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Two-dimensional modeling of a polymer electrolyte membrane fuel cell with long flow channel. Part II. Physics-based electrochemical impedance analysis

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HIGHLIGHTS

- Methodology of 'configuration of system dynamics' for impedance resolving.
- Multi-arc characteristics of impedance plot of PEMFCs.
- The first rapid impedance computation based on fully 2D model.

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ABSTRACT

The state-of-the-art electrochemical impedance spectroscopy (EIS) calculations have not yet started from fully multi-dimensional modeling. For a polymer electrolyte membrane fuel cell (PEMFC) with long flow channel, the impedance plot shows a multi-arc characteristic and some impedance arcs could merge. By using a step excitation/Fourier transform algorithm, an EIS simulation is implemented for the first time based on the full 2D PEMFC model presented in the first part of this work. All the dominant transient behaviors are able to be captured. A novel methodology called 'configuration of system dynamics', which is suitable for any electrochemical system, is then developed to resolve the physical meaning of the impedance spectra. In addition to the high-frequency arc due to charge transfer, the Nyquist plots contain additional medium/low-frequency arcs due to mass transfer in the diffusion layers and along the channel, as well as a low-frequency arc resulting from water transport in the membrane. In some case, the impedance spectra appear partly inductive due to water transport, which demonstrates the complexity of the water management of PEMFCs and the necessity of physics-based calculations.

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is a key technology for electrochemical energy conversion. One of the crucial subjects of ongoing research and development is the dynamic behavior of the PEMFC. Dynamics plays a key role not only for the application (e.g., required fast load changes for automotive traction), but particularly in the context of cell aging, where dynamic operation was observed to strongly accelerate degradation [1]. Understanding and optimizing the dynamics of electrochemistry and transport is therefore important for the further development of fuel cell technology.

Electrochemical impedance spectroscopy (EIS) is a classical tool for the dynamic analysis and fault diagnosis of PEMFCs, providing more detailed information than the conventional voltage–current characteristics. The AC impedance studies in PEMFCs have been summarized in the recent reviews [2,3]. The state-of-the-art EIS calculation is based on physical mechanisms rather than conventional equivalent circuit models [4]. With arbitrary input and output signals not limited to cell voltage and current, the physics-based impedance spectroscopy calculation allows generating the

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so-called transfer function in control theory. Springer et al. [5] firstly discussed the characterization of PEMFC using impedance spectroscopy calculation based on a 1D physicochemical model. However, Schneider et al. [6] recently suggested in experiments the existence of an additional low-frequency impedance arc due to the along-the-channel distribution of oxygen concentration, demonstrating the necessity of EIS calculation based on multi-dimensional modeling. It is predictable that this effect will be significant in a PEMFC with long flow channel. Considering this point, Kulikovsky [7] calculated the local impedance of segmented cells based on a qausi-2D model. Using a pseudo-2D approach, Mainka et al. [8] discussed the effect of oxygen depletion along the air channel on the Warburg diffusion impedance. By using a sinusoidal excitation of input signal at each frequency point, such EIS calculations were implemented frequency by frequency. Therefore, there are so far no EIS calculations starting from fully multi-dimensional modeling due to limitation of the computational cost.

There are various transient behaviors in PEMFCs, including dynamics of charge transfer in electric double layer (EDL), fluid dynamics in flow channels, dynamics of mass transfer in gas diffusion layer (GDL), dynamics of water transport in the membrane, etc. Compared to fast electrochemical reactions, the slow water transport induces complex dynamic behavior. In general, only the dominant dynamics of charge transfer in EDL and mass transfer in GDL were captured in both simulating and experimental impedance studies [5,9–13]. As a result, a typical impedance plot of PEMFCs shows a clear one- or two-arc characteristic and the dynamics of water transport is little recognized due to the small amplitude of its impedance arc. In some cases, one impedance arc is actually a combination of some different dynamics. For example, the dynamics of along-the-channel oxygen depletion and the dynamics of mass transfer in GDL could overlap in some frequency bands. How to distinguish the multi-arc impedance characteristic brings a challenge to the physics-based impedance spectroscopy calculation.

The aim of the second part of this work (this paper) is to analyze the transient behavior of PEMFCs using AC impedance spectroscopy. Using the advanced algorithm for the rapid computation of EIS based on step-excitation and Fourier transform developed by Bessler [14], we presented the first EIS calculation of PEMFCs based on a full 2D model. In the context of a PEMFC with long flow channel, all the main impedance arcs were captured and recognized. Then we developed a novel methodology to resolve the physical meaning of multiple arcs in impedance plots. The EIS calculations were carried out at three typical points representing different working regions in V–I curve.

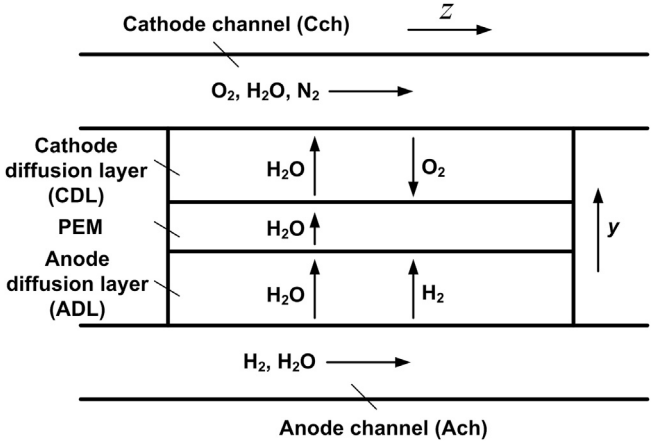

Fig. 1. Schematic of the two-dimensional modeling domain.

2. Background

2.1. Modeling framework

In the coordinate direction normal to the membrane electrode assembly and the coordinate direction along the gas flow channel, a transient 2D model has been developed in the first part of this work [15]. Fig. 1 shows a schematic of modeling domain. On the membrane level, we made a combination of the concentration solution theory and the dilute solution theory by superposing viscous flow on phenomenological equations. On the electrode level, we developed a Butler–Volmer formulation for the electrochemical kinetics of oxygen reduction reaction (ORR) starting from elementary steps. On the cell level, we used uniform governing equations for transport in free and porous flow in the gas channels and GDLs.

Mass and momentum balance in the gas channels and GDLs is governed by

$$\begin{aligned}&\frac{\partial(\varepsilon_p\rho)}{\partial t}+\nabla\cdot(\rho\mathbf{u})=0\\&\frac{\rho}{\varepsilon_p}\left(\frac{\partial\mathbf{u}}{\partial t}+(\mathbf{u}\cdot\nabla)\frac{\mathbf{u}}{\varepsilon_p}\right)=\nabla\cdot\left[-pI+\frac{\mu}{\varepsilon_p}(\nabla\mathbf{u}+(\nabla\mathbf{u})^T)-\frac{2}{3}\frac{\mu}{\varepsilon_p}(\nabla\cdot\mathbf{u})I\right]\\&\qquad\qquad-\frac{\mu}{K}\mathbf{u}+\mathbf{F}\end{aligned}\tag{1}$$

where the dependent variables are the density of gas mixture (ρ) and the superficial velocity vector ($\mathbf{u}$). The equation of state for ideal gas is used to close the system.

Species balance in the gas channels and GDLs is governed by

$$\begin{aligned}&\rho\varepsilon_p\frac{\partial\omega_i}{\partial t}+\nabla\cdot\mathbf{J}_i+\rho(\mathbf{u}\cdot\nabla)\omega_i=0\\&\mathbf{J}_i=-\rho\omega_i\sum_k D_{ik}\varepsilon_p^{1.5}\left[\nabla x_k+\frac{1}{p_A}(x_k-\omega_k)\nabla p_A\right]\\&\mathbf{N}_i=\mathbf{J}_i+\rho\mathbf{u}\omega_i,\quad x_k=\frac{\omega_k}{M_k}\Big/\sum_i\frac{\omega_i}{M_i},\quad\sum_i\omega_i=1\end{aligned}\tag{2}$$

where the dependent variables are the mass fraction of species i (ω_i).

Phenomenological equations with diffusive and viscous flow in the PEM is governed by Ref. [15]

$$\begin{aligned}&\mathbf{I}=-\kappa\nabla\phi-\frac{\kappa\xi}{F}\left[\frac{RT}{a_w}\nabla a_w+V_w\frac{\Delta p}{l_m}\mathbf{n}_y\right]-c_+F\frac{k_{p,m}}{\mu_{liq,w}}\frac{\Delta p}{l_m}\mathbf{n}_y\\&\mathbf{N}_w=-\frac{\kappa\xi}{F}\nabla\phi-\left(\frac{c_wD_{w,self}}{RT}+\frac{\kappa\xi^2}{F^2}\right)\left[\frac{RT}{a_w}\nabla a_w+V_w\frac{\Delta p}{l_m}\mathbf{n}_y\right]\\&\qquad-c_w\frac{k_{p,m}}{\mu_{liq,w}}\frac{\Delta p}{l_m}\mathbf{n}_y\end{aligned}\tag{3}$$

$$\begin{aligned}&\nabla\cdot\mathbf{I}=0\\&\frac{1}{1+b\lambda}\frac{\rho_{m,dry}}{EW}\frac{d\lambda}{da_w}\frac{\partial a_w}{\partial t}+\nabla\cdot\mathbf{N}_w=0\end{aligned}\tag{4}$$

where the dependent variables are the electrolyte potential (ϕ) and the water activity (a_w). The sorption curve of $\lambda=f(a_w)$, the dependence of characteristic variables (ξ, κ, $D_{w,self}$ and $k_{p,m}$) on the water uptake (λ), and the detailed definitions of symbols can be referred to the part work of model development [15].