PEM Fuel Cells

Session chair: Stephen Paddison,
Los Alamos National Lab, USA

ABSTRACT

The polymer electrolyte membrane (PEM) fuel is deemed one of the most promising devices for energy conversion. For the PEM fuel cell to be successfully integrated into the mass-market new materials will need to be developed, including: electrocatalysts for the fuel and air electrodes and the proton conducting membrane [1]. New materials possessing improved properties will emerge as a result of a collaborative effort between experimentalists, engineers, and theorists, the later doing both device and materials modeling. For the physical and chemical modeling of materials to play a role in the suggestion of new materials the modeling must be at the nano- and even molecular scale and ideally it should not be phenomenological but rather from Ågfirst principlesÅh. Discussed below are the various efforts in both materials and device modeling. It is hoped that as a result of this Special ICCN Session that there will be a much greater integration and collaboration between the research in materials and device modeling.

Keywords: fuel cells, PEM, modeling

PAPERS

On the Development of New Electrolytes for Fuel Cell Applications: The Role of Simulation Tools

K-D Kreuer
Max-Planck-Institut für Festkörperforschung,,
Heisenbergstr. 1, D-70569
Stuttgart, Germany

A critical part of any fuel cell is the separator material, an electrolyte conducting preferentially one kind of ion but impervious to electrons (and holes). The different types of fuel cells are even named according to the different electrolytes used as separator materials, i.e. SOFC for "solid oxide fuel cell", MCFC for "molten carbonate fuel cell", AFC for "alkaline fuel cell", PAFC for "phosphoric acid fuel cell" and PEMFC for "polymer electrolyte membrane fuel cell". During the last decade, there has been tremendous progress with respect to achieving both performance and long-term stability. While this success was essentially the result of sophisticated engineering efforts making use of available materials, the inherent properties of the materials employed to date seem to inhibit further progress of this promising technology. This presentation emphasizes the potential of various simulation techniques in the development of new electrolyte materials.

Ab initio and quantum molecular dynamics-, Monte Carlo- and phenomenological simulations combined with appropriate experimental techniques may be used as complementary tools. This will be demonstrated for the development of:

(i) highly proton conducting oxides by optimization of the crystallographic and electronic structure of acceptor-doped BaZrO3-based materials [1-4]. Such electrolytes allow the operation of solid oxide fuel cells (SOFC) at reduced temperature (500-800°C), where materials compatibility problems are significantly reduced. (ii) Solvated proton conducting polymers and composite membranes with low Onsager cross-coefficients for the coupled transport of protons and water or methanol by micro structural control. These materials are relevant for direct methanol fuel cells (DMFC), for which the so-called methanol and water "cross-over" is still the key problem to be solved [5]. (iii) Novel side-chain polymers with heterocycles (e.g. imidazole) as proton solvating moieties and high proton mobility at medium temperatures (150-250°C), where poisoning effects of available electro catalysts (e.g. Pt/Ru) are drastically reduced. As opposed to conventional membranes, the high proton mobility in these materials does not rely on the presence of water (high relative humidity) [6-9].

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Self-Consistent Mean Field Theory for Micro-domain Structure in Perfluorinated Ionomers

H.J. Ploehn
Department of Chemical Engineering
University of South Carolina

The objective of this research is to develop statistical mechanical models that can be used to predict the phase behavior and micro-domain structure of perfluorinated ionomers. Specifically, we wish to understand how the ionomer architecture controls the equilibrium microstructure. To achieve this goal, existing statistical mechanical models for linear homopolymers have been extended in order to account for co-monomers and branched chain topology. We have implemented lattice-based self-consistent mean field (SCMF) theory, programmed using an object-oriented approach, to predict the equilibrium structure in Nafion_ and Dow short-side-chain ionomers. With decreasing water content or temperature, we observe a phase transition: the spatial distributions of polymer and water transform from homogeneous to lamellar, with the domain size and coexistence conditions depending on the number of sulfonyl side-chains, their length, and their spacing along the fluorocarbon main chain. The primary phase transition occurs when the hydrophobic fluorocarbon segments segregate from the other, more hydrophilic segments. We see secondary transitions due to the segregation of ether and sulfonyl segments. The conditions for these transitions on the (concentration-temperature) phase diagram depend on the details of the molecular architecture. We must regard the results as qualitative because none of the interaction parameters have been set in accord with experimental data, nor do we account for the possibility of morphologies other than lamellar. Nevertheless, the results demonstrate that we have established the foundation to explore the relationship between polymer architecture and phase separated micro-domain structure in perfluorinated ionomers.

Theoretical Advances in Electro catalysis over Supported Nanoparticles: the Oxidation of CO and Methanol over PtRu

M. Neurock, S. Desai and J-S Filhol
Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22901

Theory has rapidly advanced to the stage where it can provide reliable information for kinetic processes carried out over well-defined surfaces in the gas phase. It has therefore been used to a growing extent to probe catalytic reactions over extended surfaces and cluster models, which mimic catalytic sites on supported nanoparticles. There have been relatively few applications, however, electro catalytic systems due to the complexity that arises from the presence of solution, electric fields and applied potentials. Herein we will discuss the development and application of ab initio methods to treat aqueous electro catalytic reactions on bimetallic nanoparticles and their application to fuel cell systems. More specifically we will focus on the electro catalytic oxidation of CO and methanol over PtRu surfaces.

The catalytic performance of both the direct methanol fuel cell and the reformate fuel cell can be significantly inhibited by the formation of CO which acts to poison active Pt surface sites. The addition of ruthenium is known to enhance CO tolerance. Ruthenium is thought to either weaken the binding of CO on the surface or activate water to form surface hydroxyl intermediates, which can in turn oxidize CO to CO2 via the bifunctional mechanism shown below:

$$H_2O^* \rightarrow OH^* + H^+ + e^-$$
$$CO^* + OH^* \rightarrow CO_2 + H^+ + e^-$$

We have used first-principle density functional theoretical calculations and ab initio molecular dynamics herein to model the oxidation of CO over different PtRu alloys. We explicitly examine both of the reactions above at various model conditions including: 1) in the vapor phase, 2) in solution, and 3) in the presence of an applied potential in order to understand each of their effects. We describe a set of extensive calculations on Pt, Ru and PtRu alloys for these systems. We find that Pt and Ru play unique roles in this chemistry, which cooperatively work together in order to facilitate the bifunctional mechanism.

Modeling PEFC Anode Performance to Include Effects of CO, Reformate Gas, and High Hydrogen Utilization

T.E. Springer
Electronic and Electrochemical Materials and Devices Group
Los Alamos National Laboratory
Los Alamos, NM 87545

We discuss a polymer electrolyte fuel cell (PEFC) model designed to calculate anode potential losses from effects of CO poisoning, of H2 dilution in reformate gas, and of hydrogen utilization up to 90% along the flow channel. We specify a cell voltage, a cathode/membrane voltage-current relation, and an anode reactant gas concentration at the flow-channel / gas-diffusion layer interface. Then one-dimensional equations simultaneously describe anode gas fluxes and concentrations through the anode gas diffusion layer and local potential and reactant concentrations in the catalyst layer and determine local current density. These equations are repetitively applied along the flow channel where local reactant utilization rather than position tracks progress until the desired utilization is achieved at the flow channel exit. We will discuss the improvement in solution robustness by adding additional difference equations to pass current density from the cathode to the anode gas diffusion layer, the introduction of CO coverage-dependent rate constants to the anode kinetic equations to reproduce measured data, and the advantage of using local utilization in the flow channel.

Effects of the Environment on the Performance of PEM Nanocatalysts

P.B. Balbuena
Department of Chemical Engineering
University of South Carolina

Understanding the mechanisms and intricacies of catalytic and electrocatalytic processes is one of the goals that must be achieved in order to optimize fuel cell performances.

Transition metal nanocatalysts have been used since the 60's, however they are in most cases the result of poorly defined fabrication procedures. Nanocatalysts not only provide reaction rates enhanced with respect to those obtained from catalysis on extended surfaces, most importantly they may be suitable for alternative reaction paths that are available only because of the singular electronic characteristics of the nano-dimensions. Besides, the feature size of nano-scale systems allows a theory-guided and a controlled atomic manipulation that should enable the fabrication of nanosystems with very precise characteristics.

An important aspect of PEM carbon-supported transition metal nanocatalysts is that they are immersed in a proton-conductive hydrated polymeric membrane through which the reactants are able to reach the catalytic surface. Although quantum and classical molecular simulations are beginning to be used for the analysis and design of materials suitable for fuel cell catalysis and electrocatalysis, in many cases the additional complexity due to the effects of the environment surrounding the catalyst/reactant system is ignored. In this talk we will discuss our recent molecular simulations work addressing the temperature and pressure effects on the shape and structure of mono and bimetallic nanoclusters deposited on graphite, as well as the interactions of the hydrated polymer membrane with such structures. Moreover, we will discuss how these effects would modify the cathodic overpotential for the electroreduction of oxygen.

Mathematical Modeling of Water Management in PEM Fuel Cells

Keith Promislow
Department of Mathematics
Simon Fraser University, Burnaby Canada V5A 1S1
kpromisl@cs.sfu.ca

Liquid water is fundamental to Polymer Electrolyte Membrane fuel cells (PEMFC). Its influence, both beneficial and parasitic, is measured on time scales from femto-seconds to hours, on length scales from Angstroms to centimeters. Its role couples it intimately to all aspects of PEM fuel cell operation: electro-chemical reaction and temperature management, ion transport in the polymer membrane, diffusive mass transport in gas diffusion layers, convective transport in headers and flow fields. A predictive mathematical model for water management must encompass, at some level, these complex interactions over the vast array of length and time scales.

This talk will give an over-all sketch of PEMFC functioning, and then will visit in detail the aspects where nano-scales impinge upon the macro-level modeling. In particular we will focus on proton transport modeling in the electrolyte membrane, the multi-phase flow in the teflonated carbon fiber material of the gas diffusion layer which backs the membrane, and the crucial effects which occur at the junction of these two layers.

Micro- and Meso-scale Phenomena in Polymer Electrolyte Fuel Cells

C-Y Wang, G.Q. Wang, U. Pasaogullari and H. Meng
Electrochemical Engine Center, and Mechanical Engineering Department
The Pennsylvania State University
University Park, PA 16802

Polymer electrolyte fuel cells are characterized by a large range of length and time scales. This talk will present recent attempts to understand micro- and meso-scopic phenomena occurring in polymer electrolyte fuel cells. These include oxygen and charge transport and water distribution in the microscopically complex catalyst layer at the pore level (microscale), water management in the membrane electrode assembly (mesoscale), and transverse water transport between channel and land areas (mesoscale). Coupled experimental and modeling studies have been performed to generate a basic understanding of these important phenomena, and results will be elaborated in this talk. In addition, parallel computations to integrate these micro- and meso-scale sub models into macroscale simulation of PEM fuel cells with complex flow field will be described.

CFD-Based PEM Fuel Cell Models and Applications

H. Liu
Department of Mechanical Engineering
University of Miami

In recent years, various fuel cell models based on computational fluid dynamics (CFD) have been developed at the Fuel Cell Laboratory, University of Miami. These 2- or 3-dimensional models account for all the major transport phenomena in all the major components of a fuel cell: two flow fields, two gas-diffusion layers, two catalyst layers and the membrane. If necessary, collector plates, cooling channels and other components can easily be included in the modeling domain. These models can provide detailed multi-dimensional distributions of gas concentrations, current density, over-potential, temperature, water content and reaction rates, as well as polarizations curves. Application of these CFD-based models to various fuel cell operating situations will be presented and the uniqueness of such multi-dimensional models will be discussed. The limitations of such models and the need for multidisciplinary research, including those in micro/nano-scales, will also be addressed.

Voltage Current Curve of a PEM Fuel Cell: Analytical and Numerical Modeling

A.A. Kulikovsky
Research Center "Juelich", IWV-3
D-52425 Juelich, Germany,
A.Kulikovsky@fz-juelich.de

First we consider 1D problem of the cathode catalyst layer (CCL) performance. The general solution is presented and simple analytical formulas for CCL polarization voltage are obtained. Based on these formulas we build a simple fitting equation for voltage current curve of a cell. All terms in this equation have clear physical meaning; coefficients are expressed in terms of basic transport and kinetic parameters.

Then we describe quasi-3D numerical model of PEM fuel cell, equipped with long channels for feed gases supply. The model is based on 2D mass and charge conservation equations in a cell cross-section, coupled by equations for along-the-channel concentration of feed gas. Typical example of "fuel cell map" (distribution of parameters in a cell cross section) is presented.

Finally, analytical and numerical models are used to analyze real experimental voltage current curve. This procedure gives kinetic and transport parameters of the cell and allows to isolate the contribution of 2D effects to voltage loss. A perspective to characterize membrane-electrode assemblies and flow fields, using voltage current curve is discussed.

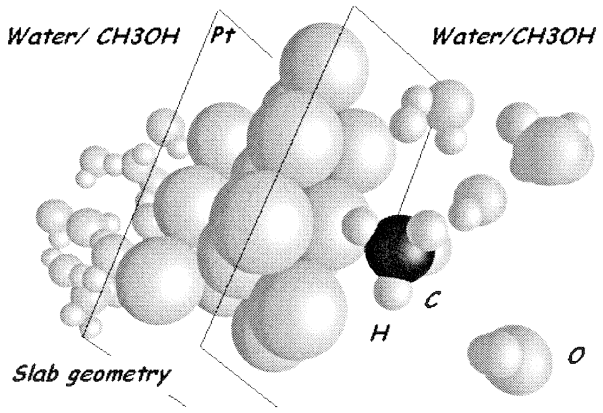
Ab-initio Molecular Dynamics of CH3OH at the H2O/Pt Interface

T.R. Mattsson[1] and S. J. Paddison[2]
[1]Surface and Interface Science Department
Sandia National Laboratories
Albuquerque, NM 87105-1415
[2]Computational Nanoscience Group, PSRL,
Motorola Inc.
Los Alamos Research Park,
Los Alamos, New Mexico 87544

Among the engineering achievements, including a reduction in the overall cost of the system, necessary for Direct Methanol Fuel Cells (DMFC) to become a competitive alternative for both portable and stationary power applications, are improved catalysts. An important step towards improving existing solutions, in turn, is a fundamental, molecular based, understanding of the catalytic processes.

Computer simulations, in particular calculations from first principles, have proven to provide key insights into gas-phase catalytic reactions. Density Functional Theory (DFT) stands out as the method of choice for this type of problems. With DFT, it is possible to describe molecular

reactions as well as an extended metallic surface without assumptions about atomic interactions. DFT has therefore been used extensively, and successfully, for explaining properties of gas-phase reactions at surfaces. The situation in a DMFC is, on the other hand, significantly more complex since the water solution and the water/ Platinum interface will substantially influence the reaction kinetics. In this talk, we present first-principles molecular dynamics simulations of methanol near the Pt/water interface. Energies, bond lengths, bond angles and correlation functions during trajectories extending several nanoseconds will be reported. The dependences on distance from the interface as well as on the orientation of the methanol molecule relative to the surface will be investigated and compared to the corresponding quantities for the gas-phase reaction.



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Computational Modelling and Structural Studies of Perfluoro Sulfonate Ionomer Membranes

James A. Elliott
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, England CB2 3QZ

Perfluoro sulfonate ionomer membranes (PIMs) consist of a "Teflon" (PTFE) backbone with sulfonic acid groups periodically substituted along the chain, and are of great commercial interest due to their peculiar ion transport properties. In particular, under certain conditions, these membranes are selectively conductive, passing cations but not anions. This makes them ideal as efficient membrane separators in redox fuel cells. It has been known for some time that the properties of PIMs derive from the microscopic phase separation of ionic material and the fluorocarbon matrix. However the precise nature of this remains controversial.

In this paper, we present data from small angle X-ray scattering (SAXS) and molecular dynamics studies that provide convincing evidence that PIMs possess an ion-clustered morphology with a structural hierarchy. In particular, a model-independent instantiation of the segregation between polar and non-polar material can be obtained from a maximum entropy interpretation of the SAXS data. Such models are consistent with surface images of membranes taken with atomic force microscopy, and molecular dynamics simulations show that these structures demonstrate selective conductivity in the presence of an applied electric field.

Advances in Modeling and Simulation of Transport Processes in PEM Fuel Cells

B. D'Aguanno, G. Murgia, L. Pisani, M. Valentini
Center for Advanced Studies, Research and Development in Sardinia, VI Strada Ovest, Z.I. Macchiareddu, 09010 Uta (CA), Italy

Mathematical models and numerical simulations treatment of PEM fuel cells have been developed to predict both the overall cell behavior, as typified by the cell potential versus the cell current density curve, and the local spatial behavior of fuel cell variables, such as the chemical species concentrations, the temperature, the pressure, the electrical potential, and their associated flow fields. Although in many specific cases the prediction aim has been fulfilled, water flooding and concentration phenomena, which are relevant at high current densities, are not yet included in mechanistic models.

Aim of this presentation is to show under which circumstances the inclusion of the porous structure of all Membrane-Electrode-Assembly regions is essential to qualitatively and quantitatively describe the cell potential at any cell current density. This will be achieved by introducing capillary theory considerations in the diffusion regions, and by considering the interplay between the "diffusion" lengths of the chemical species with the characteristic length scales of a porous medium (pore-to-pore distance, pore size, tortuosity, etc.), especially in the reactive regions.

The derived Bernardi-Verbrugge-like model is presented together with extensive applications and comparisons with experimental data. The advantages of the model in terms of solution algorithm performances are also presented and discussed.

Theoretical Study of Temporal Performance Patterns in Anodes of Polymer Electrolyte Fuel Cells

M. Eikerling
Technische Universität München, Department of Physics E19, James-Franck-Str. 1, D-85748 Garching, Germany

Transient performance patterns at anodes of polymer electrolyte fuel cells under conditions of high CO coverage are studied. The basic model, build on commonly accepted mechanisms, consists of two kinetic equations for the processes at highly dispersed Pt catalyst, involving irreversible adsorption of CO onto vacant catalyst sites, generation of adsorbed OH_{ads} via dissociative oxidation of water and recombination of CO_{ads} and OH_{ads}. The interplay of CO_{ads} balance and charge balance, involving faradic and capacitive contributions, determines the transient performance.

Critical conditions (Hopf-bifurcation point), at which self-sustained voltage oscillations occur, have been determined. They indicate the transition between stable and instable electrode performance. The analysis revealed that an autocatalytic mechanism for the formation of free catalyst surface by electro-oxidative CO removal has to be invoked in order to explain oscillatory behaviour. Instable performance is only encountered, if the number of free surface sites for OH-adsorption and mobility is larger than the number of sites on which CO adsorbs.

Further detailed analysis rationalizes effects of electrode structural parameters on performance, highlighting the impact of the surface heterogeneity factor: a larger heterogeneity helps to endure larger amounts of CO. Diagnostic capabilities of the model are demonstrated, depicting the effect of double layer capacitance and real-to-apparent-catalyst-area ratio on critical conditions. In practice, the described phenomena are expected at current densities of a few am cm^{-2} if the anodic reactant gas predominantly consists of CO.

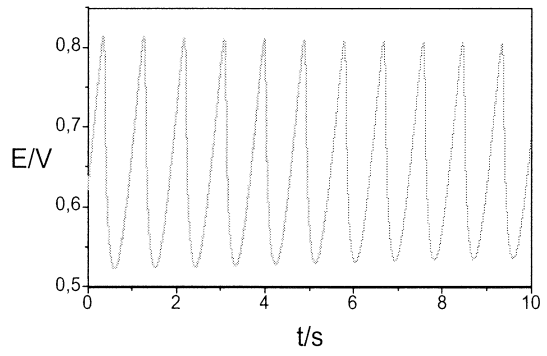

Fig. 1: Oscillation of electrode potential in methanol oxidation on Pt, calculated in the model.

A straightforward variant of the model reproduces voltage oscillations in the methanol electro-oxidation on Pt (Fig. 1), recently found in experiments [1]. In summary, our study contributes to the understanding of mechanisms underlying catalyst poisoning by adsorbed CO and it reveals routes towards their control. This first model forms the basis for extended investigations of instabilities in electrodes with alloy catalysts.

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Proton Conduction in the Polymer Electrolyte Membrane: Molecular and Statistical Mechanics Modeling

*S.J. Paddison**
Computational Nanoscience Group, PSRL, Motorola Inc.
Los Alamos Research Park,
Los Alamos, New Mexico 87544

For the PEM fuel cell to be successfully integrated into the mass-market new materials will need to be developed, including: electrocatalysts for the fuel and air electrodes and the proton conducting membrane [1]. New materials possessing improved properties will emerge as a result of a collaborative effort between experimentalists, engineers, and theorists, the later doing both device and materials modeling. For the physical and chemical modeling of materials to play a role in the suggestion of new materials the modeling must be at the nano- and even molecular scale and ideally it should not be phenomenological but rather from "first principles".

The hydrated PEM is an inhomogeneous material the morphology of which is not well characterized. As such it is a system that must be examined through modeling 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 [2-9]. The hierarchy of this multi-scale modeling is as follows: (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 applying both equilibrium and non-equilibrium statistical mechanics.

This talk will present new results and analysis of proton conduction derived from the three approaches described above and at various degrees of hydration with various membranes.

*Presently at the Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545

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