CFCD-III Schedule

March 18, 2005

Rooms

accomodation: Corbett Hall

reception, coffee breaks, breakfast: Corbett Hall 5210

talks: Max Bell Room 159

buffet lunch and dinner: Dining Room in Donald Cameron Hall

See

`http://www.banffcentre.ca/about/location/maps.htm`

for a site map.

Saturday, March 19

7:00-9:00 pm Informal reception.

Sunday, March 20

9:00-9:30 Birs director and staff, *Birs Institute Welcome*

9:30-10:00 Brian Wetton, *An overview of fuel cells: science, modelling and mathematics*

10:00-10:30 John Kenna, *Application of Mathematical and CFD models for Design Space Analysis and Optimization Studies*

10:30-11:00 coffee break

11:00-11:30 Stephen Paddison, *Molecular and Phenomenological Modeling of Polymer Electrolytes*

11:30-12:00 Adam Weber, *Macroscopic Modeling of Polymer-Electrolyte Membranes*

12:00-2:00 Lunch

1:00-2:00 Tour of the Banff Centre

2:00-2:30 Felix Buechi, *Analysis and Exploitation of Along the Channel Gradients*

2:30-3:00 Andrei Kulikovsky, *Analytical models of PEFC and DMFC: New insights into cell functioning*

3:00-3:30 Daniel Baker, *Low-Frequency Impedance of Polymer Electrolyte Fuel Cells*

3:30-4:00 coffee break

4:00-4:30 Xianguo Li, *A Comprehensive Approach to the Analysis of PEM Fuel Cells and Stacks*

4:30-5:00 Simon Liu *PEMFC Modeling: Status, Challenges and Research Needs*

Monday, March 21

9:00-9:30 Christoph Ziegler, *Simulation of cyclo-voltammograms in PEM fuel cells*

9:30-10:00 Issac Rubinstein, *Over-Limiting Conductance Through a Cation Exchange Membrane*

10:00-10:30 Tobias Schaeffer, *Mathematical modeling of Membrane Swelling*

10:30-11:00 coffee break

11:00-11:30 Jay Benziger, *The Importance of Membrane Mechanical Properties to PEM Fuel Cell Operation*

11:30-12:00 Graeme Milton, *Estimating the properties of composites*

12:00 Group Photo

12:00-2:00 Lunch

2:00-2:30 John Van Zee, *Experimental and CFD Studies of PEMFCs During Load Changes*

2:30-3:00 Sirivatch Shimpalee, *The effect of GDL's electrical conductivity on PEMFC performance*

3:00-3:30 Juergen Schumacher, *PEM Fuel Cell Modeling at the Fraunhofer Institute for Solar Energy Systems*

3:30-4:00 coffee break

4:00-4:30 Erin Kimball, *Modeling PEM Fuel Cells with Stirred Tank Reactors*

4:30-5:00 Keith Promislow, *Ignition Bifurcations in a Stirred Tank Reactor PEM Fuel Cell*

Tuesday, March 22

9:00-9:30 Jon Pharoah, *The Critical Role of the Porous Transport Layer*

9:30-10:00 Uwe Beuscher, *A One Dimensional Model of the Membrane Electrode Assembly*

10:00-10:30 Viola Birss, *Understanding and improving the performance of fuel cell cathodes*

10:30-11:00 coffee break

11:00-11:30 Hyunchul Ju, *Two-phase modeling of polymer electrolyte fuel cells*

11:30-12:00 Ziheng Zhang, *Membrane Gas Diffusion Measurements with MRI*

12:00-2:00 Lunch

2:00 onwards Outing, various destinations possible.

Wednesday, March 23

9:00-9:30 Herwig Haas, *Measurement Methods for Liquid Water Distribution and Mass Transport Properties*

9:30-10:00 Radu Bradean, *Models for Controlling MEA Water Content During Fuel Cell Operation And After Shutdown*

10:00-10:30 Jean St-Pierre, *Low cell voltage unit cell models*

10:30-11:00 coffee break

11:00-11:30 TBA

11:30-12:00 Chun Liu, *Energetic Variational Principles in Free Interfacial Motions: A Phase Field Approach*

12:00-2:00 Lunch

2:00-2:30 Peter Berg and Arian Novruzi, *A dry 1D catalyst layer model and numerical computations*

2:30-3:00 John Stockie, *Modeling the PEMFC Catalyst Layer*

3:00-3:30 Bernhard Andreaus, *Kinetic Monte Carlo simulations: A powerful tool to investigate reaction mechanisms in fuel cell electrodes*

3:30-4:00 coffee break

4:00-5:30 TBA

Thursday, March 24

9:00-9:30 Juergen Fuhrmann, *Numerical Simulation of Direct Methanol Fuel Cells*

9:30-10:00 Henning Struchtrup, *A macroscopic transport model for PEM membranes based on the microscale behavior*

10:00-10:30 Brian Carnes, *Modeling and Numerical Simulation Using the Binary Friction Membrane Model (BFM2)*

10:30-11:00 coffee break

11:00-11:30 Paul Chang, *Electrical and Thermal Coupling in Proton Exchange Membrane Fuel Cells*

11:30-12:00 Gwang-Soo Kim, *Electrical and thermal coupling in proton exchange membrane fuel cell stacks*

12:00 Lunch and Meeting End

Bernhard Andreaus *Kinetic Monte Carlo simulations: A powerful tool to investigate reaction mechanisms in fuel cell electrodes*

In the introductory part of the talk, an overview of current PEMFC modeling activities (group of M. Eikerling at SFU and IFCI) will be given, including recent efforts in catalyst layer water management as well as studies of structure formation and transport in polymer electrolyte membranes.

The main part focuses on molecular-level modeling of processes in nanoparticle electrocatalysts. Essential properties of the actual catalyst material in PEMFCs, supported Pt or Pt-alloy nanoparticles, are still not well-understood. Fundamental understanding of catalyst structure and prevailing kinetic mechanisms could, however, be highly valuable in view of improving catalyst utilization and optimizing rates of current generation. The design of nanostructured catalysts could be facilitated.

The kinetic Monte Carlo (kMC) method provides a general technique to investigate surface reaction mechanisms in electrochemical kinetics. Instead of solving a set of coupled differential equations for the reaction- diffusion system, a stochastic formulation is considered in the Monte Carlo method. Unlike conventional MC algorithms, the kMC algorithm progresses in real time steps. It allows simulating non-equilibrium processes with time- dependent reaction rates. In this way, the method lends itself ideally to the analysis of electrochemical systems and transient experimental techniques such as cyclic voltammetry and chronoamperometry.

In the present study, we perform kinetic Monte Carlo simulations of CO oxidation on supported catalyst particles with sizes in the nanometer range to elucidate the strong effects of catalyst particle size, heterogeneous surface structure and supporting material on catalytic activity. Tremendous particle-size effects have been found in recent experimental studies.

The simulations are based on the active sites concept, highlighting the role of distinguished sites with extraordinary activity (e.g. defects, step or kink sites) and finite surface mobility of adsorbed electroactive species for catalyst activity. For comparison with experimental results, potential step experiments were simulated. The Monte Carlo simulations consistently reproduce effects of particle size and electrode potential found experimentally. Small particles exhibit rather low rates of surface diffusion of adsorbed CO. In comparison with our simulations, analytical mean field models and nucleation and growth models exhibit inferior agreement with experimental data.

Daniel Baker *Low-Frequency Impedance of Polymer Electrolyte Fuel Cells*

AC impedance tools have the potential of isolating the various contributions to the fuel cell polarization curve, and methods have been demonstrated to determine pure ohmic (sum of electronic and membrane protonic) resistance as well as the protonic resistance within the cathode catalyst layer. Whereas these techniques rely on relatively high frequency impedance (1 kHz or greater), this

talk focuses on taking and interpreting impedance data in the low frequency range (<<1 kHz), the frequency range where gas-phase transport effects are expected. It will be seen that impedance spectra offer a very sensitive tool for measuring gas-phase transport resistance, but that there are still significant holes in our understanding of various other effects needed to model impedance in this frequency range. Of particular interest is a low-frequency inductive effect that becomes observable at frequencies less than around 1 Hz. This talk will discuss some preliminary efforts at measuring in this frequency range and also discuss the possible causes for this inductive effect.

Jay Benziger *The Importance of Membrane Mechanical Properties to PEM Fuel Cell Operation*

PEM fuel cells employ a polymer with ionizable substituent groups that permit proton conduction from an anode to a cathode. Protons move to the cathode under the influence of a chemical potential gradient to the cathode where they react with oxygen and electrons that pass through an external circuit to make water. The membrane resistance limits proton current. The membrane resistance depends on the water content of the membrane. In the absence of any mechanical constraints the membrane resistance is nearly independent of temperature for fixed water activity.

The dynamic response of Polymer Electrolyte Membrane (PEM) fuel cells at time scales > 1 s is dominated by changes in the water inventory in the polymer membrane and the electrocatalyst. The balance between water produced at the cathode and water removed by convection in the cathode and anode effluents alters the water content in the electrolyte membrane and in the catalysts layers. These changes affect both proton transport through the membrane and reactant transport to the membrane-electrode interface. Recent studies of the dynamical behavior of PEM fuel cells at Princeton has discovered that multiple steady states and autonomous oscillations occur in PEM fuel cells due to a positive feedback between the resistance of the polymer membrane and the water production in the fuel cell. The water produced by the fuel cell reaction equilibrates with the water in the membrane controlling the membrane resistance. Furthermore, it was also discovered that additional steady state multiplicity arises from the coupling of the mechanical properties of the polymer electrolytes and their electrical and chemical properties. There is a complex interaction between the polymer swelling due to water absorption and the membrane- electrode resistance. The constrained environment of the membrane in the fuel cell inhibits water uptake by the membrane and reduces the proton conductivity of the membrane. We demonstrate the critical need to control the construction of PEM fuel cells, if the sealing pressure is too low the membrane-electrode contact is poor, whereas if the sealing pressure is too high water squeezed out of the membrane increasing the membrane resistance.

We will describe a series of experiments that show the effects of water inventory on the dynamics of fuel cell performance. We will present a lumped parameter model of a differential PEM fuel cell that is tractable to follow the

dynamics of PEM fuel cells to changes in load, flow rate and temperature.

Peter Berg and Arian Novruzi *A dry 1D catalyst layer model and numerical computations*

We consider a macroscopic model for a dry, non-isothermal catalyst layer (CL) in a proton exchange membrane (PEM) fuel cell. It couples variables X for the 3 phases

1. C/Pt (electric potential)

2. pores (oxygen and water vapor concentrations, pressure)

3. PEM (proton concentration, water content, electric potential ϕ).

The temperature is assumed to be the same for all 3 phases and dominated by the conduction in the carbon phase. The catalyst layer fluid dynamics are described by a large nonlinear system of partial differential equations, with appropriate boundary conditions. This partial differential system is strongly nonlinear and, due to the different physical parameters, its coeffcients vary over a large range, which makes the system very stiff.

For given values of the variables at the boundaries of the catalyst layer, the system is entirely defined by the value ϕ_0 of the membrane potential at the PEM-CL interface, thus $X = X(\phi_0)$. In turn, ϕ_0 is defined by imposing the total current. This implies that the numerical solution results in two iterative methods, namely solving the system for a given ϕ_0, then iterating on ϕ_0 until the total current is matched. Each iterative method solves a nonlinear problem, so Newton method is used for each of them.

We have made some estimations of several nonlinear diffusive coeffcients and source terms, which we think have constant or linear behavior. Also, an appropriate scaling of variables leads to a nonlinear differential system of equations with constants of similar order, which leads to a better-conditioned partial differential system of equations. Our results show that the numerical method used is very well suited for such kind of nonlinear problem, which in fact represent a typical inverse problem with respect to ϕ_0. We have made a number of numerical simulations in order to identify the contribution of different key parameters (e.g. catalyst layer thickness, water evaporation from PEM into pore) to the catalyst layer fluid dynamics, and in particular to the total current.

Uwe Beuscher *A One Dimensional Model of the Membrane Electrode Assembly*

The performance of a proton exchange membrane (PEM) fuel cell is limited by electrochemical kinetics, proton conductance through the ionomeric material, electron conductance through the carbon phase, and mass transport phenomena. A detailed model is under development for studying the material and structural properties of the membrane, catalyst layer, and gas diffusion layer (GDL) of

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membrane electrode assemblies (MEAs). The Gore Electrode Model (GEM) is a one-dimensional description of all essential processes in the PEM fuel cell. The model consists of five different domains: anode GDL, anode catalyst layer, membrane, cathode catalyst layer, and cathode GDL. Transport processes that are considered in the model are proton transport in the catalyst layers and membrane, electron and gas transport in the catalyst layers and GDL, and water transport in all five domains. The focus of this paper will be a detailed description of the model as well as the presentation of current, potential, and concentration profiles throughout the MEA at various operating conditions.

Viola Birss *Understanding and improving the performance of fuel cell cathodes*

The majority of the power loss in both low temperature proton exchange membrane (PEM) fuel cells and high temperature solid oxide fuel cells (SOFC) occurs at the cathode, due to the sluggish kinetics of the oxygen reduction reaction (ORR). In PEM fuel cells, significantly higher loadings of (expensive) Pt must be used at the cathode, as compared to the anode, to compensate for the low activity of the ORR, resulting in high costs. For this reason, we are developing non-noble metal ORR catalysts using sol-gel synthesis, a simple and low cost approach known to yield nanoparticulate composite materials. These new catalysts have demonstrated very good ORR activity in acidic solutions after adsorption on carbon and subsequent heat treatment, with a maximum in performance and minimum in H2O2 generation after preparation at 700 C. In comparison, the standard cathode in SOFCs is composed of a mixture of small particles of strontium-doped lanthanum manganite (LSM) and yttria stabilized zirconia (YSZ), the ceramic electrolyte. A key observation is that the ORR Tafel slopes are very high, almost double those predicted, contributing significantly to the poor electrode performance and making reaction mechanism determination difficult. These results, as well as the effect of the sol-gel synthesis of LSM-YSZ electrodes (resulting in significantly smaller particle size) on the ORR performance, will be presented.

Radu Bradean *Models for Controlling MEA Water Content During Fuel Cell Operation And After Shutdown*

Effective fuel cell operation requires the optimization of the water content of the membrane electrode assembly (MEA) such that to meet targets for performance, freeze start, durability and reliability. In this work we present models for controlling the MEA water content that are used to provide input into the design of operating strategies of automotive fuel cell stacks. The measurements of MEA water content during fuel cell operation, stack purging after shutdown, or natural cooling after shutdown are reasonably predicted by these models.

Felix Buechi *Analysis and Exploitation of Along the Channel Gradients*

In PEFC multiple gradients evolve under operation, not only normal to the membrane electrode assembly, but also significantly along the channel. In cells of several hundreds of square centimeters of active area, the along the channel gradients are a dominant phenomena.

A fast 1+1 D model, realized in Matlab, is used for parameter space analysis of along the channel current and species distribution. The model includes treatment of heat transport in the MEA and along the channel. The model has been validated against experimental data in a wide parameter space.

The paper presents two approaches: i) reduction of the current density- decay along the channel due to falling oxygen concentration along the channel by catalyst redistribution; ii) reduction of current density gradient along the channel by adaptation of thermal gradients. While in the case of catalyst activity distribution the optimization potential seems surprisingly small, temperature distribution has a significant influence on cell performance.

Brian Carnes *Modeling and Numerical Simulation Using the Binary Friction Membrane Model (BFM2)*

Recently a model for transport of water and protons within polymer electrolyte membranes (PEMs) was developed (Fimrite et al., submitted 2004). This model, which we denote BFM2, rigorously accounts for multicomponent transport using the Binary Friction Model for transport in a porous medium and has been shown to provide an excellent fit to experimental conductivity data.

In this talk, we present a number of calculations obtained using the BFM2. We begin with a short summary of the model and then present a comparison of the model to the widely used model of Springer et al. (1991). We compare membrane resistance and water flux under various membrane saturation conditions. Next we discuss how the water transport in the membrane model (the lambda equation) can be coupled with water transport in the electrodes of a membrane-electrode assembly (MEA). We conclude with some calculations of the polarization curves and water distributions for a complete MEA model.

Paul Chang *Electrical and Thermal Coupling in Proton Exchange Membrane Fuel Cells*

A mathematical model describing the effects of electrical and thermal coupling of proton exchange membrane unit fuel cells through shared bipolar plates is developed. The unit cell model, developed by Berg et al. (2004), couples the consumption of reactants in the

flow field channels to the current density and water content in the polymer membrane. Differing current density profiles in neighboring cells leads to in-plane currents in the bipolar plates, and the redistribution of current is governed by the nonlocal voltage equations. Thermal transport is decoupled into the in- plane and cross-plane directions; this is reasonable because of the large aspect ratio of the typical fuel cell geometry and the large in-plane to cross-plane conductivity ratio. Numerical results showing the effects on stack voltage and current density due to anomalous oxidant and coolant flow rates in the center cell are shown. It is shown that both electrical and thermal coupling have a significant effect on fuel cell performance.

Juergen Fuhrmann *Numerical Simulation of Direct Methanol Fuel Cells.*

We present a numerical model for the membrane-electrode assembly of a Direct Methanol Fuel Cell (DMFC) based on the control volume method. Among other physical effects, this model includes fully resolved catalytic reaction chains, evaporation/condensation/dissolution reactions, two-phase flow of water and a gas mixture in a hydrophilic/hydrophobic porous medium, Stefan Maxwell Diffusion, solute transport, proton and electron transport, and heat transport. The model is realized using the control volume method on one- two- and three-dimensional domains.

The talk focuses on new devolopments, including model improvements, concepts for numerical bifurcation analysis, speed up and parallelization of the implementation, and new simulation examples.

Herwig Haas *Measurement Methods for Liquid Water Distribution and Mass Transport Properties*

PEM fuel cell performance attributes often depend on the distribution of water within the MEA. Liquid water in the electrodes is believed to impact the mass transport of gases to the active catalyst sites, posing limits to high current operation. For fuel cell developers, it is therefore of significant importance to manage the water distribution within the MEAs of their fuel cell stacks. Validated models are needed to aid in the design of cells, MEAs and operating conditions. PEM fuel cell models often lack validation in

respect to predicted MEA water distributions. Two experimental methods have been developed at Ballard that provide results that may serve for model validation. These experimental measurements will be shown and discussed.

Erin Kimball *Modeling PEM Fuel Cells with Stirred Tank Reactors*

Large area fuel cells and fuel cell stacks can be broken down to simple differential fuel cells that can be modeled with a simple Stirred Tank Reactor Model. We have developed a simplified lumped parameter model for the kinetics and mass transport in a differential PEM fuel cell that captures the dynamic water balance in response to changes in load, feed, and temperature. This model includes both a simplified equivalent circuit and material and energy balances that permit the dynamics of fuel cell systems to be analyzed from the differential element to a fuel cell stack with simple circuit analysis and sets of first order ODEs/DAEs. The model is easily adapted to model large area fuel cells where the dynamics of front movement for water flooding during start-up and changes in load can be tracked. We will highlight how the model matches dynamic results from a differential PEM fuel cell, and what it predicts for more complex flow patterns.

Hyunchul Ju *Two-phase modeling of polymer electrolyte fuel cells*

At high current densities and low gas flow rates, excess water is generated and condenses, filling the pores of electrodes with liquid water, and hence limiting the reactant transport to catalyst sites. This phenomenon known as "flooding" is an important limiting factor of PEFC performance. A fundamental understanding of two-phase transport in porous gas diffusion medium (DM) of PEFC is essential in order to improve performance.

In this work, we present a two-phase PEFC model that consists of four sub-models: 1) Catalytic surface coverage model to account for the active area reduction due to liquid water coverage of catalyst particles, 2) Multi- phase mixture (M2) model for liquid water transport through hydrophobic porous medium, 3) Interfacial liquid coverage (IC) model to consider the effect of liquid droplets emerging at the DM/channel interface, 4) Micro- porous layer (MPL) model to numerically predict a discontinuity in the liquid saturation pro-

file at the MPL-DM interface due to difference in the properties of two porous layers. The comprehensive two-phase model enables to gain a better understanding of liquid water transport and ensuing flooding effect on cell performance.

John Kenna *Application of Mathematical and CFD mode ls for Design Space Analysis and Optimization Studies*

An overview will be given on Ballard Power System fuel cell products and simulation models and how stack requirements are managed with the use of bounded design space analysis tools. The bounded design space methodology allows the interaction of multiple variables as well as the effect of advancing technology to be clearly visualized. Mathematical and CFD tools models physical behavior and material properties in conjunction with geometrical features. This talk will focus on the importance of coupling simulation models with physical verification data that includes establish bounded design limits. Introduction of design space tools and using DOE hydrogen energy roadmap has help focus Ballard's simulation and modeling efforts towards meeting their targets.

Gwang-Soo Kim *Electrical and thermal coupling in proton exchange membrane fuel cell stacks*

Proton exchange membrane fuel cell stack models require consideration of interactions between cells owing to non-uniformities such as cell parameters distributions and cell location/environment differences, leading to thermal, electrical and mass transfer gradients. Experiments were designed to emphasize electrical and thermal cell interactions by introducing specific anomalies. For electrical interactions, different bus bus plate materials and a partially inactive cell located at the stack center were introduced in a short stack. For thermal interactions, one of the coolant bipolar plate adjacent to the stack center cell was modified by altering the coolant flow field channel geometry. The cell voltage distribution and coolant outlet temperatures were measured and compared with model predictions. The deviations from an unmodified stack were attributed to anomalies and their magnitude was related to cell interaction damping factors, which provide useful predictive criteria for the number of cells affected by an anomaly.

Andrei Kulikovsky *Analytical models of PEFC and DMFC: New insights into cell functioning*

We report recent 1D+1D analytical and semi-analytical models of hydrogen– and direct methanol fuel cells. The models take into account transport of reactants across the cell (including methanol crossover in DMFC) and along the feed channels. The model of PEFC explains the shapes of local current density along the channeland predicts optimal composition / stoichiometry of the cathode feed. The model of DMFC reveals a new effect. At infinitely small total current in the cell, near the inlet of oxygen channel forms a "bridge", a narrow region with finite local current density. The bridge short-circuits the electrodes, thus reducing cell open-circuit voltage. The bridge forms only in the presence of methanol crossover; in an ideal cell without crossover it disappears. This phenomenon explains a well known effect of mixed potential in a DMFC. Analytical solutions are verified against numerical results and experiment.

Xianguo Li *A Comprehensive Approach to the Analysis of PEM Fuel Cells and Stacks*

Polymer electrolyte membrane (PEM) fuel cell has increasingly become the potential choice of zero-emission power source for portable, mobile and stationary co-generation applications. However, technical barriers need to be overcome before its widespread commercialization; cost reduction and performance improvement including reliability are the two key areas, that can be realized through better cell/stack design and improved understanding of the transport processes occurring inside the individual cells and stacks. In this presentation, we will present a comprehensive multi- species, multi-phase and multi-dimensional formulation of a single PEM fuel cell, with consistent and systematic formulation for all the regions involved, including the solid bipolar plates, gas flow channels, the electrode backing layers, the catalyst layers and the electrolyte membrane. Such a detailed approach allows us to extract sufficient information to the analysis of a stack of PEM fuel cells. Stack model will be presented that investigates the various stack designs and flow configurations, and the optimal stack design based on the present study will be described. Also some innovative cell/stack designs will be

featured.

Chun Liu *Energetic Variational Principles in Free Interfacial Motions: A Phase Field Approach*

In this talk, I will introduce a general energetic variational procedure for modeling the free interfacial motions in complex fluids. The method employs a phase field approach to capture the moving free interfaces. The method gives a natural coupling between the flow field and the different interfacial properties. I will discuss both modeling and analytical issues arising from the approach. Numerical results will also be presented.

Simon Liu *PEMFC Modeling: Status, Challenges and Research Needs*

This talk presents an overview of PEMFC modeling covering its current status, challenges and research needs. The capabilities of modeling software commercially available are illustrated by means of several engineering cases the authors have conducted in the past four years. It involves computational fluid dynamics, computational solid mechanics, computational electrochemical engineering, and computational materials.

Graeme Milton *Estimating the properties of composites*

We begin by setting the stage for non-experts, outlining the basic theory of linear composite materials and their effective properties. Formulae for the effective properties of layered materials and sphere and ellipsoid assemblages will be presented. Approximation schemes such as average field approximations, effective medium schemes, differential schemes, and asymptotic methods will be described, and their limitations discussed. Finally we will give a brief overview of the subject of bounds on the effective properties of composites, and the optimal microstructures which achieve them.

Stephen Paddison *Molecular and Phenomenological Modeling of Polymer Electrolytes*

Hydrated polymer electrolyte membranes (PEMs) are inhomogeneous materials. Although subject to numerous characterization

measurements, the morphology is not well understood and may change as a function of temperature, chemical composition, and amount of absorbed water. This knowledge, however, is critical as the starting point in elucidating relationships between structure and function. As the PEM functions as a separator of the electrodes and as a conductor of protons, it is a system that warrants investigation at several distinct length and time scales. Our approach has been to theoretically examine proton conduction in the PEM at three distinct length and time scales implementing three different approaches [1]. The hierarchy of this multi-scale modeling includes study of: (1) proton dissociation and hydration of hydrophilic groups in the membrane using ab initio molecular orbital theory; (2) local proton dynamics 'near' (between) the fixed sites studied with ab initio (quantum) molecular dynamics; and (3) proton diffusion and the state (permittivity) of the water within a single membrane pore or channel with equilibrium and non-equilibrium statistical mechanical models.

This talk will present an overview of recent molecular modeling investigations into the choice of the protogenic group in a PEM functioning at elevated temperature and low humidity conditions. Specifically we compare the sulfonic acid group with phosphonic acid and imidazole. Gleanings from these investigations will be used to justify the importance in understanding the factors that influence proton conduction, namely: complexity, cooperativity, and connectivity of the PEM.

1. K.-D. Kreuer, S. J. Paddison, E. Spohr, and M. Schuster, Transport in Proton Conductors for Fuel-Cell Applications: Simulations, Elementary Reactions, and Phenomenology, Chem. Rev. 104, 4637-4678 (2004).

Jon Pharoah *The Critical Role of the Porous Transport Layer*

The porous transport layer (PTL), also known as the gas diffusion layer, is the critical link between the electrochemical reactions, the balance of plant and the electrical load. Several very interesting transport phenomena occur in this layer, including the transport of heat, electrons, gaseous fuel and reactants and liquid water. The PTL is typically made of a chopped carbon fibre paper, or a weave of carbon fibre bundles and as such is virtually always anisotropic

- yet to date it has been modelled as an isotropic media. Several critical issues are discussed along with their impact on fuel cell performance: PTL permeability and the link between convective transport and flow-field design, the impact of flow field design on liquid water build-up, and the effect of orthotropic transport coeffcients. Finally, a new method for the determination of anisotropic transport coefficients is outlined and the results compared to currently used values.

Keith Promislow *Ignition Bifurcations in a Stirred Tank Reactor PEM Fuel Cell*

We present a mathematical model of ignition dynamics and bistable operation of a Stirred Tank Reactor (STR) Polymer Electrolyte Membrane (PEM) fuel cell. In dry inlet gas operation the positive feedback between current, water production, and membrane resistance within the model leads to two stable "ignited" states. Within the framework of the model these correspond to a uniform current distribution or a partially extinguished cell with localized current production. The switching between the two regimes is accompanied by hysteresis and transient behavior on the order of 2-4 hours in a small 1 cm^2 cell. We compare the numerical results to experimental data gathered by Jay Benziger and show that the steady-state distribution of membrane water is very sensitive to several parameters and is an excellent diagnostic for determining material parameters.

Issac Rubinstein *Over-Limiting Conductance Through a Cation Exchange Membrane*

Electric steady state current higher than the limiting one is readily passed through a cat-ion exchange membrane - phenomenon commonly referred to as over-limiting conductance. The mechanisms of this and of the accompanying excess electric noise remained unclear for a long time. (Possible loss of membrane permselectivity at high voltage or appearance of additional charge carriers ('water splitting') have been conclusively ruled out.) Eventually, a fair amount of indications have been accumulated, suggesting that the overlimiting behavior of the cation exchange membranes has to do with some kind of non-gravitational convective mixing that develops spontaneously in the depleted diffusion layer at the advanced stage of concentration

polarization. Electro-convection driven by nonequilibrium electro-osmotic slip at the solution/membrane interface, was suggested as a mechanism drawing together the overlimiting phenomena at cation exchange membranes.

In this presentation we summarize our recent results concerning this type of electro-convection. Theories of electro-osmotic slip of either quasi- equilibrium (first) or non-equilibrium (second) kind at a charge-selective ion exchange membrane are reviewed. Slip condition for electro-osmosis of the second kind, relevant for developed concentration polarization at a cation exchange membrane, with its related non-equilibrium electric double layer, characterized by an extended space charge region, absent in a quasi- equilibrium double layer, is derived through a boundary layer analysis of the appropriate convective electro-diffusion problem. Linear hydrodynamic stability of quiescent concentration polarization in a diffusion layer at a cation exchange electrodialysis membrane is studied. It is shown that electro-osmotic slip of the second kind, as opposed to that of the first kind, yields instability for realistic conditions. Numerical calculations for the resulting nonlinear steady state convection show that the latter provides an efficient mixing mechanism for the diffusion layer, capable of accounting for the over-limiting conductance in concentration polarization at a cat-ion exchange membrane. Our recent experiments with membrane modifications, eliminating electro-osmotic slip, rule in favor of electroosmotically induced convection as the mechanism of overlimiting conductance.

Tobias Schaeffer *Mathematical modeling of membrane swelling*

Based on the work of Grimshaw et al, we present a one-dimensional continuum model that describes changes of the hydration of polyelectrolyte membranes in response to transmembrane electric fields and changes in the ionic environment. A particular focus is the influence of the membrane swelling on the hydration of the membrane, being important for understanding the water-uptake of membranes in fuel cells.

Juergen Schumacher *PEM Fuel Cell Modeling at the the Fraunhofer Institute for Solar Energy Systems*

An overview of different PEM fuel cell modeling approaches that

are developed at the Fraunhofer institute for solar energy systems (ISE) is given. The modeling approaches adress the cell scale, the stack scale, and the system scale. A mathematical model for planar self-breathing fuel cells was developed at Fraunhofer ISE based on the FEMLAB software. The mathematical model presented is two-dimensional and non-isothermal. The validation of the model is performed by comparison of the measured overall performance of a planar self-breathing fuel cell to the predictions of the model. fc-2p is a dynamic two-phase flow model describing PEM single cells. The simulation domain is two-dimensional with an along-the-channel geometry. Two-phase transport of water in the porous gas diffusion layer and in the electrodes is considered. Moreover, the transport equations for protons and electrons are solved separately. The oxygen reduction reaction in the cathodic catalyst layer and the hydrogen oxidation reaction in the anodic catalyst layer is accounted for. Heat transport includes three source and sink terms: ohmic heating, entropic heating, and latent heat due to phase change of water. We are working on a simplified dynamic fuel cell stack model that is intended for control purposes. Balance equations for the energy and mass fluxes through a stack are developed. A simple electrical model is derived. The important couplings between energy, mass and charge transfer phenomena are considered. The model is solved using the ODE solvers provided by MATLAB. The model is suitable for on-line compution using a microcontroller platform that is integrated with an autonomous robot. Fuel cell system modeling using the Colsim package of Fraunhofer ISE is presented. The Colsim library includes a fuel cell stack model, models for reformers, power inverters, heat storage units, pumps, compressors, valves and controllers. The system description is based on an electrochemical submodel that is coupled to a thermal submodel. It is assumed that the electrical response is much faster than the thermal response of the fuel cell stack. A modified Euler algorithm is used to solve the differential equations, a so-called "plug-flow modeling" approach is realized. Thereby, finite mass elements and finite energy elements corresponding to a fixed time step are traced through closed and opened system networks.

Sirivatch Shimpalee *The effect of GDL's electrical conductivity on PEMFC performance*

The objectives of this work are to understand the importance of electrical conductivity of gas diffusion layer and its effect on the performance. In this work, in-plane realtive to thru-plane electrical conductivity including contact resistance that experimentally measured and the interaction with flow-field geometry (channel/rib spacing) with the GDL are studied. The model is exercised that evaluates the cell potential at the bi-polar plate instead of at the MEA surface. Therefore, this form of the model allows for a potential drop in the GDL.

Jean St-Pierre *Low cell voltage unit cell models*

A 4 parameter 1+1 dimensional unit cell model validated using a significantly large and varied data set was previously described. The behavior of this model in the mass transport limited regime was studied (large stoichiometry limit). The development and validation of the resulting 0 dimensional model led to a better estimate of the mass transfer parameter consistent with the value obtained from the 1+1 dimensional unit cell model. Cell behavior knowledge in the mass transfer limited region was further extended by developing a 1 dimensional unit cell model (flow field channel direction) at low cell voltages for two separate cases (general, low oxidant concentration limit). The 1 dimensional unit cell model was validated and can be used as a new method to extract mass transfer coefficient values from full size cells. Criteria were also defined to ensure model applicability.

John Stockie *Modeling the PEMFC Catalyst Layer*

Proton exchange membrane fuel cells are known to exhibit a sharp drop-off in the local potential at some limiting value of the current density. Many experimental and modeling studies of mass transport in proton exchange membrane fuel cells propose that this limiting current behaviour can be attributed to mass transport limitations in the gas diffusion layer (or GDL) owing to the presence of liquid water. Our previous modeling work indicates that it is not GDL transport that is the limiting step, but rather transport within the catalyst layer.

Our primary goal in this work is therefore to develop a model of the catalyst layer which explains this limiting current behaviour.

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Our approach is general, in that in incorporates various possible mechanisms for mass transport limitations. The results are compared to existing results from both experiments and simulations in the literature.

Henning Struchtrup *A macroscopic transport model for PEM membranes based on the microscale behavior*

Insight into the microscopic be structure and behavior of PEM membranes is used in the development of a general transport model for water and protons in PEMs based on the Binary Friction Model (BFM). In order to investigate the unknown parameters in the transport model, a simplified conductivity model (BFCM) is developed for perfluorosulfonic acid membranes. The model is first applied 1100 EW Nafion, and compared to other established membrane models, the new BFCM is shown to provide a more consistent fit to the data over the entire range of water contents and at different temperatures. The generality of the BFCM is also illustrated by applying the model to predict the conductivity of a Dow and Membrane C membrane using only rational and physically consistent changes in model parameters.

The analysis leads to possible experimental investigations and fundamental simulations to determine the model parameters required to apply the BFM to other types of membranes. One advantage of the BFM model and the associated transport model is that by fitting the BFM to conductivity data we are able to gain insight into all the transport parameters, and this could eventually be used to develop a general membrane water transport model.

John Van Zee *Experimental and CFD Studies of PEMFCs During Load Changes*

As a platform to discuss dynamic operation of Proton Exchange Membrane Fuel Cells (PEMFCs), data are presented to show how performance is affected by rapid changes in the voltage. It is shown that this dynamic behavior depends on the type of flow-field and on the voltage range of the voltage change. Pseudo second-order responses (i.e., overshoot and undershoot of the steady state current density) were observed for fixed flowrates when the fuel stoichiometries varied between 1.2 and 1.1. The undershoot of the final steady

state current (that follows an overshoot for a load increase) was observed with a standard triple-path serpentine flow- field (SFF) but not with a single-path SFF. The results also show that the dimensionless peak current and the percentage of the overshoot current depend on the starting cell voltage and on the range of the voltage change. Evidence is presented to indicate that these peak heights are limited primarily by oxygen even though the PEMFC is operating close to fuel starved conditions. The results of transient simulations with a CFD model are used to explain current overshoot and undershoot data. The variation in the distributions of current density, water content, and reacting gas concentrations are shown.

Adam Weber *Macroscopic Modeling of Polymer-Electrolyte Membranes*

In this talk, our recent model for transport in polymer-electrolyte membranes will be reviewed and discussed. This includes placing the model in the context of other published membrane models. Our model is based on a physical model that is semi-phenomenological and takes into account Schroeder's paradox. It also utilizes the wealth of knowledge contained in the literature regarding polymer-electrolyte membranes. Along with the structural changes of the membrane due to water content, the two different transport mechanisms, vapor- and liquid-equilibrated will be presented. This includes their governing equations and relevant transport properties. In addition the simultaneous occurrence of both modes will be treated. Thus, the model bridges the gap between the one- and two-phase macroscopic models currently used in the literature. Validation of the model and discussion of relevant results will also be presented. Finally, the general requirements of membrane models will be mentioned.

Brian Wetton *An overview of fuel cells: science, modelling and mathematics*

An overview of hydrogen fuel cell operation is given, concentrating on stack design for Polymer Electrolyte Membrane type cells. Some of the fundamental scientific questions related to device performance are outlined. A summary of modelling approaches and the use of modelling in the application is given. An overview of the types

of Mathematics than can be used to further understand fuel cell operation is presented.

Ziheng Zheng *Membrane Gas Diffusion Measurements with MRI*

Gas transport across polymeric membranes is fundamental to many filtering and separation technologies. To elucidate transport mechanisms, and understand the behaviors of membrane materials, accurate measurement of transport properties is required. We report a new Magnetic Resonance Imaging (MRI) methodology to measure membrane gas phase diffusion coefficients. The MRI challenges of low spin density and short gas phase relaxation times, especially for hydrogen gas, have been successfully overcome with a modified one-dimensional, Single-Point Ramped Imaging with T1 Enhancement, (SPRITE) measurement. We have measured the diffusion coefficients of both hydrogen gas and sulfur hexafluoride in a model polymeric membrane of potential interest as a gas separator in metal hydride batteries. The experimental apparatus is a modified one-dimensional diaphragm cell which permits measurement of the diffusion coefficient in experimental times of less than one minute. The H2 gas diffusion coefficient was 0.54±0.01 mm2/sec, while that of sulfur hexafluoride was 0.13±0.01 mm2/sec, at ambient conditions.

Christoph Ziegler *Simulation of cyclo-voltammograms in PEM fuel cells*

A mathematical model is developed that is based on a coupled system of partial differential equations. The model contains a dynamic and two-phase description of the proton exchange membrane fuel cell and a membrane model that accounts for Schroeder's paradox. The mass transport in the gas phase and in the liquid phase is considered as well as the phase transition between liquid water and water vapor. The transport of charges and the electrochemical reactions are part of the model. Cyclo-voltammograms are simulated and measured. A hysteresis effect is found in the measured IV- curves which can be explained by the accumulation of liquid water at the cathode side of the cell. A model based analysis of the hysteresis is given that considers key parameters of the measurement and the model.