Computational Fuel Cell Dynamics-III

Conference Organizers: Jean St.-Pierre[*], Keith Promislow[†], Brian Wetton[‡]

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Report Prepared By: Paul Chang[1]

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1 Introduction

Replacing today's fossil fuel economy with a hydrogen one would alleviate much of today's environmental and political problems. The transport and consumption of fossil fuels has contributed to oil spills, fossil fuel scarcity issues, political instability in the middle east, etc. Hydrogen consumption, on the other hand, would not since hydrogen can be produced by electrolyzing water and the latter is abundant and ubiquitous. Moreover, Proton Exchange Membrane (PEM) fuel cells (a key component of the hydrogen economy) produce only water as its byproduct, and therefore greenhouse gases and other air pollutants would cease to be produced.

Key challenges remain, however, in the transition to a hydrogen economy. Infrastructure for producing and distributing hydrogen needs to be established. An economical means for storing hydrogen needs to be developed. And, if PEM fuel cells are to supplant the internal combustion engine, PEM fuel cells need to be as (if not more) durable, efficient, economical, and powerful as the latter. Our community aims to meet this last challenge.

Cost-effective and rapid improvement of current fuel cell designs requires computationally fast and accurate fuel cell models; a pure trial-and-error approach is clearly expensive and slow. The development of fuel cell models requires the talents of a diverse group of scientists and engineers: chemists and physicists are needed to understand the fundamental chemical and mechanical processes and their interactions, mathematicans are needed to develop fast and stable numerical algorithms to solve the governing model equations, engineers are needed to implement these models to optimize fuel cell design which in turn directs future model development, and finally experimentalists are required to validate these models. Many members of our community are able to play one or more of these roles, but since few are experts in all roles, it is clear that a high degree of collaboration is needed.

The CFCD workshops hosted by Ballard Power Systems and PIMS at Simon Fraser University in June 2001, and at BIRS in April 2003, gave focus to these activities. These meetings brought together a diverse mix of scientists and engineers to exchange expertise and to find common ground, and provided future research directions. The CFCD III workshop is a continuation of these efforts, providing a forum where the latest fuel cell knowledge and technologies can be shared, and focusing the multi-disciplinary efforts of its participants. This important work will certainly lead to the development of a new generation of analytical and computational tools for PEM fuel cell design, and ultimately the realization of the hydrogen economy.

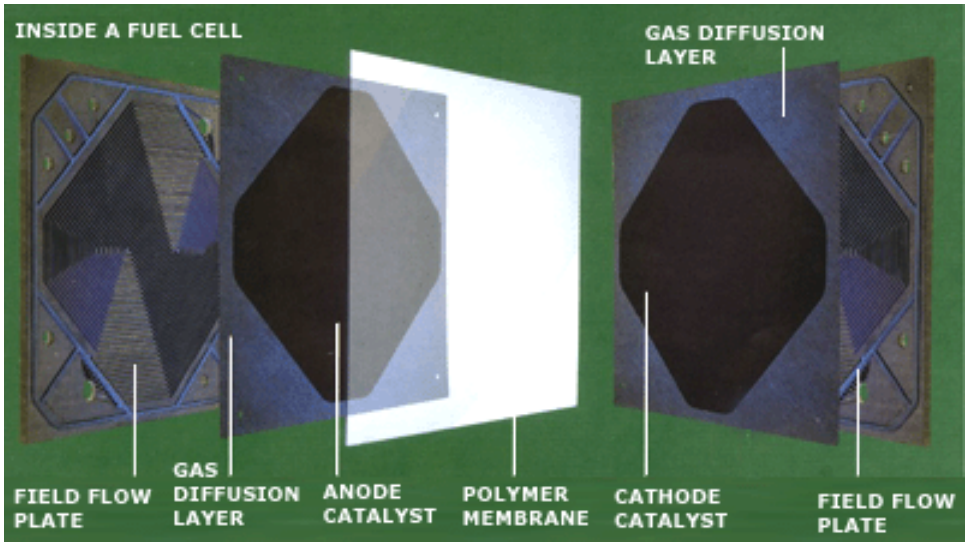

Figure 1: The layers comprising a fuel cell. [5]

2 Proton Exchange Membrane Fuel Cells and Modelling Activities

PEM fuel cells generate power by consuming hydrogen and oxygen. As earlier mentioned, hydrogen can be produced by electrolyzing water, but in cases where pure hydrogen fuel is unavailable, it can be obtained by processing available fuels including natural gas, propane, diesel, methanol, etc. Oxygen is drawn directly from air. A PEM unit cell consists of a polymer membrane sandwiched between a pair of gas diffusion layers sandwiched between a pair of bipolar plates (See Figure 1). The polymer membrane is usually made of Nafion and the gas diffusion layers are often teflonated carbon fibre paper. The bipolar plates are usually made of graphite. At the interface between the gas diffusion layer and membrane lies a catalyst layer which facilitates the power-generating electrochemical reactions. The catalyst is usually Platinum, but because Platinum is such an expensive component of the fuel cell, other catalyst materials are being developed as possible replacements.

Channels are carved in the bipolar plates which deliver hydrogen (on the anode side) and oxygen (on the cathode side) to the reaction sites. The channel configuration can be straight, serpentine, or cross-flow. The hydrogen diffuses through the gas diffusion layer to the anode catalyst sites where it disassociates into two protons and two electrons. The electrolyte membrane, being a good protonic and poor electronic conductor, allows the protons to diffuse to the cathode side while the electrons are conducted through the bipolar plates through an external circuit where useful work can be performed. The protons and electrons then meet with the oxygen, which has diffused through the cathode diffusion layer, at the cathode catalyst sites where water and heat is produced. The net electrochemical reaction is simply

$$2H_2 + O_2 \rightarrow 2H_2O. \tag{1}$$

A key advantage of PEM fuel cells is its operation at low temperatures (around $70^\circ C$). However, this necessitates a catalyst layer as the activation potential for the electrochemical reactions is much too high at these temperatures. Reducing Platinum loadings at the electrodes, or the complete replacement thereof, is a priority for the fuel cell community due to high cost of Platinum; but to do so without degrading the power output capabilities of the fuel cell requires an understanding of the fundamental processes which drive the catalyzed reactions. Existing approaches to modelling the catalyst layer include interface models in which the

*Ballard Power Systems
†Michigan State University
‡University of British Columbia
[1]University of British Columbia

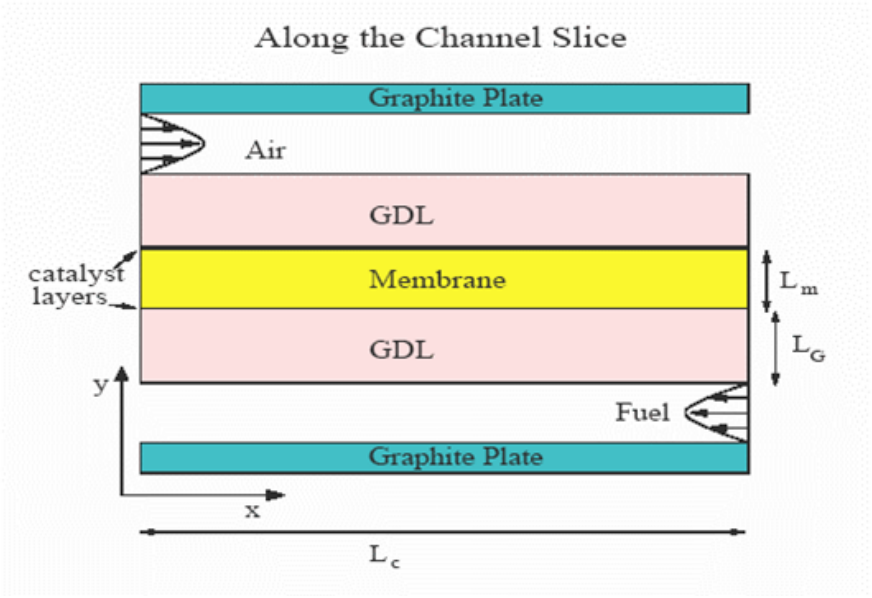

Figure 2: A 2D unit cell slice.

layer is infinitesimally thin, microscopic or single-pore models in which the layer consists of pores filled with gas and pores filled with electrolyte and catalyst, and agglomerate models in which the layer is composed of spherical agglomerates of carbon grains supporting Platinum. Research in this area is active and ongoing.

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. While the membrane must be well hydrated to allow the protons to cross over, the overproduction of liquid water may saturate the surrounding porous electrodes, flood the gas channels, and lead to a pronounced drop in local 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. The understanding of water management is also key to optimizing fuel cell design.

Many efforts have been undertaken to develop fuel cell models which incorporate these effects. These models can be roughly classified as either fully three dimensional, or reduced dimensional where quantities are averaged in one or more directions. There are also models which look at specific aspects of the fuel cell.

In recent years, several large computational fluid dynamics (CFD) code vendors have become interested in developing comprehensive three dimensional fuel cell computational models. Some examples are the modules developed by CFX [2], StarCD [4], and the more academic FEMLAB [3]. 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 also 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 gas diffusion layers will be difficult to capture accurately in these general packages. It is apparent that larger scale problems such as electrical coupling of unit cells in the stack and long time transients will have to be handled by specialized codes.

Reduced dimensional models exploit the high aspect ratio of the unit cell, roughly 1000 to 1 down channel versus thru membrane, and solve for quantities averaged in a particular direction. For instance, unit cell models which assume a straight channel design and average in the cross channel direction are comprised of two one-dimensional models for transport along the channel and thru the membrane electrode assembly, coupled through their boundary conditions. With such simplified geometries, these models are computationally speedier than their CFD counterparts, yet certain higher dimensional effects may not be captured with these models. A 2D slice of such a unit cell model is shown in Figure 2. It should be mentioned that this type of

fuel cell, which uses pure hydrogen, is one of many design approaches.

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

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

3 Presentation Highlights

The following is a summary of the presentations presented at our workshop.

- *Bernhard Andreaus (Simon Fraser University):* Performs kinetic Monte Carlo simulations of CO oxidation on supported catalyst particles in the nanometer range. The goal is to improve our understanding of the catalyst structure and the prevailing kinetic mechanisms, which can help us improve catalyst utilization and optimze rates of current generation.

- *Daniel Baker (General Motors):* AC impedance tools have the potential of isolating the various contributions to the fuel cell polarization curve. Daniel Baker presented some findings in the low frequency range (much less than 1 KHz), and showed that the impedance spectra in this frequency range offers a very sensitive tool for measuring gas-phase transport resistance. Of particular interest is a low-frequency inductive effect that becomes observable at frequencies less than around 1 Hz. On another note, General Motors will build an environmental chamber for car testing at the University of Ontario Institute of Technology. It will include temperature and relative humidity control. Quoted as the best facility in North America when completed.

- *Jay Benziger (Princeton University):* Recent studies at Princeton have 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. 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. Control of the construction of PEM fuel cells is key: if the sealing pressure is too low the membrane-electrode contact is poor, whereas if the sealing pressure is too high water is squeezed out of the membrane thus increasing membrane resistance. A series of experiments that show the effects of water inventory on the dynamics of fuel cell performance was presented, as well as a lumped parameter model of a differential PEM fuel cell. A model explaining these experimental results was also developed by Keith Promislow.

- *Peter Berg (University of Ontario IT) and Arian Novruzi (University of Ottawa):* Presented a dry, non-isothermal, macroscopic model for the catalyst layer. The model couples variables for these three phases: 1) electric potential for the Carbon/Platinum, 2) oxygen and water vapor concentrations and pressure in the pores, and 3) proton concentration, water content, electric potential in the membrane.

- *Uwe Beuscher (W. L. Gore and Associates, Inc.):* A detailed model is under development for studying the material and structural properties of the membrane, catalyst layer, and gas diffusion layer. The Gore Electrode Model (GEM) is a one-dimensional description of all essential processes in the PEM fuel cell. Transport processes that are considered include proton transport in the catalyst layers and membrane, electron and gas transport in the catalyst layers and gas diffusion layers, and water transport in all these domains. Need for degradation modeling mentioned.

- *Viola Birss (University of Calgary):* Developing non-noble metal ORR catalysts using sol-gel synthesis, a simple and low cost approach known to yield nanoparticulate composite materals. 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 H_2O_2 generation after prepartion at $700°C$.

- *Radu Bradean (Ballard Power Systems):* Presented a model for controlling the MEA water content. Such a model is 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, and natural cooling after shutdown is reasonably predicted by the model.

- *Felix Buechi (Paul Scherrer Institute):* Presented a fast 1+1D model used for parameter space analysis of along-the-channel current and species distribution. The model accounts for heat transport in the MEA and along the channel, and has been validated against experimental data in a wide parameter space. Measured electrical interactions with a two cell stack and a non straight channel design.

- *Brian Carnes (University of Victoria):* Presented a general model, named BFM2, for the transport of water and protons within PEMs. It rigorously accounts for multicomponent transport using the Binary Friction Model for transport in a porous medium. The model was shown to provide an excellent fit to experimental conductivity data. Mentioned the need for ionomer (different properties than manufactured membranes) and membrane property measurements including the direct relationship between conductivity and water content at different operating conditions.

- *Paul Chang (University of British Columbia):* Presented a stack model which accounts for electrical and thermal coupling effects between unit cells. This model is comprised of a four parameter 1+1D unit cell model which was validated using a significantly large and varied data set. A two dimensional end plate model is also included. Runs with simulated anomalies were presented, where a unit cell received substantially less coolant flux and oxidant flux than its neighbours. Experimental validation presented by Gwang-Soo Kim.

- *Juergen Fuhrmann (Weierstrass Institute Berlin):* Presented a model for Direct Methanol Fuel Cells using the control volume method. The 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, and Stefan Maxwell diffusion.

- *Herwig Haas (Ballard Power Systems):* PEM fuel cell models often lack validation in respect to predicted MEA water distributions. Two experimental methods have been developed at Ballard which can serve to validate these models. These methods were presented and discussed.

- *Erin Kimball (Princeton University):* Presented a simplified lumped parameter Stirred Tank Reactor model for the kinetics and mass transport in a differential PEM fuel cell; this model captures the dynamic water balance in response to changes in load, feed, and temperature. Highlighted how the model matches dynamic results from a differential PEM fuel cell, and what it predicts for more complex flow patterns.

- *Hyunchul Ju (Pennsylvania State University):* Presented a model for two-phase flow (of water) which accounts for catalyst active area reduction due to liquid water coverage, liquid water transport through hydrophobic porous media, and liquid water droplets emerging at the gas diffusion layer/channel interface. Emphasis on understanding water transport and effects on flooding.

- *John Kenna (Ballard Power Systems):* Gave an overview of 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. Introduction of design space tools and using DOE hydrogen energy roadmap has helped focus Ballard's simulation and modeling efforts towards meeting their targets.

- *Gwang-Soo Kim (Ballard Power Systems):* Presented experimental results which elucidated the electrical and thermal cell interactions which occur in a stack. Specific anomalies were introduced for this purpose. For electrical interactions, different bus plate materials and a partially inactive cell was introduced. For thermal interactions, the geometry of the coolant flow field channel in a bipolar plate was modified. Results were compared with model predictions.

- *Andrei Kulikovsky (Research Center Jülich):* Presented a 1+1D model of PEM and direct methanol fuel cells. The direct methanol fuel cell model reveals a new effect where, for infinitely small total current, a "bridge" of finite local current density forms near the inlet of the oxygen gas channel. This bridge forms only in the presence of methanol crossover, and short-circuits the electrodes. This phenomenon explains a well known effect of mixed potential in direct methanol fuel cells.

- *Xianguo Li (University of Waterloo):* Presented a fuel cell stack model which takes into account a variety of factors. A new flow field design was also proposed. Need for significant data was mentioned including cell voltage and pressure drop measurements under significant mass transfer control (low stoichiometries, wide range of temperatures and relative humidities including over-saturation).

- *Chun Liu (Pennsylvania State University):* Introduced 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, and gives a natural coupling between the flow field and the different interfacial properties.

- *Simon Liu (National Research Council Canada):* Presented an overview of PEM fuel cell modelling activites at NRC. The capabilities of commercial modeling software are illustrated by means of several engineering case studies the authors have conducted in the past four years, involving computational fluid dynamics, computational solid mechanics, computation electrochemical engineering, and computational materials. Need for an increased level of activity in two phase flow modelling was mentioned.

- *Graeme Milton (University of Utah):* Outlined the basic theory of linear composite materials and their effective properties. Discussed approximation schemes such as average field approximations, effective medium schemes, differential schemes, and asymptotic methods. A brief overview of the subject of bounds on the effective properties of composites, and the optimal microstructures which achieve them. Authored a book on the subject [1].

- *John Pharoah (Queens University):* Presented a gas diffusion layer model and investigated the effects of several properties of the gas diffusion layer on fuel cell performance, including thermal conductivity, mass diffusivity, and relative permeability. A new method for the determination of anistropic transport coefficients was outlined, and the results were compared to currently used values.

- *Keith Promislow (Michigan State University):* Presented a model of ignition dynamics and bistable operation of a Stirred Tank Reactor PEM fuel cell. In dry inlet gas operation, the positive feedback between current, water production, and membrane resistance leads to two stable "ignited" states, which correspond to a uniform current distribution or a partially extinguished cell with localized current production. Comparison with experimental data gathered by Jay Benziger.

- *Isaac Rubinstein (Ben Gurion University):* Over-limiting conductance is a phenomenon where steady state current higher than the limiting one is readily passed through a cation exchange membrane. Electro-convection driven by nonequilibrium electroosmotic slip at the solution/membrane interface was suggested as a mechanism drawing together the overlimiting phenomena at cation exchange membranes. Numerical calculations and experimental results were shown which support this case.

- *Tobias Schaeffer (City University of New York):* Based on the work of Grimshaw et al., Tobias Schaeffer presented a 1D transient model for membrane swelling and contraction, and the effects these changes have on membrane hydration. Results were compared with a simple ex situ type test with a membrane immersed in a solution.

- *Juergen Schumacher (Fraunhofer Institute for Solar Energy Systems):* Overview of different modeling approaches at the Fraunhofer Institute for Solar Energy Systems at the unit cell, stack and system scales. These models include a two dimensional non-isothermal model for planar self-breathing fuel cells (validated with experimental results), a dynamic two-phase flow model for unit cells, and a simplified dynamic stack model with energy, mass, and charge transfer phenomena. Fuel cell system modeling using the Colsim package of Fraunhofer ISE was also presented, which includes a fuel cell stack model, models for reformers, power inverters, heat storage units, pumps, compressors, valves, and controllers.

- *Sirivatch Shimpalee (University of South Carolina):* Presented a model which relates the electrical conductivity of the gas diffusion layer to fuel cell performance. Relative in-plane to thru-plane electrical conductivity including contact resistance are experimentally measured, and the interaction of flow-field geometry with the gas diffusion layer is also studied.
- *Jean St.-Pierre (Ballard Power Systems):* Presented a simplified 1D unit cell model for low cell voltages which elucidates our understanding of unit cell behaviour in the mass transfer limited regime. This model was validated and can be used to extract mass transfer coefficients from full size unit cells. Criteria were also defined to ensure model applicability.
- *John Stockie (Simon Fraser University):* Previous work has shown that mass transport limitations in the catalyst layer, rather than the gas diffusion layer, is responsible for limiting current density behaviour. A catalyst layer model which captures this effect is presented, and results are compared to existing results from both experiments and simulations in the literature.
- *Henning Struchtrup (University of Victoria):* Presented a simplified conductivity model, named BFCM, for perfluorosulfonic acid membranes to investigate the unknown parameters in the general transport model BFM2 (See Brian Carnes). This model was shown to provide a more consistent fit to 1100 EW Nafion than other established models, and was able to predict the conductivity of a Dow and Membrane C membrane.
- *John Van Zee (University of South Carolina):* Presented experimental data relating PEM fuel cell performance to rapid changes in the voltage. This dynamic behaviour depends on the type of flow-field and the voltage range of the voltage change. Overshoot and undershoot of the steady state current density profile were observed for fixed flowrates when the fuel stoichiometry varied between 1.2 and 1.1. The dimensionless peak current and percentage of overshoot current is shown to depend on starting cell voltage and the range of voltage change. These peaks are limited primarily by oxygen, even though operating conditions are close to fuel starved conditions.
- *Adam Weber (Lawrence Berkeley National Laboratory):* Presented a model for transport in PEMs. It is based on a physical model that is semi-phenomenological and takes into account Schroeder's paradox. The model addresses two different transport mechanisms, vapor- and liquid-equilibrated, as well as the simultaneous occurrence of both modes. The model thus bridges the gap between one- and two-phase macroscopic models currently used in the literature.
- *Brian Wetton (University of British Columbia):* An overview of PEM fuel cell operation is given, with emphasis on stack design. Some of the fundamental scientific questions related to device performance are outlined, and a summary of modelling approaches and the use of modelling in the application is given.
- *Ziheng Zheng (University of New Brunswick):* A new Magnetic Resonance Imaging (MRI) methodology was presented 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. The diffusion coefficients of both hydrogen gas and sulfur hexafluoride were measured in a model polymeric membrane, which is of potential interest as a gas separator in metal hydride batteries.
- *Christoph Ziegler (Fraunhofer Institute for Solar Energy Systems):* Presented a dynamic, two-phase flow model which accounts for Schroeder's paradox. Cyclo-voltammograms are simulated and measured, and a hysteresis effect is found in the measured IV-curves. This is likely due to the accumulation of liquid water at the cathode side of the cell.

4 Personal Remarks from the Organizers

There are other notable fuel cell meetings: the Gordon Conference on Fuel Cells, the American Society of Mechanical Engineering meetings on Fuel Cell Science, and sessions at the larger Electrochemical Society

meetings. There are also several possibilities for general meetings on industrial mathematics: the SIAM annual meetings and the larger ICIAM meetings every four years. However, at both of these kinds of meeting, the mathematical researcher with a focus on the fuel cell application is an outsider. The CFCD series of meetings at BIRS is a chance for this activity to be at the centre, with participation of experts in mathematical areas that will be used in the next generation of models, and application experts to identify where modelling activity should be focussed. BIRS provides a really wonderful opportunity for these communities to meet.

We would like to thank the staff and directorship of BIRS for their enthusiastic support of our workshop. Banff was the perfect setting to hold this workshop: the majestic scenery, the recreational facilties, the food attracted many top-notch participants who otherwise might not have come. Given the opportunity, we would welcome the chance to hold our next meeting at BIRS again.

References

[1] Graeme Milton. **The Theory of Composites.** Cambridge University Press, 2002.

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