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Author

Weber, Adam Z.

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On a Pioneering Polymer Electrolyte Fuel Cell Model

Adam Z Weber

Lawrence Berkeley National Laboratory, Berkeley, CA

Jeremy P. Meyers

Department of Mechanical Engineering, University of Texas, Austin, TX

Introduction

In the early 1990s, research in the area of polymer-electrolyte fuel cells (PEFCs) increased dramatically, in both breadth and depth, due to their promise of efficient and clean energy conversion. The sudden increase in interest that this technology received at the time was due in no small part to the demonstration of high-performance catalyst layers with much lower platinum loadings than had been previously been considered possible, specifically enabled by some of the pioneering work performed by Raistrick and his co-workers on ionomer-containing catalyst layers at Los Alamos National Laboratory. (1, 2) The group at Los Alamos conducted experiments into the key materials that enabled and yet still limited fuel cell performance: oxygen reduction reaction on platinum catalysts, and water movement and migration in the proton-exchange membranes (still largely PFSA membranes such as Nafion).

At about the same time, advances in computer technology were enabling increased complexity of mathematical modeling of underlying phenomena in electrochemical systems. Both the testing of PEFC's and the complexity of mathematical models increased throughout the 1990's and into the first decade of the 21st century. As computers have become faster and less expensive, so too has mathematical modeling become more numerically based and complex. The development of models has allowed researchers to examine coupled, simultaneous phenomena in the cell, and to understand how changes in one rate can affect another. The PEFC modeling literature has increased from one or two models published per year to well over a hundred models a year. However, most of these models can trace their heritage back to a model that was developed by Springer, Zawodzinski, and Gottesfeld in 1991. (3)

"Polymer Electrolyte Fuel Cell Model" is a seminal work that continues to form the basis for modern modeling efforts, especially models concerning the membrane and its behavior at the continuum level. The paper is complete with experimental data, modeling equations, model validation, and optimization scenarios. While the treatment of the underlying phenomena is limited to isothermal, single-phase conditions, and one-dimensional flow, it represents the key interactions within the membrane at the center of the PEFC. It focuses on analyzing the water balance within the cell and clearly demonstrates the complex interactions of water diffusion and electro-osmotic flux. This interplay is still a highly researched topic today, nearly 20 years after the model's original publication. Cell-level and system-level water balance are key to the development of efficient PEFCs going forward, particularly as researchers address the need to simplify humidification and recycle configurations while increasing the operating temperature of the stack to minimize radiator requirements. The paper provided the framework for many other groups as can be seen in the hundreds of citations by other modeling-based papers, and has subsequently been made more complex with time to include more phenomena and dimensions. It also serves as the basis for many different commercial PEFC modeling programs and codes.

Model

The schematic diagram of the model included in the paper is shown below in Figure 1. The model includes three distinct sections: a cathode backing region, an anode backing region, and the membrane in between. The reactions are carried out at the backing-layer/membrane interface on each side of the cell. Although cell-level models had been developed for batteries and even for other types of fuel cells, its application to PEFCs was still relatively immature. Aside from some empirical curve-fitting, the first PEFC models focused on the interactions within the catalyst layers and drew heavily from phosphoric acid research. The Springer model was the first one to truly examine water management in the membrane of a working fuel cell.

The model includes Stefan-Maxwell diffusion in the diffusion media, and while its treatment of the electrode kinetics neglects any distributed reaction zone in the catalyst layer, and considers only the dependence of oxygen content at the catalyst layer/gas diffusion layer interface, this model managed to capture quite a bit of what was occurring in a PEFC based primarily on the level of hydration of the membrane and the effective partial pressure of oxygen in the cathode catalyst layer. While subsequent models have sought to explain how the reaction rate varies through the thickness of the catalyst layer, and have refined our understanding of flooding in the cathode diffusion media, this model captured a lot of the basic physics and revealed explicitly the tradeoff between too little and too much water in the system.

Treatment of ionomeric membranes

While some attempts had been made earlier to model a cell or particular components of one with the most notable probably those of Verbrugge and Hill (4), and Fuller and Newman (5), no one had yet distilled a complete cell sandwich model composed of diffusion media, catalyst layers, and membrane. While the Springer model treated conditions that were relatively mild, (i.e., 1-D, single-phase flow, no detailed reaction-rate distribution, and isothermal) it still utilized many of the underlying equations for multicomponent diffusion and electrokinetic phenomena.

The model laid the foundation for more recent -and more complicated- descriptions in which the basic model has been rendered more complex, both in dimensionality and in the number of coupled phenomena (even subsequently by the authors), yet retaining much of the basic physics. The membrane treatment is highlighted and linked to the tradeoffs inherent in PEFC water management. Although it did not directly model liquid water, it discussed it, and utilized data where it was not as critical (membrane dehydration being more dominant in the model simulations).

The most lasting and important impact of the model was the treatment of the membrane. The use of a diffusion-type, single-phase equation of has run into limitations, and authors have since sought to describe the existence of multiple modes of transport and even distinct phases within the proton-exchange membrane. The authors elected to treat the water in the polymer as a dissolved species in the single membrane phase, as opposed to a condensed liquid in pores moving under a hydraulic pressure gradient.

The model also popularized the use of λ ($\bar{\lambda}$) as a modeling parameter, a function of which all of the various transport properties can be expressed. This serves as an expression of concentration, in the same way that electrolyte concentration expresses the chemical state of a liquid electrolyte. In this fashion, it allowed for variable properties in the membrane such as conductivity and the water diffusion coefficient.

The value of λ serves as a measurement of the water content of the membrane, the number of moles of water per equivalent of acid in the membrane. It is equivalent to a concentration in a system where water can easily move into and out of the system, but where the quantity of membrane is fixed by the design of the cell.

Thermodynamic and transport data

In addition to the validation data provided, the Springer paper distilled the various membrane transport-property measurements occurring at Los Alamos National Laboratory at that time. In some cases, transport property data was extrapolated or assumed to maintain a trend or value beyond the range where measurements had been taken place, but the trends were established and noted. In particular, the fit of water content to water vapor activity expressed in Equation [16] has been used in countless papers and presentations to correlate membrane water content and gas-phase humidity. The work the authors did to reduce data to a polynomial function has ensured that subsequent researchers could quickly and easily estimate the level of hydration in PFSA membranes of this type.

The paper provided relatively straightforward values for the diffusion coefficient of water, protonic conductivity, and electro-osmotic coefficient n_{drag} , all from various experimental analyses and functions of water content. Many of these expressions are still used in the modeling community today, with a preponderance of the debate centered on determining water content rather than the precise functional forms. It should be noted that some of the functional forms were quickly supplanted by more refined measurements in just a few years: a few years later, the authors would make measurements of the transport number of water that supplanted the assumption of a linearly varying drag coefficient included in Equation [18]. (6) The use of NMR to measure diffusion coefficients is subject to some scrutiny, but provides a means of measuring a diffusion coefficient in a system where liquid-phase measurements of the relaxation of concentration profiles are not possible.

In this model, the nature of water content and transport properties on membrane histories is neglected. In subsequent papers, it is shown that membrane history and the membrane surface properties play a role in setting the overall hydration level and transient behavior, but these aspects were not yet addressed, and would only later be discovered. Also, by operating in a single-phase region, the details of Schroeder's paradox, the apparent discrepancy between water uptake at 100% saturation in the vapor phase and that for pure liquid water, are neglected.

Results

The model demonstrates how one can use polarization curves for validation and how one can use a model to explore optimization strategies and variable space not readily experimentally available. It is remarkable that many of the conclusions and water balance figures are the same as those found today with much more complex and coupled phenomena modeled. In the years since the model was first published, in-situ measurements and diagnostic techniques have become much more capable and refined, but at the time of publication, there were no ways to visualize water content within the cell or to estimate potential distributions through the thickness of the membrane. Only by modeling could researchers look "inside" the polymer electrolyte and isolate the effects of various phenomena.

Some of the key results are polarization curves broken into overall cell voltage and the ionic resistance of the system. The model is particularly helpful in illustrating the coupled effects which dictate performance: the factor of β is the ratio of water flux to protonic flux. In the case of a cell with the same water activity on both sides and no generation of water at the cathode, the factor β would be identically equal to the value of the electroosmotic drag coefficient. When water is generated on the cathode in a real cell, however, back-diffusion comes into play, and the interplay between diffusion, drag, and gas-phase mass transport resistance dictates the overall performance and identifies where the optimum hydration level resides.

Conclusions

"Polymer Electrolyte Fuel Cell Model" ushered in a new era in understanding of PEFC operation and phenomena. It stands at the forefront of a now rich community dedicated to the use of mathematical modeling to describe, explain, and optimize performance of fuel cells. It is easy to forget in today's age of fast computers, commercial software packages, and cheap multicore processors, how specialized modeling was only twenty years ago. This paper stands the test of time both in analysis and presentation, demonstrating that relatively simple analyses, if done correctly, can provide extensive knowledge and insights into PEFC operation. The principles described and established in the paper hold true today. It is also still a heavily cited paper where it is averaging about 150 citations per year over the last decade, which also demonstrates the emphasis on modeling, PEFCs, and the advent of cheaper, more robust technology.

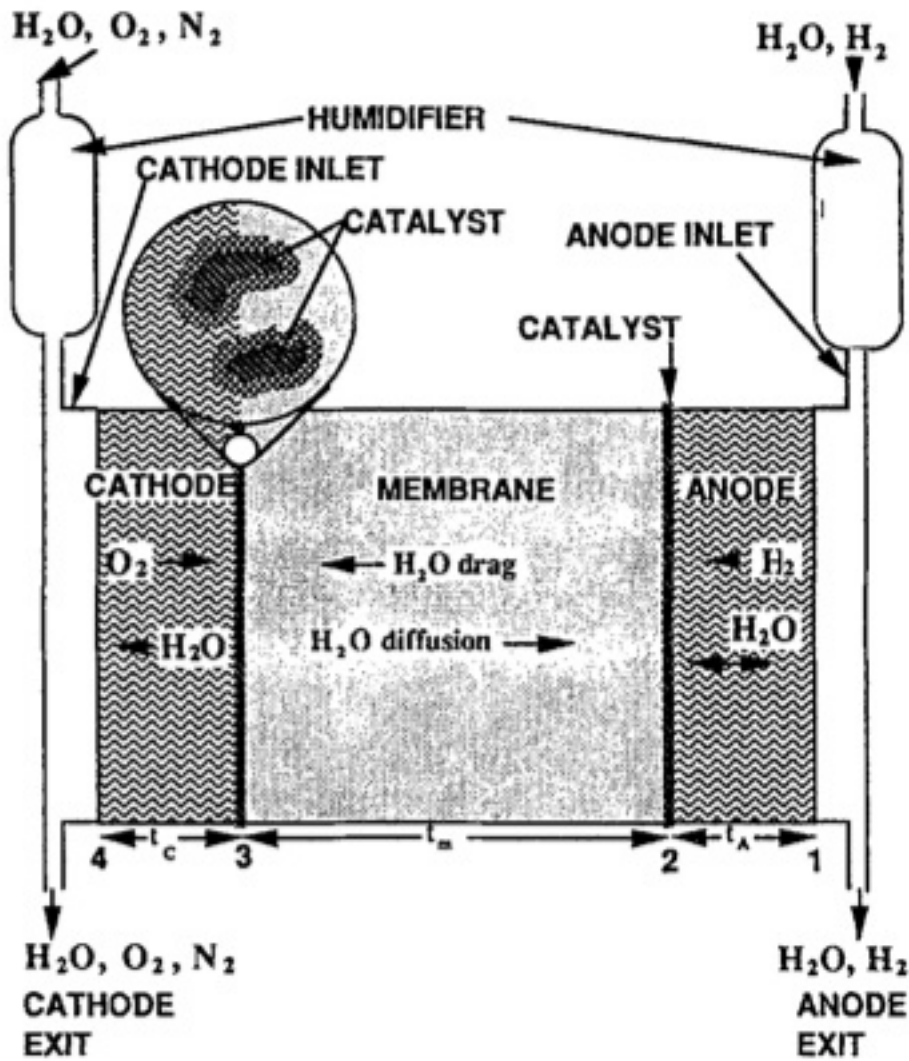


Figure 1. Schematic of model. The model is comprised of three distinct regions (cathode backing region, membrane, and anode backing region) for transport with planar catalyst layers. The backing regions describe multicomponent gas-phase transport, and the membrane region includes diffusion and electroosmotic drag for water transport.

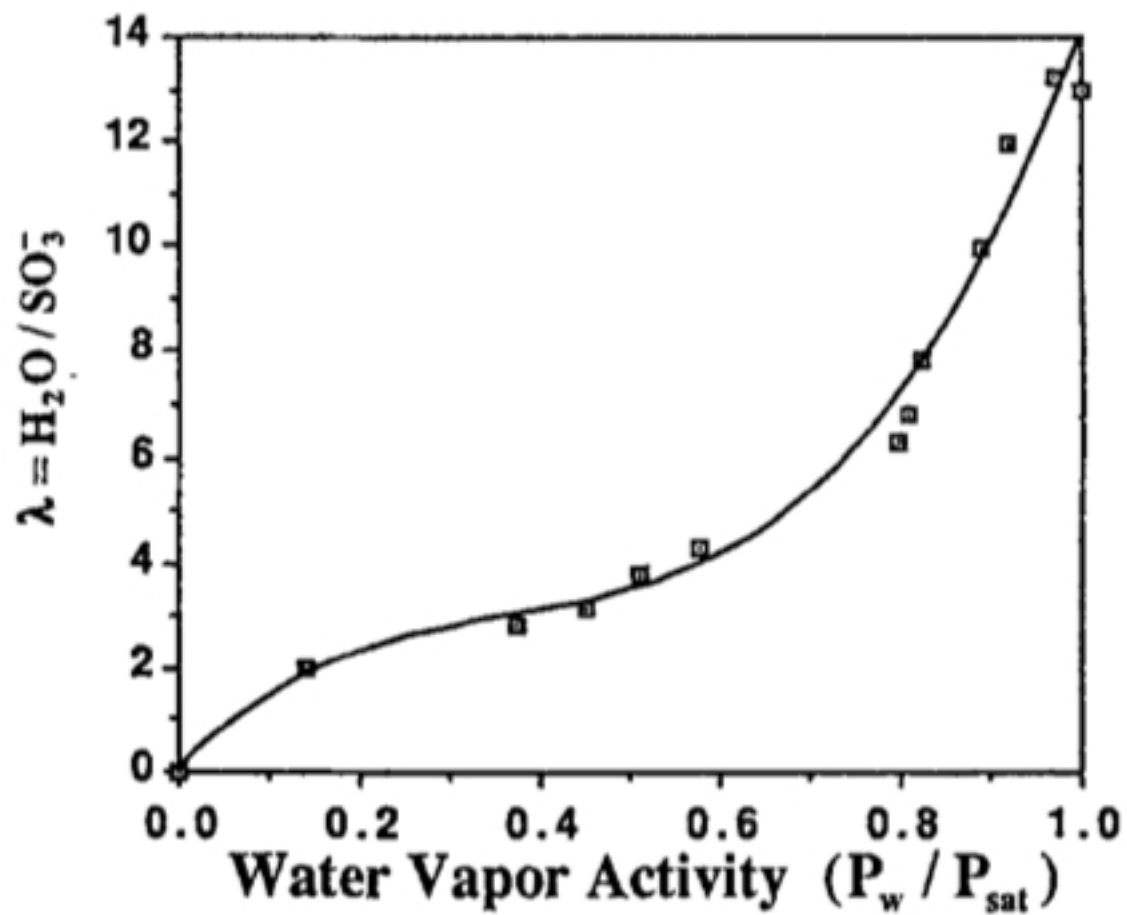


Figure 2. Water uptake versus water vapor activity in the Nafion membrane. The solid line is a fit to the measured data and this fit has been cited and used in many subsequent models and analyses.

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