A recurrent formula for calculating an impedance of the cathode catalyst layer in a polymer electrolyte fuel cell

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Abstract: A recurrent formula for estimating an impedance of the cathode catalyst layer with fast oxygen transport in a polymer electrolyte fuel cell is derived. The catalyst layer is divided into N sub-layers and application of the charge conservation law enables to obtain the nonlinear recurrent relation $Z_n = f(Z_{n-1})$, where Z_n is the accumulated impedance of all sub-layers up to the n-th one. Numerical solution of this relation gives the total impedance of the catalyst layer with taking into account variation of the static overpotential of the oxygen reduction reaction along the depth of this layer. The model is simple, robust and two orders of magnitude faster than the standard model based on numerical solution of the differential equation.

Keywords: polymer electrolyte fuel cell, impedance, modeling.

Рекуррентная формула для вычисления импеданса катодного каталитического слоя в топливном элементе с полимерным электролитом

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Аннотация: Получена рекуррентная формула для вычисления импеданса катодного каталитического слоя с быстрым переносом кислорода в топливном элементе с полимерным электролитом. Каталитический слой разбивается на N подслоев, и применение закона сохранения заряда позволяет получить нелинейное рекуррентное соотношение $Z_n = f(Z_{n-1})$, где Z_n — суммарный импеданс всех подслоев вплоть до n-го включительно. Численное решение этого соотношения дает полный импеданс каталитического слоя с учетом переменного вдоль него статического перенапряжения реакции восстановления кислорода. Модель проста, надежна и на два порядка быстрее, чем стандартная модель, основанная на решении дифференциального уравнения.

Ключевые слова: топливные элементы с полимерным электролитом, импеданс, моделирование.

1. Introduction. The electrochemical impedance spectroscopy (EIS) is a unique non-invasive, non-destructive, *in operando* tool for characterization of polymer electrolyte membrane fuel cells (PEMFC) [1]. It is not surprising that over the past decade, a number of papers on EIS spectroscopy of PEMFCs has been growing exponentially.

Thanks to commercial EIS-meters, the PEMFC impedance measurement is a routine procedure. However, understanding of spectra requires a rather sophisticated modeling. In recent years, a large interest in development of the physics-based impedance models has been demonstrated. Models of this type are based on the transient conservation equations in the porous layers and cathode channel of a cell (see recent reviews [2, 3]). In general, the standard procedures of linearization and Fourier-transform of transient mass and charge conservation equations lead to impedance model, which includes numerical solution of boundary value problems (BVPs) [4]. The core of any impedance model for the cell is a model for cathode catalyst layer (CCL) impedance, which, generally speaking, should take into account oxygen and proton transport, double layer charging/discharging and a faradaic reaction. At low cell currents, the models for CCL impedance can be solved analytically; however, analytical solutions are typically valid under strong assumption of a small variation of static parameters along the CCL depth [5, 6]. The high-current impedance modeling includes numerical solution of a coupled linear BVPs for perturbation amplitudes of overpotential and oxygen concentrations in the CCL, which severely slows down the least-squares procedure for spectra fitting. The coefficients of BVPs are functions of distance through the CCL depth obeying to strongly nonlinear BVPs (see discussions below).

An alternative approach for calculation of the CCL impedance is construction of transmission line (TL) model consisting of a large number of repeated resistive and capacitive elements representing transport and kinetic processes. Recently, a TL model has been developed and used for fitting experimental impedance spectra of a segmented cell operated with neat oxygen [7]. The TL modeling usually leads to accurate results; however, some elements (processes) in the repeating TL fragment may be missing. The advantage of TL approach is the simplicity and ease of numerical implementation.

Below, we report a novel technique for modeling of the CCL impedance. As the first step, the CCL with fast oxygen transport is considered. We split the CCL into a number N of sub-layers and assume that the static overpotential of the oxygen reduction reaction (ORR) η^0 is constant in each sub-layer. This assumption is equivalent to stepwise approximation of the function $\eta^0(x)$, where x is the distance through the CCL. In this approximation, a nonlinear recurrent formula relating the impedance of n sub-layers with the impedance of $(n-1)$ sub-layers is derived from the proton charge conservation equation in the sub-layer. Using this formula N times, one gets the CCL impedance. The model is based on the physical conservation equation, it is simple and robust, as it does not involve numerical BVP solvers. Calculation shows that this model is nearly two orders of magnitude faster than the standard impedance model based on BVP solvers.

2. Model. The linearized and Fourier-transformed conservation equation of the proton charge in the CCL with fast O_2 transport is [8]

$$\varepsilon^2 \frac{\partial^2 \tilde{\eta}^1}{\partial \tilde{x}^2} = \left(i\tilde{\omega} + \tilde{c}_0 \exp \tilde{\eta}^0 \right) \tilde{\eta}^1, \quad \tilde{\eta}^1(1) = \tilde{\eta}_1^1, \quad \left. \frac{\partial \tilde{\eta}^1}{\partial \tilde{x}} \right|_{\tilde{x}=1} = 0, \tag{1}$$

where the dimensionless variables are defined in accordance with

$$\tilde{x} = \frac{x}{l_t}, \quad \tilde{\eta} = \frac{\eta}{b}, \quad \tilde{c} = \frac{c}{c_h^{in}}, \quad \tilde{\omega} = \frac{\omega C_{dl} b}{i_*}. \tag{2}$$

Here x is the coordinate through the CCL counted from the membrane, η is the positive by convention ORR overpotential, c and c_h^{in} are the local and reference oxygen concentrations respectively, ω is the angular frequency of the applied alternating current (AC) signal, l_t is the CCL thickness, b is the ORR Tafel slope, i_* is the volumetric ORR exchange current density, C_{dl} is the double layer capacitance, the superscripts 0 and 1 stand for the static variables and perturbation amplitudes in the $\tilde{\omega}$-space, ε is the dimensionless Newman's reaction penetration depth

$$\varepsilon = \sqrt{\frac{\sigma_p b}{i_* l_t^2}}, \tag{3}$$

where σ_p is the CCL proton conductivity. One should also introduce the following dimensionless variables that will be used in this work:

$$\tilde{j} = \frac{j l_t}{\sigma_p b}, \quad \tilde{Z} = \frac{Z \sigma_p}{l_t}, \tag{4}$$

where j is the proton current density and Z is the impedance.

The boundary conditions to Eq.(1) imply the applied perturbation $\tilde{\eta}_1^1$ and zero perturbation of proton current $\tilde{j}^1 = -\partial\tilde{\eta}^1/\partial\tilde{x}$ at the CCL/gas diffusion layer (GDL) interface. The fast oxygen transport means that the static oxygen concentration is uniform throughout the CCL depth: $\tilde{c}^0 = \tilde{c}_1^0$, where $\tilde{c}_1^0$ is the concentration at the CCL/GDL interface. However, due to the finite proton conductivity, the static overpotential $\tilde{\eta}^0$ is a function of $\tilde{x}$, which under high cell current has a peak on the membrane surface. The shape of $\tilde{\eta}^0(\tilde{x})$ satisfies to the static charge conservation equation

$$\varepsilon^2 \frac{\partial^2 \tilde{\eta}^0}{\partial \tilde{x}^2} = \tilde{c}_1^0 \exp \tilde{\eta}^0, \quad \tilde{\eta}^0(0) = \tilde{\eta}_0, \quad \left.\frac{\partial \tilde{\eta}^0}{\partial \tilde{x}}\right|_{\tilde{x}=1} = 0, \tag{5}$$

which is strongly nonlinear. The analytical solution for $\tilde{\eta}^0(\tilde{x})$ was found in [9,10] and read:

$$\tilde{\eta}^0 = \ln\left(\frac{\varepsilon^2 \beta^2}{2\tilde{c}_1^0}\left(1 + \tan^2\left(\frac{\beta}{2}(1-\tilde{x})\right)\right)\right), \tag{6}$$

where β is a solution of equation

$$\beta \tan\left(\frac{\beta}{2}\right) = \tilde{j}_0, \quad 0 \leqslant \beta < \pi \tag{7}$$

and $\tilde{j}_0$ is the static total current density.

Analytical solution of Eq.(1) with the coefficient given by Eq.(6) may hardly be derived and the straightforward way to calculate the CCL impedance

$$\tilde{Z} = -\left.\frac{\tilde{\eta}^1}{\partial\tilde{\eta}^1/\partial\tilde{x}}\right|_{\tilde{x}=0} \tag{8}$$

involves numerical solution of Eq.(1).

However, to avoid numerical integration of Eq.(1), the following idea can be employed. We divide the CCL into N sub-layers and assume that $\tilde{\eta}^0$ is constant in each

Figure 1. The scheme of the catalyst layer division into N sub-layers. The function $\tilde{\eta}^0(\tilde{x})$ is approximated by the stepwise function, which is constant in each sub-layer (not shown).

sub-layer (Figure 1). This is equivalent to stepwise approximation of the function $\tilde{\eta}^0(\tilde{x})$. Let the sub-layers be numerated in reverse order, with the fist sub-layer located at the CCL/GDL interface ($\tilde{x} = 1$) and the last one at the membrane surface ($\tilde{x} = 0$) (Figure 1).

By analogy with Eq.(1), the problem for $\tilde{\eta}^1$ in the n-th sub-layer $\tilde{x} \in [a, b]$ is

$$\varepsilon^2 \frac{\partial^2 \tilde{\eta}^1}{\partial \tilde{x}^2} = \left(\mathrm{i}\tilde{\omega} + \tilde{c}_0 \exp \tilde{\eta}_n^0\right) \tilde{\eta}^1, \quad \tilde{\eta}^1(b) = \tilde{\eta}_b^1, \quad \left.\frac{\partial \tilde{\eta}^1}{\partial \tilde{x}}\right|_{\tilde{x}=b} = -\tilde{j}_b^1, \tag{9}$$

where $\tilde{\eta}_n^0$ is the value of the static ORR overpotential in the n-th sub-layer, $\tilde{\eta}_b^1$ and $\tilde{j}_b^1$ are the overpotential and the proton current perturbation amplitudes at the interface of the $n|(n-1)$ sub-layers. The accumulated impedance of all layers up to the n-th one is

$$\tilde{Z}_n = -\left.\frac{\tilde{\eta}^1}{\partial\tilde{\eta}^1/\partial\tilde{x}}\right|_{\tilde{x}=a}. \tag{10}$$

The problem (9) is a linear one with constant coefficients and, therefore, it can readily be solved. Solving Eq.(9), calculating the impedance $\tilde{Z}_n$ from Eq.(10) and taking into account that $\tilde{\eta}_b^1/\tilde{j}_b^1 = \tilde{Z}_{n-1}$ on the right side of the n-th sub-layer, we arrive at the following recurrent relation

$$\tilde{Z}_n = \frac{\tilde{Z}_{n-1} + \tanh\left(\tilde{l}_n\sqrt{\phi_n}\right)/\sqrt{\phi_n}}{1 + \tilde{Z}_{n-1}\sqrt{\phi_n}\tanh\left(\tilde{l}_n\sqrt{\phi_n}\right)}, \quad \phi_n = \frac{1}{\varepsilon^2}\left(\mathrm{i}\tilde{\omega} + \tilde{c}^0 \exp \tilde{\eta}_n^0\right), \tag{11}$$

where $\tilde{l}_n = \tilde{x}_n^* - \tilde{x}_{n-1}^*$ is the thickness of the n-th sub-layer and $\tilde{\eta}_n^0$ is calculated from Eq.(6) at the sub-layer midpoint $\tilde{x} = (\tilde{x}_n^* + \tilde{x}_{n-1}^*)/2$. Note that according to convention, $\{\tilde{x}_n^*\} = \{1 - \tilde{l}_1, 1 - 2\tilde{l}_1, \ldots, 0\}$ (Figure 1).

Figure 2. (a) Solid line – the CCL impedance calculated with 10 sub-layers in accordance with the recurrence relation Eq.(11). Points – the CCL impedance computed with help of Eq.(8) and by the direct numerical integration of Eq.(1). In both cases, the static shape of $\tilde{\eta}^0$ is evaluated from Eq.(6). (b) Real and imaginary parts of the impedance from (a) as a function of frequency ω.

At the CCL/GDL interface $\tilde{j}_1 = 0$ and, hence, $\tilde{Z}_0 = \infty$ on the right side of the first sub-layer (at $\tilde{x} = 1$). Thus, using Eq.(11), we get an initial value of $\tilde{Z}_1$

$$\tilde{Z}_1 = \frac{1}{\sqrt{\phi_1}\tanh\left(\tilde{l}_1\sqrt{\phi_1}\right)}, \quad \phi_1 = \frac{1}{\varepsilon^2}\left(i\tilde{\omega} + \tilde{c}^0 \exp\tilde{\eta}_1^0\right), \tag{12}$$

enabling to evaluate the impedance $\tilde{Z}_n$ at $n = 2, \ldots, N$.

3. Results and discussion. The relation (11) is a nonlinear recurrent relation, which cannot be solved. However, the numerical implementation of Eq.(11) is simple and robust; for instance, it may be solved using recursion. The comparison of spectra computed from Eq.(11) with 10 sub-layers and those obtained by the direct numerical integration of Eq.(1) is shown in Figure 2. Parameters for the calculation are listed in Table 1. Parameter β was calculated using *fsolve* procedure from Python Scipy library. The shape of the static ORR overpotential $\tilde{\eta}^0$ utilized in both calculations is demonstrated in Figure 3.

As can be seen, the solution of Eq.(11) with $N = 10$ is almost indistinguishable from the exact numerical result. Meanwhile, in the case of 10 sub-layers, the calculation with the recurrence relation is nearly two orders of magnitude faster than using the model based on direct numerical ODE solver.

Such a fast method for calculation of the CCL impedance can be crucial for using in 2D problems with non-uniform distribution of overpotential over the cell active surface area. Note that for simplicity, the thicknesses of all sub-layers were assumed to be the same. Generally speaking, this is not necessary, since the equation (11) is valid for the layers of arbitrary thickness. In some cases, it may be beneficial to use a non-uniform sub-layers grid to better resolve the region of a large $\tilde{\eta}^0$ gradient.

Table 1. Geometrical and operating parameters of the cell.

CCL thickness l_t, cm	$10 \cdot 10^{-4}$
ORR Tafel slope, V / exp	0.03
ORR exchange current density i_*, A cm^{-3}	10^{-3}
Double layer capacitance C_{dl}, F cm^{-3}	20
CCL proton conductivity σ_p, S cm^{-1}	0.01
Cell current density j_0, A cm^{-2}	0.5
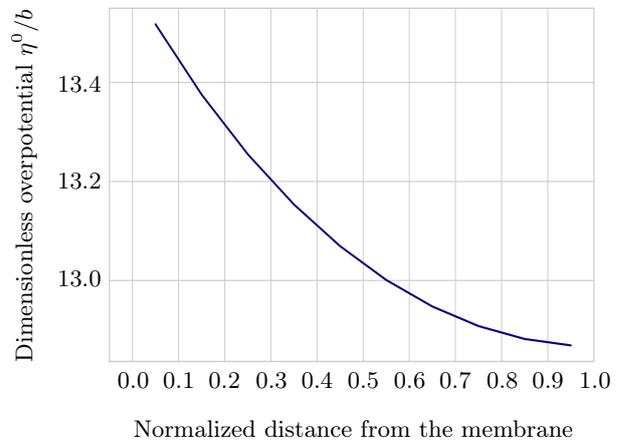
Figure 3. The shape of the dimensionless static ORR overpotential through the CCL depth. The membrane is located at $\tilde{x} = 0$.

Finally, it is worth noting that the idea leading to Eq.(11) can be used to derive a recurrent relation for the CCL with finite rates of proton and oxygen transport. This work is in progress.

4. Conclusions. A recurrent equation for impedance of the cathode catalyst layer with fast oxygen transport and finite rate of proton transport in a polymer electrolyte fuel cell is derived. This equation allows to calculate the impedance spectrum of the catalyst layer almost two orders of magnitude faster than the standard method based on the numerical solution of the differential equation for the perturbation amplitude of the overpotential of the oxygen reduction reaction.

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