

A Dynamic Spherical Agglomerate Model for Proton Exchange Membrane Fuel Cells (PEMFC)

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Abstract

There has been growing interest in the modelling of proton exchange membrane fuel cells (PEMFC). While some steady-state models have been proposed, literature is scarce in PEMFC two-phase dynamic models and transient studies. Typical dynamic models for the fuel cell are empirical current-voltage dynamic models. The internal transients associated with reactant and product species and other components are usually neglected. Further, systems engineering studies such as process control, dynamic optimization, identification of faults and other operational problems in fuel cell studies are missing to a large extent.

A detailed dynamic model for spherical agglomerate in a PEMFC is presented in this work. The dynamic model will include detailed mathematical equations for O_2 and H^+ ions. The model will be unique from the earlier proposed models, as it will include not only the dynamics, but also detailed mathematical equations for transport and electrochemical kinetics. Preliminary results using the dynamic model of spherical agglomerate are presented in this paper.

Keywords: PEMFC, dynamic model, fuel cell, spherical agglomerates.

1. Introduction and Background

There has been considerable interest in the modeling of proton exchange membrane fuel cells (PEMFC) and a number of PEMFC models have been proposed in the literature over the last two decades. The seminal works in PEMFC modeling were published by Springer et al. (1991) and Bernardi and Verbrugge (1991, 1992). These models were one dimensional and accounted for steady state mass transport and electrochemical kinetics. Subsequently, several authors have studied both simplified and complex models in terms of dimensionality and physicochemical phenomena. A thorough review of the scientific and engineering aspects of PEMFC deployment can be found in Costamagna and Srinivasan (2001a, 2001b).

Typically, the models proposed in literature assume that the product water is either in liquid state or vapour and correspondingly the model equations are written. But they do not account for either phase change or accumulation of liquid water within the electrodes. Over the last few years, some of the researchers have studied the effect of

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two-phase flow models inside PEM fuel cells to gain a better understanding of the phenomena of electrode flooding and phase change. One of the first models to include information on liquid water saturation and predict flooding was that proposed by Baschuk and Li (2000). It was one-dimensional steady-state model in which the degree of water flooding was determined by matching the predictions with experimental polarization curve. Dutta et al. (2001) extended their single-phase three-dimensional model to include liquid water as a component. He et al. (2000) presented a steady state, isothermal, two-phase two-dimensional model using interdigitated flow field. This model was subsequently extended by Natarajan et al. (2001) to study the transients of liquid water transport inside the cathode gas diffusion layer. The transient model by Natarajan et al. (2001) was further extended by Natarajan and Nguyen (2003) to include the third dimension i.e., along the length of the channel. Some of the other contributions on two-dimensional multiphase cathode models are by Wang et al. (2001), You et al. (2002), Berning (2003), which are based on two-phase flow mixture theory by Wang et al. (1997). A common feature to be noted in all the above-mentioned models is that the reaction or catalyst layer is not modeled in detail. The catalyst layer is treated as an ultra-thin layer, thus neglecting the transport of reactant gases and products. The cathode and anode catalyst layers are treated as source/sink of product water/reactant gases, respectively. Hence, while writing the species conservation equations in the gas diffusion layers, appropriate boundary conditions are imposed based on electrochemical kinetics at the interface between the diffusion layer and the catalyst layer. Though neglecting the catalyst layers reduces the number of equations and complexity of the PEMFC model, the models will not be capable of predicting local effects inside reaction layers. Hence, a detailed dynamic model for spherical agglomerate is developed in this research work.

Literature is scarce in PEMFC dynamic models and transient studies. Dynamic models are not usually as detailed as the steady-state models. Typically, dynamic models for the fuel cell are empirical current-voltage formulations embedded in a complete system model for a particular application. Dynamic models proposed in the literature take into account only the overall dynamics of the fuel cell. The internal transients associated with reactant and product species and other components are usually neglected (Amphlett et al. (1996), Hubertus et al. (1998)). A one-dimensional dynamic model for a gas diffusion electrode of PEMFC was proposed by Bevers et al. (1997). A two-dimensional dynamic model for the cathode of a PEMFC was proposed by Natarajan and Nguyen (2001). Ceraolo et al. (2003) proposed a simplified dynamic model based on physico-chemical knowledge of the phenomena occurring inside a PEMFC. From the above review it is evident that PEMFC dynamic models are scarce in literature and moreover, their utility has been limited to minimal transient studies of the transport phenomena and electrochemistry.

2. Spherical Agglomerate Dynamic Model

In this research, our aim is to gain better insight into the dynamic operation of PEM fuel cell. Moreover, a detailed understanding of the transient characteristics of the various physico-chemical phenomena will also be undertaken. For this, we will develop detailed dynamic model for a complete PEMFC cell, consisting of anode, cathode and the

membrane. The model will be developed based on first principles, the merits of which are: (i) it provides insight into the fundamental limiting mechanisms, (ii) allows for different physico-chemical phenomena to be easily incorporated, and (iii) can predict behavior of cells over wide range of operating conditions. Some of the unique features of the proposed model are: (i) the model accounts for the dynamics of various phenomena, (ii) it is multicomponent and multidimensional, (iii) nonisothermal in nature to predict temperature gradients inside the cell, and (iv) two-phase effects based on water saturation are considered inside the catalyst layer, diffusion layer and gas flow channels.

A schematic of the half-cell in a PEMFC is illustrated in Fig. 1. The proton exchange membrane fuel cells consist of a polymer electrolyte in the form of a thin, permeable membrane. The cell operates at about 80° C with hydrogen on the anode side and oxygen/air on the cathode side. Hydrogen atoms are ionized in the anode and the positively charged protons diffuse through the membrane and migrate to the cathode. The electrons produced at the anode traverse through an external circuit to the cathode. At the cathode catalyst layer, the electrons, protons and oxygen combine to produce water. The mechanisms influencing the distribution of water within a cell are: (i) diffusion of H₂O (from cathode to anode due to concentration gradient), (ii) electro-osmosis (transport due to movement of H⁺ ions from anode to cathode), (iii) evaporation / condensation (due to liquid water saturation), and (iv) moisture pick-up by exiting gases

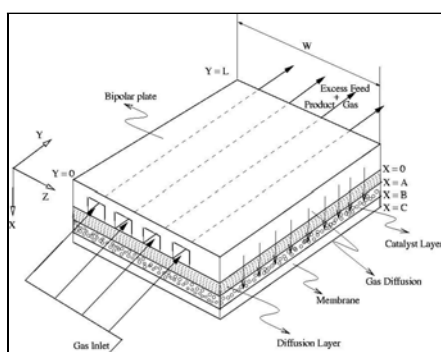


Figure 1. Schematic of a PEM half-cell

Table 1. Two-phase PEMFC modelling assumptions

Section	Modelling
Gas flow channel	Two-phase flow, multicomponent mixture, nonisothermal conditions to account for evaporation/condensation of water
Diffusion layer	Two-phase flow, multicomponent mixture, nonisothermal conditions to account for evaporation/condensation of water
Reaction layer	Two-phase flow, multicomponent mixture, nonisothermal conditions to account for evaporation/condensation of water
Spherical agglomerate	Transport of dissolved oxygen, water and hydrogen ions
Membrane layer	Transport of water and hydrogen ions

The dynamic model equations for each section of the PEM fuel cell are not detailed in this paper due to space limitations. However, the assumptions that are made, the effects that are modelled using the dynamic equations are provided in Table 1.

Simulation studies were carried out on the dynamic model of spherical agglomerate. In spherical agglomerate, conservation equations are written for dissolved O₂, and H⁺ ions. The assumptions that are inherent in the dynamic model for spherical agglomerate are: (i) the polymer within micropores of the agglomerate is assumed to be completely hydrated, (ii) since the size of an agglomerate is small, pressure gradients and convective terms are assumed to be negligible, and (iii) Butler-Volmer equation is considered for oxygen reduction reaction at the surface of platinum. The corresponding dynamic model equations are illustrated in Table 2.

Table 2. Model equations for spherical agglomerate

Model Equation	Comments
Model equations for O_2	
$\frac{\partial}{\partial t}(c_{O_2,agg}\epsilon_{agg}\epsilon_{mem}) = -\nabla \cdot \mathbf{N}_{O_2,agg} + R_{O_2,agg}$	O_2 Conservation
$\mathbf{N}_{O_2,agg} = -D_{O_2,agg} \frac{\partial c_{O_2,agg}}{\partial r}$	Nernst-Plank Equation
$R_{O_2,agg} = -\frac{a_a}{nF} i_o \left\{ \frac{c_{O_2,agg}}{c_{O_2}} \exp\left(-\frac{\alpha n \eta_{agg} F}{RT}\right) - \frac{c_{H_2O,agg}}{c_{H_2O}} \exp\left(\frac{(1-\alpha)n \eta_{agg} F}{RT}\right) \right\}$	$= R_{orr}$
Model equations for conservation of H^+	
$\frac{\partial}{\partial t}(q_{H^+,agg}\epsilon_{agg}\epsilon_{mem}) = -\nabla \cdot \mathbf{N}_{H^+,agg} + R_{H^+,agg}$	In terms of $\frac{Coul}{cm^2 \cdot s}$ H^+ Conservation
$\mathbf{N}_{H^+,agg} = -z_{H^+} F \frac{D_{H^+,agg}}{RT} c_{H^+,agg} \nabla \eta_{agg} - D_{H^+,agg} \nabla c_{H^+,agg}$	H^+ superficial molar flux
$\mathbf{N}_{H^+,agg} = \mathbf{j}_{agg} / F$	Current density and flux
$\mathbf{j}_{agg} = -\kappa_e \nabla(\eta_{agg})$	Charge flux
$R_{H^+,agg} = -a_a i_o \left\{ \frac{c_{O_2,agg}}{c_{O_2}} \exp\left(-\frac{\alpha n \eta_{agg} F}{RT}\right) - \frac{c_{H_2O,agg}}{c_{H_2O}} \exp\left(\frac{(1-\alpha)n \eta_{agg} F}{RT}\right) \right\}$	$= nFR_{orr}$
$\frac{\partial}{\partial t}(C_{agg}\eta_{agg}\epsilon_{agg}\epsilon_{mem}) = -\nabla \cdot \mathbf{j}_{agg} + R_{H^+,agg}$ $= \kappa_e \nabla^2 \eta_{agg} + R_{H^+,agg}$	Charge conservation
Initial Condition	
$t = 0: c_{O_2,agg} = c_{O_2}^s \quad \forall r$	Saturated condition
$\eta_{agg} = \eta_o \quad \forall r$	System start-up
Boundary Conditions	
$r = r_{agg}: c_{O_2,agg} = K_{O_2} p_{O_2,r} \quad \forall t$	Equilibrium at interface
$\eta_{agg} = \eta_o + A \sin(2.0\pi f t) \quad \forall t$	Depends on operating condition
$r = 0: \frac{\partial c_{O_2,agg}}{\partial r} = 0 \quad \forall t$	Symmetry condition
$\frac{\partial \eta_{agg}}{\partial r} = 0 \quad \forall t$	Symmetry condition

Results and Discussion

The agglomerate model was set up in Maple (version 9) and was solved using the method of lines. The dynamics and transients of $C_{O_2,agg}$, η_{agg} , and $J_{agg,cum}$ are studied as a function of both steady DC overpotential η_o and when a small amplitude sine wave is imposed on η_o . The dynamic plots of $C_{O_2,agg}$, η_{agg} , and $J_{agg,cum}$ for $\eta_{agg} = \eta_o + A \sin(2\pi f t)$ with $\eta_o = -0.10$ and -0.15 V are given in Figs. 2-7. From a comparison of corresponding figures, it can be seen that at higher overpotentials, more reaction takes place from the surface of the agglomerate. Hence, the contribution of the agglomerate core to current is less. From simulations carried out with $\eta_o > -0.20$ V, it was observed that the current generated from the agglomerate core is negligible.

From the above results, it can be concluded that the extent of current generated from different regions inside the spherical agglomerate is strongly influenced by the surface overpotential. The above spherical agglomerate model will be extended to include the dynamics associated with H_2O . Including the accumulation of water will help in understanding the variation of membrane conductivity within the agglomerate and the local effects associated with two-phase transformations. The work related to the two-phase dynamic model for the complete PEMFC is also currently under progress.

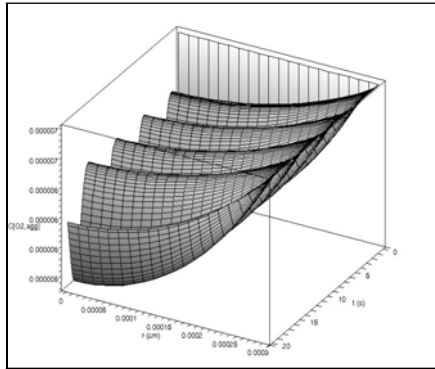


Figure 2. Concentration of O_2 Inside Agglomerate. $\eta_{agg} = -0.10 + A \sin(2.0\pi ft) V$

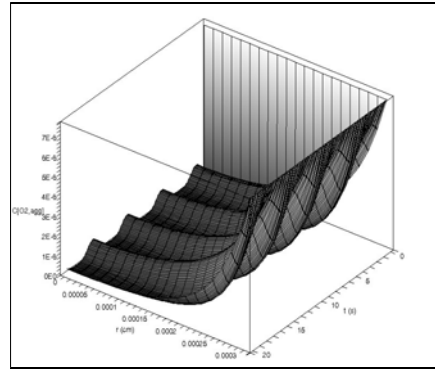


Figure 3. Concentration of O_2 Inside Agglomerate. $\eta_{agg} = -0.15 + A \sin(2.0\pi ft) V$

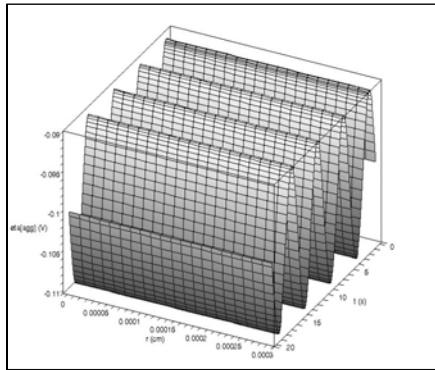


Figure 4. Variation of η_{agg} inside agglomerate. $\eta_{agg} = -0.10 + A \sin(2.0\pi ft) V$

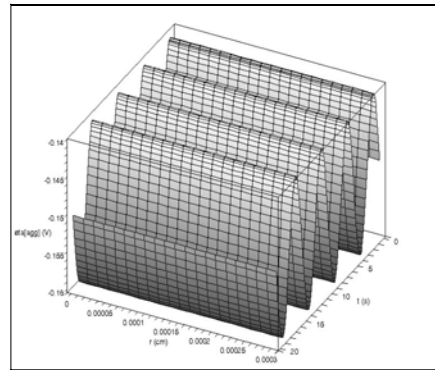


Figure 5. Variation of η_{agg} inside agglomerate. $\eta_{agg} = -0.15 + A \sin(2.0\pi ft) V$

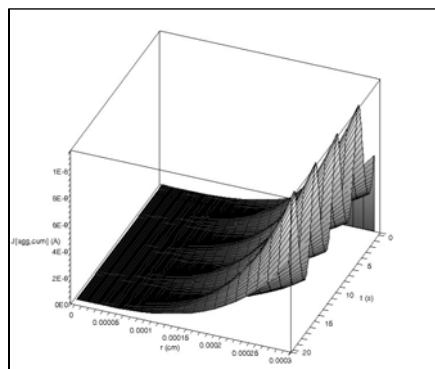


Figure 6. Cumulative current inside agglomerate. $\eta_{agg} = -0.10 + A \sin(2.0\pi ft) V$

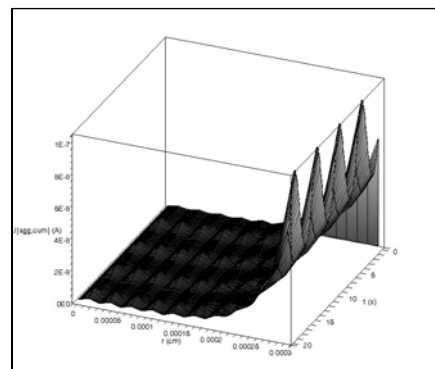


Figure 7. Cumulative current inside agglomerate. $\eta_{agg} = -0.15 + A \sin(2.0\pi ft) V$

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