Computational Fuel Cell Dynamics-II

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1 Introduction

The world's major automotive manufactures are engaged in an historic race to develop Proton Exchange Membrane (PEM) fuel cells as clean, high-efficiency alternatives to internal combustion engines for automotive power. PEM fuel cell technology not only holds out the promise of a more environmentally friendly automobile, but also of an extremely versatile power generation system with a broad spectrum of applications.

For such an important application, one rich in interesting phenomena, PEM fuel cells has attracted relatively little interest from modelers, both analytic and computational. Until the last few years, the number of rigorous attempts at modeling fuel cell performance were few (see [10, 6, 8, 12, 4] for some of the "classic" ones). Certainly the field had received little attention from mathematicians. However, the importance of this activity was clear: to develop understanding of fuel cell processes and their interactions; to develop computational fuel cell models to permit faster and more cost efficient design optimization.

The CFCD meeting hosted by PIMS and Ballard Power Systems at Simon Fraser University in June 2001 was an attempt to give focus to this activity. This meeting brought together mathematicians, engineers, and industry representatives in the PEM fuel cell community to exchange expertise and find common ground. It was the goal of the CFCD-II workshop to build upon this effort, uniting researchers from computational and applied mathematics, chemical engineering, mechanical engineering, polymer chemistry, and electrochemical engineering; setting a framework for future research directions, and seeding multi-disciplinary efforts which will lead to the development of a new generation of analytical and computational tools for PEM fuel cell design.

2 Proton Exchange Fuel Cell Membrane Overview

PEM fuel cells generate electric potential by separating the oxidation of hydrogen into two catalysed steps performed on opposite sides of an electrolyte membrane. The end products are water, water vapor, and heat. A 2D slice of a unit cell is shown in Figure 1. The humidified reactant gases, air (the oxidant) and hydrogen (the fuel) flow in channels cut into graphite plates (the 3D structure of the unit cell is shown in Figure 2). The gases flow through the gas diffusion electrodes (GDEs) which are often teflonated carbon fibre paper. At the GDE/membrane interface is a Platinum catalyst layer.
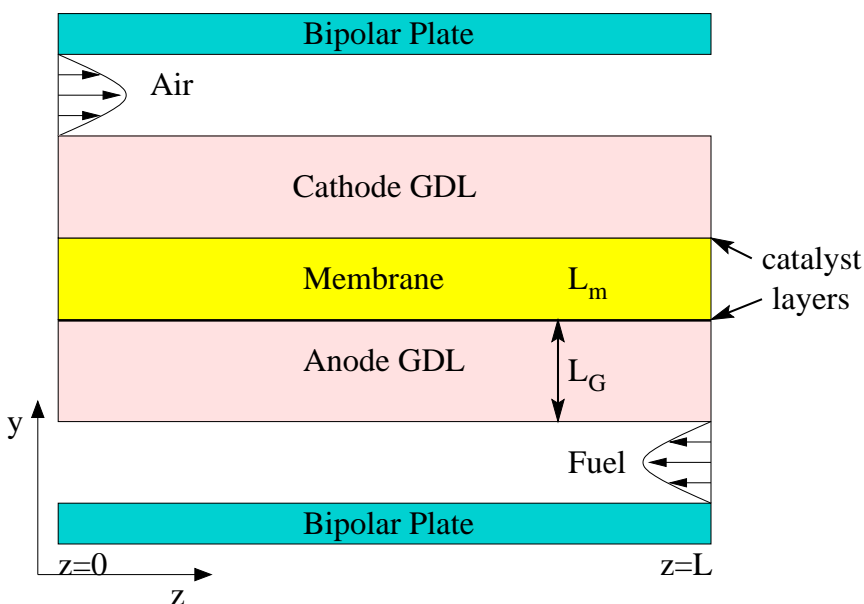
Along the Channel Slice

Figure 1: Unit Cell Slice.

On the hydrogen (anode) side the catalyst helps the hydrogen more easily dissasociate into protons and electrons. The membrane is a good protonic conductor but a very poor electron conductor. The protons can diffuse across the membrane and the electrons go around an external circuit doing useful work. On the other side of the membrane (the cathode) the protons combine with oxygen molecules and the returning electrons to produce water. This reaction is also catalysed by Platinum. It is this reaction which provides the energy to generate the voltage of the circuit.

The unit cell presented here with straight channels is the simplest possible arrangement. In many unit cell designs, the flow fields are arranged in a serpentine way and are the alignment is not the same on anode and cathode. There are additional electrical and thermal coupling effects when unit cells are arranged in series in a fuel cell stack. It should also be mentioned that this type of cell, with pure hydrogen, is only one approach to design.

The electrolyte membrane is a complex polymer comprised of Teflon spines from which typically hydrophilic SO_3^- groups extend. These are arranged in a nanoscale configuration which facilitates the selective diffusivity of the membrane, enabling the fuel cell to perform close to the thermodynamic limit for efficiency. The membrane must be well hydrated to function, however overproduction of liquid water may saturate the surrounding porous electrodes and leads to pronounced drops in power density. The control of the motion and distribution of liquid water in both the nano-structure of the membrane and the surrounding fibrous electrodes is referred to as water management, and is critical to effective cell operation.

3   Computational Fuel Cell Modeling

A proper modeling of the transport process requires understanding of the interactions of water and ions within the polymer membrane. These issues lead to intriguing mathematical phenomena at the limit of continuum mechanics, including degenerate free-boundary problems requiring novel computational methods. The development of a predictive computational model of water management requires an understanding of the fundamentals of liquid transport in nano-scale pores, in turn demanding development of innovative numerical schemes to adapt to the widely disparate time and length scales present in the system.
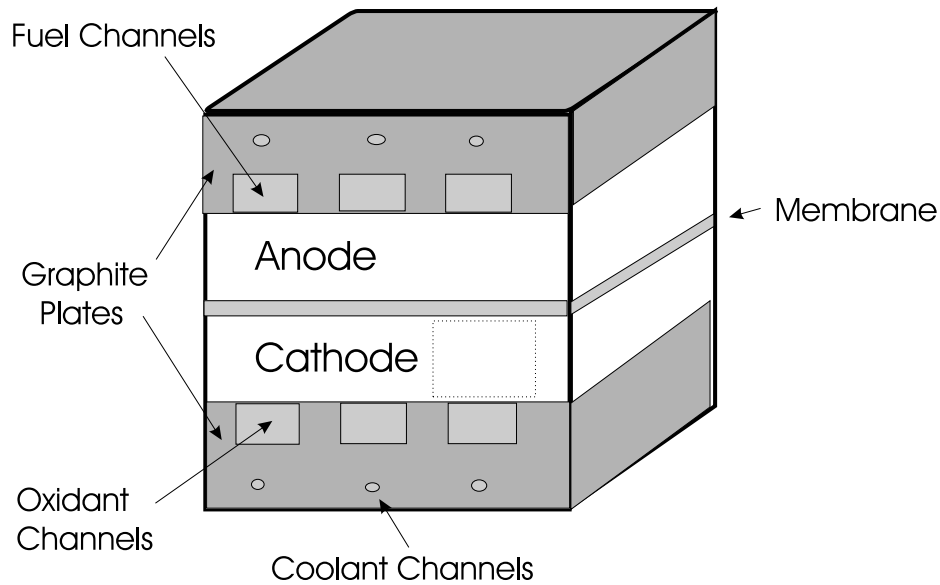
Figure 2: The 3D structure of the unit cell.

In the last two years, several large computational fluid dynamics (CFD) code vendors have become interested in developing comprehensive fuel cell computational models. Some examples are the modules developed by CFX [3], StarCD [11] and the more academic FEMLAB [5]. These CFD codes provide convenient 3D meshing and visualization tools and robust solvers for the traditional fluid dynamics elements of fuel cell models. These codes will provide a platform for validated models of elements unique to fuel cells to be integrated into the "big picture". However, preliminary models suggest that the delicate balance of temperature, condensation and liquid water transport in the GDEs will be difficult to capture accurately in these general packages. Also, larger scale problems such as electrical coupling of cells in stacks and long time transients will have to be handled by specialized codes.

A collaboration between modeling and experimental work is needed in the development of models for fuel cells, as in other similar fields. Experimental work can serve first to guide and validate models and allow parameters to be fit. In turn, models can identify critical parameters that be the subject of experimental measurement or the target for materials engineering.

Some of the more important aspects of fuel cell modeling are listed below.

Mass transport of species in membrane materials: water mobility and proton motion through Nafion and similar PEM products. Some of the questions of interest here have been considered by researchers in biological membranes. Various effects can be considered, ranging from molecular level models, hydraulic pumping, nano-technology and capillary forces.

Condensation and two phase flow models for gas diffusion layers: based on hydrophobicity and capillary forces combined with porosity and permeability factors associated with GDL were presented. This coupling of forces leads to difficulties in predicting water formation within the various regions of the GDL and catalyst areas. These parameters are extremely difficult to measure and correlate to model results.

Capillary, hydrophobicity and rivulet modeling: depicting parameters such as pressure fronts and water droplet formations coupled with various geometry and shapes is an issue. Capillary effects can be a dominating effect when coupled with poorly matched micro-channels and header configuration.

Unit cell modeling: Mathematical solutions with simplified geometry to avoid time consuming CFD solutions. These models can be simplified by using a 2 dimension geometrical model

with 1-dimensional transport through the MEA. This 'trick' allows for quicker solution times assuming minimal channel effects on flow.

4   Presentation highlights (by alphabetical order)

Jeffery Allen (National Aeronautics and Space Administration) This presentation addressed the need for gravity insensitive fuel cells for space applications. Under these conditions, capillary forces are predominant. However, for terrestrial applications, capillary forces are also important partly due to the small flow channel sizes. Capillary flow in square channels was experimentally investigated and measurements were compared to theoretical analyses. On the basis of the results obtained, further work in several areas were recommended (two phase flow in complex non circular geometries under capillary force control, stability of liquid films, liquid water separation).

Daniel Baker (General Motors) AC impedance was discussed as a potential diagnostic tool (see [2]). to measure in situ local membrane resistance/electrode humidification. It was claimed that separation of the membrane resistance from other resistances (contact, GDL, etc) could be achieved by varying operating conditions). Cable inductance effect at high frequencies was taken into account by adding a small inductance to the model. Current perturbations were used instead of voltage perturbations (more convenient for stack measurements). Measurements were also made with a segmented cell (10 x 10 segments) but only at a single frequency to monitor the membrane resistance. Discrepancies were found between CFD code predictions (StarCD) and measurements which were ascribed to either membrane conductivity values and liquid water presence. The effect of lateral currents between different segments was not assessed.

Jay Benziger (Princeton University) This presentation discussed fuel cell control issues. Most experimental data/models assume either current or voltage control. However, resistance control is more appropriate (a load resistance is changed during transients). This case was studied for a PEMFC CSTR (continuous stirred tank reactor) which is achieved by the use of high stoichiometries and cooling flow rates. A simple model was developed assuming operation in the ohmic regime. Experiments included transients with dry reactants and different initial membrane water contents (obtained with prescribed reactant relative humidities prior to the transient experiments). Interestingly, multiple steady states were found which offer an additional method to probe PEMFC behavior.

Felix Buchi (Paul Scherrer Institute) A model similar in scope (simple 1+1 D model) to the one presented by Brian Wetton was discussed. However, there were some differences between the models. Buchi used the Stefan Maxwell equations to model gas diffusion in GDLs as opposed to a simple mass transfer coefficient. Also, the electro-osmotic drag coefficient was assumed to be a constant but because of the different membrane behavior treatment led to the need to discretize the dimension through the membrane which was not necessary in the Wetton's model (analytical equations describe that particular direction).

Ravindra Datta (Worcester Polytechnic Institute) A membrane model was described (water content) but was largely based on a previous paper [7]. The main differences were the inclusion of two modifications: multi-step equilibrium between water molecules and proton, inclusion of a contact angle (claimed to be responsible for the Schroeder's paradox). Also, a membrane conductivity model was also presented which includes the membrane water content model.

Ned Djilali (University of Victoria) A description of a two phase CFD code (steady state, single cell) was discussed. Code convergence was established in 3 steps (no liquid water, liquid water, phase change). The need for a catalyst layer model was highlighted.

Joseph Ferhibach (Worcester Polytechnic Institute) The discussion centered about the use of electrochemical potentials to reduce the number of variables needed for modeling. The

molten carbonate fuel cell was previously used to demonstrate the validity of this technique. The PEMFC has not yet been modeled using this approach.

Jurgen Furhmann (WIAS, Berlin) This presentation addressed the mathematical details behind a direct methanol fuel cell model (see next presentation by Klaus Gaertner). This is an academic (not commercial) finite element method (FEM) code that performs sophisticated quasi-Newton iterations using implicit time stepping to achieve fast calculation of the model, which is very stiff due to the liquid water motion in the GDL.

Klaus Gaertner (WIAS, Berlin) A detailed direct methanol fuel cell model was presented (assumptions and physical description of the phenomena). Methanol is fed in the cell as a vapor and as a result some of the conclusions are not directly applicable to PEMFC electrode liquid water accumulation issue at high current densities. However, future work will include an extension to PEMFC. Additionally, the discussion brought up the need to measure the capillary pressure as a function of water content for GDL type materials (a key element to model liquid water in GDLs). This was confirmed by a number of other participants as the only available relationships were derived for soils and related materials which are not directly applicable.

Gerhard Hummer (National Institute of Health) Molecular dynamics was used to understand water movement in pores associated with living cell processes (transfer of water during oxygen consumption along hydrophobic pores). Similar processes occur in kidneys (filtration). Water transport was modeled using carbon nanotubes. Interestingly, proton diffusion in those carbon nanotubes (water transport is one dimensional) occurs 40 times faster than in bulk water. This research could potentially contribute to better designed proton exchange membranes.

Xianguo Li (University of Waterloo) Two models were presented: flow distribution in stacks and cell performance with reformate fuel. The key model parameter was the flow resistance. Model results led to the suggestion of modifying the cell design along the stack to ensure uniform reactant distribution to each cell (impractical from a manufacturing point of view). This work has not yet been published. As for the reformate fuel model, the computed results highlighted at least one deficiency as air bleed values of up to 30% were required to manage trace amounts of CO.

Tim Myers (University of Cape Town) This presentation addressed thin film flows. However, pressure driven flows were not discussed but are considered as future work.

Boaz Nadler (Yale University) This presentation also addressed ion movement in protein channels with the objective to predict their function if the structure is known. The discussion centered around the determination of the proper equations to describe the physical phenomena (extension of the Boltzmann distribution/ Langevin treatment to continuity equations). In effect, the author is trying to include molecular structure effects into a continuum description. This treatment could benefit proton exchange membrane modeling activities.

Stephen Paddison (Los Alamos National Laboratory) This presentation was a summary of previous work aimed at the understanding of membrane properties (electro-osmotic drag, water content and transport, high temperature membranes with low water content requirements) using several techniques which are length scale dependent (ab initio computations, molecular dynamics, statistical thermodynamics) and which can lead to experimental correlations between molecular structures and material properties, and material design specifications. Both Nafion and PEEK (poly-ether-ether-ketones) chemistries were discussed. Nafion side chains do not interact with water (hydrophobic). However, if the side chain is an hydrocarbon, interactions with water are present (hydrophilic). The dissociation of the hydrogen atom from the sulfonate site does not occur with only 1 or 2 water molecules per sulfonate site. Hydrogen dissociation occurs with 3 or more water molecules per sulfonate site. With 6 water molecules per sulfonate site, the proton is separated from the sulfonate site negative charge. Lower water contents at which proton separation occur are better to achieve conductivity at low reactant relative humidities. From this point of view, the separation between proton and sulfonate

site is greater for Nafion than PEEK (the strong base behavior of the PEEK aromatic ring imparts an hydrophilic behavior which reduces separation). As a consequence, low strength base functionalities should be considered to ensure maximum membrane conductivity. Good agreement was obtained between measured and computed proton diffusion coefficients.

Reginald Paul (University of Calgary) This researcher conducts joint work with Stephen Paddison (modeling proton movement within membrane channels).

Keith Promislow (Simon Fraser University) This presentation set the stage for the conference summarizing fuel cell phenomena and physical models used as representations. There was a brief discussion about the water concentration difference across the membrane which generates a potential difference (about 10 mV). The gap existing between the engineering and modeling world was also highlighted (for example, the use of mathematical approximations which do not necessarily represent physical phenomena). Evidence for the existence of this gap include the difficulty in finding people who are knowledgeable about modeling and experimental aspects of fuel cells. Finally, the need to relate measurement parameters to model variables was highlighted (need to relate macroscopic parameters to microscopic parameters).

Isaak Rubinstein (Ben Gurion University) This presentation addressed a membrane modification for separation processes [9]. The detailed mathematical analysis of ionic transport was new to almost everyone in the audience.

John Stockie (University of New Brunswick) A model for the water content of the electrodes was presented but is not currently validated.

Trung Van Nguyen (University of Kansas) This presentation targeted the use of inter-digitated flow field to characterize the presence of liquid water in GDLs (increased pressure drop). References electrodes were also used (GDEs on the reference electrode side were wider and offset by more than three times the membrane thickness with respect to the GDE on the other side to ensure minimum disturbance [1]). Transient experiments were used and, overpotentials as well as pressure drops were monitored which showed simultaneous increases in value (ascribed to liquid water accumulation). The liquid water accumulation process is slow (approximately 30 minutes).

John Van Zee (University of South Carolina) This presentation summarized efforts to develop a CFD tool to describe PEMFCs. Some model features were questioned or are debatable. An interaction between reactant humidity and cell compression was mentioned. StarCD [11] includes transient functionality coupled with the presence of liquid water (cases with high levels of liquid water were not run). This liquid water is modeled as a thin film. The quantity of liquid water present in cells was not measured. The model is useful to predict cell behavior but is not currently fully validated. The model showed that liquid water localization is dependent on flow field design. 2° C difference between channel and membrane was also reported.

Brian Wetton (University of British Columbia) This presentation summarized the development of a simple PEMFC model co-developed with Ballard. Henry's law coefficient, presently assuming water as the solvent, was questioned (value should be revised assuming Nafion as the solvent). It was also suggested that model fitting could be carried out in two steps for both low and high current densities.

Jinchao Xu (Pennsylvania State University) This presentation addressed general numerical issues related to adaptive mesh refinement and efficient (multi-grid) solution techniques for a general class of partial differential equation problems. The exciting developments in so-called alebraic multigrid, in which improved solvers can be found automatically from existing discretizations, were outlined. Several impressive examples were shown of the effectiveness of this technique in speeding up the solution of existing discretized problems.

5   A Personal Note from the Organizers

All the participants thoroughly enjoyed their stay at the Birs facility. The venue is superb and the scenery, the hospitality and the food were fantastic. The cachet of Banff brought a number of the more important participants in the field that might not otherwise have attended. The beauty (and isolation) of the location kept many there longer than they had originally planned. The scientific discussions continued long after the talks were over, in the meeting rooms, the hiking trails, and by the "donation" fridge. It was a meeting that will shape the future of our fledgling field for years to come. Our thanks to the staff and directorship of Birs for this opportunity.

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