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Impedance Spectroscopy Study of the PEM Fuel Cell Cathode with Nonuniform Nafion Loading

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We report modeling and experimental study of impedance of the PEM fuel cell cathode with nonuniform ionomer loading. A physics-based model for the high-frequency impedance is developed and analytical solution for impedance is derived. Assuming that the CCL proton conductivity σ_p exponentially decays from the membrane surface, we fit the model to experimental spectra of the cell measured at the open circuit conditions. Fitting gives the characteristic scale of the σ_p decay, the average CCL proton conductivity and the double layer capacitance.

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Fuel cell impedance can, in principle, give parameters of virtually all kinetic and transport processes running in the cell. Perhaps, there is no other experimental technique giving comparable to impedance amount of information on the cell function. However, understanding impedance spectra requires quite sophisticated modeling. Over the past decade, interest in impedance studies of fuel cells has been growing exponentially. Of particular interest are physical impedance models,^{1–18} as these models help to extract the transport and kinetic parameters from the cell impedance.

A major contribution to PEMFC impedance gives the cathode side. At small cell currents, the contribution of the oxygen transport in the gas-diffusion layer to the cell impedance is small. In PEMFCs at open circuit, this contribution is much less than the cathode catalyst layer (CCL) impedance due to hydrogen crossover¹⁹ (see also below). Thus, at small currents and in particular at open circuit voltage (OCV), the cell impedance spectrum depends on the processes in the CCL only.

Of special interest is the high-frequency (HF) impedance, as in this frequency domain, slow oxygen transport and faradaic processes are “frozen”, i.e., they do not respond to the rapid variation of AC potential. The standard macrohomogeneous model shows that in the HF range, the impedance of a uniform CCL exhibits a straight line with the 45° slope.² This line is a signature of proton transport in the layer: projection of this line onto the real axis yields the CCL proton resistivity $R_p = l_t/(3\sigma_p)$, which allows one to calculate the CCL proton conductivity σ_p directly from the impedance spectrum.^{20,21} Here l_t is the CCL thickness.

However, in a number of works, measured HF impedance strongly differs from the 45° straight line. The HF part of the spectrum either has a form of an arc, which is independent of the cell current density,^{22,23} or it exhibits almost a straight line with the slope significantly exceeding $\pi/4$.²⁴ Recently, Gerteisen¹⁷ developed a numerical model, which explains formation of these HF features by nonuniform CCL properties. In particular, the quasi-straight line has been explained in¹⁷ by exponentially decaying toward the GDL proton conductivity of the layer, while the current-independent arc forms as a concerted action of a nonuniform σ_p and double layer capacitance C_{dl} . Malko et al.²⁴ explained the measured HF quasi-straight line in the spectrum of their electrode using a similar concept of impedance of a single pore with nonuniform Nafion coverage along the pore length.

An impedance study of PEMFC cathodes with possibly non-uniform Nafion loading has been reported by Lefebvre²⁵ and Li and

Pickup.²⁶ Both groups used an equivalent transmission line to fit the experimental spectra from several cathodes with different Nafion content. A rapidly decaying toward the GDL shape of the proton conductivity has been reported; much lower proton conductivity at the CCL/GDL interface was explained in²⁶ by penetration of catalyst to the pores of the GDL in combination with formation of isolated Nafion “islands” in this region. It should be noted that the experiments in Ref. 26 were performed under fixed cell potential and varying current density, depending on Nafion content.

Steady-state models^{27–29} and experiments^{30–33} show that the CCL with growing toward the membrane Nafion content (proton conductivity) improves the cell performance. This explains interest in gradient electrodes from the fuel cell industry. Below, we develop analytical model of HF impedance of the CCL with nonuniform Nafion loading. We show that at high frequencies of the applied signal, the equations of transient macrohomogeneous model can be greatly simplified and analytical solution for the HF impedance can be obtained. Further, we use this solution for fitting impedance spectra of a PEMFC measured at open circuit conditions. We assume that the proton conductivity σ_p decays exponentially through the CCL depth; the reference case of uniform Nafion loading is described by the exponent with zero power. Fitting the model CCL impedance to the high-frequency points of the spectra gives the characteristic scale of σ_p decay, the CCL proton conductivity at the membrane surface, and the double layer capacitance of the electrode. All these parameters are “reference” values at the open-circuit conditions.

Model

Basic equations.—Let the x -coordinate with the origin at the membrane surface be directed through the CCL depth (Figure 1). In this work, we assume that the proton conductivity is a function of x :

$$\sigma_p(x) = \sigma_0 s(x) \quad [1]$$

where σ_0 is the conductivity at the membrane interface (at $x = 0$), and $s(\bar{x})$ is the dimensionless shape function of x . The analysis below is based on the transient macrohomogeneous CCL model

$$C_{dl} \frac{\partial \eta}{\partial t} + \frac{\partial j}{\partial x} = -2i_* \left(\frac{c}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right) \quad [2]$$

$$j = -\sigma_0 s(x) \frac{\partial \eta}{\partial x} \quad [3]$$

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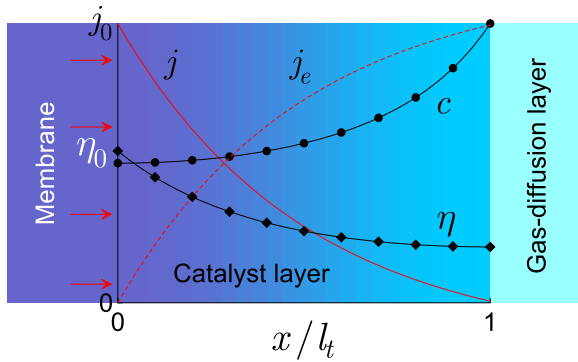


Figure 1. Schematic of the cathode catalyst layer and the x -coordinate. Note that the ORR overpotential η is positive by convention. The gradient of Nafion loading is depicted as the gradient of blue color.

$$\frac{\partial c}{\partial t} - D_{ox} \frac{\partial^2 c}{\partial x^2} = -\frac{2i_*}{4F} \left(\frac{c}{c_{ref}} \right) \sinh \left(\frac{\eta}{b} \right) \quad [4]$$

Here, C_{dl} is the double layer volumetric capacitance ($F \text{ cm}^{-3}$), η is the ORR overpotential, positive by convention, t is time, j is the local proton current density, i_* is the volumetric exchange current density ($A \text{ cm}^{-3}$), c is the local oxygen concentration, c_{ref} is its reference concentration, b is the Tafel slope, D_{ox} is the oxygen effective diffusion coefficient in the CCL. Eq. 2 is the proton charge conservation equation, Eq. 3 is the Ohm's law relating the proton current density to the gradient of overpotential, and Eq. 4 is the oxygen transport equation in the CCL with the Fick's law of diffusion. In the context of fuel cell electrode, the model above has been introduced and studied by Newman and Tobias.³⁴ Detailed discussion of Eqs. 2–4 is given in Ref. 35.

Substitution of Eq. 3 into Eq. 2 gives the diffusion-type equation for the overpotential. Linearization and Fourier-transform of the resulting system leads to the following pair of linear equations for the small-amplitude perturbations of overpotential η^1 and oxygen concentration c^1 (see³⁵ for details):

$$\varepsilon^2 \frac{\partial}{\partial \tilde{x}} \left(s(\tilde{x}) \frac{\partial \tilde{\eta}^1}{\partial \tilde{x}} \right) = \sinh(\tilde{\eta}^0) \tilde{c}^1 + (\tilde{c}^0 \cosh \tilde{\eta}^0 + i\tilde{\omega}) \tilde{\eta}^1 \quad [5]$$

$$\varepsilon^2 \tilde{D}_{ox} \frac{\partial^2 \tilde{c}^1}{\partial \tilde{x}^2} = (\sinh \tilde{\eta}^0 + i\tilde{\omega} \mu^2) \tilde{c}^1 + \tilde{c}^0 \cosh(\tilde{\eta}^0) \tilde{\eta}^1 \quad [6]$$

where the superscripts 0 and 1 mark the steady-state solution and the amplitude of a small harmonic perturbation, respectively,

$$\varepsilon = \sqrt{\frac{\sigma_0 b}{2i_* l_t}}, \quad \mu = \sqrt{\frac{4F c_{ref}}{C_{dl} b}} \quad [7]$$

and the following dimensionless variables are used

$$\tilde{x} = \frac{x}{l_t}, \quad \tilde{t} = \frac{t}{t_*}, \quad \tilde{\eta} = \frac{\eta}{b}, \quad \tilde{j} = \frac{j}{j_p}, \quad \tilde{c} = \frac{c}{c_{ref}} \quad [8]$$

$$\tilde{D}_{ox} = \frac{D_{ox}}{D_*}, \quad \tilde{Z} = \frac{Z \sigma_0}{l_t}, \quad \tilde{\omega} = \omega t_* \quad [8]$$

Here $\omega = 2\pi f$ is the angular frequency of the applied signal,

$$t_* = \frac{C_{dl} b}{2i_*}, \quad j_p = \frac{\sigma_0 b}{l_t}, \quad D_* = \frac{\sigma_0 b}{4F c_{ref}} \quad [9]$$

are the scaling parameters for time, current density, and diffusion coefficient, respectively.

The CCL impedance $\tilde{Z}$ is given by

$$\tilde{Z} = - \left. \frac{\tilde{\eta}^1}{s(\tilde{x}) \partial \tilde{\eta}^1 / \partial \tilde{x}} \right|_{\tilde{x}=0} \quad [10]$$

High-frequency limit.—In this work we will focus on the high-frequency limit of Eqs. 5,6. In this limit, all the terms on the right side of Eq. 5, except $i\tilde{\omega} \tilde{\eta}^1$ can be neglected, and this equation simplifies to

$$\varepsilon^2 \frac{\partial}{\partial \tilde{x}} \left(s(\tilde{x}) \frac{\partial \tilde{\eta}^1}{\partial \tilde{x}} \right) = i\tilde{\omega} \tilde{\eta}^1 \quad [11]$$

As can be seen, Eq. 11 does not contain $\tilde{c}^1$, which simply means that the oxygen concentration remains unperturbed if the frequency of the applied signal is high enough (the exact condition is formulated below). Eq. 11 thus decouples from the system. Note that Eq. 11 does not contain the static overpotential $\tilde{\eta}^0$, which means that this equation is valid for all cell currents, provided that the frequency of the applied signal is high.

Dividing both parts of Eq. 11 by ε^2 we get an equation

$$\frac{\partial}{\partial \tilde{x}} \left(s(\tilde{x}) \frac{\partial \tilde{\eta}^1}{\partial \tilde{x}} \right) = i\tilde{\Omega} \tilde{\eta}^1, \quad \tilde{\eta}^1(1) = \tilde{\eta}_1, \quad \left. \frac{\partial \tilde{\eta}^1}{\partial \tilde{x}} \right|_{\tilde{x}=1} = 0 \quad [12]$$

which depends on a single parameter, the reduced dimensionless frequency $\tilde{\Omega}$:

$$\tilde{\Omega} = \frac{\tilde{\omega}}{\varepsilon^2} = \frac{\omega C_{dl} l_t^2}{\sigma_0} \quad [13]$$

Note that the factor $C_{dl} l_t^2 / \sigma_0$ in Eq. 13 is the characteristic time for the relaxation of charge stored in the double layer. The first boundary condition in Eq. 12 fixes the amplitude of applied at $\tilde{x} = 1$ perturbation, and the second condition means zero proton current through the CCL/GDL interface.

Eq. 12 can be transformed to a first-order equation for the local admittance $\tilde{Y}$. Introducing $\tilde{Y}(\tilde{x})$ according to

$$\tilde{Y} = -\frac{s}{\tilde{\eta}} \frac{\partial \tilde{\eta}}{\partial \tilde{x}}, \quad [14]$$

substituting $-s \partial \tilde{\eta} / \partial \tilde{x} = \tilde{\eta} \tilde{Y}$ on the left side of Eq. 12, after simple transformations we get

$$\frac{\partial \tilde{Y}}{\partial \tilde{x}} - \frac{\tilde{Y}^2}{s} = -i\tilde{\Omega}, \quad \tilde{Y}(1) = 0 \quad [15]$$

Here, the boundary condition follows from the second boundary condition in Eq. 12. From the definition of $\tilde{Y}$, Eq. 14, it follows that

$$\tilde{Z} = \frac{1}{\tilde{Y}(0)} \quad [16]$$

Useful solutions to Eq. 15 can be obtained if we guess some shape function $s(\tilde{x})$. Our experimental data (see below) suggest exponentially decaying toward the GDL $s(\tilde{x})$:

$$s(\tilde{x}) = \exp(-\beta \tilde{x}) \quad [17]$$

where $\beta \geq 0$ is the inverse characteristic decay length. Note that $\beta = 0$ describes the case of uniform Nafion loading. Solving Eq. 15 and calculating impedance, Eq. 16, we find

$$\tilde{Z}_{HF} = \left(\sqrt{\frac{i}{\tilde{\Omega}}} \right) \frac{Y_0 \left(q e^{\frac{\beta}{2}} \right) J_1(q) - Y_1(q) J_0 \left(q e^{\frac{\beta}{2}} \right)}{Y_0(q) J_0 \left(q e^{\frac{\beta}{2}} \right) - Y_0 \left(q e^{\frac{\beta}{2}} \right) J_0(q)} \quad [18]$$

where

$$q = \frac{2\sqrt{-i\tilde{\Omega}}}{\beta} \quad [19]$$

and J , Y are the Bessel functions of the first and second kind, respectively. In dimension form, this impedance reads

$$Z_{HF} = \left(\sqrt{\frac{i}{\omega \sigma_0 C_{dl}}} \right) \frac{Y_0 \left(q e^{\frac{\beta}{2}} \right) J_1(q) - Y_1(q) J_0 \left(q e^{\frac{\beta}{2}} \right)}{Y_0(q) J_0 \left(q e^{\frac{\beta}{2}} \right) - Y_0 \left(q e^{\frac{\beta}{2}} \right) J_0(q)} \quad [20]$$

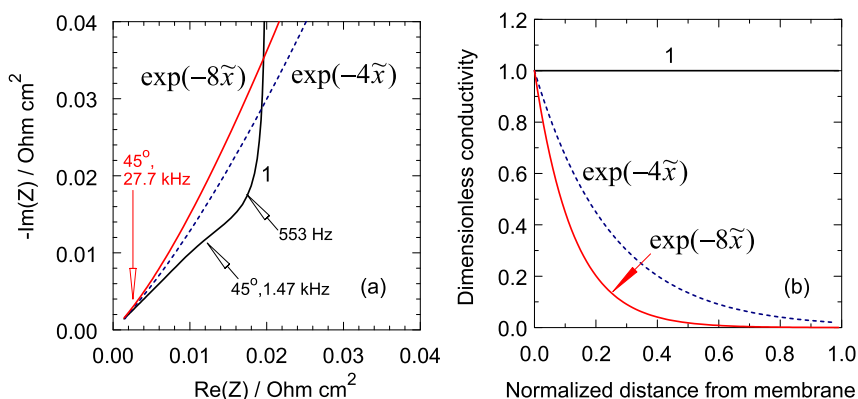


Figure 2. (a) High-frequency part of model impedance spectra, Eq. 18, corresponding to uniform ionomer loading (1), and to exponentially decaying through the CCL depth proton conductivity ($\beta = 4$ and 8). (b) The respective shapes of the proton conductivity through the CCL depth. The other parameters for calculations are $\sigma_0 = 0.02 \Omega^{-1} \text{ cm}^{-1}$, $C_{dl} = 20 \text{ F cm}^{-3}$, and $l_t = 10^{-3} \text{ cm}$.

with

$$q = \frac{2}{\beta} \sqrt{-\frac{i\omega C_{dl} l_t^2}{\sigma_0}}, \quad [21]$$

The limits of validity of Eq. 18 follow from a simple analysis of terms on the right side of Eq. 5. Clearly, $\tilde{c}^1 \ll 1$ and close to the OCV, $\tilde{c}^0 \simeq 1$; thus, the frequency-independent terms can be neglected if

$$\tilde{\omega} \gg \cosh \tilde{\eta}^0 \quad [22]$$

or, in dimension form,

$$\omega \gg \frac{2i_* \cosh(\eta^0/b)}{C_{dl} b} \quad [23]$$

At zero current in the load, the CCL still converts an equivalent current density of hydrogen crossover. In other words, in PEM fuel cells, true OCV conditions cannot be achieved and the cathode works in the Tafel regime even if the current in the load is zero.¹⁹ Thus, we may neglect the reverse exponent in Eq. 23, which leads to

$$\omega \gg \frac{i_* \exp(\eta^0/b)}{C_{dl} b} \quad [24]$$

As the oxygen concentration is close to the reference value, the Tafel equation reduces to $j_{\text{cross}} = l_t i_* \exp(\eta^0/b)$, where j_{cross} is the equivalent current density of hydrogen crossover. Using this in Eq. 24, we finally find

$$\omega \gg \frac{j_{\text{cross}}}{C_{dl} b l_t} \quad [25]$$

It is advisable to estimate the right side of Eq. 25. A typical current density of hydrogen crossover is about 0.003 A cm^{-2} . With $C_{dl} = 20 \text{ F cm}^{-3}$, $b = 0.03 \text{ V}$ and $l_t = 10^{-3} \text{ cm}$, we get $\omega \gg 5 \text{ s}^{-1}$, which is equivalent to the regular frequencies

$$f \gg 1 \text{ Hz} \quad [26]$$

Thus, Eq. 18 can be fitted to the part of the OCV spectrum above 10 Hz. Note that though the validity condition Eq. 25 for the impedance (18) depends on j_{cross} , the impedance $\tilde{Z}_{HF}$ itself does not contain j_{cross} .

Experimental

The experiments have been performed using a segmented cell system developed at Hawaii Natural Energy Institute (HNEI) and GRanalytix test station. The segmented cell system employs close loop Hall sensors (Honeywell CSNN 191) for current sensing and allows us to perform simultaneous measurements of spatial electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV) and cyclic voltammetry (CV). The system details are provided in our previous papers.^{16,36}

The segmented flow field of a cell consists of ten 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 the segmented and the standard flow field on the anode side. The reactant streams were arranged in a co-flow configuration, and segment 1 is the inlet segment, and segment 10 is the outlet.

The cell was operated with commercially available 100 cm^2 catalyst coated membrane from Gore with the thickness of $40\text{--}42 \text{ }\mu\text{m}$. The thickness of the reinforced membrane was $16\text{--}18 \text{ }\mu\text{m}$. The Pt/C loading of the anode and cathode electrodes was 0.4 mgPt cm^{-2} . Sigracet 25 BC (thickness $235 \text{ }\mu\text{m}$, 80% porosity) was used as the anode and cathode gas diffusion layers (GDLs). 25 BC consists of carbon paper substrate and microporous layer with the thickness of $40\text{--}45 \text{ }\mu\text{m}$. Segmented GDL was used on the cathode side, whereas a uniform GDL was applied at the anode. The total active area of membrane/electrode assembly (MEA) was 76 cm^2 . The gasket material was made of Teflon, with the thicknesses of $125 \text{ }\mu\text{m}$ for the anode and cathode.

To perform EIS at open circuit voltage a 4-quadrant amplifier (4QA) has been employed instead of the normally used load bank. The 4QA can source and sink current, therefore it ensures that the average current over one perturbation period is truly zero. The segmented cell was assembled, conditioned and tested. The anode/cathode testing conditions for the EIS measurements were hydrogen/air at $1.0/1.0 \text{ l min}^{-1}$, 100/50% relative humidity and back pressure of 150 kPa . The cell temperature was 60°C . The frequency range for the EIS was 0.1 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. Spatial EIS are measured simultaneously from 10 segments and from the whole cell, thereby providing good statistics for fitting parameters (see below).

Hydrogen crossover current was measured by LSV using a Solartron SI 1287/electrochemical interface as a voltage source. The LSV was performed at the same operating conditions as EIS, while hydrogen and nitrogen were supplied to the reference/counter and working electrodes, respectively. The voltage sweep was applied from 0.1 to 0.4 V vs the reference hydrogen electrode at a scan rate of 0.1 mV s^{-1} .

Results and Discussion

Figure 2 shows the high-frequency part of the model spectra, Eq. 18, corresponding to $\beta = 0$ (uniform ionomer loading) and to exponentially decaying shapes of the proton conductivity ($\beta = 4$ and $\beta = 8$). As can be seen, with the frequency growth, the spectrum for $\beta = 0$ forms a well-known straight line with the 45° slope; however, the spectra corresponding to $\beta = 4$ and 8 look like a straight line with larger slope, which increases with β . A more detailed view of this effect is depicted in Figure 3, which shows that the phase angle of impedance Eq. 18 increases with β , though it tends to 45° as $\omega \rightarrow \infty$. Note that the phase angle of the uniformly-loaded spectrum changes rapidly in the frequency range $\omega \simeq 10^2\text{--}10^4 \text{ s}^{-1}$, and it reaches the

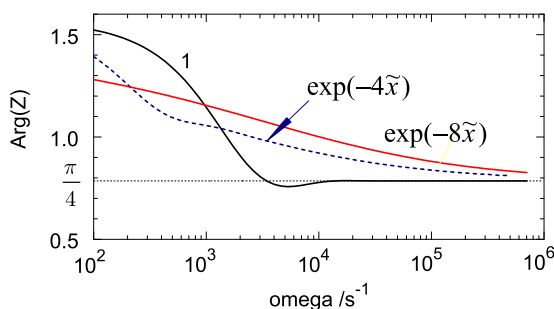


Figure 3. Bode plot of the phase angle of the model high-frequency impedance for the three indicated shapes of the proton conductivity through the CCL thickness x . The larger the gradient of σ_p along x , the larger the phase angle of the HF part of the spectrum. Note that the phase angles for $\beta = 4$ and 8 vary rather slowly with ω , which gives an impression that the respective part of the Nyquist spectrum is close to the straight line (see Figure 2a).

value of 45° at $\omega \simeq 10^4 \text{ s}^{-1}$. In contrast, the phase angle of the other two spectra in Figure 3 vary rather slowly in the range of $\omega \simeq 10^3$ – 10^5 s^{-1} , and they approach the 45° -slope asymptotically at $\omega > 10^6 \text{ s}^{-1}$, which is typically out of the frequency range used in impedance studies of fuel cells (Figure 3).

Next, Eq. 18 has been fitted to the HF part of experimental spectra. The spectra have been measured at zero current in the external load; as discussed above, this corresponds to the CCL operation at the current density of hydrogen crossover. This current was measured to be about 3 mA cm^{-2} , which limits validity of Eq. 18 by the frequency $f \simeq 10 \text{ Hz}$.

The fitting has been performed in Maple environment using a built-in Maple procedure *NonlinearFit*. The experimental and fitted curves for the whole cell and for the segments 1 to 3 are shown in Figure 4. The parameters resulted from fitting are depicted in Figure 5; their mean over the cell surface values are summarized in Table I. As can be seen, the values of β group quite well around the mean of 7.3 (Figure 5a). Large β indicates quite strong nonuniformity of the proton conductivity through the CCL depth. The proton conductivity at the membrane interface σ_0 varies in the range from 0.09 to $0.23 \Omega^{-1} \text{ cm}^{-1}$ (Figure 5b). This spread can be explained by “fuzzy” boundary between the CCL and membrane. However, the mean value of σ_0 of $0.13 \Omega^{-1} \text{ cm}^{-1}$ agrees well with the conductivity of fully humidified Nafion at 60°C .³⁷ The mean over the cell surface shape of the proton conductivity through the CCL depth is depicted in Figure 6. It is worth noting that the average over x proton conductivity is $0.018 \Omega^{-1} \text{ cm}^{-1}$, which correlates with the literature data.²⁰ The double layer capacitance is $28 \pm 2 \text{ F cm}^{-2}$ (Figure 5c and Table I). This value is in good agreement with that obtained from impedance at a finite cell current density.³⁸

A very few literature data exist on impedance of gradient electrodes (see introduction section). The reason is that making a reproducible electrode with the prescribed shape of Nafion loading is only possible using an expensive spray coating machines. These machines are

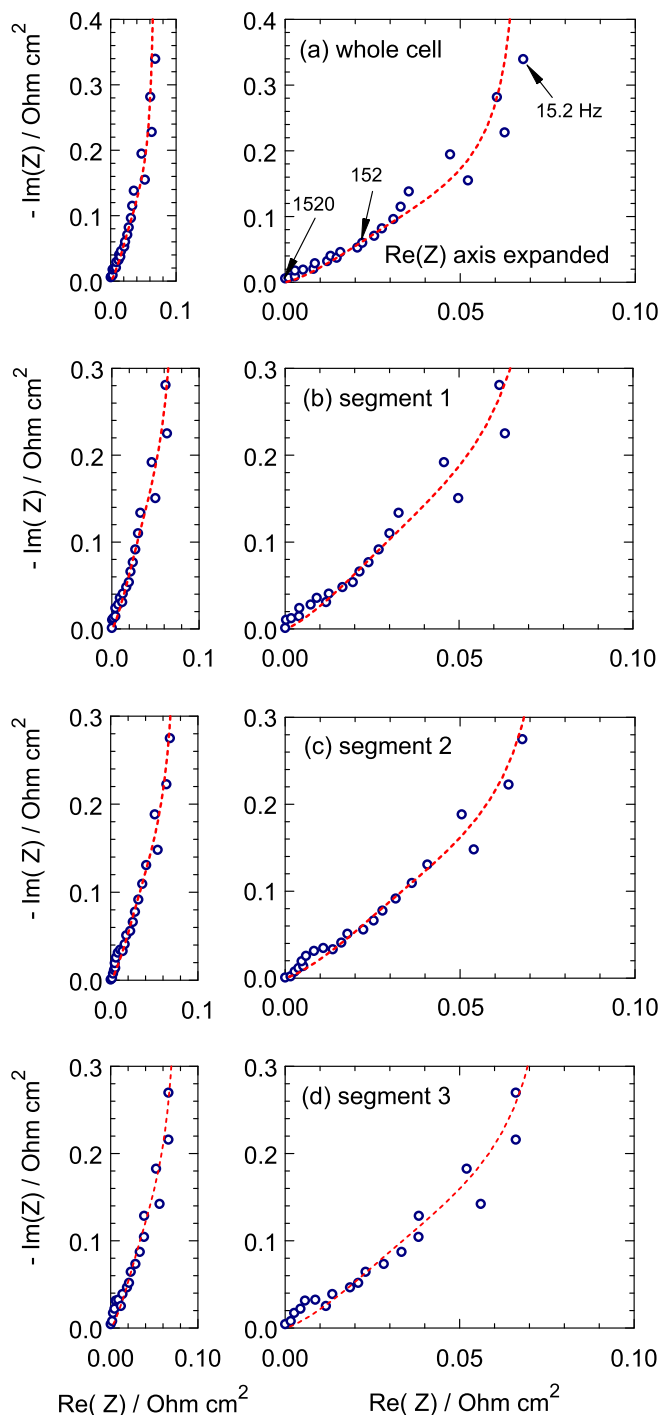


Figure 4. Experimental (points) and fitted model impedance (dashed lines) for the whole cell and for the segments 1 to 3. The left panels show the Nyquist spectra in the coordinates with equal scales along the real and imaginary axis. The right panels show the same spectra with the stretched real coordinate, to represent the details. Arrows in the frame (a) indicate frequencies f , Hz.

Table I. The cell parameters resulted from impedance fitting; the hydrogen crossover current density j_{cross} was measured by linear sweep voltammetry and the CCL thickness l_t was obtained by scanning electron microscopy.

Characteristic scale of the exponent in Eq. 17 β	7.3 ± 0.4
CCL proton conductivity at the membrane interface σ_0 , $\Omega^{-1} \text{ cm}^{-1}$	0.12 ± 0.03
Double layer capacitance C_{dl} , F cm^{-2}	28 ± 2
Catalyst layer thickness l_t , cm	0.0012 ± 0.0004
Current density of hydrogen crossover j_{cross} , mA cm^{-2}	3.1 ± 0.5

available on the market, however, not many labs have this equipment. It seems that traditional methods of electrode preparation lead to uncontrollable gradients of a Nafion content during drying or thermal processing.^{25,26}

The advantage of the HF@OCV technique discussed in this work is twofold. First, in typical PEMFC, it can be used for analysis of impedance at the frequencies above 10 Hz. The standard frequency range in fuel cell impedance studies extends up to 10 kHz; thus,

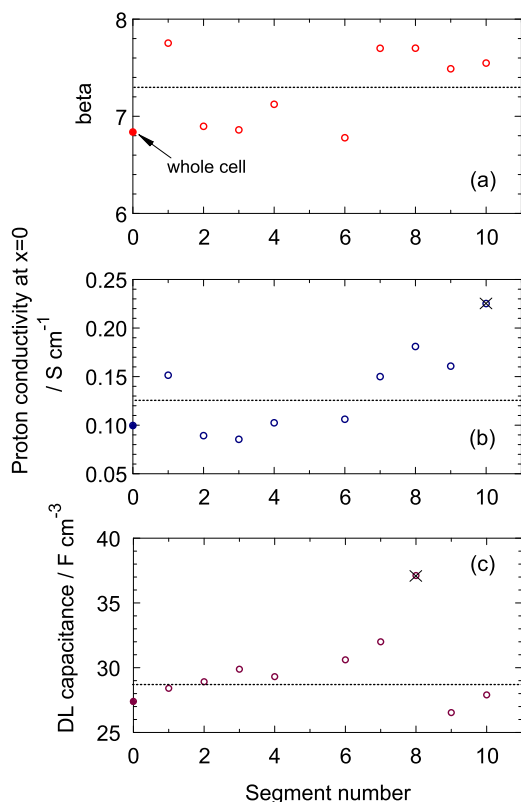


Figure 5. The fitting parameters for individual segments. Parameters for the whole cell are depicted as zero segment (filled circles). The parameters excluded from calculation of mean values are marked by crosses.

the method above is applicable to the OCV impedance data in the frequency window covering three decades, from 10 Hz to 10 kHz. This greatly improves reliability of the method. Second, in the HF domain, the inertial oxygen transport and faradaic processes are “frozen”, i.e., the signal changes so fast, that these processes do not respond. This is the best situation to determine the transport parameter for ions, which respond immediately to the HF potential, and the double layer capacitance, which is being charged by the ions. Last but not least, the method provides “reference” values of β , σ_0 and C_{dl} at zero cell current density, when the amount of water in the CCL is determined solely by external humidification of the cathode stream.

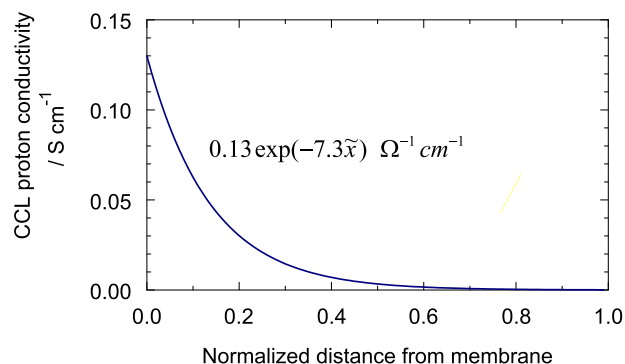


Figure 6. The averaged over the cell surface shape of the CCL proton conductivity through the CCL depth.

Conclusions

A model for the high-frequency impedance of the cathode catalyst layer with nonuniform Nafion loading is developed. Under the assumption of exponential decay of the CCL proton conductivity σ_p from the membrane surface, an analytical solution for the CCL impedance is derived. The impedance exhibits a quasi-straight line in the HF range, with the slope of the line depending on the characteristic scale of σ_p decay along the x -coordinate through the CCL depth. The model impedance is fitted to the HF part of the experimental Nyquist spectra obtained from the segmented PEM fuel cell at the open-circuit conditions. Fitting gives the characteristic scale of σ_p decay along x , the CCL proton conductivity at the membrane interface, and the double layer capacitance C_{dl} .

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Lists of Symbols

$\sim$	Marks dimensionless variables
b	ORR Tafel slope, V
C_{dl}	Double layer volumetric capacitance, $F\text{ cm}^{-3}$
c	Oxygen molar concentration in the CCL, mol cm^{-3}
c_{ref}	Reference oxygen molar concentration, mol cm^{-3}
D_{ox}	Effective oxygen diffusion coefficient in the CCL, $\text{cm}^2\text{ s}^{-1}$
F	Faraday constant, $C\text{ mol}^{-1}$
f	Regular frequency, Hz
j_0	Local cell current density, $A\text{ cm}^{-2}$
j_{cross}	Current density of hydrogen crossover, $A\text{ cm}^{-2}$
i	Imaginary unit
i_*	Volumetric exchange current density, $A\text{ cm}^{-3}$
l_t	Catalyst layer thickness, cm
q	Auxiliary parameter, Eq. 19
$s(x)$	Dimensionless shape of the CCL proton conductivity, Eq. 17
R_p	Proton resistivity of the CCL, $\Omega\text{ cm}^2$
t	Time, s
t_*	Characteristic time of double layer charging, s, Eq. 9
x	Coordinate through the CCL, cm
Z	CCL impedance, $\Omega\text{ cm}^2$
Z_{HF}	High-frequency CCL impedance, $\Omega\text{ cm}^2$

Subscripts

0	Membrane/CCL interface
1	CCL/GDL interface
HF	High-frequency
t	Catalyst layer
*	Characteristic value

Superscripts

0	Steady-state value
1	Small-amplitude perturbation

Greek

β	Characteristic parameter of σ_p decay, Eq. 17
ε	Newman's dimensionless reaction penetration depth, Eq. 7

μ	Dimensionless parameter, Eq. 7
σ_p	CCL ionic conductivity, $\Omega^{-1} \text{ cm}^{-1}$
σ_0	CCL ionic conductivity at the membrane surface, $\Omega^{-1} \text{ cm}^{-1}$
$\tilde{\omega}$	Reduced dimensionless frequency, Eq. 13
ω	Angular frequency ($\omega = 2\pi f$), s^{-1}

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