is the oxygen flux through the unit agglomerate surface. With this, Eq. 3 transforms to

\[
\frac{\partial c_{ox}}{\partial t} - D_{ox} \frac{\partial^2 c_{ox}}{\partial x^2} = -\frac{3N_N}{R_a}
\]

[6]

Below, we will see that the right side of Eq. 6 depends on the local overpotential \( \eta \), which varies with \( x \). The proton charge balance equation, including Ohm’s law for the proton transport is

\[
C_a \frac{\partial \eta}{\partial t} - \sigma_p \frac{\partial^2 \eta}{\partial x^2} = -4F \frac{3N_N}{R_a}
\]

[7]

Here, the right side describes the “sink” of overpotential consistent with the sink of oxygen in Eq. 6. Physically, the rates of oxygen consumption and proton current conversion along the pore axis must be coupled by the Faraday law. The chain of Equations 1, 2, 6 and 7 describe oxygen transport along the void pore in the CCL, with the
sink through to the Nafion film to the water-filled agglomerates of Pt/C particles.

It is convenient to introduce dimensionless variables

\[
\tilde{r} = \frac{r}{R_a}, \quad \tilde{x} = \frac{x}{l_f}, \quad \tilde{t} = \frac{t}{t_e}, \quad \tilde{\epsilon} = \frac{c}{\epsilon_{ref}}, \quad \tilde{\eta} = \frac{\eta}{b},
\]

where the characteristic time \( t_e \) is given by

\[
t_e = \frac{4F\epsilon_{ref}}{i_e} \quad [9]
\]

With the dimensionless variables, the system 1, 2, 6, 7 transforms to the agglomerate model

\[
\frac{\partial \tilde{c}_{\alpha}}{\partial \tilde{t}} + \tilde{D}_N \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{c}_{\alpha}}{\partial \tilde{r}} \right) = -\tilde{c}_{\alpha} \exp(\tilde{\eta}) \quad [10]
\]

and the pore (CCL) model

\[
\frac{\partial \tilde{c}_a}{\partial \tilde{t}} + \tilde{D}_a \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{c}_a}{\partial \tilde{r}} \right) = -3\tilde{\eta}_N \quad [12]
\]

where the parameters \( \delta, \beta, \) and \( \epsilon \) are given by

\[
\delta = \frac{R_a}{l_f} \quad \beta = \sqrt{\frac{C_0 b}{4F\epsilon_{ref}}} \quad \epsilon = \sqrt{\frac{\sigma b}{2\tilde{\omega} l_f^2}} \quad [14]
\]

and the flux \( \tilde{\eta}_N \) is nondimensionalized according to

\[
\tilde{\eta}_N = \frac{4F\eta_N}{i_e R_a} \quad [15]
\]

The boundary conditions to the system 10, 11 express continuity of the oxygen concentration and flux at the Nafion/agglomerate interior interface (\( \tilde{r} = 1 - \epsilon \)), and symmetry of the oxygen concentration profile at \( \tilde{r} = 0 \):

\[
\tilde{D}_N \frac{\partial \tilde{c}_{\alpha}}{\partial \tilde{r}} \bigg|_{\tilde{r}=1-\epsilon} = \tilde{D}_a \frac{\partial \tilde{c}_a}{\partial \tilde{r}} \bigg|_{\tilde{r}=1-\epsilon}, \quad \tilde{c}_{\alpha}(1) = \tilde{c}_a(1) \quad [16]
\]

\[
\tilde{D}_a \frac{\partial \tilde{c}_a}{\partial \tilde{r}} \bigg|_{\tilde{r}=0} = 0, \quad \tilde{c}_a(1-\epsilon) = \tilde{c}_a(1-\epsilon) \quad [17]
\]

Here,

\[
\epsilon = \frac{d_N}{R_a} \quad [18]
\]

is the dimensionless thickness of the Nafion film, and \( \tilde{c}_{\alpha} \) is the dimensionless concentration of oxygen dissolved in Nafion on the film outer surface. This concentration is related to the gaseous oxygen concentration in the void pores of the CCL \( \tilde{c}_{\alpha} \) by the Henry’s law with the constant \( k_{\alpha} \) (mol/mol):

\[
\tilde{c}_{\alpha} = K_{\alpha} \tilde{c}_{\alpha} \quad [19]
\]

The boundary conditions to Eqs. 12 and 13 are

\[
\frac{\partial \tilde{c}_{\alpha}}{\partial \tilde{x}} \bigg|_{\tilde{x}=0} = 0, \quad \tilde{c}_{\alpha}(1) = \tilde{c}_1 \quad [20]
\]

\[
\tilde{\eta}(0) = \tilde{\eta}_0, \quad \frac{\partial \tilde{\eta}}{\partial \tilde{x}} \bigg|_{\tilde{x}=1} = 0 \quad [21]
\]

The first of Eq. 20 means zero oxygen flux in the membrane, while the second fixes the oxygen concentration at the CCL/GDL interface. The first of Eq. 21 fixes the total ORR overpotential at the membrane interface, and the second expresses zero proton current to the GDL.

**Linearization and Fourier transform.**—To obtain the CCL impedance, we apply a small-amplitude harmonic perturbation of potential to the CCL. Due to smallness of the AC signal, the response of the system is linear and harmonic, and we can write

\[
\tilde{\eta} = \tilde{\eta}_0(\tilde{t}) + \tilde{\eta}_1(\tilde{t}, \tilde{x}) \exp(i\tilde{\omega}t), \quad \tilde{\eta}_1 \ll 1
\]

\[
\tilde{c}_{\alpha} = \tilde{c}_{\alpha 0}^0(\tilde{t}) + \tilde{c}_{\alpha 1}^1(\tilde{t}, \tilde{x}) \exp(i\tilde{\omega}t), \quad \tilde{c}_{\alpha 1}^1 \ll 1
\]

\[
\tilde{c}_a = \tilde{c}_a(\tilde{t}) + \tilde{c}_a^1(\tilde{t}, \tilde{x}) \exp(i\tilde{\omega}t), \quad \tilde{c}_a^1 \ll 1
\]

where \( \tilde{\omega} = \omega t_e \) is the dimensionless angular frequency of the applied signal, and the superscripts 0 and 1 indicate the steady-state profile and the small-amplitude perturbation, respectively.

The equations for static shapes are obtained from Eqs. 10–13 by chalking out the time derivatives. Substituting 22 into the system 10–13, subtracting the static equations and neglecting the terms with the perturbation products, we get a system of linear equations for the perturbation amplitudes of the agglomerate model

\[
\tilde{D}_N \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{c}_1^1}{\partial \tilde{r}} \right) = \left( \tilde{c}_1^1 + \tilde{c}_a^1 \tilde{\eta}_1 \right) \exp \tilde{\eta}_0 + i\tilde{\omega} \tilde{c}_1^1 \quad [23]
\]

\[
\tilde{D}_a \frac{\partial}{\partial \tilde{r}} \left( \tilde{r} \frac{\partial \tilde{c}_\alpha 1^1}{\partial \tilde{r}} \right) = \tilde{c}_\alpha 1^1 \tilde{\eta}_1 + i\tilde{\omega} \tilde{c}_\alpha 1^1 \quad [24]
\]

and for these amplitudes of the CCL model

\[
\tilde{D}_a \frac{\partial^2 \tilde{c}_1^1}{\partial \tilde{x}^2} = 3\tilde{\eta}_N^1 + i\tilde{\omega} \tilde{c}_\alpha 1^1 \quad [25]
\]

\[
2\epsilon^2 \frac{\partial^2 \tilde{c}_\alpha 1^1}{\partial \tilde{x}^2} = 3\tilde{\eta}_N^1 + i\tilde{\omega} \tilde{c}_\alpha 1^1 \quad [26]
\]

Here,

\[
\tilde{\eta}_N^1 = \tilde{D}_N \frac{\partial \tilde{c}_1^1}{\partial \tilde{r}} \bigg|_{\tilde{r}=1} \quad [27]
\]

is the flux of dissolved oxygen permeation through the outer surface of Nafion film. The boundary conditions to the system 23–26 are

\[
\tilde{D}_a \frac{\partial \tilde{c}_1^1}{\partial \tilde{r}} \bigg|_{\tilde{r}=1-\epsilon} = \tilde{D}_a \frac{\partial \tilde{c}_\alpha 1^1}{\partial \tilde{r}} \bigg|_{\tilde{r}=1-\epsilon}, \quad \tilde{c}_\alpha 1^1(1) = K_{\alpha} \tilde{c}_a 1^1(\tilde{x}) \quad [28]
\]

\[
\frac{\partial \tilde{c}_1^1}{\partial \tilde{x}} \bigg|_{\tilde{x}=0} = 0, \quad \tilde{c}_\alpha 1^1(1-\epsilon) = \tilde{c}_\alpha 1^1(1-\epsilon) \quad [29]
\]

and

\[
\frac{\partial \tilde{c}_\alpha 1^1}{\partial \tilde{x}} \bigg|_{\tilde{x}=1} = 0, \quad \tilde{c}_\alpha 1^1(1) = 0 \quad [30]
\]

As can be seen, the problem 23–26 is split into the local problem for \( \tilde{c}_1^1 \) and \( \tilde{c}_\alpha 1^1 \) in a single agglomerate and the global problem for the through-plane shapes of \( \tilde{c}_1^1 \) and \( \tilde{\eta}_1 \). The local problem is given by Eqs. 23, 24 with \( \tilde{\eta}_1(\tilde{x}) \) being a parameter. The global CCL problem is given by Eqs. 25, 26, with \( \tilde{\eta}_N^1 \) resulting from solution of the local problem.
Solution for the local oxygen flux.—The static shapes of the oxygen concentration in the agglomerate and in Nafion film are

\[
\begin{align*}
\tilde{c}_a^0 &= \frac{\alpha_a}{\tilde{r}} \sinh \left( \tilde{r} \sqrt{\frac{\exp \tilde{\eta}_0}{D_a}} \right) \\
\tilde{c}_N^0 &= \frac{\alpha_N}{\tilde{r}} \sinh \left( \tilde{r} \sqrt{\frac{\exp \tilde{\eta}_0}{D_N}} \right) + \frac{\beta_N}{\tilde{r}} \cosh \left( \tilde{r} \sqrt{\frac{\exp \tilde{\eta}_0}{D_N}} \right)
\end{align*}
\]  

Due to agglomerate smallness, the overpotential \( \tilde{\eta} \) is assumed to be independent of \( \tilde{r} \). The expressions for coefficients in Eqs. 32, 33 are very cumbersome and not displayed here. Exact solution to the problem for the perturbation amplitudes \( \tilde{c}_a^0 \) and \( \tilde{c}_N^0 \) can be obtained with the aid of mathematical software. For the CCL problem, we get only an expression for the perturbation of the oxygen concentration flux \( \tilde{N}_a^1 \) through the Nafion film outer surface, Eq. 27. This flux can be represented as

\[
\tilde{N}_a^1(1) = \tilde{N}_a^1 \tilde{\eta}^1 + \tilde{N}_a^1 \tilde{c}_a^1
\]  

Unfortunately, the exact expressions for the coefficients \( \tilde{N}_a^1 \) and \( \tilde{N}_a^1 \) are very cumbersome. However, in this problem, \( D_a \) and \( D_N \) are large, while \( \epsilon \) is small. Performing asymptotic expansion of the exact \( \tilde{N}_a^1(1) \) over \( D_a \), Taylor series expansion over \( \epsilon \), and neglecting the terms on the order of \( O(D_a^{-2}) \), \( O(D_a^{-1}D_N^{-1}) \) and \( O(\epsilon^2) \), we come to a compact result

\[
\begin{align*}
\tilde{N}_a^1 &\approx \frac{1}{3} K_{\tilde{\eta}} e_{\tilde{\eta}a} \exp(\tilde{\eta}0) \left( 1 - \epsilon (2 \exp \tilde{\eta}0 + i\tilde{\omega}) \right) \\
\tilde{N}_a^1 &\approx \frac{1}{3} K_{\tilde{c}} e_{\tilde{\eta}a} \exp(\tilde{\eta}0 + i\tilde{\omega}) \left( 1 - \epsilon (\exp(\tilde{\eta}0 + i\tilde{\omega}) \right)
\end{align*}
\]

Note that at leading order, the terms with \( D_a^{-1} \) vanish, as \( D_a \gg D_N \). Note also that in the limit of \( D_a \to \infty \), Eqs. 35, 36 simplify to \( \tilde{N}_a^1 \approx K_{\tilde{\eta}} e_{\tilde{\eta}a} \exp(\tilde{\eta}0) ) / 3 \), \( \tilde{N}_a^1 \approx K_{\tilde{c}} e_{\tilde{\eta}a} \exp(\tilde{\eta}0 + i\tilde{\omega}) / 3 \), and in Eqs. 25, 26 we get the standard macro–homogeneous expressions for the Tafel ORR rate.

**Results and Discussion**

Fast oxygen transport through the CCL depth.—Before we proceed to numerical solution of the CCL system, it is advisable to consider the limit of fast oxygen transport through the CCL depth. Note that considering this limit only makes sense if the cell current density is small; the respective criterion is given in the next section. In this case, in the system, we can set \( \tilde{c}_a = 0 \) (fast oxygen transport), and \( \tilde{c}_N = \tilde{c} = \) const, \( \tilde{\eta}^0 = \tilde{\eta}_0 = \) const (small cell current density). With these changes, \( \tilde{N}_a^0 \), \( \tilde{N}_a^0 \), is independent of \( \tilde{x} \) parameter and Eq. 26 can easily be solved. By definition, the CCL impedance is

\[
\tilde{Z}_{\text{cell}} = -\frac{\partial}{\partial \tilde{x}} \tilde{Z}_{\text{cell}} \left|_{\tilde{x}=0} \right.
\]

Using here the solution to Eq. 26 we get

\[
\tilde{Z}_{\text{cell}} = \frac{1}{2 \pi e \phi \tan \phi}, \quad \phi = \sqrt{\frac{(3\tilde{N}_a^1 + \tilde{\omega}^2)}{2e^2}}
\]

The spectrum of impedance Eq. 38 is shown in Figure 4 together with the charge–transfer and proton transport impedance \( \tilde{Z}_{\text{tr}+p} \) corresponding to zero oxygen transport losses in the agglomerate. The spectrum of \( \tilde{Z}_{\text{tr}+p} \) is obtained from Eq. 38 by passing to the limit \( D_N \to \infty \). Noting that at small cell currents, the polarization curve of the CCL is given by the Tafel equation

\[
K_{\text{oc}} e \exp(\tilde{\eta}0) = \tilde{j}_0
\]  

for the coupled charge–transfer and proton transport impedance \( \tilde{Z}_{\text{tr}+p} \) we find

\[
\tilde{Z}_{\text{tr}+p} = -\frac{1}{2 \pi e \phi \tan \phi}, \quad \phi = \sqrt{\frac{(3\tilde{N}_a^1 + \tilde{\omega}^2)}{2e^2}}
\]

In dimension form this impedance reads

\[
\tilde{Z}_{\text{tr}+p} = -\frac{1}{\sigma \phi \tan \phi}, \quad \phi = \sqrt{\frac{(3\tilde{N}_a^1 + \tilde{\omega}^2)}{2e^2}}
\]

The charge–transfer and total \( \tilde{Z}_{\text{cell}} \) spectra are very close to each other (Figure 4). Note that the difference is visible due to the upper estimate of the CCL thickness of 30 nm taken for the calculations; for a more realistic value of \( d_{\text{tr}} = 10 \) nm, the spectra in Figure 4 would be indistinguishable. Nonetheless, Figure 4 gives us a hope that for higher currents and lower oxygen concentrations, the effect of Nafion film could be measurable.

From Eq. 38 we can obtain the formula for the CCL static resistivity \( R_{\text{cell}} \). In PEMFCs, the parameter \( \epsilon \) is large, typically \( \epsilon \approx 10^{-5} \). Setting in Eq. 38 \( \tilde{j}_0 = 0 \), expanding the result over \( \epsilon \) and calculating asymptotic expansion over \( \epsilon \), we get

\[
R_{\text{cell}} = \frac{1}{6e} + \frac{1}{\tilde{j}_0} + \frac{2e}{3 \tilde{j}_0} \frac{d_{\text{oc}}}{d_{\text{oc}} e_{\tilde{\eta}a} \tilde{c}_1} \]

In dimension form, Eq. 42 reads

\[
R_{\text{cell}} = \frac{1}{3 \sigma} + \frac{1}{\tilde{j}_0} + \frac{2 \tilde{j}_0 R_{\text{oc}} \tilde{b}}{3(4 \tilde{j}_0 R_{\text{oc}} \tilde{c}_1) \tilde{j}_1}
\]

The first term on the right side is the CCL resistivity to proton transport. The second term is the Faraday charge–transfer resistivity. The third term represents the oxygen transport resistivity of the Nafion film.

Remarkably, the Nafion film resistivity is inversely proportional to the CCL thickness \( l_{\text{tr}} \). Eq. 43 helps to understand this effect. Indeed, individual agglomerates are connected to the pore volume as parallel resistivities; thus, the longer the representative pore, the more agglomerates we have along the pore, and the smaller the total resistivity of the agglomerates ensemble.

Subtracting \( \tilde{Z}_{\text{tr}+p} \) from \( \tilde{Z}_{\text{cell}} \), we get an explicit expression for the Nafion film impedance

\[
\tilde{Z}_N = \frac{1}{2 \pi e} \left( \frac{1}{\phi \tan \phi} - \frac{1}{\tilde{j}_0} \right)
\]

where \( \phi \) and \( \tilde{j}_0 \) are given in Eqs. 38 and 40. Eq. 44 can be simplified: expanding the right side over small \( \epsilon \), and calculating asymptotic
In this case, and of the through–plane shows that Eq. 5 (solid line) and numerical (points) CCL

...we can get the characteristic (summit) frequency

\[ \omega_N = \frac{j_0}{3} \left( \frac{8b^2 - 2\sqrt{9b^2 - 8b^2\epsilon_s + 2\epsilon_s^2}}{\epsilon_s} \right) \]

where \( \epsilon_s = K_{ox}c_1 \). With the parameters in Table I and \( j_0 = 40 \text{ mA cm}^{-2} \), for the regular frequency \( f_N = \omega_N/(2\pi) \) we get \( f_N \approx 6 \text{ Hz} \).

**Finite rate of oxygen transport through the CCL depth.—Small cell current density.—** The cell current density is small, if it obeys

\[ R_{cl} = \frac{l_i}{3\sigma_p} + \frac{b}{j_0} + \frac{2d_N R_b}{3(4F_D K_{ox}c_1l_i)} + \frac{b l_i}{3(4F_D K_{ox}c_1)} \]

This equation can also be obtained by passing to the limit of magnitude lower than \( R_{cl} \).

It is useful to compare the characteristic summit frequencies of the oxygen transport in Nafion film, Eq. 47 and of the through–plane oxygen transport. The latter frequency is given by

\[ \omega_{ox} \sim \frac{2.54 D_{ox}}{l_i^2} + \frac{j_0}{4Fc_1l_i} \]
With the data from Table I and the current density of 50 mA cm⁻², we get \( j_0 = \omega_0 \alpha (2\pi) \approx 40 \text{ Hz} \). The value of \( f_N \) estimated above is 6 Hz, i.e., the Nafion film and through–plane transport impedances are well separated in the frequency domain. However, the frequency gap between \( f_N \) and \( f_0 \) would be zero for the oxygen diffusion coefficient \( D_{ox} \approx 1.5 \cdot 10^{-5} \text{ cm}^2 \text{s}^{-1} \), which is quite a realistic value for standard Pt/C electrodes. In that case both the transport losses are indistinguishable by impedance methods.

Medium cell current density.—Eqs. 35, 36 are derived assuming that \( D_a \) is large. In 32, \( D_a \) appears in the combination \( \exp(\eta^0) / D_a \). Thus, the approximation of large \( D_a \) works as long as \( \exp(\eta^0) \ll D_a \); this limits the cell current density by the value of 250 mA cm⁻². For the currents just below this value, we have to solve the Equations 25, 26, taking into account that the expression for the flux \( 3 \hat{\eta} \)).

The CCL impedance spectra resulting from solution of the general problem 25, 26 with the static shapes from Eqs. 55, 56 are shown in Figure 7. As can be seen, the Nafion film contribution to the CCL impedance is small but visible already at the cell current density on the order of 100 mA cm⁻², and it increases with the current (Figure 7).

![Figure 7](image)

Figure 7. Lines – the spectra corresponding to zero transport losses in the Nafion film. Points – the spectra, which include the Nafion film impedance. The parameters for calculations are listed in Table I.

Figure 8 shows the components of the total CCL impedance at the current density of 235 mA cm⁻². The largest contribution gives the oxygen transport through the CCL depth; the contribution of the Nafion film impedance is about 10% (Figure 8). The impedances in Figure 8 are represented as separate arcs by shifting \( Z_{ox} \) and \( Z_N \) to the right along the real axis by the resistivities \( R_{c+} \) and \( R_{c+} + R_m \), respectively. This can be done using the model equations; however, separation of the impedances from the experimental spectrum is a much more difficult task. We note again, that the separation of \( Z_N \) and \( Z_{ox} \) is only possible if the characteristic frequencies \( \omega_N \) and \( \omega_{ox} \) are different.

It should also be noted that the spectra in Figure 8 are plotted for the upper estimates of \( D_m \) and \( d_m \) (Table I). For more realistic values of three to four times lower \( D_m \) and three times lower \( d_m \), the contribution of \( Z_N \) to the total impedance would be less than 1%. The experimental impedance spectra becomes progressively noisy with the increase in the cell current density, and reliable determination of \( Z_N \) with the standard 10 μm–thick CCL seems to be rather problematic. However, Eq. 53 shows that with the decrease in the CCL thickness \( l \), the contribution of \( Z_N \) to the total CCL impedance decreases, while the contribution of \( Z_{ox} \) increases. This gives us a chance to determine \( Z_N \) by fitting the impedance models above to experimental spectra from MEA with the thin, low–loaded catalyst layers.

Fitting.—Finally, the following numerical experiment has been performed. An impedance spectrum for the current density \( j_b = 100 \text{ mA cm}^{-2} \) has been generated using Eq. 49 and the parameters indicated in brackets in Table II. The total spectrum and its components are shown in Figure 9a. Then, the imaginary part of the spectrum has been perturbed by adding a 3% random noise and the model of Eq. 49 has been fitted to the perturbed spectrum. The fitting has been performed using the Maple least–squares procedure NonlinearFit.

The perturbed and fitted spectra, and the components of the fitted spectrum are shown in Figure 9b. As can be seen, the fitted spectrum and its components are quite close to the “exact” spectra in Figure 9a. The fitting and prescribed parameters are listed in Table II. The Nafion film impedance, Eq. 46, depends on the ratio of the parameters

![Figure 8](image)

Figure 8. Solid line – the total CCL impedance, short–dashed line – the charge–transfer impedance, including proton transport impedance, long–dashed line – the through–plane oxygen transport impedance, dotted line – the Nafion film impedance. The cell current density is 240 mA cm⁻², the parameters for calculations are listed in Table I.

<table>
<thead>
<tr>
<th>Table II. Fitted and prescribed (indicated in brackets) parameters. The other parameters are listed in Table I.</th>
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<tbody>
<tr>
<td>The ratio ( D_N / D_a ), s cm⁻¹</td>
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<tr>
<td>Oxygen diffusion coefficient through the CCL depth ( D_{ox} ), cm² s⁻¹</td>
</tr>
<tr>
<td>ORR Tafel slope ( b ), V</td>
</tr>
<tr>
<td>CCL proton conductivity ( \sigma_p ), Ω cm⁻¹</td>
</tr>
</tbody>
</table>
the characteristic frequencies of the oxygen transport in the Nafion film and in the CCL pores are nearly the same, and the respective impedances cannot be separated. For larger current densities, the system of equations for perturbation amplitudes is solved numerically. With the growth of the cell current, the contribution of Nafion film impedance increases up to 10% of the total CCL impedance. The Nafion film impedance can best be measured by fitting the model equations of this work to impedance of a low–loaded, thin CCL, in which the effect of the through–plane oxygen transport is small.

### Conclusions

A physics-based model for impedance of the cathode catalyst layer is developed. The model takes into account oxygen transport through the CCL depth, and through the Nafion film covering agglomerates of Pt/C particles. Transient mass and charge conservation equations are linearized and Fourier–transformed to get a system of linear equations for small perturbation amplitudes. In the case of small cell current density and fast oxygen transport through the CCL, the system is solved and analytical expressions for the CCL impedance and static resistivity are derived. With typical CCL parameters, at small currents, the contribution of the Nafion film to the CCL impedance appears to be small. Furthermore, for the Nafion film thickness of 10 nm and through–plane oxygen diffusivity on the order of $10^{-5}$ cm$^2$ s$^{-1}$, the fitted values of $\alpha$, $\eta$, and $\beta$ are less accurate; nonetheless, these values are determined with 10% accuracy. Taking into account a very small value of $Z_N$ (Figure 9a), this experiment gives us a hope that even small $Z_N$ can be found from fitting real experimental spectra.

To conclude discussions, a following note should be made. The non–zero ORR rate in the Nafion film is justified by the following arguments. Formally, the “gap” in the ORR rate due to Nafion film would make it difficult to link the local agglomerate and the through–plane problems. In the present formulation, a simple equation for the divergence of the oxygen flux in Eq. 3 results from condition that in the limit of infinite $D_N$ and $D_N$, this divergence should reduce to the macro–homogeneous expression $i_s(c/C) \exp(\eta/b)$. In the absence of ORR rate in the Nafion film, this condition does not hold, as the “gap” in the oxygen conversion inside the Nafion film contradicts to the macro–homogeneous paradigm. Second, in real fuel cells, Pt is dissolved during operation and it migrates to membrane, where it is re–deposited, sometimes forming quite a dense band. This process may lead to deposition of Pt in the Nafion film covering agglomerates. As this film is thin, Pt particles may have an electric contact with the main cluster of Pt/C particles, and hence ORR would run also in the film.

### List of Symbols

- $K_N$ Marks dimensionless variables
- $b$ ORR Tafel slope $b = RT/\alpha F$, V
- $C_{dl}$ Double layer volumetric capacitance, F cm$^{-3}$
- $c_{ox}$ Oxygen molar concentration in the CCL pores, mol cm$^{-3}$
- $c_a$ Oxygen molar concentration in the agglomerate, mol cm$^{-3}$
- $c_N$ Oxygen molar concentration in Nafion film, mol cm$^{-3}$
- $c_{ref}$ Reference oxygen molar concentration, mol cm$^{-3}$
- $D_{ox}$ Effective oxygen diffusion coefficient in the CCL pores, cm$^2$ s$^{-1}$
- $D_N$ Oxygen diffusion coefficient in the agglomerate, cm$^2$ s$^{-1}$
- $d_N$ Oxygen diffusion coefficient in the Nafion film, cm$^2$ s$^{-1}$
- $d_N$ Nafion film thickness, cm
- $F$ Faraday constant, C mol$^{-1}$
- $j$ Local proton current density in the CCL, A cm$^{-2}$
- $j_0$ Cell current density, A cm$^{-2}$
- $i$ Imaginary unit
- $i_s$ Volumetric exchange current density, A cm$^{-3}$
- $l_c$ Catalyst layer thickness, cm
- $N_N$ Oxygen flux through the outer side of Nafion film, mol cm$^{-2}$ s$^{-1}$
- $N_N^1$, $N_N^{10}$ Coefficients in Eq. 34
- $\alpha_N$, $\beta_N$ Dimensionless coefficients in Eq. 33
- $\delta$ Dimensionless ratio $\delta = R_N/l_c$, Eq. 14
- $\epsilon$ Dimensionless ratio $\epsilon = l_s/R_a$
- $\eta$ Local ORR overpotential (positive by convention), V
- $\beta$ Dimensionless parameter, Eq. 14
- $\sigma_p$ CCL ionic conductivity, $\Omega^{-1}$ cm$^{-1}$
- $\phi$ Dimensionless parameter, Eq. 38
- $\omega$ Angular frequency ($\omega = 2\pi f$), s$^{-1}$
- $\omega_{ox}$ Characteristic frequency of oxygen transport in the CCL, s$^{-1}$, Eq. 54
- $\omega_N$ Characteristic frequency of oxygen transport in the Nafion film, s$^{-1}$, Eq. 47

### Subscripts

0 Membrane/CCL interface


