

Direct numerical simulation (DNS) modeling of PEFC electrodes Part I. Regular microstructure

Guoqing Wang¹, Partha P. Mukherjee, Chao-Yang Wang*

*Electrochemical Engine Center (ECEC) and Department of Mechanical & Nuclear Engineering, The Pennsylvania State University,
University Park, PA 16802, USA*

Received 26 July 2005; received in revised form 1 September 2005; accepted 2 September 2005
Available online 10 October 2005

Abstract

A direct numerical simulation (DNS) model is developed to achieve pore-level description of polymer electrolyte fuel cell (PEFC) electrodes. The DNS method solves point-wise accurate conservation equations directly on an electrode microstructure comprising of various phases and hence utilizes the intrinsic transport properties of each phase. Idealized two- and three-dimensional regular microstructures are constructed to represent the porous cathode catalyst layer. Various voltage losses identified from the simulation results are compared with experimental observations. This pore-scale model is further applied to study the morphological effects, such as pore size, layer thickness and porosity, on the performance of the cathode catalyst layer.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Polymer electrolyte fuel cell; Cathode catalyst layer; Pore-level description; Direct numerical simulation (DNS)

1. Introduction

In polymer electrolyte fuel cells (PEFC), two thin electrodes, usually referred to as the catalyst layers (CL), are attached to an ionomeric membrane, typically Nafion[®], to form the membrane electrode assembly (MEA), which constitutes the heart of a fuel cell. The fuel (i.e. hydrogen) and oxidant (i.e. oxygen) react electrochemically in the active catalyst layers to produce electricity, water and waste heat. The hydrogen oxidation reaction (HOR) occurs in the anode catalyst layer, while oxygen reduction reaction (ORR) takes place in the cathode catalyst layer. Despite significant developments, major voltage losses in the PEFC include sluggish kinetics of the ORR and transport limitations of protons and oxidizing species in the cathode catalyst layer. Therefore, it is imperative to fully understand pore-level phenomena taking place in the cathode catalyst layer.

A typical cathode catalyst layer of a PEFC consists of a solid matrix of Pt/carbon particles providing pathways for electron conduction to the reaction site, an ionomer network providing

pathways for proton transport and a network of open pores for oxygen and product water transport. Additionally, the ionomer acts as a binder for the structure and provides stability and mechanical strength to the catalyst layer. The electrochemical reaction takes place at the triple-phase boundary forming an active catalyzed interface, where oxygen is consumed together with protons and electrons, producing water along with waste heat. The cathodic half-reaction, i.e. the ORR, is given by:



Thus, the cathode catalyst layer is a complex porous structure comprising of three phases. An excellent account on the structures and functions of the catalyst layer was given by Gottesfeld and Zawodzinski [1].

Various modeling approaches have been used for catalyst layers. In most of the macroscopic models in the literature [2–5], developed for the polymer electrolyte fuel cell, the active catalyst layer was not the main focus, rather treated either as an ultra-thin layer in terms of an interface or as a macrohomogeneous porous layer. Essentially based on the theory of volume averaging, these models specifically developed for PEFC catalyst layers, can be further categorized as a homogeneous model, a film model and an agglomerate model. Springer and Gottesfeld [6], Eikerling and Kornyshev [7], Perry et al. [8] presented

* Corresponding author. Tel.: +1 814 863 4762; fax: +1 814 863 4848.
E-mail address: cw31@psu.edu (C.-Y. Wang).

¹ Present address: Plugpower Inc., 968 Albany-Shaker Road, Latham, NY 12110, USA.

some comprehensive analytical and numerical solutions for the cathode catalyst layer under various conditions. Recently, Wang [9] and Weber and Newman [10] provided excellent overviews of the various catalyst layer models.

However, these models do not address the local pore-scale phenomena. In their work, Pisani et al. [11] constructed an analytical pore-scale model to study the effects of catalyst layer pore structure on performance over idealized, one-dimensional (1-D) pore geometry. Their emphasis was to ascertain the pore-scale phenomena, for example, the variation of the reactant concentration within the electrolyte phase at the pore-level and decouple these primary variables varying at the pore-level from the ones, which show no pore-scale variation. Preferential non-homogeneity was inducted into the model by defining an effective reaction rate through a modified analytical expression of the Butler–Volmer equation deduced separately for each of the simplified geometries under consideration. Although, they tried to show the effect of the non-homogeneous porous structure through partly accounting for the modified reaction rate, their approach lacked a unified pore-level description of the species and charge transport. The objective of the present work is to demonstrate, for the first time, the development and implementation of a direct numerical simulation (DNS) model on idealized two- and three-dimensional (2- and 3-D) catalyst layer microstructures and assess the effects of morphological parameters on the performance of the cathode catalyst layer through a systematic pore-scale description of the underlying transport processes.

2. DNS model

The DNS model has essentially two steps: the first step is the construction of the catalyst layer microstructure describing the underlying micro-morphology comprising of various phases and the next step is to solve the transport equations for charge and species conservation directly on the microstructure. For the ORR to occur, a typical cathode catalyst layer is assumed to consist of uniformly dispersed Pt particles between the electronic phase (i.e. carbon) and the electrolyte phase (i.e. Nafion[®]) forming an active reaction interface, which is further accessible, by oxygen. Various symbols used in the following subsections are defined in the nomenclature.

2.1. Idealized 2-D microstructure

According to the basic features of the catalyst layer microstructure described above, a 2-D realization of it is constructed as shown in Fig. 1. In the schematic diagram, x -direction is across the catalyst layer thickness and y -direction represents a periodic repeating unit of the actual catalyst layer. In the physical system, a thin film of ionomer is assumed to exist between the electronic phase and the gas phase forming an active catalyzed interface. Protons migrate into the CL from the membrane side on the left boundary (i.e. $x = 0$) and oxygen diffuses into the layer through the gas diffusion layer (GDL) on the right boundary (i.e. $x = x_L$). Oxygen thereafter dissolves in the electrolyte film and is consumed at the catalyzed interface along with protons and elec-

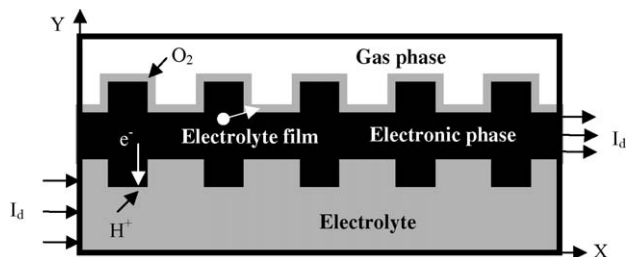


Fig. 1. Schematic diagram of the 2-D computational domain.

trons due to the ORR. The catalyst layer thickness is considered to be 20 μm in the present study.

2.1.1. Model assumptions

As a first step toward modeling the cathode catalyst layer using the DNS approach, the following assumptions are made:

- At the reaction interface, thermodynamic equilibrium is assumed to exist between the oxygen concentration in gas phase and that dissolved in the electrolyte phase. O_2 diffusion resistance through the electrolyte film is ignored due to the small thickness of the film (estimated to be ~ 5 nm).
- The mass balance of product water is not considered, assuming that water is in the gas phase due to heat generation in the CL and diffuses out of CL sufficiently fast. This assumption may bring considerable error at large current densities, which will be justified later.
- The proton conductivity in the electrolyte phase is treated as a constant, though it actually depends on the water content in the ionomer.
- Isothermal and steady state operation.

2.1.2. Governing equations

A single set of governing differential equations valid for all the phases is developed; therefore, no internal boundary condition is required to be specified at the phase interfaces. Due to slow kinetics of the ORR, the rate of electrochemical reaction assumes Tafel kinetics as:

$$j = -i_0 \frac{c_{\text{O}_2}}{c_{\text{O}_2, \text{ref}}} \exp\left(\frac{\alpha_c F}{RT} \eta\right) \quad (2)$$

The overpotential, η , is defined as:

$$\eta = \phi_s - \phi_e - V_{\text{oc}} \quad (3)$$

where ϕ_s and ϕ_e stand for the electronic and electrolyte phase potentials at the reaction site, respectively. V_{oc} is the reference open-circuit potential of the cathode under the specified operation temperature.

The charge conservation for electron and proton and oxygen conservation equations can be described, respectively, as:

$$\nabla \cdot (\sigma \nabla \phi_s) + a \int_{\Gamma} j \delta(x - x_{\text{interface}}) ds = 0 \quad (4)$$

$$\nabla \cdot (\kappa \nabla \phi_e) + a \int_{\Gamma} j \delta(x - x_{\text{interface}}) ds = 0 \quad (5)$$

Download English Version:

<https://daneshyari.com/en/article/196665>

Download Persian Version:

<https://daneshyari.com/article/196665>

[Daneshyari.com](https://daneshyari.com)