



Physical modeling of polymer-electrolyte membrane fuel cells: Understanding water management and impedance spectra

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HIGHLIGHTS

- A transient PEMFC model resolving all layers of the cell in 2D is developed.
- It is validated in various conditions with a single set of parameters.
- Water management is investigated in co- and counter flow.
- Impedance spectra are analyzed from physical modeling.
- Induction is caused by changing ionomer properties and PtOx formation.

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ABSTRACT

A transient 2D physical continuum-level model for analyzing polymer electrolyte membrane fuel cell (PEMFC) performance is developed and implemented into the new numerical framework NEOPARD-X. The model incorporates non-isothermal, compositional multiphase flow in both electrodes coupled to transport of water, protons and dissolved gaseous species in the polymer electrolyte membrane (PEM). Ionic and electrical charge transport is considered and a detailed model for the oxygen reduction reaction (ORR) combined with models for platinum oxide formation and oxygen transport in the ionomer thin-films of the catalyst layers (CLs) is applied. The model is validated by performance curves and impedance spectroscopic experiments, performed under various operating conditions, with a single set of parameters and used to study water management in co- and counter-flow operation. Based on electrochemical impedance spectra (EIS) simulations, the physical processes which govern the PEMFC performance are analyzed in detail. It is concluded that the contribution of diffusion through the porous electrodes to the overall cell impedance is minor, but concentration gradients along the channel have a strong impact. Inductive phenomena at low frequencies are identified from physics-based modeling. Induction is caused by humidity dependent ionomer properties and platinum oxide formation on the catalyst surface.

1. Introduction

Polymer electrolyte membrane fuel cells are promising systems for energy-conversion in particular for automotive applications. Over the last decades, the cell performance and durability has been improved significantly. However, durability remains still an issue. Thus, multi-scale modeling of PEMFC performance and degradation phenomena is a field of active research [1] with the aim to enable the technological breakthrough. Continuum-level modeling has helped to identify the physical processes which govern the cell performance. Still, improved models for the description of multiphase flow, catalyst layers and the

ionomer properties are needed [2].

For the macroscopic description of the PEM, physical models for the sorption isotherm, determining the equilibrium water content in the membrane as a function of water activity, are applied. The existence of Schroeder's paradox for the membrane [3], i.e. increased water uptake of a liquid-equilibrated membrane compared to a vapor-equilibrated state, is under debate [1]. A possible explanation for the phenomenon is the existence of an 'extended surface layer' [4] which rapidly re-structures upon contact with liquid water. However, physical models describing the process are missing. Based on the equilibrium state, the kinetics of water uptake are modeled using mass transfer coefficients

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which may depend on the temperature, humidity and the mechanical properties of the membrane [5–9]. The models for water transport inside the membrane take into account diffusive transport [10], convection [11–13], or transport due to gradients of the chemical potential [14–16].

The most complex layers of the PEMFC are the catalyst layers (CLs). The electrochemical half-cell reactions are mostly described using Butler-Volmer (BV) equations. For the ORR, a doubling of the Tafel slope has been observed [17–20] which has been taken into account by the use of different transfer coefficients, depending on the cell voltage [21,22]. Alternatively, for the ORR, elementary kinetic ‘double-trap’ models are applied [23–26]. Due to the confined pore space in this layer, Knudsen diffusion has to be considered in the gas phase [2]. In addition to the flow of liquid water, oxygen transport resistances in the ionomer need to be considered [27–29]. Agglomerate models [21,22,30–33] have aimed to describe these resistances using efficiency factors in combination with BV equations and the Thiele modulus. In some models, the effective agglomerate surface has been assumed to be two orders of magnitude lower than the electrochemically active surface area (ECSA) and extremely large agglomerate radii were employed to fit experimental data. This indicates that a relevant resistance has been missing in these models. Further, in Ref. [34], it was concluded that in state-of-the-art CLs, with agglomerate radii smaller than 100 nm, agglomerate effects manifest themselves only below 0.1 V and are therefore negligible. Consequently, novel ionomer film models, which describe the oxygen transport resistance in ionomer thin-films have been developed [35].

For the rigorous simulation of gas and liquid transport in the gas diffusion layer (GDL), a multiphase Darcy approach has been applied [36–39], which requires correlations for the relative permeability and capillary-pressure-saturation-relation. Alternatively, the multiphase mixture model [40] has been used in order to speed up the computations. However, the interfaces between single and two-phase regions are not tracked rigorously and no net benefit is seen for PEMFC modeling using this approach [2].

To obtain a reliable cell-level model of a PEMFC, the best models for the description of ionomer properties, electrochemistry and transport need to be united. The combined model should be able to describe all experimental observations and still be as simple as possible. In this work, we aim to develop such a model, by relaxing many crucial assumptions made in recent PEMFC models.

As discussed above, many PEMFC models do not treat two-phase flow rigorously. Instead, liquid water is often assumed to exist as droplets in the gas phase [10]. In this case, the gas phase is supersaturated and the water activity is allowed to exceed unity. In this work’s formulation, two-phase flow is treated rigorously.

For the ORR, most often overly simplified BV equations are employed which are not able to capture the reaction kinetics in different voltage regimes. Further, the spatial resolution of the CLs is often neglected. However, as will be shown in this study, this assumption needs to be relaxed in order to obtain realistic results. To describe mass transport losses, the oxygen transport resistances in the ionomer thin-films, covering the carbon and platinum in the CLs, need to be taken into account. All important aspects of the electrode models, governing the cell performance, are combined in this work.

Finally, the model needs to be validated with dedicated experiments. A valid model will be able to describe all observations with a single set of realistic parameters. Many PEMFC models published today are poorly validated. In this study, the importance of validation under a broad range of operating conditions is emphasized. In addition to polarization curves, EIS should be used for model validation. Therefore, a transient model is developed in this work.

The paper is organized as follows. The model description, the numerical framework and the experiments are presented in Sections 2–4, respectively. The results are discussed in Section 5. The model validation, presented in Fig. 2 is the basis for the subsequent results. It is

essential for significant model predictions under conditions that have not been measured and supports simulation results that are experimentally not accessible. After the model validation, we allow ourselves to present simulation results which are not comparable with experiments. With the results depicted in Fig. 3, we start to rationalize the validation results and highlight the importance of the spatial resolution of the CLs in PEMFC modeling. With Fig. 4 we dive deeply into the analysis of PEMFC water management and illustrate how internal humidification [41] proceeds, especially in counter flow mode. The rigorous treatment of multi-phase flow is demonstrated in Fig. 5. All this paves the way for the impedance analysis, the central findings of the paper, which are presented in Figs. 6 and 7.

2. Mathematical model

The mathematical model is based on the following assumptions:

1. Each layer of the membrane electrode assembly (MEA) can be described as a macro-homogeneous medium with effective transport properties
2. The relevant transport processes in the gas channels (GCs) and the porous layers of the cell are the same: convection, diffusion and capillary transport.
3. Gravitational forces can be neglected.
4. Fluid phases in the porous domains are in local chemical equilibrium.
5. At the PEM/CL interface, local chemical equilibrium between the membrane and the porous electrodes holds.
6. Local thermal equilibrium holds.
7. Gases are ideal.

The kinetics of water evaporation and condensation at the PEM/CL interface influence the water transport through the membrane [5–9,42–44]. Since the validation of the sorption kinetics is difficult and for the sake of simplicity, the assumptions of chemical and thermal equilibrium at this interface were made. The influence of sorption kinetics on the water transport will be investigated in the future.

The cell is divided into nine layers which are all spatially resolved. The cell geometry, represented in 2D with an along-the-channel domain, is depicted in Fig. 1, along with the physical processes considered in each layer.

2.1. Governing equations

The general form of the conservation equations, which are solved for each quantity κ (species mass, charge and energy) is derived from the Reynold’s transport theorem [45,46]. It is given by

$$\frac{\partial \xi^\kappa}{\partial t} + \nabla \cdot \Psi^\kappa - q^\kappa = 0, \quad (1)$$

where ξ^κ denotes the density or concentration, Ψ^κ the flux density and q^κ the supply/production of species κ respectively. In the following, they will be discussed separately for the PEM and the porous electrodes.

2.2. Membrane transport

To describe the transport of water, protons and dissolved gaseous species in the PEM, the model of Weber and Newman [16], which is based on concentrated solution theory [47] is applied. Since the original formulation applies to a steady-state and the present formulation is transient, in addition to the flux densities, expressions for the concentration ξ^κ need to be provided. For water, the molar concentration is given by

$$\xi^{\text{H}_2\text{O}} = c^{\text{H}_2\text{O}} = \frac{\phi_{\text{PEM}} \rho_{\text{PEM,dry}} \lambda^{\text{H}_2\text{O}}}{EW}. \quad (2)$$

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