Comparison of Two Physical Models for Fitting PEM Fuel Cell Impedance Spectra Measured at a Low Air Flow Stoichiometry

Tatyana Reshetenkoa,∗ and Andrei Kulikovskyb,c,∗

a Hawaii Natural Energy Institute, University of Hawaii, Honolulu, Hawaii 96822, USA
b Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK–3: Electrochemical Process Engineering, D-52425 Jülich, Germany

c Lomonosov Moscow State University, Research Computing Center, 119991 Moscow, Russia

Local impedance spectra of a segmented PEM fuel cell operated at an air flow stoichiometry of λ = 2 are measured. The local spectra are fitted with the recent 1D and quasi–2D (q2D) physical models for PEMFC impedance. The q2D model takes into account oxygen transport in the gas channel, while the 1D model ignores this transport assuming infinite stoichiometry of the air flow. Analysis of the q2D expression for the GDL electrode impedance Zgdl at λ → ∞ shows that the contribution of Zgdl to the total cell impedance rapidly decays with the frequency growth. We derive an equation for the boundary frequency flim, above which this contribution is small. We show that the 1D model can be fitted to the high–frequency part (f > flim) of a spectrum acquired at λ = 2, ignoring the low–frequency arc due to the oxygen transport in the channel. Comparison of fitting parameters resulted from the 1D and q2D models confirms this idea.

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Polymer electrolyte membrane fuel cells (PEMFCs) generate electricity due to splitting the hydrogen–oxygen combustion reaction into two half–reactions producing and consuming charged particles. Understanding transport and kinetic potential losses in these cells is crucial for cell design. Electrochemical impedance spectroscopy (EIS) provides a unique opportunity to separate contributions of different processes into the total potential loss in a cell.1,2 Deciphering experimental impedance spectra requires modeling though.

The simplest and fastest way to rationalize the spectra is the transmission line modeling (TLM). This approach aims at construction of equivalent electric circuit, which has a spectrum close to the measured one. The circuit is usually assembled out of $R$, $C$, and $L$–elements, and out of a number of elements representing classic impedances of electrochemical systems. Two well–known examples are the Warburg element,3 which describes impedance of a transport layer attached to a planar electrode, and Gerischer element4 representing impedance of a transport layer with the distributed chemical reaction. The TLM has been widely used in fuel cell studies (see e.g. Refs. 5 and 6); however, validity of this approach cannot be rigorously proved. First, the circuit is usually assembled out of $R$, $C$, and $L$–elements, and out of a number of elements representing classic impedances of electrochemical systems. Two well–known examples are the Warburg element,3 which describes impedance of a transport layer attached to a planar electrode, and Gerischer element4 representing impedance of a transport layer with the distributed chemical reaction. The TLM has been widely used in fuel cell studies (see e.g. Refs. 5 and 6); however, validity of this approach cannot be rigorously proved. First, there is no guarantee, that the selected equivalent circuit is unique. Second, the classic solutions for impedance of a system with the planar electrode are, in general, not applicable to a porous catalyst layer with the distributed electrochemical reaction.7,8 In addition, determination of the cell physical transport and kinetic parameters from the equivalent circuit elements is usually beyond the scope of the TLM.

This explains growing interest in physical modeling of PEMFC impedance.9–22 Generally, a physical impedance model can be obtained from any transient performance model of a cell by making a standard procedure of linearization and Fourier–transform (see e.g. Ref. 23 for mathematical details). The resulting system of linear equations for the perturbation amplitudes is, in general, a complex–valued boundary–value problem (BVP). We solve BVP discussed above by means of fitting this model to the experimental spectra acquired at a high stoichiometry of the air flow.29

Most of the physical impedance models ignore the impedance due to the air flow in the channel. This approach is justified if the air (oxygen) stoichiometry $\lambda$ of the flow is large. However, in real situations, PEMFCs operate at $\lambda \approx 2$, and the “channel” impedance could be quite significant.30–32 Recently, we developed a new quasi–2D model for impedance of a PEMFC with the straight air channel has been developed.8 This model includes the effect of the air flow in the channel on the cell impedance. Below, this model will be referred to as the q2D model.

In this work, we use the 1D7 and the q2D8 models as the tools for PEMFC characterization at a low stoichiometry of the air flow. We show that with the growth of the frequency of the exciting signal, the impedance due to the air flow in the channel vanishes. We calculate the frequency $f_{\text{lim}}$, above which this contribution is negligible. It follows, that the points with $f > f_{\text{lim}}$ of a low–stoichiometry spectrum can be fitted using the 1D model. Next, we fit the 1D and the q2D models to the local experimental spectra of the segmented cell operated at the air flow stoichiometry of $\lambda = 2$. Comparison of fitting parameters resulted from the two models validates the idea of using the 1D model for fitting a part of the spectra with $f > f_{\text{lim}}$.

Experimental

The experiments have been performed using Hawaii Natural Energy Institute’s (HNEI) segmented cell system.33 The segmented cell approach used in this study follows the ideas developed in Refs. 34–37. HNEI’s system is partially based on the design,34 using closed loop Hall sensors (Honeywell CSNN 191) and an improved data acquisition system, which allows us to perform simultaneous measurements of spatial EIS, linear sweep voltammetry and cyclic voltammetry.35 This diagnostic tool is operated as a single fuel cell using a GRandalytics test station. Standardized single fuel cell testing protocols were used for recording spatially resolved data. All experiments were carried out under galvanostatic control of the total cell current.

The segmented cell system consists of the cell hardware, the custom designed current transducer system, the data acquisition device and a single cell test station.33 The system allows the collection from 10 current channels in a high (standard) current mode and from 10 channels in a low current mode. The standard current mode enables

* Electrochemical Society Active Member.

E–mail: A.Kulikovsky@fz-juelich.de

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the measurement of segment current densities up to 2 A cm$^{-2}$. The low current mode yields measurement of current up to 50 mA cm$^{-2}$, which is typical for electrochemical diagnostics. Voltage and current signal data collection was performed with a National Instrument PXI data acquisition instrument operating on HNEI–developed LabView programs.

The segmented cell hardware consists of ten flow field segments forming a continuous path along ten parallel serpentine channels. Each segment is equipped with its own current collector and GDL and it has an area of 7.6 cm$^2$. The segmented hardware is applicable to either the anode or the cathode. The same channel designs are used for both the segmented and the standard flow fields (the reactant streams were arranged in a co-flow configuration).

The segmented cell was operated with commercially available 100 cm$^2$ membrane/electrode assembly (MEA) from Gore. The Pt/C loading of the anode and cathode electrodes was 0.4 mgPt cm$^{-2}$. Sigracet 25 BC was used as the anode and cathode gas diffusion layers (GDLs). The cathode used a segmented GDL and gasket configuration, whereas a uniform GDL was applied at the anode. The total active area of MEA was 76 cm$^2$. The gasket material was made of Teflon, with thicknesses of 125 μm for the anode and cathode.

The segmented cell was assembled, conditioned and tested by making the polarization curve measurements. The anode/cathode conditions were hydrogen/air at 2/2 and 2/10 stoichiometry, 100/50% relative humidity and ambient pressure. The cell temperature was 70°C. The frequency range for the EIS measurements was 0.05 Hz to 10 kHz and the amplitude of the sinusoidal current perturbation corresponded to the amplitude of the cell voltage response of 10 mV or lower. The impedance spectra were collected at the cell current density of 50 mA cm$^{-2}$.

Model

Model parameters and impedances.—The 2D model$^9$ has been developed for the linear segmented cell shown schematically in Figure 1. The total impedance $Z_e$ of the cathode side (Figure 1) is a sum of parallel local impedances

$$\frac{1}{Z_e} = \sum_{n=1}^{N} \frac{1}{Z_{ccl,n} + Z_{gdl,n}}$$

where $Z_{ccl,n}$ is the local impedance of the cathode catalyst layer (CCL), $Z_{gdl,n}$ is the local impedance of the gas–diffusion layer (GDL), and $N$ is the number of segments. In the limit of infinite number of segments, Eq. 1 transforms to

$$\frac{1}{Z_e} = \frac{1}{L} \int_0^L \frac{dz}{Z_{ccl}(z) + Z_{gdl}(z)}$$

where $Z_{ccl}(z)$ and $Z_{gdl}(z)$ are continuous functions of the coordinate $z$ along the air channel, and $L$ is the channel length. In the following, we will also use the total GDL impedance $Z_{gdl}$ defined as

$$\frac{1}{Z_{gdl}} = \frac{1}{L} \int_0^L \frac{dz}{Z_{gdl}(z)}$$

and the shifted along the real axis GDL impedance $Z_{gdl,s}$, calculated using the following relation

$$\frac{1}{Z_{gdl,s}} = \frac{1}{L} \int_0^L \frac{dz}{R_{cel} + Z_{gdl}}$$

where

$$R_{cel} = \frac{l_i}{3\sigma \mu} + \frac{b}{j_0}$$

is the static resistivity of the CCL with fast oxygen transport. Here $j_0 = f_s J_1^{1/2} N/L$ is the local current density in the cell and $f_s = -\lambda \ln \left(1 - \frac{1}{\lambda} \right)$ is a function of the air flow stoichiometry $\lambda$ defined as

$$\lambda = \frac{4F h^2 c_{in}^o}{L J}$$

In the equations above, $l_i$ is the CCL thickness, $b$ is the ORR Tafel slope, $\sigma$ is the CCL proton conductivity, $j_0$ is the local cell current density, $h$ is the channel height, $v^o$ is the inlet flow velocity, $c_{in}^o$ is the inlet oxygen molar concentration, and $J$ is the mean current density in the cell.

Analytical expressions for $Z_{ccl}$ and $Z_{gdl}$ were obtained in Ref. 23 and Ref. 7, respectively. Note that both the local $Z_{gdl}$ and the total $Z_{gdl}$ GDL impedances include the impedance due to the air flow in the channel. Equations 7 show that $Z_{ccl}$ and $Z_{gdl}$ depend on the oxygen concentration perturbation $c_{in}^o$ in the channel, while $Z_{ccl}(z)$ is independent of $c_{in}^o$ and hence it does not include the channel impedance. Therefore, the term “GDL impedance” is used below to denote the impedance of the system “GDL + flow field”, i.e., the general equation for the GDL impedance includes the impedance due to the oxygen transport in the channel.

In the context of this work, of special interest is the total GDL impedance at infinite air stoichiometry $Z_{gdl}^{\infty}$

$$\frac{\dot{Z}_{gdl}^{\infty}}{\dot{Z}_{gdl}} = \frac{\tan (\omega t \sqrt{k - i\Omega/B \dot{Z}_{gdl}})}{\mu \sqrt{k - i\Omega/B \dot{Z}_{gdl}(\dot{Z}_{gdl} - \dot{J}\Delta F) + i\Omega/J})}$$

where tilde marks the dimensionless variables

$$\dot{t}_b = \frac{t_b}{\tau_r}, \quad \dot{J} = \frac{J_i}{\sigma \beta b}, \quad \dot{Z} = \frac{Z_{in} - \dot{Z}_b}{\mu}, \quad \dot{J}_b = \frac{4F Db c_{in}^o}{a \beta b}$$

The reduced dimensionless frequency $\Omega$ is given by

$$\tilde{\omega} = \frac{\omega}{\tau_r}$$

where

$$\omega = \frac{C_{in} b}{2\tau_r}$$

Note that $\tau_r$ is the characteristic time of double layer charging.

The parameters $\epsilon$ and $\mu$ are

$$\epsilon = \sqrt{\frac{\sigma \beta b}{2I J^2}}$$

and

$$\mu = \frac{4F c_{in}^o}{C_{in} b}$$

Here $b$ is the GDL thickness, $\omega$ is the circular frequency of the exciting signal ($\omega = 2\pi f$), $C_{in}$ is the double layer volumetric capacitance (F cm$^{-3}$), $I$ is the ORR volumetric exchange current density (A cm$^{-3}$), and $f$ is the frequency range for the EIS measurements. The reduced dimensionless frequency $\tilde{\omega}$ is given by

$$\tilde{\omega} = \frac{\omega}{\tau_r}$$
and $D_b$ is the oxygen diffusion coefficient in the GDL. The superscript \textit{gdl} marks the values at the channel inlet, and the subscripts $h$, $b$ and $t$ mark the values in the channel, GDL and CCL respectively.

The q2D model\cite{7} and, in particular, Eq. 9 have been obtained assuming oxygen transport in the CCL. This limits the cell current densities, for which the model is applicable (see Discussion section). 1D model,\cite{7} which is taken below for comparison with the q2D model, has been designed assuming that the contribution of oxygen transport to the total cell impedance is small, but non-negligible. Accurate least-squares fitting algorithm based on 1D model is able to capture these small contributions and it gives the respective transport parameters (see Ref. 7 for further discussion). Note also that at high $\lambda$, all the local GDL impedances in Figure 1 are the same, and hence Eq. 9 describes both the local and the total GDL impedances. It is also worth noting that Eq. 9 differs from the Warburg impedance for the transport layer of a finite thickness, due to the presence of the frequency-dependent factor $(1 + i\Omega / J)$ in the denominator (see Ref. 8 for detailed discussion).

**At what frequencies is the GDL impedance important?**—To answer this question, we have to calculate the modulus $|\tilde{Z}_{\text{gdl}}^{\infty}|$. Direct calculation of $|\tilde{Z}_{\text{gdl}}^{\infty}|$ from Eq. 9 leads to a rational expression containing the terms with sin– and cos–functions, and with hyperbolic sinh– and cosh–functions of the same argument, given by the left side of Eq. 15. If this argument exceeds 2

$$\frac{2\Omega}{D_b} > 2,$$  \hspace{1cm}  [15]

the terms with the sin– and cos–functions can be neglected, and we come to

$$|\tilde{Z}_{\text{gdl}}^{\infty}| \simeq \frac{1}{\mu(D_b - Jb)} \frac{J^2 D_b}{\Omega(\Omega^2 + J^2)}.$$ \hspace{1cm}  [16]

In dimensional form, Eq. 15 gives the minimal frequency $f_{\text{min}}$, at which Eq. 16 holds:

$$l_b \frac{4\pi}{D_b} > 2, \quad \text{or} \quad f > f_{\text{min}} = \frac{D_b}{\pi l_b^2}$$ \hspace{1cm}  [17]

For the set of parameters in Tables I, II, Eq. 17 gives $f_{\text{min}} \simeq 6.58$ Hz. It is advisable to estimate $|\tilde{Z}_{\text{gdl}}^{\infty}|$ at the frequencies satisfying to Eq. 17. At small current densities $J \ll 1$, the CCL charge-transfer resistivity $1/J$ is much greater than unity. Thus, the condition $|\tilde{Z}_{\text{gdl}}^{\infty}| = 1$ gives the minimal frequency $\Omega_\ast$, at which the contribution of $Z_{\text{gdl}}^{\infty}$ to the total impedance becomes small. Equating 16 to unity and solving the resulting cubic equation for $\Omega$, we get a single real root of this equation:

$$\Omega_\ast = \frac{1}{6} \left( \frac{12J^2(\sqrt{12A^4J^2 + 81D_b^2} + 9D_b)}{A^2} \right)^{1/3} - \left( \frac{(12A^4J^2)^{3/2}}{\sqrt{12A^4J^2 + 81D_b^2} + 9D_b} \right)^{1/3}$$ \hspace{1cm}  [18]

where

$$A = \mu(D_b - Jb).$$ \hspace{1cm}  [19]

From Eq. 16 it follows that $|\tilde{Z}_{\text{gdl}}^{\infty}|$ decays with $\Omega$ as $\Omega^{-3/2}$; thus, for $\Omega > \Omega_\ast$, the contribution of the GDL impedance to the total cell impedance is small and it progressively decreases with $\Omega$. The dimensional regular frequency $f_\ast$, corresponding to $\Omega_\ast$ is

$$f_\ast = \frac{\varepsilon \Omega}{2\pi \tau} = \frac{\sigma \Omega}{2\pi l_b^2 C_{\text{gdl}}}.$$ \hspace{1cm}  [20]

With the data from Tables I, II, Eq. 20 gives

$$f_\ast \simeq 3.74 \text{ Hz}.$$ \hspace{1cm}  

Noting that Eq. 17 must also be fulfilled, we finally get the following condition for the regular frequencies, at which $|\tilde{Z}_{\text{gdl}}^{\infty}|$ is small:

$$f > f_{\text{lim}} = \max \left\{ f_{\text{min}} = \frac{D_b}{\pi l_b^2}, \quad f_\ast = \frac{\sigma \Omega}{2\pi l_b^2 C_{\text{gdl}}} \right\}$$ \hspace{1cm}  [21]

With the data in Tables I, II, Eq. 21 holds for the frequencies $f > 10$ Hz.

Note that the condition Eq. 17 is sufficient, but not necessary. This condition determines validity of Eq. 16, which simplifies the analysis above. If, however, the GDL diffusivity $D_b$ is large, Eq. 17 could be restrictive. For $D_b \rightarrow \infty$, from Eq. 9 we find

$$|\tilde{Z}_{\text{gdl}}^{\infty}| \simeq \frac{\tilde{I}_b}{D_b \sqrt{1 + (\Omega/J)^2}}, \quad D_b \rightarrow \infty$$

From this equation it follows, that at large $D_b$, $|\tilde{Z}_{\text{gdl}}^{\infty}| < 1$ at all frequencies $\Omega$, or, equivalently, at all regular frequencies $f$.

Clearly, at any finite stoichiometry $\lambda$, the total GDL impedance $Z_{\text{gdl}}^{\ast}$ satisfies to

$$|\tilde{Z}_{\text{gdl}}^{\infty}| > |\tilde{Z}_{\text{gdl}}^{\ast}|$$ \hspace{1cm}  [22]

At low frequencies, the inequality \textit{22} holds with a large margin, as finite $\lambda$ dramatically increases $|\tilde{Z}_{\text{gdl}}^{\ast}|$ due to a finite rate of oxygen transport in the channel (Figure 2a). However, with the growth of the frequency $\Omega$, $|\tilde{Z}_{\text{gdl}}^{\ast}|$ tends to $|\tilde{Z}_{\text{gdl}}^{\infty}|$.

This effect is illustrated in Figure 2, which shows the model spectra of the total dimensionless cell impedance $Z_\ast$, Eq. 2, at various stoichiometries of the air flow. Figures 2b, 2c show the spectra of the shifted total GDL impedance $Z_{\text{gdl},s}$, Eq. 4, for the several values of $\lambda$. As can be seen, starting from a certain frequency, the finite–$\lambda$ GDL impedance $Z_{\text{gdl},s}$ approaches the infinite–$\lambda$ impedance $Z_{\text{gdl},s}$, represented by the curve for $\lambda = 100$ in Figure 2c. The higher the stoichiometry $\lambda$, the closer to $Z_{\text{gdl}}^{\infty}$, is located the respective curve $Z_{\text{gdl},s}$ (Figure 2c). Thus, at a certain frequency, the inequality in Eq. 22 transforms into “approximately equals to” sign. From this frequency on, both the sides of Eq. 22 are close to each other and small, and according to Eq. 16, the decay as a power function of $\Omega$, $|\tilde{Z}_{\text{gdl}}^{\ast}| \simeq |\tilde{Z}_{\text{gdl}}^{\infty}| \sim \Omega^{-3/2}$ (Figure 2c).

The data plotted in Figure 2 show that the frequency separating the regions of exponential and power decay of $\tilde{Z}_{\text{gdl}}^{\ast}$ with $\Omega = f_\ast$, Table I. PEM fuel cell physical and operational parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDL thickness $l_b$, cm</td>
<td>0.022</td>
</tr>
<tr>
<td>CCL thickness $l_c$, cm</td>
<td>0.0015</td>
</tr>
<tr>
<td>Channel height $h$, cm</td>
<td>0.1</td>
</tr>
<tr>
<td>Cell temperature $T$, K</td>
<td>273 + 70</td>
</tr>
<tr>
<td>Mean current density $J$, A cm$^{-2}$</td>
<td>0.05</td>
</tr>
<tr>
<td>Oxygen stoichiometry $\lambda$</td>
<td>2.0</td>
</tr>
<tr>
<td>Exchange current density $i_e$, A cm$^{-3}$</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table II. The average cell parameters resulted from impedance spectra fitting. The cell current density is 50 mA cm$^{-2}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope $b$, V</td>
<td>0.031</td>
</tr>
<tr>
<td>CCL proton conductivity $\sigma_p$, $\Omega^{-1}$ cm$^{-1}$</td>
<td>0.02</td>
</tr>
<tr>
<td>Double layer capacitance $C_{\text{d}}$, F cm$^{-3}$</td>
<td>22</td>
</tr>
<tr>
<td>Oxygen diffusion coefficient in the CCL $C_{\text{d}}$, D cm$^{-3}$ s$^{-1}$</td>
<td>0.6 - 10$^{-4}$</td>
</tr>
<tr>
<td>Oxygen diffusion coefficient in the GDL $D_{\text{gdl}}$, cm$^{-2}$ s$^{-1}$</td>
<td>0.01 (variable) 0.008 (variable)</td>
</tr>
<tr>
<td>Average effective air stoichiometry</td>
<td>6.28</td>
</tr>
</tbody>
</table>

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part of the impedance spectrum for fitting the 1D model\textsuperscript{7} to GDL impedances, as integration along
\[ z = \lambda \text{ Re} \left( \tilde{Z} \right) \]
Clearly, the same is true for the local part of the spectrum only.
\( \tilde{Z} \)

Eq. 20 (arrows in Figure 2c). Unfortunately, we were not able to

Fast decay of this contribution with the frequency growth. (c) Zoomed window in (b). Parameters for calculations are listed in Tables I, II.

The q2D model\textsuperscript{8} fitted to the full set of the experimental

Figure 2. (a) q2D model spectra for the indicated values of the flow stoichiometry \( \lambda \). Note the coordinates \( J \tilde{Z} \). (b) Contributions due to the oxygen transport in the GDL and channel to the total impedance spectra. Note a very fast decay of this contribution with the frequency growth. (c) Zoomed window in (b). Parameters for calculations are listed in Tables I, II.

For comparison, the “ideal” 1D distribution of local current (Eq. 6) corresponding to the straight-channel cell\textsuperscript{19} is also shown in this Figure. The experimental and fitted spectra of the whole fuel cell for the current density of 50 mA cm\textsuperscript{-2} and the stoichiometry of \( \lambda = 2 \) are shown in Figure 5.

The q2D model was fitted to the data assuming that the flow stoichiometry \( \lambda \) is a fitting parameter. We were not able to obtain good quality of fitting with the fixed stoichiometry of \( \lambda = 2 \). The reason is that the q2D model is constructed for a linear cell with a straight air channel, while in experiment we employed a true 2D cell with meander–like channels.\textsuperscript{38} In a cell with the meander–like flow field, oxygen is transported between the adjacent turns of the meander due to under–rib diffusion and convection; these processes are ignored in the q2D model. Indeed, Figure 4 shows that in segments 6–9, the local current exceeds the 1D value. We attribute this effect to under–rib oxygen transport in the cell, which homogenizes oxygen distribution over the cell surface. Treating \( \lambda \) as a fitting parameter allows us to obtain the effective stoichiometry \( \lambda_{e f f} \), which in effective manner describes the quality of the oxygen distribution over the cell surface. For the air stoichiometry of \( \lambda = 2 \), the average value of \( \lambda_{e f f} \) is 6.28 (Table II). This issue will be discussed in more detail in a separate publication.

Based on the quality of fitting, two domains can be distinguished in the cell. The first domain resides close to the oxygen channel inlet (segments 1 to 4). In this domain, both the 1D and q2D models fit the data reasonably well (Figure 3). In the second domain located in the middle and “remote” parts of the cell (segments 5–10) the quality of data fitting by the q2D model\textsuperscript{10} progressively worsens toward the outlet. In 10-th segment, no successful fitting was obtained with this model (Figure 3). In contrast, in all the segments, the solid curves representing the 1D model\textsuperscript{1} fit well the “faradaic” arc (Figure 3).

Comparison of the fitting parameters obtained with the two models is shown in Figure 6; the open circles represent the q2D model, while the filled circles correspond to the 1D model. Dotted lines show the average over the cell surface parameters from the 1D model (Figure 6). The results from the two models are close to each other; however, due to higher quality of data fitting, the 1D model results seem to be more reliable, as they exhibit smaller variation over the cell surface. The Tafel slopes resulted from the two models are close.

### Fitting Results and Discussion

**Low air flow stoichiometry (\( \lambda = 2 \)).**—Before fitting, the raw impedance spectra have been processed according to the following protocol. The high–frequency points with the positive imaginary part have been excluded from consideration, as these points exhibit the effect of cable inductance. Further, the remaining high–frequency points (in the frequency range between 1 kHz and 123 Hz) have also been excluded from fitting. These points exhibit the arc of yet undefined nature.\textsuperscript{39,40} Similar arc has been detected in our experiments with the pure oxygen feed.\textsuperscript{29} Here this arc is less pronounced; nonetheless, it “hides” the high–frequency straight line with the 45\textdegree–slope, which describes proton transport in the CCL.\textsuperscript{23,41}

Generally, there are two options to treat this arc. The first one is to model the arc by a parallel RC–circuit; this approach has been taken in Ref. 29. It gives good quality of spectra fitting in the high–frequency (HF) domain; however, the resulting CCL proton conductivity \( \sigma_p \) seems to be overestimated by a factor of two to three.\textsuperscript{29} In this work, we simply ignored the HF arc points by setting in the fitting algorithms the respective weight factors to zero. This approach results in minimal variation of \( \sigma_p \) between different segments, as discussed below; moreover, the values of \( \sigma_p \) agree well with the literature data. It is important to emphasize that both the approaches affect only the value of \( \sigma_p \), leaving the other parameters practically intact.

Least–squares fitting has been performed in Maple environment using the matrix form of NonlinearFit procedure. Fitting of a single impedance spectrum using 1D and q2D models takes less than one minute on a standard PC. The Maple worksheet with the 1D model fitting code is available for download at https://github.com/akulikovsky/Fitting_Procs/issues/1. Figure 3 shows the experimental spectra (points) of individual segments fitted using the two models: the dashed lines represent the q2D model\textsuperscript{8} fitted to the full set of the experimental points, while the solid lines show the 1D model\textsuperscript{7} fitted to the points satisfying to Eq. 21. While fitting the 1D model, the measured local current density in the segments was used and the local oxygen concentration in the channel was calculated according to\textsuperscript{38}

\[
c_h(z) = c_{h0} \left( 1 - \frac{1}{\lambda} \right)^{z/L} \tag{23}
\]

Measured local current density in each segment is shown in Figure 4. For comparison, the “ideal” 1D distribution of local current (Eq. 6) corresponding to the straight–channel cell\textsuperscript{19} is also shown in this Figure. The experimental and fitted spectra of the whole fuel cell for the current density of 50 mA cm\textsuperscript{-2} and the stoichiometry of \( \lambda = 2 \) are shown in Figure 5.

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Comparison of the fitting parameters obtained with the two models is shown in Figure 6; the open circles represent the q2D model, while the filled circles correspond to the 1D model. Dotted lines show the average over the cell surface parameters from the 1D model (Figure 6). The results from the two models are close to each other; however, due to higher quality of data fitting, the 1D model results seem to be more reliable, as they exhibit smaller variation over the cell surface. The Tafel slopes resulted from the two models are close.
Figure 3. The experimental (points) and fitted (lines) spectra for the oxygen stoichiometry of $\lambda = 2$. Oxygen inlet is at segment 1; the bold arrows indicate the direction of the air flow. Dashed lines show the q2D model fitted to the complete set of experimental points. The solid lines exhibit the 1D model fitted to the sufficiently high–frequency points, with $f$ satisfying to Eq. 21. The data for the last segment 10 has not been fitted by the q2D model due to large noise in the low–frequency points. Inside each frame, small arrows indicate the most low–frequency point used for the 1D model fitting.

Figure 4. Measured (points) and model, Eq. 6, local current densities in the cell.

The 1D model gives fairly uniform CCL proton conductivity over the cell surface (Figure 6b), with the surface–average value of 0.02 $\Omega^{-1}$ cm$^{-1}$. This value is close to $\sigma_p$ reported in Ref. 41 (0.01 to 0.03 $\Omega^{-1}$ cm$^{-1}$) from impedance measurements. The q2D model gives somewhat lower surface–average $\sigma_p$, though it is close to 0.02 $\Omega^{-1}$ cm$^{-1}$ (Figure 6b). The double layer capacitances from the 1D and the q2D models are also close to each other; the surface–average value of 22 F cm$^{-3}$ agrees well with the literature data41 (Figure 6c). The 1D model gives the oxygen diffusion coefficient $D_{ox}$ in the CCL, a parameter, which cannot be obtained from the q2D model (Figure 6d). The average over the cell surface value of $D_{ox}$ is about $6 \cdot 10^{-5}$ cm$^2$ s$^{-1}$, which agrees with the oxygen diffusivity in water at 70 $\degree$C.42 Molecular dynamics simulations of Malek, Mashio and Eikerling43 show that the thickness of Nafion film covering Pt/C agglomerates in the CCL does not exceed ten nanometers. Elementary estimate shows that oxygen penetrates through such a thin film without size–able losses. Thus, most of the oxygen transport losses in the CCL occur in the void space between Pt/C agglomerates. The value of $D_{ox}$

to each other (Figure 6a). The variation of $b$ along the channel from the 1D model is minimal and it follows the shape of the local current density (cf. filled circles in Figure 6a and in Figure 4).
The surface-average are indicated in Figure 6 as zero segment points. The right panel shows the solid lines – 1D model fitted to the filled circles only. The fitting parameters are indicated in Figure 6 as zero segment points. The right panel shows the high-frequency part of the spectrum.

above suggests that this space is severely flooded (see also Discussion section).

The shape of the oxygen diffusivity $D_{o}$ in the GDL along the oxygen channel, which results from the 1D model is shown in Figure 6d. The surface–average value of this parameter is about 0.01 cm$^2$ s$^{-1}$; however, $D_{o}$ exhibits distinct decay toward the channel outlet, which suggests progressive GDL flooding along $z$ (Figure 6d). The surface–average $D_{o} \simeq 0.01$ cm$^2$ s$^{-1}$ seems to be reasonable, as the GDL in our cell is equipped with the micro–porous layer (MPL), which lowers the effective diffusivity of the system “GDL+MPL”. In our experiments, the MPL thickness is $\sim 50$ μm, and the MPL has similar to the CCL values of porosity and pore size.44–49 Note that no data on in situ measurements of $D_{o}$ are available in literature.

The “GDL” oxygen diffusivity resulted from the q2D model is indicated in Figure 6e together with the average diffusion coefficient $D_{eff}$ in the CCL and the GDL, resulted from the 1D model. The latter parameter has been calculated according to

$$\frac{l_{t} + l_{b}}{D_{eff}} = \frac{l_{t}}{D_{o}^{CCL}} + \frac{l_{b}}{D_{o}^{GDL}}$$

[24]

As can be seen, calculated $D_{eff}$ is close to the value of the “GDL diffusivity”, resulted from the q2D model (Figure 6e). This suggests, that the q2D model gives, in fact, the average (effective) oxygen diffusion coefficient in the CCL and the GDL. The oxygen transport in the CCL is ignored in the q2D model, and this model assigns the respective transport loss to the GDL. Similar effect has been observed in Refs. 28 and 7. In Ref. 28, the impedance model of the CCL only was fitted to the experimental spectrum; in Ref 7, the “CCL+GDL” model was fitted to the same spectrum. In both the cases, oxygen transport in the CCL was taken into account. The results show that the GDL transport loss, which is ignored in the CCL-only model, simply reduces the effective CCL oxygen diffusivity, not changing the other model parameters. We can cautiously conclude, that the neglect of either CCL, or GDL oxygen diffusion in the impedance models discussed changes only the diffusion coefficient of the layer, which has been taken into account. In other words, by ignoring the oxygen transport in the CCL in the q2D model, we only get lower value of the oxygen diffusion coefficient in the GDL from this model, not changing the other physical parameters.

The parameters resulted from fitting the spectra of the whole fuel cell (Figure 5) are shown in Figure 6 as the zero-segment data. These parameters are not far from the surface–average data, indicated by the dashed lines in Figure 6. Thus, the results of this work are valid for the spectra measured with standard non-segmented cells.

High air flow stoichiometry ($\lambda = 10$)—The idea of using the 1D model for fitting the HF part of the low-lambda spectra can be verified by measuring the local spectra for the same MEA under high stoichiometry of the flow, when the $\lambda$-effects vanish. Comparison of the 1D fitting parameters for these spectra to the parameters obtained in the previous subsection could justify this approach.

The experimental and fitted 1D model local spectra for $\lambda = 10$ are shown in Figure 7. Note a quite well expressed second (low–frequency) arc in the last segments (7 to 10). This arc arises due to progressive worsening of the oxygen transport in the GDL in the direction of air flow. Even at the current density of 50 mA cm$^{-2}$, liquid water tends to accumulate in the last segments of the cell, and it reduces the GDL oxygen diffusivity in these segments. This effect is clearly seen in Figure 8, which shows the fitting parameters for the curves in Figure 7. The GDL diffusion coefficient $D_{o}$ decreases.
Figure 7. The experimental (points) and fitted 1D model (lines) spectra for the flow stoichiometry of $\lambda = 10$. Oxygen inlet is at segment 1; arrows indicate the direction of the air flow.

toward the channel outlet (Figure 8d). The same trend exhibits $D_b$ in Figure 6d.

The other parameters in Figure 8 agree with those obtained in the regime with $\lambda = 2$ (Figure 6). The only exception is the CCL proton conductivity, which appears to be twice lower in the regime with $\lambda = 10$ (cf. Figures 6b and 8b). Note that the spread of the points in Figure 8b is minimal, i.e., $\sigma_p$ is fairly uniform along the cell surface. Lower conductivity in the regime with $\lambda = 10$ can be explained by a faster rate of liquid water removal from the cell by the air flow of a higher velocity.

Twice lower $\sigma_p$ in the regime with $\lambda = 10$ qualitatively agrees with the growth of the high–frequency resistivity (HFR) of the cell, defined as the shift of the raw impedance spectra from the origin of coordinate along the real axis. The dominating part of this resistivity is due to the proton transport in membrane. Table III shows that the higher air flow velocity lowers the membrane proton conductivity, seemingly due to faster liquid water removal from the cell.

Discussion.—Both the 1D and the q2D models are valid provided that the cell current density $J$ is low:7,8

$$J \ll \min \left\{ \frac{j_\ast}{l}, \frac{j_D}{l} = \frac{4FD_o c_1}{l_i} \right\}$$

Here, $j_\ast$ and $j_D$ are the characteristic current densities for proton and oxygen transport in the CCL, respectively, and $c_1$ is the oxygen concentration at the CCL/GDL interface. For the estimate, at the cell current density of 50 mA cm$^{-2}$ we can neglect the oxygen transport losses in the GDL and set $c_1$ equal to the oxygen concentration in air. With the parameters in Table I and in Figure 6, we get $j_\ast \simeq 450$ mA cm$^{-2}$ and $j_D \simeq 100$ mA cm$^{-2}$. Thus, the inequalities $J \ll j_\ast$ and $J < j_D$ hold rather than Eq. 25, which means that the experimental spectra could be slightly depressed due to the oxygen transport in the CCL. This depression has been ignored in the analysis above.
The effective CCL oxygen diffusivity would be about 0.11. Thus, if all the oxygen were transported in the dissolved form, the effective average oxygen diffusion coefficient in the CCL could be corrected based on the following arguments.

- Low value of the oxygen diffusion coefficient in the CCL
- Tafel slope doubling due to oxygen transport in the CCL occurs.

We derive an equation for the boundary frequency \( \omega_{\text{lim}} \) and show that starting from \( f > \omega_{\text{lim}} \), the contribution of the oxygen transport in the system “channel + GDL” to the total cell impedance is small. This allows us to fit the 1D model to the points with \( f > \omega_{\text{lim}} \) only. Therefore, the q2D model has been fitted to the full set of impedance points, while the 1D model has been fitted to the points with \( f > \omega_{\text{lim}} \) only. The quality of curve fitting with the 1D model appears to be high. The fitting parameters resulted from the 1D and q2D models agree well, though the q2D model gives larger spread of parameters between the individual segments.

In addition, the local spectra for \( \lambda = 10 \) have been measured and fitted using the 1D model. The resulting set of fitting parameters agrees well with the set obtained in the case of \( \lambda = 2 \), except the CCL proton conductivity, which appears to be twice lower. We attribute this to a faster rate of liquid water removal from the cell by the air flow of a higher velocity. We conclude that the 1D model can be used for characterization of a PEM fuel cell running at a low stoichiometry of the air flow, provided that the impedance points satisfying to Eq. \( \lambda \) have been measured and fitted using the 1D model. The quality of curve fitting with the 1D model appears to be high. The fitting parameters resulted from the 1D and q2D models agree well, though the q2D model gives larger spread of parameters between the individual segments.

Table III. The local high-frequency resistivity of the cell (\( \Omega \cdot \text{cm}^2 \)) in the regimes with the air flow stoichiometry 2 and 10.

<table>
<thead>
<tr>
<th>Segment</th>
<th>HFR@( \lambda ) = 2</th>
<th>HFR@( \lambda ) = 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>0.0607</td>
<td>0.0719</td>
</tr>
<tr>
<td>02</td>
<td>0.0626</td>
<td>0.0755</td>
</tr>
<tr>
<td>03</td>
<td>0.0637</td>
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<td>04</td>
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<tr>
<td>05</td>
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<td>0.0704</td>
</tr>
<tr>
<td>06</td>
<td>0.0538</td>
<td>0.0684</td>
</tr>
<tr>
<td>07</td>
<td>0.0553</td>
<td>0.0697</td>
</tr>
<tr>
<td>08</td>
<td>0.0510</td>
<td>0.0642</td>
</tr>
<tr>
<td>09</td>
<td>0.0514</td>
<td>0.0613</td>
</tr>
<tr>
<td>10</td>
<td>0.0527</td>
<td>0.0610</td>
</tr>
</tbody>
</table>

Conclusions

We measure local impedance spectra of the segmented cell operated at the air flow stoichiometry of \( \lambda = 2 \). The spectra have been fitted using the two recent physical models for the PEMFC impedance. The 1D model assumes infinite rate of the oxygen transport in the channel, while the quasi-2D model takes into account a finite rate of this transport. Analysis of the q2D equation for the total GDL impedance at an infinite stoichiometry of the air flow shows that this impedance rapidly decays with the growth of the frequency of the exciting signal.

Acknowledgments

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List of Symbols

- \( f \) - Regular frequency, Hz
- \( f_{\lambda} \) - Function of the oxygen stoichiometry \( \lambda \), Eq. 7
- \( F \) - Faraday constant, C mol\(^{-1}\)
- \( j \) - Mean current density in the cell, A cm\(^{-2}\)
- \( j_0 \) - Local cell current density, A cm\(^{-2}\)
- \( \lambda \) - Marks dimensionless variables
- \( b \) - Tafel slope, V
- \( C_{\text{dl}} \) - Double layer volumetric capacitance, F cm\(^{-3}\)
- \( c \) - Oxygen molar concentration in the CCL, mol cm\(^{-3}\)
- \( c_b \) - Oxygen molar concentration in the channel, mol cm\(^{-3}\)
- \( c_{\text{ch}} \) - Oxygen molar concentration at the channel inlet, mol cm\(^{-3}\)
- \( D_{\text{ox}} \) - Oxygen diffusion coefficient in the CCL, cm\(^2\) s\(^{-1}\)
- \( D_{\text{GDL}} \) - Oxygen diffusion coefficient in the GDL, cm\(^2\) s\(^{-1}\)
- \( \mathrm{H}_F \) - Henry constant
- \( \Omega \) - Total cell impedance, \( \Omega \cdot \text{cm}^2 \)
- \( \Omega_{\text{lim}} \) - Boundary frequency
- \( \Omega_1 \) - Frequency of the exciting signal
- \( \chi_{\text{cell}} \) - Mean cell electrical resistance, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{GDL}} \) - Mean GDL electrical resistance, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{CCL}} \) - Mean CCL electrical resistance, \( \Omega \cdot \text{cm}^2 \)
- \( \Omega_{\text{CL}} \) - Total electrical resistance of the cell, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{inlet}} \) - Electrical resistance of the channel inlet, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{channel}} \) - Electrical resistance of the channel, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{GDL}} \) - Electrical resistance of the GDL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{CCL}} \) - Electrical resistance of the CCL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{channel}} \) - Electrical resistance of the channel, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{GDL}} \) - Electrical resistance of the GDL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{CCL}} \) - Electrical resistance of the CCL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{channel}} \) - Electrical resistance of the channel, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{GDL}} \) - Electrical resistance of the GDL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{CCL}} \) - Electrical resistance of the CCL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{channel}} \) - Electrical resistance of the channel, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{GDL}} \) - Electrical resistance of the GDL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{CCL}} \) - Electrical resistance of the CCL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{channel}} \) - Electrical resistance of the channel, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{GDL}} \) - Electrical resistance of the GDL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{CCL}} \) - Electrical resistance of the CCL, \( \Omega \cdot \text{cm}^2 \)
- \( \chi_{\text{channel}} \) - Electrical resistance of the channel, \( \Omega \cdot \text{cm}^2 \)
Small–amplitude perturbation

Characteristic current density for proton transport in the CCL, Eq. 25, A cm\(^{-2}\)

Characteristic current density for oxygen transport in the CCL, Eq. 25, A cm\(^{-2}\)

Channel height, cm

Imaginary unit

Volumetric exchange current density, A cm\(^{-3}\)

Channel length, cm

Catalyst layer thickness, cm

Number of segments of the segmented cathode

Static differential resistivity of the CCL, \(\Omega\) cm\(^2\)

Time, s

Characteristic time, s, Eq. 12

Air flow velocity in the channel, cm s\(^{-1}\)

Coordinate through the cell, cm

Coordinate along the channel, cm

Total impedance of the cathode side, \(\Omega\) cm\(^2\)

Local CCL impedance, \(\Omega\) cm\(^2\)

Local GDL impedance, \(\Omega\) cm\(^2\)

Total GDL impedance, Eq. 3, \(\Omega\) cm\(^2\)

Total shifted GDL impedance, Eq. 4, \(\Omega\) cm\(^2\)

Newman’s dimensionless reaction penetration depth, Eq. 13

ORR overpotential (positive by convention), V

Dimensionless parameter, Eq. 14

CCL ionic conductivity, \(\Omega\) cm\(^{-1}\) cm\(^{-1}\)

Dimensionless reduced circular frequency, Eq. 11

Circular frequency (\(\omega = 2\pi f\)), s\(^{-1}\)

Greek letters:

\(\varepsilon\) - Newman’s dimensionless reaction penetration depth, Eq. 13

\(\eta\) - ORR overpotential (positive by convention), V

\(\lambda\) - Stoichiometry of the oxygen flow, Eq. 8

\(\mu\) - Dimensionless parameter, Eq. 14

\(\sigma_p\) - CCL ionic conductivity, \(\Omega\) cm\(^{-1}\) cm\(^{-1}\)

\(\Omega\) - Dimensionless reduced circular frequency, Eq. 11

\(\omega\) - Circular frequency (\(\omega = 2\pi f\)), s\(^{-1}\)

Subscripts:

0 - Membrane/CCL interface

1 - CCL/GDL interface

b - GDL

c - cathode

t - Catalyst layer

\(\ast\) - Characteristic value

Superscripts:

1 - Small–amplitude perturbation

\(\infty\) - Infinite oxygen stoichiometry

\(in\) - Oxygen channel inlet

References:


