One of the best in situ methods for fuel cell characterization is electrochemical impedance spectroscopy (EIS). Application of a small AC potential perturbation to a working fuel cell allows one to separate contributions of various transport and kinetic processes running in the cell thanks to difference in time constants associated with the physical processes. However, understanding experimental impedance spectra requires quite sophisticated modeling. Over recent years, a lot of efforts has been done to develop physical models for a PEMFC impedance. Most of these models are numerical and they are slow to be used in algorithms for spectra fitting. A “faster” alternative is a model impedances have been derived in previous works; however, discarding the low-frequency (LF) points does not allow us to determine the oxygen diffusion coefficient in the gas-diffusion layer (GDL) and the resistivity due to oxygen transport in the channel.

In this work, we develop a most general physics-based analytical model for low-current PEM fuel cell impedance, which takes into account oxygen transport in the channel. The model is fast: fitting the model impedance to the experimental Nyquist spectrum takes about 2 minutes on a 2-GHz notebook.

Analytical expressions for all these impedances are derived assuming that the mean cell current density \( J \) is small. This means that the following relation must hold

\[
J \ll \min \left\{ \frac{\sigma_p b}{l_t}, \frac{4FD_{\text{ox}} c_1}{l_t} \right\}
\]

Here, \( \sigma_p \) is the mean through the CCL proton conductivity, \( b \) is the ORR Tafel slope, \( l_t \) is the CCL thickness, \( D_{\text{ox}} \) is the effective oxygen diffusion coefficient in the CCL, and \( c_1 \) is the oxygen concentration at the CCL/GDL interface. Eq. 1 means that \( J \) must be much less than the characteristic current densities for the proton and oxygen transport in the CCL. For typical PEMFC parameters (Table I) and the CCL thickness of 10⁻³ cm, Eq. 1 holds for the cell current densities below 100 mA cm⁻².

**Faradaic and proton transport impedance.** The expression for the combined charge transfer (faradaic) and proton transport impedance \( Z_{ct+p} \) is:

\[
Z_{ct+p} = \frac{l_t}{\sigma_p} \left( \frac{2}{\beta r} \right) \left( \frac{J_0(\phi)Y_0(\phi) - J_0(\phi)Y_0(\phi)}{J_0(\phi)Y_0(\phi)} \right)
\]

where

\[
\phi = \exp \left( \frac{\beta}{2} \right) \xi, \quad \xi = 2 \sqrt{\frac{j_0 l_t}{\sigma_p b} - \frac{i \omega C_d l_t^2}{\sigma_0}}.
\]

Here, \( J_0, Y_0, j_0 \) are the Bessel functions of the first and second kind, respectively, \( j_0 \) is the local cell current density (see below), \( C_d \) is the double layer capacitance, \( \sigma_p \) is the CCL proton conductivity at the CCL/membrane interface, and \( \omega \) is the angular frequency of the applied signal (\( \omega = 2\pi f, \) \( f \) is the regular frequency in Hz). Eq. 2 has been derived assuming that the proton conductivity \( \sigma_p \) decays exponentially through the CCL depth:

\[
\sigma_p = \sigma_0 \exp(-\beta x/l_t)
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Eq. 25</th>
<th>Eq. 23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope ( b ), mV</td>
<td>31.5</td>
<td>31.7</td>
</tr>
<tr>
<td>Mean proton conductivity ( \sigma_p ), ( \Omega^{-1} \text{cm}^{-1} )</td>
<td>0.0310</td>
<td>0.0347</td>
</tr>
<tr>
<td>Double layer capacitance ( C_d ), F cm⁻³</td>
<td>30.0</td>
<td>29.7</td>
</tr>
<tr>
<td>CCL oxygen diffusivity ( D_{\text{ox}} ), cm² s⁻¹</td>
<td>1.00 · 10⁻⁴</td>
<td>1.37 · 10⁻⁴</td>
</tr>
<tr>
<td>GDL oxygen diffusivity ( D_{\text{ox}} ), cm² s⁻¹</td>
<td>2.18 · 10⁻³</td>
<td>2.03 · 10⁻³</td>
</tr>
<tr>
<td>Effective air stoichiometry ( \lambda )</td>
<td>3.80</td>
<td>3.94</td>
</tr>
<tr>
<td>Parameter ( \beta ) in Eq. 4</td>
<td>7.20</td>
<td>7.30</td>
</tr>
</tbody>
</table>

The impedance due to oxygen transport in the GDL and channel.

Analytical expressions for all these impedances are derived assuming that the mean cell current density \( J \) is small. This means that the following relation must hold

\[
J \ll \min \left\{ \frac{\sigma_p b}{l_t}, \frac{4FD_{\text{ox}} c_1}{l_t} \right\}
\]

Here, \( \sigma_p \) is the mean through the CCL depth proton conductivity, \( b \) is the ORR Tafel slope, \( l_t \) is the CCL thickness, \( D_{\text{ox}} \) is the effective oxygen diffusion coefficient in the CCL, and \( c_1 \) is the oxygen concentration at the CCL/GDL interface. Eq. 1 means that \( J \) must be much less than the characteristic current densities for the proton and oxygen transport in the CCL. For typical PEMFC parameters (Table I) and the CCL thickness of 10⁻³ cm, Eq. 1 holds for the cell current densities below 100 mA cm⁻².
where $\beta$ is a dimensionless inverse characteristic scale of the exponent, $x$ is the distance from the membrane.

**Impedance due to oxygen transport in the catalyst layer.**—The low-current impedance due to oxygen transport in the CCL $Z_{\text{ox}}$ is given by

$$Z_{\text{ox}} = \frac{b}{j_0} \left( Z_W - \frac{\omega_0^\text{ct} \rho f}{\omega_0} + i \omega \left( \frac{1}{\omega_0} + \frac{1}{\omega_0^\text{ct}} \right) \right) \left( 1 + \frac{i \omega \rho f}{\omega_0} \right) \left( 1 + \frac{i \omega \rho f}{\omega_0^\text{ct}} \right) \left( 1 + \frac{i \omega \rho f}{\omega_0^\text{ct}} + \frac{1}{\omega_0^\text{ct}} \right)$$

where

$$\omega_0^\text{ct} = \frac{j_0}{4Fc_l l_\text{c}}, \quad \omega_0^\text{ct} = \frac{j_0}{C_{\text{bl}} b l_\text{c}},$$

are the characteristic frequencies,

$$Z_W = \frac{\tanh \left( \sqrt{j_0 + 4Fc_l l_\text{c}}/j_0 \right)}{\sqrt{j_0 + 4Fc_l l_\text{c}}/j_0}$$

is the dimensionless Warburg-like impedance, and $j_0$ is given in Eq. 1. Eq. 5 is obtained assuming that the undisturbed oxygen concentration and ORR overpotential are nearly constant throughout the CCL depth.\textsuperscript{27} Both assumptions hold when the cell current density obeys to Eq. 1.

**Impedance due to oxygen transport in the GDL and channel.**

In this section, the sign tilde marks dimensionless variables and parameters, defined as

$$\tilde{J}_0 = \frac{j_0 l_\text{c}}{\sigma_b}, \quad \tilde{\eta}_1 = \frac{\eta_1}{b}, \quad \tilde{l}_b = \frac{l_b}{l_\text{c}}, \quad \tilde{D}_b = \frac{4FD_b c_l^{\text{eq}}}{\sigma_b}, \quad \tilde{Z} = \frac{Z_{\text{ox}}}{l_\text{c}}$$

and the dimensionless frequency $\Omega$ is given by

$$\Omega = \frac{\alpha c_{\text{eq}} l_\text{c}^2}{\sigma_b}$$

Here, $l_\text{b}$ is the GDL thickness, $D_b$ is the effective oxygen diffusion coefficient in the GDL, $\eta_1$ is the amplitude of the applied potential perturbation, and $c_{\text{eq}}^0$ is the inlet oxygen concentration.

The combined local impedance due to oxygen transport in the channel and GDL $Z_{\text{gdl+e}}$ is given by the following chain of expressions:\textsuperscript{20}

$$Z_{\text{gdl+e}} = \frac{i}{\eta_1^0} \left( \frac{\tilde{c}_1^0 \tilde{\eta}_1^0}{\tilde{c}_1^0} \tilde{\eta}_1^0 - 1 \right)$$

where

$$\eta_1^0 = c_{\text{eq}}^0 \left( 1 - \frac{j_0 l_\text{c}}{D_b} \right).$$

and the static oxygen concentration at the CCL/GDL interface $c_1^0$ is given by

$$c_1^0 = \frac{c_1^0}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \left( \frac{j_0 c_1^0}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \sqrt{-i\Omega \mu} \right)^{-1} \left( \frac{c_1^0}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \sqrt{-i\Omega \mu} \right)^{-1}$$

where

$$\tilde{c}_1^0 = \frac{c_1^0}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \left( \frac{j_0 c_1^0}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \sqrt{-i\Omega \mu} \right)^{-1} \left( \frac{c_1^0}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \sqrt{-i\Omega \mu} \right)^{-1}$$

and the static oxygen concentration at the CCL/GDL interface $c_1$ is given by

$$c_1 = \frac{c_1}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \left( \frac{j_0 c_1}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \sqrt{-i\Omega \mu} \right)^{-1} \left( \frac{c_1}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \sqrt{-i\Omega \mu} \right)^{-1} \left( \frac{c_1}{\cos \left( \sqrt{-i\Omega \mu} \right)} - \sqrt{-i\Omega \mu} \right)^{-1}$$

The parameter $c_1$ depends on the perturbation of the local oxygen concentration in the channel $c_1$, which is

$$c_1^0 = c_1^0 \left( \frac{\gamma J}{f_s, J + \chi} + \frac{1}{\chi} (\beta + \alpha) \right) \exp \left( \frac{\chi^2}{\lambda J} \right)$$

where

$$\gamma J = \frac{J l_\text{c}}{\sigma_b}, \quad \chi = \frac{z^2}{L}$$

is the dimensionless mean cell current density and distance along the channel, respectively, $L$ is the channel length, $\lambda$ is the air (oxygen) flow stoichiometry

$$\lambda = \frac{4Fhe_{h \text{eq}}}{LJ}$$

is the inlet air flow velocity, $h$ is the channel depth, and $f_s = -\lambda \ln \left( 1 - \frac{1}{\lambda} \right)$.

Parameter $\chi$ is

$$\chi = -i\eta^0 \left( \sqrt{-i\Omega} \mu + \mu \sqrt{-i\Omega} \tan \left( \mu l_\text{c} \psi \right) - \frac{i f_s \sqrt{-i\Omega} \tan \left( \sqrt{-i\Omega} \mu \right)}{\Omega \cos^2 \left( \mu l_\text{c} \psi \right) - f_s \sqrt{-i\Omega} \tan \left( \sqrt{-i\Omega} \mu \right)} \right)$$

The local cell current density $j_0$ and the static oxygen concentration in the channel $c_1$ depend on the distance along the channel $\tilde{z}_0$:

$$j_0 = f_s J \left( 1 - \frac{1}{\lambda} \right)$$

$$c_1^0 = c_1^0 \left( 1 - \frac{1}{\lambda} \right)$$

This completely defines $Z_{\text{gdl+e}}$, Eq. 10. From Eqs. 15 and 13 it follows that $c_1^0 \sim \tilde{\eta}_1^0$ and hence $c_1^0 \sim \tilde{\eta}_1^0$; thus, the impedance (10) is independent of the applied potential perturbation $\eta_1^0$, provided that $\eta_1^0$ is small.

**Total impedance of the cathode side.**—Eqs. 2, 5 and 10 give the components of the local impedance of the cathode side $Z_{\text{loc}}$:

$$Z_{\text{loc}} = Z_{\text{ct+p}} + Z_{\text{ox}} + Z_{\text{gdl+e}}.$$  \hspace{1cm} \text{(22)}$$

Note that all the three terms in this sum depend on the distance along the channel through this dependence of $j_0$, Eq. 21; in addition, $Z_{\text{gdl+e}}$ depends on $\tilde{z}_0$ also through $c_1^0$, Eq. 15. Suppose that the cell is segmented into $N$ segments, each one having the local impedance $Z_{\text{loc}}$. Noting that all the segments are connected in parallel and taking the limit $N \to \infty$, for the total impedance of the cathode side we obtain

$$\frac{1}{Z_{\text{loc}}} = \int_0^\infty \frac{d\tilde{z}}{Z_{\text{loc}}}$$  \hspace{1cm} \text{(23)}$$

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Generally, the integral in Eq. 23 has to be calculated numerically, which dramatically slows down the fitting procedure (see below). However, numerical tests show that a good approximation of this integral can be obtained as following. Consider the equation \( j_0 = J \), or, taking into account Eq. 21

\[
f_J J \left(1 - \frac{1}{\bar{z}} \right) = J
\]

Solving this equation for \( \bar{z} \) we get a point \( \bar{z}_s \), where the local current density equals the mean current density:

\[
\bar{z}_s = \frac{\lambda \ln (f_s)}{f_s} \quad [24]
\]

where \( f_s \) is given by Eq. 18. Calculations show that for \( \lambda \geq 2 \), an accurate approximation of integral 23 is

\[
\int_0^1 \frac{d\bar{z}}{Z_{\text{loc}}} \simeq \frac{1}{Z_{\text{loc}}(\bar{z}_s)}
\]

From Eq. 23 we, thus, get

\[
Z_{\text{tot}} \simeq Z_{\text{loc}}(\bar{z}_s) \quad [25]
\]

Eq. 25 leads to much faster fitting code, as discussed below.

** Results and Discussion**

The model impedances have been fitted to an experimental spectrum of a PEM FC (Figure 1). Fitting has been performed in Maple environment using a built-in fitting procedure *NonlinearFit*. To start the fitting process, initial values for the fitting parameters have been specified, which give the model spectrum reasonably close to the experimental one. The merit function was the sum of squares (\( \text{Re}(Z) - \text{Re}(Z_{\text{exp}}) \))^2 + (\( \text{Im}(Z) - \text{Im}(Z_{\text{exp}}) \))^2, where the subscript \( \text{exp} \) denotes the experimental values. Note that the sum of squares above is minimized for every frequency point \( \omega \), which means that optimization is performed simultaneously in the Nyquist and Bode coordinates.

The spectrum has been measured at the cell current density of 100 mA cm\(^{-2}\), the experimental conditions are indicated in the caption to Figure 1; more details are given in Ref. 21. Note that in Ref. 21, the spectra have been measured from individual segments and from the whole cell; here we use the data for the whole cell. The LF arc in Figure 1 represents the combined oxygen transport in the GDL and cathode channel. Two variants of the model above have been fitted: approximate Eq. 25 (open circles in Figure 1), and Eq. 23 using numerical calculation of integral (dashed line in Figure 1). As can be seen, for both model variants the quality of fitting is very good; only the region between the LF and faradaic arcs is fitted not quite well (Figure 1). Note that the fitting points of the model Eq. 25 (open circles) are shown for the same frequencies as the measured points (filled circles). It is also seen that approximate Eq. 25 gives the curve which is very close to the “exact” curve from Eq. 23; however, the approximate model is nearly two orders of magnitude faster, than the exact model (2-3 min vs 3 hours on a standard PC).

Figure 1b shows the components of the total cathode side impedance. The GDL \( Z_{\text{gdl}} \) and channel impedance \( Z_c \) have been separated by setting \( \lambda = 1000 \) in Eq. 10; this gives the “pure” GDL impedance \( Z_{\text{gdl}} \). The channel impedance is then obtained as \( Z_c = Z_{\text{tot}} - Z_{\text{gdl}} \). As can be seen, the GDL and channel impedances are quite large. The fitting parameters resulted from the two model variants are listed in Table I. First we note, that both the models give almost the same parameters. Further, the Tafel slope and the mean proton conductivity agree well with the literature data.\(^{11,12} \) The double layer capacitance is 50% higher, than the value reported for this MEA in Ref. 21. Here, however, we used a more accurate equation for the impedance \( Z_{\text{ct}+p} \), which takes into account a rapid decay of the proton conductivity through the CCL depth, while in Ref. 21 this parameter was assumed to be independent of the distance from membrane. This leads to somewhat higher \( \sigma_p \) and \( C_{\text{ct}+p} \), as compared to Ref. 21. The oxygen diffusion coefficients in the CCL and GDL by the order of magnitude agree with those reported,\(^{21} \) taking into account that \( D_{\text{ox}} \) increases with the cell current density.\(^{31} \)

Note that the air stoichiometry \( \lambda \) has been declared as a fitting parameter. The reason is that Eqs. 21 and 15 have been derived for the cell with the straight channel. In experiment, however, the cell with the meander-like channel has been used.\(^{31} \) In this flow field, oxygen is transported under the rib between two adjacent turns of meander, which homogenizes the distribution of oxygen concentration along the cell surface. Experimental shape of local current along the channel of the meander-like flow field shows formation of plateau of \( j_0 \) in the middle of the channel (Figure 4 of Ref. 21). This plateau arises seemingly due to under-rib convection of oxygen and it changes the value of integral in Eq. 23. In our 1D+1D model, this “homogenization” of local current is effectively accounted for by higher air flow stoichiometry.

Another example of fitting is shown in Figure 2, which displays experimental and fitted Eq. 25 spectra of a high-temperature PEM fuel...
pared to that impedance in a low-T PEMFC (Figure 1b). This is explained by the five times thicker CCL in the HT-PEMFC.

To conclude we note that the shape of the low-frequency arc in the spectrum strongly depends on the stoichiometry of the air flow, and on the oxygen diffusion coefficient in the GDL. Thus, fitting the spectra using the model above allows us to reliably determine the GDL oxygen diffusivity and the resistivity due to oxygen transport in the channel.

Conclusions

A fast physics-based model for impedance of a PEM fuel cell operated under low stoichiometry of the air flow is developed. The model includes the charge-transfer and the proton transport impedance, and the oxygen transport impedances in the catalyst layer, gas diffusion layer, and in the cathode channel. The model is fast: fitting the model impedance to a single experimental spectrum takes about 2 min on a standard PC. The fitting returns seven parameters: the ORR Tafel slope, the mean proton conductivity of the CCL, the double layer capacitance, the oxygen diffusion coefficients in the CCL and GDL, the effective air flow stoichiometry, and the parameter describing the rate of proton conductivity decay with the distance from the membrane. The effective air flow stoichiometry is introduced to take into account the under-rib oxygen flow in the meander-like flow field.

Acknowledgments

The author is grateful to Dr. Tatyana Reshetenko (University of Hawaii) and to Dr. Mikhail Kondratenko (Moscow State University) for the experimental data and many useful discussions.

List of Symbols

- \( b \) ORR Tafel slope, V
- \( C_{dl} \) Double layer volumetric capacitance, F cm\(^{-3}\)
- \( c \) Oxygen molar concentration, mol cm\(^{-3}\)
- \( c_{ho} \) Reference oxygen concentration (concentration at the channel inlet), mol cm\(^{-3}\)
- \( D_{o} \) Effective oxygen diffusion coefficient in the GDL, cm\(^{-2}\) s\(^{-1}\)
- \( D_{ox} \) Effective oxygen diffusion coefficient in the CCL, cm\(^{-2}\) s\(^{-1}\)
- \( F \) Faraday constant, C mol\(^{-1}\)
- \( f \) Regular frequency, Hz
- \( J \) Mean cell current density, A cm\(^{-2}\)
- \( j_{0}, j_{1} \) Bessel functions of the first kind
- \( j_{o} \) Local cell current density, A cm\(^{-2}\)
- \( j_{ox} \) Characteristic current density for oxygen transport in the CCL, A cm\(^{-2}\)
- \( J_{p} \) Characteristic current density for proton transport in the CCL, A cm\(^{-2}\)
- \( h \) Channel depth, cm
- \( i \) Imaginary unit
- \( i_{o} \) Volumetric exchange current density, A cm\(^{-3}\)
- \( L \) Channel length, cm
- \( l_{i} \) Catalyst layer thickness, cm
- \( t \) Time, s
- \( v^{in} \) Inlet flow velocity, cm s\(^{-1}\)
- \( x \) Coordinate through the CCL, cm
- \( Y_{0}, Y_{1} \) Bessel functions of the second kind
- \( Z \) CCL impedance, \( \Omega \) cm\(^{-2}\)
- \( Z_{ct+p} \) Charge-transfer and proton transport impedance, \( \Omega \) cm\(^{-2}\)
- \( Z_{loc} \) Local impedance of the cathode side, \( \Omega \) cm\(^{-2}\)
- \( Z_{ox} \) Oxygen transport impedance in the CCL, \( \Omega \) cm\(^{-2}\)
- \( Z_{ox+cc} \) Oxygen transport impedance in the GDL and channel, \( \Omega \) cm\(^{-2}\)
- \( z \) Coordinate along the air channel, cm

---

**Table II. The fitting parameters for HT-PEMFC, Figure 2.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope ( b ), mV</td>
<td>42.1</td>
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<tr>
<td>Mean proton conductivity ( \sigma_{p} ), ( \Omega^{-1} ) cm(^{-1})</td>
<td>0.0536</td>
</tr>
<tr>
<td>Double layer capacitance ( C_{dl} ), F cm(^{-3})</td>
<td>18.5</td>
</tr>
<tr>
<td>CCL oxygen diffusivity ( D_{ox} ), cm(^{2}) s(^{-1})</td>
<td>0.892 \cdot 10^{-4}</td>
</tr>
<tr>
<td>GDL oxygen diffusivity ( D_{ox} ), cm(^{2}) s(^{-1})</td>
<td>6.53 \cdot 10^{-3}</td>
</tr>
<tr>
<td>Effective air stoichiometry ( \lambda )</td>
<td>3.37</td>
</tr>
<tr>
<td>Parameter ( \beta ) in Eq. 4</td>
<td>3.05</td>
</tr>
</tbody>
</table>
Greek

\[ \alpha \] Dimensionless parameter, Eq. 20
\[ \beta \] Characteristic parameter of \( \sigma_p \) decay, Eq. 4
\[ \gamma \] Dimensionless parameter, Eq. 20
\[ \lambda \] Air flow stoichiometry, Eq. 17
\[ \mu \] Dimensionless parameter, Eq. 14
\[ \rho \] Dimensionless parameter, Eq. 20
\[ \sigma \] CCL ionic conductivity, \( \Omega^{-1} \) cm\(^{-1} \)
\[ \sigma_0 \] Auxiliary dimensionless parameter, Eq. 3
\[ \sigma_p \] Auxiliary dimensionless parameter, Eq. 11
\[ \chi \] Dimensionless parameter, Eq. 19
\[ \psi \] Dimensionless parameter, Eq. 14
\[ \Omega \] Reduced dimensionless frequency, Eq. 9
\[ \omega \] Angular frequency (\( \omega = 2 \pi f \)), s\(^{-1} \)

Subscripts

0 Membrane/CCL interface
1 CCL/GDL interface
\( h \) Air channel
\( t \) Catalyst layer
* Characteristic value

Superscripts

\~ Marks dimensionless variables
0 Steady-state value
l Small-amplitude perturbation

References


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