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A simple transient model for a high temperature PEM fuel cell impedance

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ABSTRACT

We develop a pseudo two-dimensional, isothermal transient model for a high temperature proton exchange membrane fuel cell. It takes into account the dynamic change of oxygen concentration in the cathode gas diffusion layer and in the cathode channel. The model can be used to simulate and analyze electrochemical impedance spectra of the cell in both potentiostatic and galvanostatic modes, current interrupt results and step changes in the cell current or potential. The model is validated by fitting experimental data.

1. Introduction. Transient operation of a PEMFC

In real applications fuel cells (FC) are operated at variable conditions and loading. To describe behavior of the system one needs a transient model which takes into account dynamic variation of operation parameters and modes [1]. Dynamic simulation helps to estimate parameters and properties which are difficult to measure *in situ*; these values can differ from *ex situ* measurements.

One of the applications of transient modeling is understanding the results of experimental electrochemical impedance spectroscopy (EIS) of fuel cells [2–4]. In this method, a system is subjected to a small amplitude harmonic current or potential perturbation. As a result, the system potential or current are harmonically alternating at the frequency of the exciting signal with a certain phase shift:

$$
\begin{aligned}
&J = J_{cell} + J_0 \sin(\omega t) \Rightarrow E = E_{cell} + E_0 \sin(\omega t + \phi_E) \\
&E = E_{cell} + E_0 \sin(\omega t) \Rightarrow J = J_{cell} + J_0 \sin(\omega t + \phi_J) \\
&Z = Z_0(\cos\phi + \imath \sin\phi)
\end{aligned}
\quad (1)
$$

The cell impedance is a ratio of complex Fourier-amplitudes of potential to current disturbances. The results of EIS can be represented by means of Nyquist and Bode plots. In Nyquist plot, the x-coordinate is for the real part of the impedance, while the y-coordinate is for the imaginary part. In Bode plots, the absolute value of impedance and phase shift are shown as functions of frequencies.

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The physical model for the cell impedance is obtained from the transient model of the cell performance. In high temperature proton exchange membrane fuel cell (HT-PEMFC), most of the potential loss originates from the cathode side; thus, a transient performance model of the cell cathode is necessary to model the cell impedance. A physical dynamic model should consider not only the system response to harmonic perturbation of current density or potential, but it should also predict the system response to finite step changes in cell current or potential.

A thorough review of models for EIS analysis of conventional low temperature PEMFC can be found in Ref. [5]. One of the first numerical EIS models of FC cathode has been developed in a fundamental work [6]. This model accounts for the oxygen transport in the gas diffusion layer (GDL), and the processes in the cathode catalyst layer (CCL). A model for impedance of a porous electrode with cylindrical pores is developed in Ref. [7]; it takes into account both concentration and overvoltage gradients. One of the first analytical impedance models of the macrohomogeneous CCL in a PEM fuel cell has been developed in Ref. [8]; this model is an extension of the previous steady-state CCL performance model of the same authors [9]. In Refs. [10,11] a transient model is developed to predict the response of porous gas diffusion electrode in current interrupt and EIS experiments; the gas diffusion electrode is considered as a spherical agglomerate structure. The model for impedance of the whole PEMFC with a spherical agglomerate CCL is presented in Ref. [12], the gaseous transport in the cathode GDL and catalyst layer is described by Stefan–Maxwell equations. An analytical solution for impedance of a porous macrohomogeneous electrode is obtained in Ref. [13] taking into account concentration and potential gradients. An impedance model of a PEMFC with the focus on high current densities region is presented in Ref. [14]; the model takes into account mass transport limitations in the cathode GDL and catalyst layer. The modeling results in Ref. [14] are qualitatively compared to experimental data. Ref. [15] reports a model for large-scale PEMFC which takes into account oxygen consumption in the channel. Note, however, that this model assumes infinitely fast oxygen transport along the channel. In Ref. [16] the role of pore-size distribution on the impedance response of a porous electrode is investigated.

The results of EIS are often interpreted by means of equivalent circuit method. For example, Ref. [17] uses a transmission line model to obtain various contributions to the total polarization overpotential. Note that in this model, the oxygen transport loss in the CCL is neglected. In Ref. [18] a transmission line model is used to describe a catalyst layer with agglomerate structure and evaluate its degradation. The authors of Ref. [18] consider low current density region and compare model results to the results of destructive tests. However, different parts of a fuel cell can work in different regimes simultaneously (see, for example, Ref. [19]) which means that they should be described by different equivalent circuits [4]. Therefore a physical model can be more adequate to describe the impedance of the whole fuel cell.

There is only a few computationally inexpensive transient models of HT-PEMFC. In a phenomenological control-oriented model [20] the dynamic behavior of a system is governed by double layer capacity only, no dynamic transport process are accounted for and only step changes in loading are considered. A recent model [21] for FC impedance accounts for both the anode and cathode parts of a cell, but it ignores the oxygen consumption along the cathode channel. The transient three-dimensional, non-isothermal model [22] is based on commercial software; it requires resource-demanding computations.

In this work, we report a simple and fast physical transient model of the HT-PEM fuel cell cathode. The model equations are discretized and solved numerically to find a transient response to certain changes in cell current or potential. The model Nyquist curves are fitted to experimental impedance spectra and the parameters resulted from fitting are discussed. Overall, the model is suitable for fast processing of experimental impedance spectra. It can be also used to analyze the effects of parameters and properties on the cell transient behavior and impedance.

2. Model

The model below is based on the earlier developed stationary [23–25] and transient models [25,26]. In this work, we use a more accurate model for the cathode polarization overpotential, which takes into account finite proton conductivity of the electrode [27]. The model is derived from the conservation laws and it does not require high performance computing facilities. Our "1D + 1D" model takes into account the dynamic change of oxygen concentration in the cathode gas diffusion layer and in the channel. The model is applicable to step changes of cell potential or current and for the direct simulation of EIS. The schematic of the modeled system is shown in Fig. 1.

2.1. Assumptions

- The temperature and total gaseous pressure in the cell are constant.

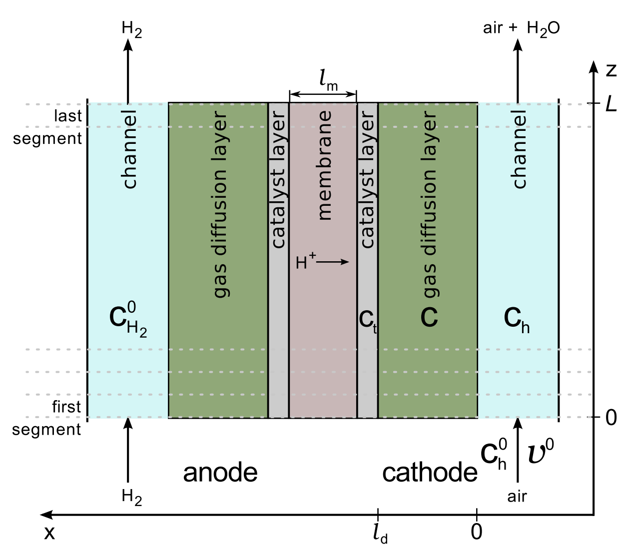

Fig. 1 – Schematic of a fuel cell.

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