

## Transport Issues in Polymer Electrolyte Fuel Cells

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### Abstract

This paper describes recent attempts to define and understand important transport issues that control performance and durability of polymer electrolyte fuel cells. The transport phenomena occurring in fuel cells are characterized by a large range of length and time scales. As examples, we will discuss oxygen/proton transport and water distribution in the microscopically complex catalyst layer at the pore level (microscale,  $\sim\mu\text{m}$ ), water management in the membrane-electrode assembly (MEA) (mesoscale,  $\sim\text{mm}$ ), lateral diffusive transport of species and electron transport in the gas diffusion layer over the land between two neighboring gas channels (mesoscale), and multi-dimensional flow, thermal transport, and multi-component species transport on the macroscale ( $\sim\text{cm}$ ). In addition, a comprehensive physico-chemical modeling framework of combining electrochemistry with multi-scale transport is presented for an industrial-scale fuel cell. Areas for future research into transport issues in fuel cells are pointed out wherever appropriate.

### 1. Introduction

Proton exchange membrane (PEM) fuel cells can potentially replace the internal combustion engine because they are clean, energy-efficient, quiet, and have rapid start up transient due to low-temperature operation. A PEM fuel cell consists of an anode, a membrane, and a cathode. The membrane, typically about a few tens  $\mu\text{m}$  thick, is also the electrolyte and made of proton-conducting polymers. The anode and cathode are prepared by applying a small amount of catalyst, typically platinum black or carbon-supported platinum, to both surfaces of a thin polymer electrolyte. The catalyst-coated membrane is then sandwiched between anode and cathode gas diffusion layers (GDL), and the three components are bonded together to produce an integral membrane/electrode assembly (MEA). The anode and

cathode GDLs are contacted on the backside by flow plates with channels that permit oxidizer and fuel flow. The anode flow channel supplies either gaseous fuel (e.g. hydrogen) or liquid fuel (e.g. methanol), whereas air or oxygen is fed into the cathode flow plate. The fuel flowing through the anode channel dissociates at the catalyst layer into protons and free electrons. The protons migrate through the PEM to the cathode where they combine with oxygen from the oxidizer and electrons flowing from the anode through the external circuit, to form water.

Fuel cell science and technology cuts across multiple disciplines, including materials science, interfacial science, transport phenomena, electrochemistry and catalysis. Through a decade-long R&D and tremendous progress, it appears that currently available fuel cell materials will be adequate for near-term markets with highest cost entry points. As a result, the fuel cell and automotive industries are currently placing their focus on fuel cell design and engineering for improved performance and durability. This new focus has led to an urgent need for identification, understanding, prediction and optimization of various transport processes of chemicals, product water, protons and electrons that occur on disparate length scales in PEM fuel cells. This note presents select transport issues that are currently being pursued by an interdisciplinary group of researchers along with their industrial collaborators at Penn State Electrochemical Engine Center (ECEC).

### 2. Transport Issues

#### *2.1 Pore-Level Transport of Oxygen, Water and Protons in Catalyst Layer*

The catalyst layer of a thickness around 10  $\mu\text{m}$  is a critical component of PEM fuel cells. Gottesfeld [1] provided a good overview of the catalyst layer structure and functions. Oxygen reduction reaction (ORR) occurs in the cathode

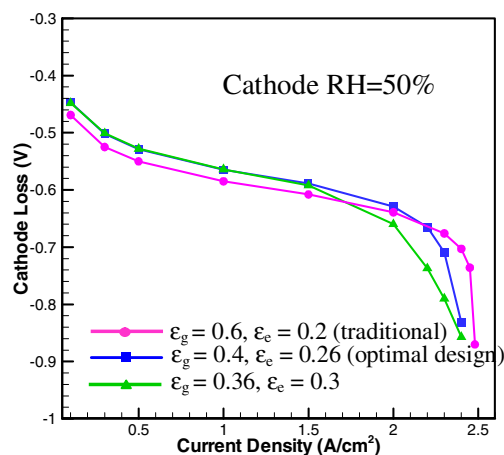
catalyst layer, and the hydrogen oxidation reaction (HOR) takes place in the anode catalyst layer. Both reactions require active catalyst sites to break the molecular bond in the diatomic gaseous reactant molecules because of the low temperature environment of PEM fuel cells. HOR has orders of magnitude higher kinetic rate constant than ORR, which leads to ORR being one of the largest voltage losses in the PEM fuel cell. Due to the acid nature of the membrane electrolyte and low temperature operation, Pt or Pt-alloys are the best known catalysts. In order to enable ORR in the cathode catalyst layer, the layer must provide access for oxygen molecules, protons, and electrons. Therefore, the catalyst layer usually consists of: (1) the polymer electrolyte (its amount is also called Nafion content,  $\epsilon_e$ ) to provide a passage for protons to be transported in or out, (2) metal catalysts dispersed on carbon (the electronic phase volume fraction,  $\epsilon_s$ ) to provide a means for electron conduction, and (3) sufficient porosity ( $\epsilon_g$ ) for the  $O_2$  gas to be transferred to the catalyzed sites. The sum of all volume fractions is equal to unity; i.e.  $\epsilon_e + \epsilon_s + \epsilon_g = 1$ , and individual volume fractions must be optimized to provide the best overall performance of a catalyst layer.

ECEC has developed a direct numerical simulation (DNS) model to describe the transport of protons, electrons, oxygen and product water at the pore level (of the order of 100 nm) within a microscopically complex catalyst layer [2]. This model is based on a numerical mesh created by either a digitized catalyst layer micrograph or a computer-generated random pore structure controlled by a specified porosity and an average pore size, and subsequently performs direct simulation of reactant and product transport with reaction at the pore level. Such a DNS model is being used by the industry as an alternative to experimental trial-and-error for the optimization of compositions and microstructure of a high-performance catalyst layer. Figure 1 shows the cathode voltage loss as a result of kinetic polarization, ohmic polarization, and mass transport polarization, for a commonly used catalyst layer composition (circles), an optimized design (squares), and a less optimal design (triangles). The three-dimensional contour of the  $O_2$  concentration on the right illustrates that the less optimized design exhibits restrictive oxygen transport into the catalyst layer due to a too small porosity.

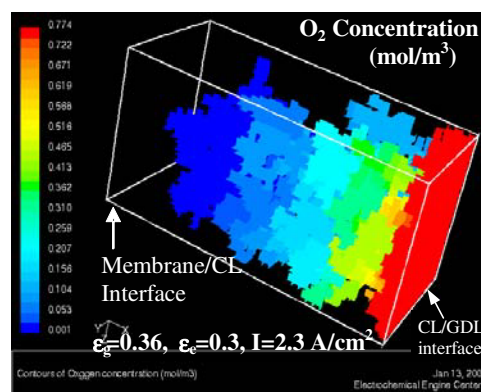
## 2.2 Co-Transport of Protons and Water in MEA

Water management is a key to high performance and longevity of PEM fuel cells. This is because currently available membranes such as Nafion require water in order to exhibit good proton conductivity. Figure 2 depicts a complete picture of water transport and generation in the MEA as well as the water uptake by reactant gas flowing through anode and cathode gas channels, respectively. Water is typically supplied in the gas feed streams at both anode and cathode through external humidification; however, the most recent industrial practice has been to keep the gas inlet relative humidity to a minimum extent possible, without drying out the polymer membrane. This allows for the reduction in the cost and volume of external humidifiers. Within MEA, two modes of

water transport are operative, electro-osmosis that drags a certain number (between 1 and 2.5) of water molecules along with each proton, and molecular diffusion driven by the water concentration gradient set up between the anode and cathode sides of the MEA. In addition, water is produced on the cathode side of MEA due to oxygen reduction reaction.



(a)



(b)

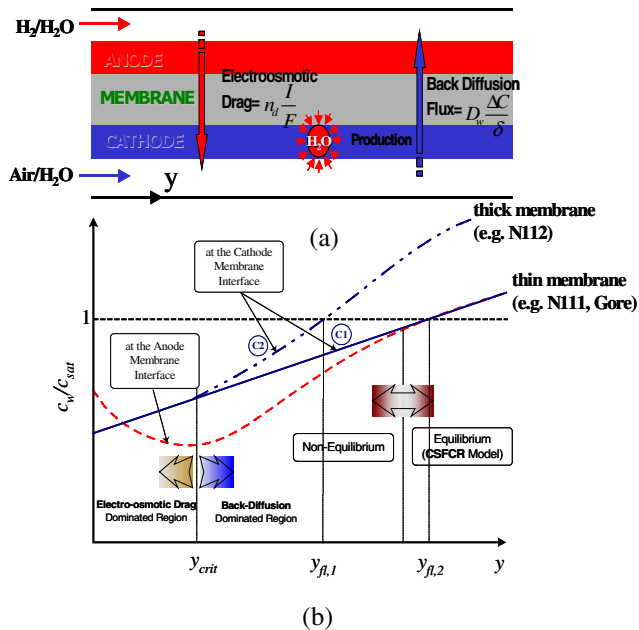
**Figure 1.** (a) Cathode voltage loss as predicted by direct numerical simulation of proton, oxygen and water transport in a catalyst layer at the pore level, and (b) a three-dimensional oxygen concentration distribution in a random microstructure of the catalyst layer.

The complex interplay of water transport and generation within MEA leads to two characteristics of water concentration profiles inside anode and cathode channels along the flow direction. These are shown in Figure 2(b) as the dimensionless quantity normalized by the saturated water vapor concentration (a function of temperature and pressure only). It can be seen that the anode water profile undergoes a decrease initially, meaning losing water to the cathode side due to the electro-osmotic drag. Thus an electro-osmotic drag control regime can be defined based on this behavior. After the minimum point, the anode water concentration will

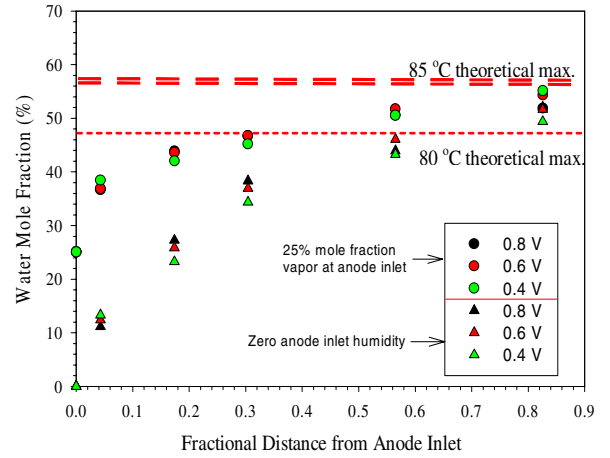
increase as a result of enhanced back diffusion due to the cathode water concentration continually increasing from the oxygen reduction reaction. On the cathode side, the water profile can typically take two routes, depending primarily upon the membrane thickness. For thin membranes (i.e. less than 25  $\mu\text{m}$ ), the back diffusion is so strong that it makes the anode and cathode water profiles reach equilibration. At this point, water distributes uniformly within the entire fuel cell, making a continuous stirred fuel cell reactor model applicable for simple analysis of PEM fuel cell dynamics [3]. On the other hand, thick membranes greater than 25  $\mu\text{m}$  tend to make the water concentrations on both sides of MEA more diverging from each other, as is illustrated in Fig.2.

Using an on-line gas chromatograph (GC) and an instrumented fuel cell, ECEC researchers have measured the water distribution along both anode and cathode channels, for the first time [4]. Figures 3a and 3b show the experimental data in the anode and cathode channels, respectively. These data combined with a fundamental water transport model provide a valuable tool to understand and design water management strategies for PEM fuel cells [3].

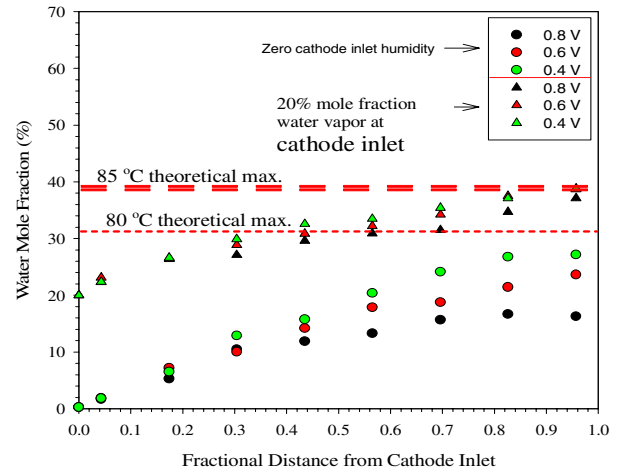
Figure 2 also nicely describes two possible scenarios of electrode flooding. Defining the onset of electrode flooding by the dimensionless water concentration reaching unity (i.e. gas becomes saturated), Fig.2 shows that both anode and cathode will be flooded by liquid water condensed from the gas phase for thin membranes, but for thick membranes only the cathode is susceptible to flooding by liquid water.



**Figure 2.** (a) A two-dimensional sketch of water management in a PEM fuel cell whereby the membrane-electrode assembly separates the anode feed channel from the cathode, and (b) a diagram of water uptake profiles in anode and cathode channels as well as definition of various regimes of water transport.



(a)



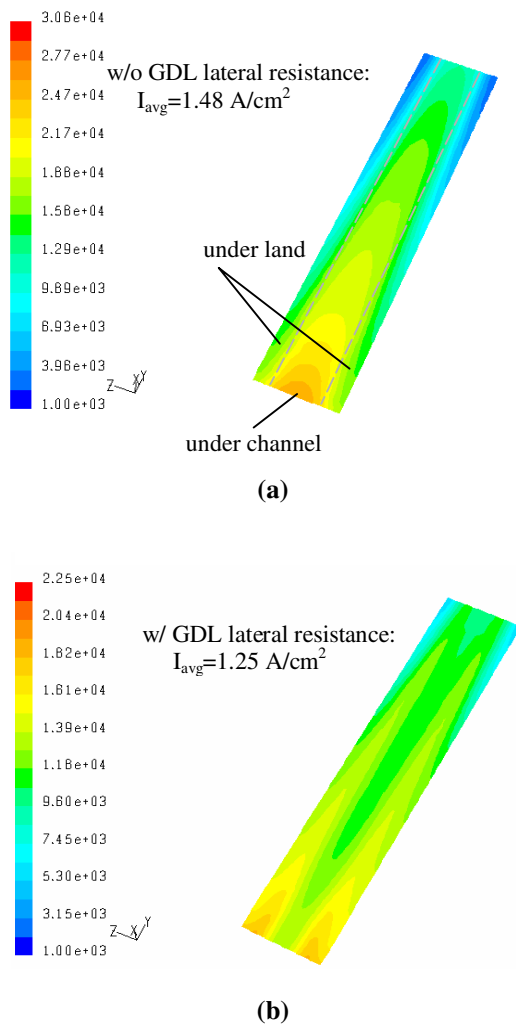
(b)

**Figure 3.** Water mole fraction distributions in anode and cathode gas channels of an operating fuel cell measured by a micro-GC: (a) anode gas channel, and (b) cathode gas channel. The cell temperature is 80°C, and anode/cathode pressure of 1atm, and stoichiometry of 1.5 and 2.0 @ 1A/cm<sup>2</sup>.

### 2.3 Lateral Species/Electron Transport in Gas Diffusion Layer

The gas diffusion layer (GDL) provides dual functions: to supply reactants to the catalyst layer uniformly and to conduct electrons in and out. The lateral transport of species and electrons is referred to as the transport processes occurring in the in-plane direction of MEA between the channel area and the region covered by the land separating two neighboring channels. Here, we are primarily concerned with a mesoscopic scale of approximately one millimeter. On this mesoscale, non-uniform current distribution may result primarily from the low diffusion rate of oxygen in the restricted area covered by the land and GDL resistance to

lateral electron flow. Figure 4 displays the current density distributions in a single-channel fuel cell predicted by a most recent model of Meng and Wang [5]. As can be seen, without accounting for the lateral electron transport in GDL, the current density is highest in the middle of the channel because the reaction zone there has the easiest access to oxygen. However, once considering the electronic resistivity of GDL in the in-plane direction, the highest current density region is shifted towards the edges of the channel because these locations have the best combination of easy access to oxygen and short path for electron transport onto the current-collecting land. This new study clearly establishes the necessity to include the lateral electron transport on a mesoscale in a comprehensive fuel cell model for high-fidelity computer simulations.



**Figure 4.** Current distribution in a straight-channel fuel cell with the 1mm wide channel bounded by two half-width lands (0.5 mm wide) on the edges at the cell voltage of 0.6 V: (a) without GDL electronic resistance, and (b) with GDL electronic resistance.

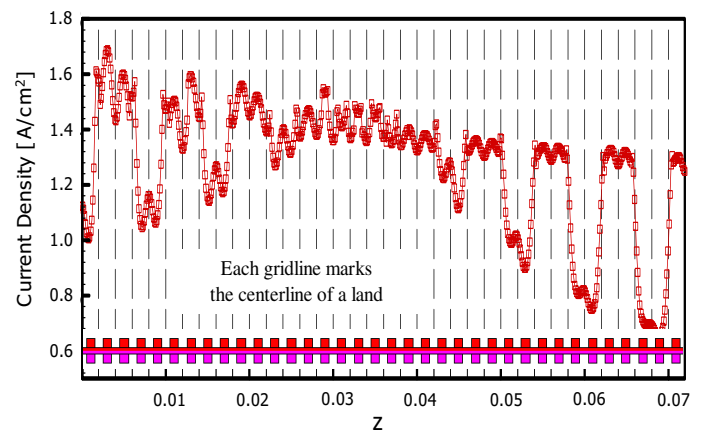
## 2.4 Thermal Transport

A PEM fuel cell produces roughly a similar amount of waste heat to its electrical power (such that the energy-conversion efficiency is close to 50%). This is a fairly large amount of heat generation. Heat generation in PEM fuel cells stems from the irreversibility of the electrochemical reactions, ohmic resistance, and mass-transport overpotentials [6]. Furthermore, the polymer membrane has low tolerance for temperature deviation from its operating point. Hydration of polymer membrane also strongly depends upon the temperature as the water vapor saturation pressure is an exponent function of temperature. Thus thermal management of a fuel cell is inherently coupled with water management, and the two factors combine to ensure high performance and longevity of a PEM fuel cell.

ECEC researchers have developed a unique technique to embed micro-thermocouples in a multi-layered membrane of an operating PEM fuel cell so that the membrane temperature can be measured *in-situ* [7]. An array of up to 10 thermocouples can also be instrumented into a single membrane for temperature distribution measurements. These new data in conjunction with a parallel modeling effort have helped in probing the thermal environment of PEM fuel cells for the first time [3].

## 2.4 Multi-scale Simulation of Industrial-size Fuel Cells

Once sufficient understanding of transport issues occurring at various length scales is obtained, this knowledge can be incorporated with electrochemistry to establish a comprehensive simulation tool for industrial-scale fuel cells featuring tens of flow channels. Such a large-scale simulation is now being made possible by parallel computing on PC clusters using millions of computational cells [8]. Figure 5 shows a current distribution for a 36-channel fuel cell predicted by such a comprehensive fuel cell model using 2,560,000 grid-points. Both large-scale and mesoscale variations in the current distribution are visible.



**Figure 5.** Current density profile in the mid-channel cross-section of a 36-channel fuel cell.

### 3. Summary

Transport in low-temperature PEM fuel cells is an important and physically rich subject. Despite that experimental and modeling capabilities are emerging, presently this is still a largely unexplored area. Much remains to be done before one can utilize the knowledge of multi-scale transport phenomena occurring in PEM fuel cells directly in the cell design and product development.

### Acknowledgements

The author would like to acknowledge the contributions of his present and former graduate students, research associates and industrial collaborators. The writing of this paper was made possible, in part, through the support of NSF under grant no. CTS-9733662, DOE under cooperative agreement no. DEFC26-01NT41098, as well as General Motors, Toyota, Nissan, Hyundai Motor Co., and ConocoPhillips.

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