Workshop on Research Challenges for Low-temperature Fuel Cells

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Table of Contents

Introduction

Our society's power and energy demand is met largely through the combustion of fossil fuels. The world economy relies upon on a limited resource; trends suggest that global energy use is expected to double in the coming decades. At the same time, concerns about the effects of anthropogenic carbon dioxide and criteria pollutants and about energy security continue to mount. Meeting our energy needs in a sustainable manner is a historic challenge that will cause us to diverge from the pattern of the last couple of centuries. To this end, several U.S. research universities, Stanford's Global Climate & Energy Project, Georgia Institute of Technology, and MIT to name a few, have recently launched major initiatives to intensify their efforts in energy research. The U.S. Department of Energy has also introduced a broad hydrogen-fuel initiative.

Storage and conversion of energy becomes increasingly relevant as we move towards greater reliance on renewable energy sources. Fuel cells are an efficient means to convert chemical energy into electrical energy with little or no emissions. Fuel cells are therefore expected to be an important energy technology for the future. Typically fuel cells are categorized by their electrolyte and therefore by the temperature of operation. This report focuses on low temperature fuel cells—here low temperature is taken to be less than 200 ºC. For low temperature fuel cells the predominant electrolytes are perfluorinated sulfonic acid membranes, or proton exchange membranes (PEM). The most common is Nafion™, a perfluorinated ionomer first developed by DuPont.

The principal application for these low-temperature fuel cells will be transportation. Table 1 shows the high-level requirements as defined by DOE. In particular, low-temperature fuel cells are best suited for operation on hydrogen. Recent reports have identified the development of cost-effective, durable, and safe fuel-cell systems as a key research challenges in the 21st Century.[1,2] Here we will address in more

detail the technical barriers visible on the horizon and outline a specific research agenda to address the gaps between product requirements and present capabilities.

For transportation applications in a future hydrogen economy, the key competition will be batteries. Interestingly, batteries are simultaneously the major competitor and a complementary technology to fuel cells. The source of hydrogen for a fuel-cell system may be from the electrolysis of water using energy from nuclear power or a renewable source, thermolysis or photolysis of water, or from a reformed hydrocarbon fuel. The fuel cell stack, pumps, blowers, *etc*. along with a hydrogen-storage system are essentially an energy-storage system equivalent to a battery. The difference between the two storage systems is that the fuel-cell system is recharged with hydrogen rather than with electrical energy. The battery will be more efficient in converting electrical energy into chemical and back, achieving round-trip efficiencies of 80 percent or more. A state-of-the-art fuel-cell/electrolyzer system cannot approach similar efficiencies. However, rechargeable batteries have a specific energy of about 100-120 Wh/kg with a long-term goal of 200 Wh/kg, and typical vehicle requirement of near 300 Wh/kg. The key advantage for the fuel cell system will be greater energy density, which translates directly to better range. This comparison is shown in figure 1 for a 100 kW fuel cell assuming 0.65 kW/kg (DOE 2010 goal) More than likely the vehicle system will be a hybrid—the extent of hybridization and specific system architecture will depend on the relative successes in improving hydrogen storage, reducing fuel-cell costs, and in increasing the energy density of secondary batteries.

Tremendous progress has been made in the development of low-temperature fuel cells. Two noteworthy advancements were the introduction of perfluorinated ionomer

membrane and the improvement of electrode structures that increase catalyst utilization.[3] At the same time, numerous incremental improvements have been made. Nonetheless, it is clear that present technology falls far short of the ultimate requirements, and significant effort in fundamental understanding is warranted.

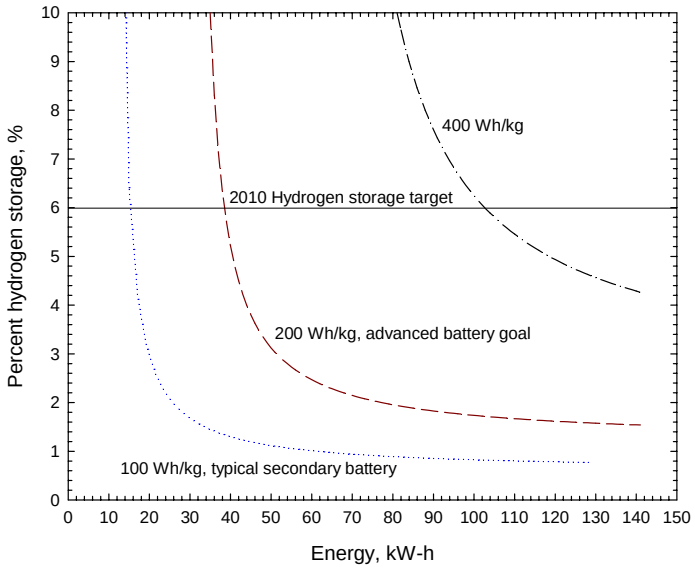


Figure 1.

Recently Steele and Heinzel suggested that in order to meet the targets a wholesale review of materials of construction is needed.[4]

	Units	2005	2010
Energy efficiency @ 25% of rated power	**%**	**60**	**60**
Energy efficiency @ rated power	**%**	**50**	**50**
Power density excluding hydrogen storage	**W/liter**	**500**	**650**
Specific power excluding hydrogen storage	**W/kg**	**500**	**650**
Powerplant cost (@ 500,000 units per year)	**$/kW$_e$**	**125**	**45**
Transient response (time from 10% to 90% of rated power)	**sec**	**2**	**1**
Emissions		**none**	**none**
Durability	**hours**	**2000**	**5000**
Cold start-up time to 90% rated power @ -20 C ambient temperature	**sec**	**60**	**30**
@ +20 C ambient temperature	**sec**	**30**	**15**
Survivability	**^{o}C**	**-30**	**-40**
Stack cost (@ 500,000 units per year)	**$/kWe**	**65**	**30**
Precious metal loading	**g/kW**	**2.7**	**0.3**

"Embedded requirements" (estimates)

low power/ high power cycles	1,000,000
start stop cycles	20,000
max allowable stack temperature	90-120 C
system water volume	< 1 liter

Table 1. Summary of Requirements

Workshop Organization

The National Science Foundation and the Electrochemical Society sponsored a two-day workshop to define the basic science needs addressing challenges for low-temperature fuel cells. The starting point for the discussion was the assessment of the status of low-temperature fuel cells, the end-use requirements, capabilities and limitations of existing systems for energy conversion. This information was obtained through an exchange between scientists and engineers and experts in the automotive and energy companies.

Following opening remarks by Dr. Geoff Prentice (NSF program manager), five 40 minute keynote presentations that scoped the main aspects of the research challenges were made. The subtopics were 1) proton conductors, 2) electrocatalysis, 3) transport, particularly at temperatures below the freezing point of water, 4) modeling and simulation, and 5) systems integration. Advances in these core areas are needed to address the key challenges for low-temperature fuel cells in durability, operability, efficiency, power density, and cost. However, we did not attempt to address specific product deficiencies; rather our objective is to identify more fundamental technical challenges that underlie the gaps. Therefore the specific objectives are 1) to identify gaps in low-temperature fuel-cell technologies, 2) describe technical approaches to meet these critical research needs, and 3) establish an agenda for basic research in low-temperature fuel cells. Following the five plenary talks, the participants were divided into five break-out groups that met that afternoon and the following day. A complete list of participants is provided at the end of this document. On the second day, each breakout group presented a summary of their findings to the entire group. This report documents the findings and recommendations for each subtopic and some general recommendations.

Proton Conductors

The Department of Energy's Hydrogen Fuel Initiative suggests that for fuel cells to become viable energy-delivery devices, there is a need to operate them at low humidity and temperatures around 120 °C, something current membranes cannot achieve. Thus, new membranes must be synthesized with good ionic conductivity and durability and low gas permeation. Such a combination poses a challenge for polymer scientists due to the lack of fundamental knowledge of structure-function relationships for this class of polymers. Even though the development of high temperature membranes (*i.e.*, > 100 ºC) has been an active area of research, the progress has been slow, and we should now consider the viability of present approaches. A similar effort was made to develop higher temperature polymers for lithium batteries with limited success. Are the characterization techniques and molecular level modeling tools adequate and are they being used appropriately? Do we have the necessary interdisciplinary teams working on these challenges?

A further important issue related to these membranes is their stability and durability. Polymer degradation occurs in Nafion®, even though it is considered to be highly stable. Thinning of membranes and detection of fluoride ions in product water provide direct evidence of chemical attack.[5] Degradation is believed to result from the formation of hydrogen peroxide, subsequent free-radical formation, and polymer attack, likely at residual H-containing end groups.[6] This mechanism is strongly influenced by the water content of the membrane, permeability to oxygen and hydrogen, and the electrochemical environment. Mechanical stress, either induced by swelling with water or

by mechanical forces from the cell construction, is also believed to contribute to the degradation; however, no overarching theory yet explains this degradation. Although qualitative information is emerging, scant fundamental understanding of the mechanisms has been elucidated. By correlating the structure and morphology of membranes with the chemical attack, permeability of gases, and proton conduction, one may thus guide, by means of macroscopic and molecular level modeling, the development of new membrane materials that operate at low humidity and higher temperatures with acceptable durability. The key challenges related to proton conduction identified were:

- Fundamental issues in transport and permeability. How are gases going through the membrane and what are the effects of interfaces in multi-component systems?
- Design over morphology and structure, specifically new experimental techniques and coupled modeling, including time-resolved studies that correlate with simulations of dynamics, control over morphology, and control of the interfacial surface structure
- Membrane responses to multiple stresses such as fundamental studies of responses of polymers to thermal, mechanical, electrochemical, and redox stresses over time.
- How does the membrane respond over time in an fuel-cell-like environment? Does the initial state influence property responses? How do specific interfacial defects relate to specific failure modes in the device?
- Design over chemical structure (proton conduction). Examples include new amphoteric systems, the origins of oxygen stability. Model materials that provide insight into mechanisms of proton conduction for instance.

Electrocatalysis

Low-temperature acid fuel cells use platinum supported on carbon for electrocatalysis. Reduction of loadings of platinum or other precious metal in electrodes has been identified as essential in order to reduce system costs.[7] Today, platinum and its alloys are the only catalysts that show reasonable kinetics for oxygen reduction in low-

temperature acid electrolytes. What's more, the polarization losses at the oxygen electrode are the largest source of inefficiency. Consequently, in addition to cost, improving the catalytic activity may be the most promising avenue to further improvements in power density and efficiency. At the same time, there are new questions about the stability of platinum and the associated support materials in a fuel-cell environment.[8] Two issues of catalyst stability are dissolution and support corrosion. Oxygen reduction selectivity and the consequences of peroxide generation are also important factors in membrane durability.

Without question, the oxygen reduction reaction deserves the overwhelming majority of attention for future research. It is well known that the activation polarization is the largest (about 0.4 V) and that the most precious metal is needed at the cathode. In contrast, the hydrogen reaction is so fast that very little (~ 0.05 $mgPt/cm^2$) is required. Over the last decade as the interest in low-temperature fuel cells grew, so too did investigations of CO tolerance. CO is well known for strongly adsorbing on to a platinum surface. Nevertheless, as one researcher put it we should "resist the sirens lure of focusing on CO and CO-like molecules." It appears that the performance losses due to impurities are largely reversible, *i.e.*, one can readily mitigate the poisoning effects of ammonia or CO. Although the effects of low levels of fuel impurities are important, they can largely be managed at the system level and these effects are second order—the details are highly coupled to operational conditions. Direct methanol fuel cells will be restricted to low power applications. Oxidation of methanol and other potential fuels is important, but oxygen reduction should be the focus.

At a high level, a target of less than 0.2 g Pt per kW are needed, or 20 g Pt for a 100 kW power plant, to meet cost targets for automotive applications. This equates to more than 0.44 A/mg Pt at 0.9 V (reference to hydrogen) on oxygen, and 0.9 W/cm^2 at 0.65 V. We recommend in studying or evaluating catalyst activity that researches use oxygen rather than air. Air is kinetically controlled only at current densities below about 0.1 A/cm^2. Automotive targets require development of catalysts that are nearly 4 times more active than present Pt materials.

Catalytic activity

There are two approaches to meeting the cost and efficiency requirements: reducing the use of platinum and simultaneously maintaining or improving activity, or use of non-precious metal catalysts (assuming of course that they are less costly). For reducing the loadings, the options are 1) increase surface area of catalysts, 2) increasing the utilization of platinum in electrode structure, and 3) improving the specific activity of the platinum. Today cutting-edge catalysts layers use platinum nanoparticles supported on carbon. Carbon black comprise aggregates of about 40 nm primary particles and the platinum particles are about 2-4 nm in size. The electrochemical surface area in a electrode today is about 60-90 m^2/g, and the theoretical limit is 240 m^2/g. Oxygen reduction activity per surface platinum atom is less for small particles than for large particles or continuous surfaces,[9] and no improvement in mass activity is seen above 80 m^2/g. Therefore the point of diminishing return has been reached through improved dispersion of platinum.

What are the prospects for improving catalyst activity at low temperature with existing materials? One approach to improving the intrinsic activity of catalysts has been the use of alloy catalysts.[10] The effects that catalyst particle size (typically on the order of a nanometer), d-band filling, and crystal lattice parameters have on activity for oxygen reduction are reasonably well understood. This understanding has been the basis for the development of alloy catalysts. Platinum alloys can about double the activity of platinum alone, (add some references). How might we achieve another doubling? Based on work of Ross *et al*., it is evident that not only the surface composition, but also surface structure and sublayer composition are key factors to obtaining the highest possible activity. The alloying component changes the electronic properties of platinum, which implies different adsorptive properties of the platinum. A platinum skin structure has the most pronounced effect where platinum atoms in the first outermost layer are spread over a cobalt enriched underlayer. An optimized catalyst has both controlled particle size and shape. Key paths now must control the composition of the layer under surface platinum, control the size and more important the shape of the particles, and control the isotherm for OH_{ads}.

Many of these approaches have been explored for a couple of decades or more with modest improvements in catalytic activity. In some cases alloy catalysts are used commercially, but is this still a fruitful area of research? Combinatorial methods for identification of new alloys have had limited success—composition is only one of the variables. Ternary systems may be explored. Another proposed method to increase the utilization of Pt is to create a skin structure of Pt on a base material, such as Ni.[11] The

structure of the catalyst, support, and ionomer interface is critical. We need better tools to identify the true picture of their interactions.

Durability

Durability is hampered by loss of platinum surface area and degradation of non-platinum catalysts. During cycling one repeatedly forms and reduces an oxide layer, which redistributes platinum atoms on the surface. There is a small domain of corrosion, see the Pourbaix diagram for platinum, through which the cell potential passes during cyling. Is the loss of platinum are dominated by dissolution equilibrium or by Pt dissolution during passivation/depassivation? Pt/Co has shown decreased surface area loss, but still may not meet the target of less than 40 % area loss over life of fuel cell. How can one manage the electrocatalyst and interfacial durability? What are the relationships between structure and stability? Can we find better spectroscopic methods? Could we model segregation as a function of particle size and shape?

For low-loaded catalysts peroxide can diffuse away from catalyst layer before reacting to form water. A significant amount of peroxide is formed from a low loading of platinum at normal potentials.[12] Therefore one must keep an eye on peroxide formation for low-loaded catalysts.

$$O_2 + 2e^- + 2H^+ \longrightarrow H_2O_2$$
$$H_2O_2 + 2e^- + 2H^+ \longrightarrow 2H_2O$$

Are non-carbon supports available that will give high surface area platinum and be more resistant to corrosion? Further modeling of parallel paths for oxygen reduction and peroxide formation are needed. Can we employ ESR for *in-situ* detection?

Fundamental tasks and priorities

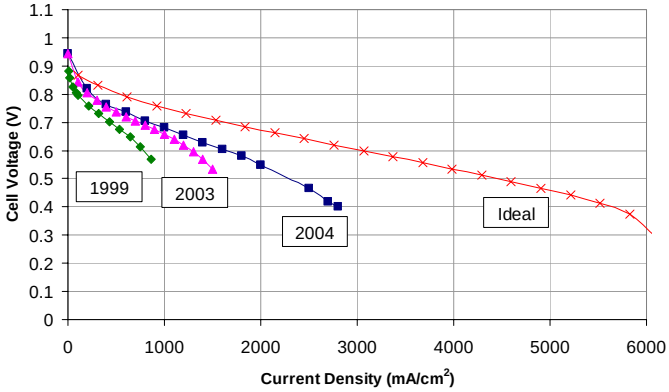
Above all, a fundamental understanding of the catalyst surface is needed in order to identify new systems with higher activity, improved stability of electrocatalysts, and to predict the properties of these systems. Most of the fundamental work in electrocatalysis focuses on single crystals. Single crystal experiments will remain important for elucidating fundamental mechanisms and validating *ab initio* models. Further work in linking these single-crystal results with those of polycrystalline catalysts found in fuel cells is critical. With highly dispersed catalysts, a large fraction of the Pt is on the surface, and the bulk properties are not representative. The segregation tendency of alloying elements, for instance, is very dependent on the external environment the catalyst particle sees, as well as on the applied potential. As such, the surface composition and structure will be strongly influenced by the operating conditions of the electrode. First principles computations are particularly well suited to study these problems as segregation energies can be calculated under well controlled conditions of oxidation, water adsorption, *etc*. This will give insight into the evolution a Pt-alloy catalyst is expected to undergo in fuel-cell operation. Combining this with rate information, obtained either through experiments, or with first principles computations, will give a predictive model for the stability of catalysts.

While modeling and theory of low-temperature catalysts has focused mainly on the catalytic activity and overpotential, little emphasis has been placed on understanding the atomistic mechanisms that determine catalyst stability. An understanding of the surface structure of Pt and Pt-alloy catalysts is crucial for any rational design of better catalysts. For instance, present models for sintering or ripening of catalyst particles are inadequate. How can we elucidate further the mechanisms for performance loss of electrocatalysts due to platinum deactivation, dissolution, and migration? How should we develop tools based on first principle models that would allow design of new catalyst materials, and predict their stability? We believe that in this area, a combination of first principles computations and targeted experiments can rapidly identify the important effects in stability, and consequently suggest better catalysts.

It is clear that a fundamental understanding of the catalyst surface is crucial in order to identify new systems with improved stability and to predict their performance. Suggested directions for catalysis include better understanding of the structure property relationships. More work to model the lateral-adsorbate interactions is warranted. A better understanding of the nature of the overpotential at a molecular level is needed. Additionally, understanding local water activity and kinetics is lacking. Will the key to improve catalyst activity depend on the development of new electrolytes? What are the support interactions and exploration on non-carbon or modified carbon supports.

Transport

To a large degree transport limitations in low-temperature fuel



cells have been reduced to the point where they no longer represent a large fraction of the efficiency loss. Figure 2 shows the improvements made in cell performance for one manufacturer. The ideal curve is a model that assumes no liquid-phase diffusion occlusion of gas-phase transport in the electrode. This is particularly true under well-controlled, steady-state conditions. Two aspects of transport are important for future work, nonetheless. First, water transport during transients, and in particular for freezing/thawing conditions. The second is correlating the change in transport properties with degradation of materials. In addition, there is limited ability to define and fabricate the appropriate electrode microstructure without extensive trial and error.

Present low-temperature fuel cells rely on a solid, liquid, and gas phase. Within electrode structures a complex interconnecting network of the three phases allows for facile electronic and ionic conduction and transport of reactants and product water. Pores range in size from tens of micrometers for gas diffusion media to nanometers within the ionomers and catalysts supports. A further complication for existing low-temperature acid fuel cells is that the product water is formed as a liquid. Compared to multi-component diffusion of gases transport of liquid water in the porous structure of the fuel cell is not well understood. By necessity, the porous media is not saturated, and it is well known that the permeability depends strongly on the fill level and that a critical percolation threshold may exist below which transport stops. Furthermore, the surface energy of the cell materials will change with potential and with degradation or ageing of the cell. This surface energy of course dramatically affects the wettability of the electrode structure.

The effect of very low temperatures on fuel cells has been little studied. How do temperatures below 0 °C affect the transport of water, for instance? While this is well studied for soils, where the porous nature is partially analogous to that found in fuel cells, no work has been reported on the effect of water transport in a fuel cell under a temperature gradient, particularly near the freezing point of water.

At the same time basic information on the state of water in ionomers, and electrode structures below 0 °C are not known. What are the forces associated with phase changes, how will these be affected by the water content? Does the rate of freezing play a critical role?

- The ionomer/catalyst interface within the electrode was identified by all members as an area of utmost importance with reference to heat, mass and ion transport. Mass transport through a polymeric skin around the catalyst layer can impede mass transport, especially at targeted low humidity conditions. Similarly, temperatures at the catalyst particle could be higher than that in the bulk, leading to acceleration in degradation mechanisms

- Multi-phase mass transport within the flow-field channels, the gas diffusion layer, the catalyst layer and interfaces therein was also identified as an area where further knowledge and understanding (both theoretical and experimental) were needed. The emphasis here was on “multi-phase” (including freeze related issues)

- The present experimental approach has largely been based on trail and error. A need for a more fundamental understanding of transport phenomena in the above mentioned locations was emphasized

- One primary challenge was the unavailability of adequate experimental techniques to probe important interfaces such as the one between the ionomer and the electrocatalyst in the interface. The need to develop such experimental probes was identified as an area of key importance for future funding

- The current modeling approach was deemed to be less than adequate – borrowing models from fields such as soil science were seen as a stopgap. The importance of developing a multi-scale model for each component was stressed. It was recognized that this would need to be a multiple PI effort, with scales ranging from *ab-initio* modeling (very difficult in terms of computational time) to

macroscopic modeling. Developing such multi-scale, multi-phase transport models was identified as an area of key importance for future funding

- While steady state models would be a good starting point, the importance of modeling transients was stressed

- Durability was identified as an important area for future research–*i.e*. how do structures and transport mechanisms change with operating time?–the need for new and novel diagnostic tools was also felt while discussing this issue. While ex-situ tools would be a good start, the need for in-situ diagnostics was emphasized

- At a more fundamental level, the need to relate component bulk and surface structure to transport properties was stressed. The difficulty in determining accurate structural information was recognized (need new experimental tools). The use of model structures as a start was proposed

- The use of neutron scattering as a method to probe model interfaces was proposed. Other techniques proposed include designing transparent cells to observe water transport, in-situ sensors to monitor temperature and species transport and pressure drop related diagnostics to monitor flooding

- There was broad agreement with the membrane group on issues related to ion and water transport through the membrane, and the importance of the ionomer / electrocatalyst interface.

- An RFP soliciting proposals to develop new experimental diagnostics (ex and in-situ), multi-scale models, establish structure / property relationships and investigate durability effects at component level was thought to be an appropriate means of promoting further thought and development in transport related issues

Modeling and Simulation

Modeling and simulation are critical tools for the rational design of new materials and novel structures. What's more, the ability to predict performance will help develop better system designs and appropriate control strategies, to mitigate degradation mechanisms for instance. It is necessary to develop models at several length scales, ranging from the first-principle models of catalyst surfaces and polymers to macroscopic models of entire cells and systems. Models must also span an immense range of time scales: from heterogeneous, electron-transfer reactions, to reactant diffusion, to dynamics

transients of hybrid systems, to long-term degradation mechanisms. Furthermore, transport of mass and energy, electrical conductance, electrode kinetics, and structural mechanics are relevant in the electrode structure. This coupling suggests that these processes may need to be considered simultaneously. The accurate treatment of relevant phenomena balanced against the computational intensity is the principal challenge for modeling. Advances in methods, particularly for 1st principles calculations, and improvements in computational power will increase the importance of modeling and simulations for years to come.

Today, many of these models are being developed, but perhaps too little effort has been expended in linking these models and approaches together in a way that preserves the underlying physics but is computationally robust. For instance, simulations with electronic degrees of freedom are generally restricted to fragments of polymers or small systems of about 100 atoms. For classical molecular dynamics, the current limits are in the order of thousands to millions of atoms, using the advantages of parallelized codes. What's more, predictive capabilities of present models are often lacking. The tremendous range of time-scales and characteristic lengths requires hierarchical approaches—no single model will suffice. Research to connect the atomistic, mesoscopic, and continuum descriptions is occurring,[13] but further emphasis is needed for electrochemical systems. Multi-scale modeling of porous electrodes based on micro-structural, thermo-mechanical, and electrochemical principles should be able to predict the effect of structure/architecture on thermal, mechanical, and electrochemical behavior of porous electrodes and to provide guidelines for rational design of optimal structures of porous electrodes for high performance, long life and durability. What are the barriers to the

development of predictive models for optimization of porous electrode structures for rapid mass and charge transport?

Figure 3 shows classes of models, ranging from macroscopic models to first principles calculations. For all intents and purposes macroscopic modeling is mature. *Electrochemical Systems*,[14] provides the most authoritative reference on transport phenomena for systems of interest here. These macroscopic models are extraordinarily useful for elucidating important phenomena, training one's intuition, and for providing a sound framework for experiments. Weber and Newman provide a recent review for PEM fuel cells.[15] There are unquestionably challenges in identifying the specific structure of an electrode and determining physical properties for instance, but the underlying physics required for macroscopic modeling is generally known. One area where macroscopic modeling could have greater impact is in understanding degradation mechanisms. Today, many of the models for degradation have little physical basis, and therefore no predictive capability. This is an area where greater emphasis on educating the scientist and engineers is warranted. At the same time, we believe that in terms of fundamental advances there are greater opportunities at the micro or nano-scale.

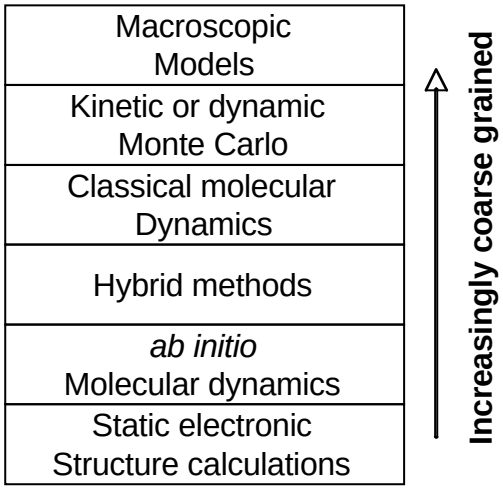


Figure 3.

Stochastic methods, such as Monte Carlo theory, have been used extensively to examine the dynamics of particles, to model transport in polymer systems for instance. Molecular dynamic simulations of Nafion™ and similar polymers have been accomplished with up to a few thousand atoms and over time scales of the order of 1 ns. The objectives are to predict microstructure of the membranes, water uptake, and

estimate the transport properties using independently derived electronic structures. Kreuer *et al.*[16] provide a recent summary of modeling of transport in proton conductors. As noted earlier, the molecular dynamic approaches do not treat electronic behavior, and therefore would not be adequate for catalyst simulation for instance. Hybrid methods, such as ONIOM, have more recently been applied to large systems,[17]but have not been used widely for electrochemical systems. Density functional theory (DFT) and other first-principles approaches are more and more being applied to electrochemical systems.[18,19,20,21,22,23,24] The advances made in the last few years have been impressive, but we are far from simulating even remotely complex electrochemical systems. Here, we break the technical gaps into two parts, method development and specific *ab initio* challenges.

To advance broad method development, one of the most valuable changes would be better coordination and collaboration between experiments and theory. That is, identifying critical experiments that could be modeled and vice versa. Another key need is making a bridge between microscale models and the macroscale. The immense range of characteristic times and length scales require different modeling approaches as shown in figure 3 and sound methods to connect these together will be essential. A further critical area is overcoming the timescale challenge of microscale or *ab initio* models.

Specific challenges for *ab initio* modeling of electrochemical systems include 1) the rigorous treatment of electrode potential in calculations, 2) inclusion of solvent, counter-ion, and effects of pH, and 3) the accurate treatment of chemisorption and charge transfer. The treatment of potential for electrochemical systems is variable and often inconsistent. We desire a potential based on thermodynamics, and the familiar electrostatic potential is of limited use in condensed phases typical of electrochemical systems. In fact there is no known way to separate out electrical and chemical contributions to the free energy. Whereas in a thermodynamic treatment, the use of the electrostatic potential may be avoided, the electrical state must be included to address

transport and kinetic phenomena. The approach that leads to well-defined and measurable quantities is through a reversible reference electrode. This methodology is used extensively in macroscopic models.[14] Zhang *et al*.[25] uses a thermodynamic cycle to determine the electrode potential, but this still requires some experimental data and approximates the solvent as a continuum. A more rigorous treatment of the individual thermodynamic steps is needed.

A third area where modeling is thought to have a large impact is understanding catalyst performance. Foremost is of course elucidating the origin of the overpotential on the oxygen electrode, as discussed earlier. How can we use first principle methods to describe the thermodynamics and kinetics of nanoparticles? How can one treat defects? What can be gained toward development of non-precious metal catalysts, specifically their stability, activity, and site density.

A fourth area is membranes, understanding proton transport in bulk and at catalyst interface. What are the degradation mechanisms? How should be model capillary condensation? Capillary condensation has been determined with reasonable accuracy using classical Monte Carlo or Molecular Dynamics methods. There are many papers on this topic from the 80's and 90's to understand capillary condensation of gases such as methane, ethane, and others inside micropores using MC, MD, and classical density functional theory. These same methods could be used for the fuel-cell systems.

Finally, approaches to simulating more complex electrochemical interfaces must be developed. We need to integrate molecular descriptions of catalysts, electrolytes, and supports, treat the growth of oxides and multiple electron transfer reactions.

How should macroscopic and first-principles models, namely *ab initio* calculation of catalyst surfaces, be united? How might molecular modeling of polymers at low temperatures contribute to our understanding of macroscopic properties below 0 ºC? Is more effort needed to link the polymer and catalyst structures, for instance, with the model results? In general, even within a discipline, researchers focus on one facet of the

modeling and have little interaction with those working at different length or time scales. Specific challenges are outlined below.

- Development of strategies for hierarchical models. Integration of molecular descriptions of catalysts, electrolytes, and supports.
- Treatment of multiple electron-transfer reactions.
- Physics based models for degradation phenomena. Ability to predict performance beyond regions of test data.
- Approaches to characterize the complex structures of interfaces for macroscopic models.
- Better coordination of first principle modelers and experimentalists
- Rigorous methodology to treat electrochemical potential for *ab initio* calculations.
- Accurate treatment of chemisorption and charge transfer
- Inclusion of solvent, counter-ion, and pH effects.
- Prediction of CV diagram for platinum in acid electrolyte from first principles

Systems integration

Here we identify the system as a collection of interrelated components that must work together to perform some function. Thus examples of systems would include not only a thermal-management system or the entire power plant, but cell stack assemblies, membrane electrode assemblies (MEAs), and even electrodes and catalysts. The manner and degree of system integration play an instrumental role in the development of low-temperature fuel cells. One of the key roles of systems analysis is optimizing between many objectives; that is, balancing the many requirements identified in Table 1. These

interactions are depicted in the cartoon below—it is at the system level that the many objectives must be traded and optimized. The key areas for improvement are

- High power density
- Efficiency
- Durability
- Hot-day operation
- Cost reduction and system simplification

Figure 4 shows the efficiency of a PEM power plant. Most commonly fuel-cell system efficiency is defined as the net electrical output divided by the lower heating value of the fuel. Because these data represent a power plant and not just the fuel cell stack, the efficiency goes to zero at low power. Regardless of net electrical output some power is needed to support ancillary equipment such as cooling pumps, air blowers, controllers, *etc*. These parasitic loads dominate at low power. In contrast, at high power these loads may be small compared to the fuel-cell output; and for all intents and purposes, the polarization losses in the cell stack determine system efficiency.

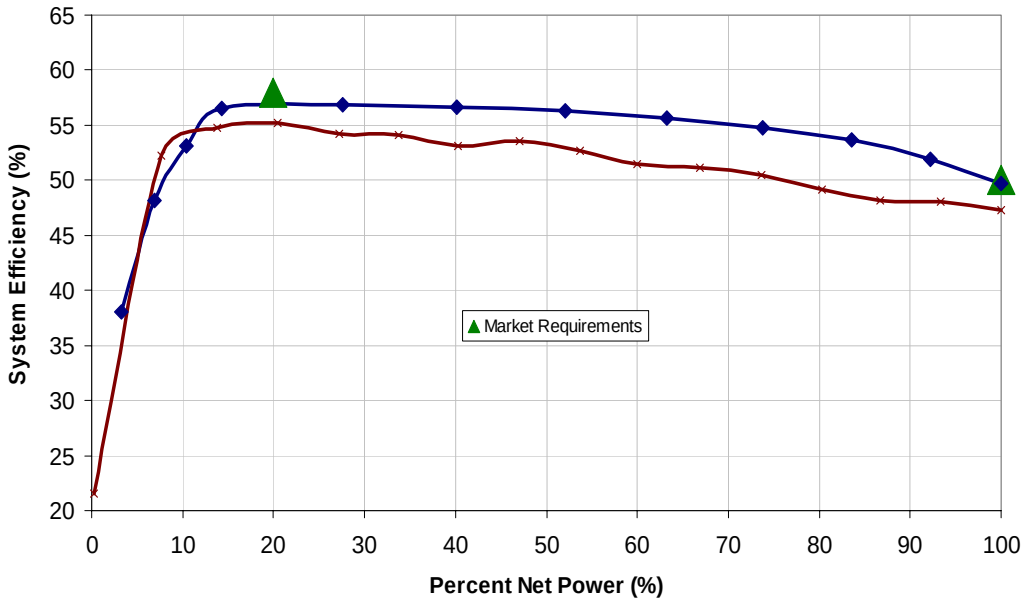


Figure 4.

Considering that a transportation system is going to have the most frequent demand at low power levels (valid for urban as well as highway driving schedules) this system has been designed to maximize efficiency at relatively low loads. This schematic of a system and the thinking about component integration is the representation of a system with which we are most familiar. It should be clear that system-level efficiency must be emphasized as a key metric to compete against hybrid vehicles and PZEV's

We should, however, think more broadly about systems and about integrating components together. The MEA, although often thought of as a purchased component, is itself a complex system. It is typically made up of a membrane, two electrodes, and gas diffusion media. It has to perform many functions: conduct protons, collect current, provide access of reactants to catalyst sites, remove product water, seal between reactants and the environment, *etc*. In these capacities the MEA must work with other sub-systems, such as bipolar plates, air delivery, and thermal management, to provide these functions and meet the higher-level requirements. Components within the MEA cannot be designed independently, nor can the MEA be designed separate from the larger system. Just as with the overall system, trades must be made between durability and performance and cost.

In a typical design process, requirements flow from product, the vehicle for example, to components, such as the fuel-cell power plant, and then to subcomponents. Component requirements are determined by decomposing higher-level system requirements. To do this effectively, one must understand clearly the coupling of subsystems and have sufficiently detailed models that allow one to trade between

competing requirements. If a certain system efficiency is specified, based on the known power requirements for air blowers and cooling fan, one might impose a efficiency (voltage) on the cell stack. Often this decomposition is viewed as a unidirectional cascade from product requirements to detailed specifications. In reality, these interactions are often complex. Frequently, early in the design process sufficient data are not available to determine accurately the effect of these couplings. For instance, heat rejection from the automobile will be facilitated by operation at higher temperatures, a temperature of 120 ºC is considered adequate for existing cooling systems. Higher temperatures will also bring improved reaction kinetics, but may severely accelerate degradation of membranes and catalysts. Understanding this coupling is important not only the design process, but it can also affect the research directions needed. For the last few years many efforts have gone into identifying high-temperature membranes, and it only recently that concerns about degradation have been raised and research directed toward better understanding of the fundamentals. How can one more formally address these interactions?

Sosa *et al.* describe a methodology that tries to capture the numerous and sometimes subtle interactions that occur during the design process.[26] This design system matrix, DSM, helps clarify the interactions, interdependencies and interfaces between elements in a system. This type of approach can be particularly useful for an immature technology that is being developed simultaneously across many fronts. The low level of technology readiness will often mean that data found later in the design process, then forcing one to visit earlier assumptions and adjust the conclusions of system trades. Within mature organizations, this is implicitly if not explicitly understood. For specialized researchers, more often than not, these interrelationships are not well

internalized. A better understanding of the coupling is vital, but equally important is to organize research and development such that the appropriate interactions between scientists and engineers occur. Researchers on high temperature membranes need to understand how their results may affect catalyst stability for instance.

In a system evaluation and design how might one account for: uncertainty, life-cycle design, feasibility, and technology infusion? Multiobjective optimization and probabilistic techniques are appropriate for non-deterministic systems. At times designing for many objectives, like those shown in table 1, may be straightforward; but frequently it can be difficult to balance these in a dynamic development environment. Simultaneously trading between efficiency, power density, transient response, durability, cost calls for a more sophisticated modeling methodologies. The Technology Identification, Evaluation and Selection (TIES) methodology developed for aeronautical systems is one example that provides for a formal approach for system evaluation and design that accounts for components such as uncertainty, life-cycle design, feasibility, and technology infusion.[27] TIES provides a methodical approach where technically feasible alternatives can be identified with accuracy and speed to reduce design cycle time, and subsequently, life cycle costs. This methodology is most effective in the early design phases. In addition to its use as a design tool, this methodology permits one to evaluate the effect of new technologies in development—thus identifying avenues of research that will have the greatest impact at the lowest risk.

It is not practical to integrate many detailed physics-based models for individual components or subcomponents into one large model for system design. What rules should we use to develop approximate representations of complex phenomena that capture the

core attributes of more complex models but are able to be used in parametric modeling of entire systems? Basic design rules for fuel cell systems and manufacturing are not readily available, and parametric modeling and visualization techniques that might help to guide decision makers and policy setters are not well developed.

Furthermore, the importance of transient responses to transportation systems cannot be overstated. Transportation systems are seldom at steady state. How the sub-systems integrate together will affect performance and durability. Understanding and designing systems around transient response capability is critical. This must be taken into account when making the trades between requirements. It is not simply that the system must be able to respond to power demands. How the system meets these demands has a large impact on durability and cost. Below are some examples of where a systems approach is expected to have the greatest impact.

Water management.

Water management of the cell stack is perhaps the most critical powerplant-level aspect of fuel cell powerplant performance. As has often been lamented, with the current class of materials, it is desirable to operate on a "knife edge" of relative humidity.

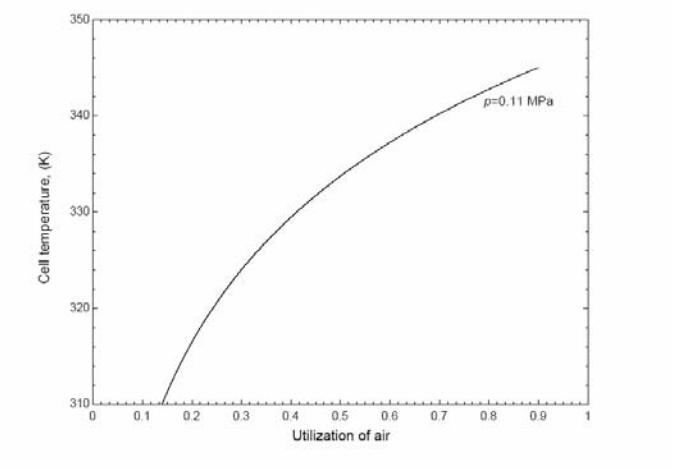


Figure 5.

Figure 5 shows the relationship between cell temperature and air utilization assuming that all the water is removed as a vapor. For a given temperature only a single point will be in water balance, not too dry, lest the membrane dry out and lower ionic conductivity; not too wet, lest electrode flooding restrict access of reactants to the catalyst layer.Water management is intimately coupled with thermal management of the system, as relative humidity will be dictated by local water content and by local temperatures.

It is critical to design water- and thermal-management schemes that are robust to transients, and that can meet the performance and efficiency targets at both low power and high power. Generally speaking, at lower currents, the cell stack operates at a considerably cooler temperature than at rated power, because considerably less waste heat is generated at low power. For a powerplant that operates at constant stoichiometric ratio, then, a cell operating at low power will have a considerably higher relative humidity (or a greater degree of liquid saturation) than will a cell at rated power. The liquid water that is present at cooler conditions can be removed by two-phase flow in the gas channels by maintaining a high velocity in the channels, but high velocities do tend to lead to higher pressure drops, which will lower overall system efficiency, and will tend to be exacerbated at higher flowrates.

In order to be able to respond rapidly, there needs to be a close coupling between the stack and the external water management system. One needs to identify schemes by which local water content and thermal management can respond rapidly to changes in load and external conditions. There is a continued need for simplified, transient-capable humidification and water-removal schemes that are likely only achievable by

simultaneous stack and system design. Water distribution systems capable of delivering water to the regions of the cell where it is needed, as it is needed, rather than simply delivering water vapor at a fixed dewpoint to the cathode inlet, would likely result in considerable improvements in performance and membrane durability. As alluded to in the section on proton conduction, many of these issues would be alleviated by identification of an anhydrous proton conductor that is also robust to exposure to liquid water, but these materials have proved elusive to date.

Durability.

The issues of water management discussed in the previous section certainly have implications on membrane durability, based upon data shown that fluoride emission rates in perfluorinated membranes are a strong function of relative humidity. Differences in relative humidity are also likely to change pH in the electrolyte, which can have strong implications on proposed decay mechanisms, such as platinum dissolution and carbon corrosion.

Another critical aspect of system design with strong implications on the durability of the cell stack is uniformity of fuel distribution. Potential cycling has been shown to have a strong effect on platinum stability, and localized fuel starvation has been shown to shift electrode potentials to sufficiently high values to induce corrosion of the carbon supports. Uniformity of fuel distribution across all cells and regions of the cells in both steady-state and transient conditions is critical to fuel cell performance robustness. The

distribution of fuel to all channels over the entire driving cycle is critical for ensuring that the stack is not permanently damaged by localized starvation events.

Component elimination.

Next-generation systems need to insert more functionality in the stack, or to eliminate the need for that functionality. For instance, many powerplants employ a hydrogen recycle to increase gas velocity and maintain margin on hydrogen inventory to allow fast transient capability, but the hydrogen recycle blower is a potential point of failure, and is a liability when starting from the frozen state, because the fuel exit stream tends to be saturated with liquid water, and can condense and freeze during startup, Hydrogen content in the fuel stream tends to be detected indirectly, because of the shortcomings of present-day hydrogen sensors. Rapid and robust hydrogen sensors are necessary if direct detection schemes are to be employed.

Systems integration is intrinsically an interdisciplinary activity. Here is the best opportunity to integrate scientific, engineering, and economic information. Too often in practice, however, the approach to system design is not sufficiently interdisciplinary, and the tools are often lacking to trade effectively within the appropriate constraints between numerous requirements for emerging technologies. What are the key barriers to better system integration? Education plays a pivotal role in how one thinks about technical challenges and how problems are framed. Are additional initiatives needed in education to foster more and interdisciplinary research in systems engineering? In the most general sense, technical gaps can be addressed either through material changes or system design.

It is sometimes unclear how best to weight the relative likelihood of success between a strategy that is constrained by material properties and that demands system-level changes to accommodate those properties, and one that is constrained by preferred system configuration, that imposes demands to material properties by material discovery and modification.

Summary and General Recommendations

We need more open and better ties to industrial research. Today the bulk of real-world experience with fuel-cell systems resides within commercial companies and only a small amount of the work is published. Greater support from governmental agencies for industrial collaboration and communication is suggested.

We need to renew interest at educational institutions in electrochemistry and electrochemical engineering. Storage and conversion of energy are vital to meeting societies energy needs today and will be even more critical in the future. More scientists and engineers trained in electrochemistry, and more training that cuts across traditional academic disciplines is sought.

Fundamental understanding of transport in polymers needs greater development. The oxygen reduction reaction unquestionably deserves the most attention for further electrocatalysis work. In both instances, more emphasis on modeling and on more emphasis in linking different modeling approaches together is needed. We continue to be surprised by the amount of overlap between the topics and the need for greater interdisciplinary collaboration.

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Workshop Attendees

Muhammad Arif	National Institute of Standards & Technology
Jorge A Ayala	Columbian Chemicals Company
Perla Balbuena	Texas A&M University
Wu Bi	Georgia Institute of Technology
Oleg Borodin	University of Utah
Scott Calabrese Barton	Columbia University
Song-yul (Ben) Choe	Auburn University
Deryn Chu	U.S. Army Research Laboratory
Stephen Creager	Clemson University
Kathi Epping	U.S. Dept of Energy
Gonzalo Escobedo	DuPont Fuel Cells
Tom Fuller	Georgia Institute of Technology
Nancy L Garland	U.S. Dept of Energy
Girish Gopalakrishnan	University of Notre Dame
Pat Hagans	United Technologies Research Center
Donna L Ho	U.S. Dept of Energy
Gyeong Hwang	University of Texas
Maria Inman	Faraday Technology, Inc.
David Jacobson	National Institute of Standards & Technology
William Johnson	W.L. Gore & Associates
Paul Kenis	University of Illinois
John Kerr	Lawrence Berkeley National Laboratory
Pete Ludovice	Georgia Institute of Technology
Nicola Marzari	Massachusetts Institute of Technology
Paul Maupin	U.S. Dept of Energy
J. Will Medlin	University of Colorado
Matthew Mench	Penn State University
Sanjeev Mukerjee	Northeastern University
Trung V Nguyen	University of Kansas
Vijay Ramani	Illinois Institute of Technology
Gabriel A Rincon-Mora	Georgia Institute of Technology
Yang Shao-Horn	Massachusetts Institute of Technology
Rachel A Segalman	UC Berkeley
Chunsheng Wang	Tennessee Technological University
Frederick T Wagner	General Motors
Junxiao (Charlie) Wu	Mississippi State University
Dean Wheeler	Brigham Young University
Thomas A Zawodzinski	Case Western Reserve University