
V.N.15 A Unified Computational, Theoretical and Experimental Investigation of Proton Transport through the Electrode/Electrolyte Interface of Proton Exchange Membrane Fuel Cell Systems

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Objectives

The first objective of this research is to develop a fundamental understanding of the molecular-level mechanism for proton transport across the electrode/electrolyte interface of hydrogen-powered Proton Exchange Membrane (PEM) fuel cells. This is to be achieved using a combination of molecular simulation and experimental tools. The second objective of this research is to apply this molecular-level understanding toward the development of a predictive model for proton transport across the electrode/electrolyte interface, which can be integrated into existing macroscopic models of fuel cell power generation. The third objective of this research is to communicate this molecular-level understanding with experts in Membrane Electrode Assembly (MEA) manufacturing to provide feedback for the future direction of the fundamental studies.

Technical Barriers

Current macroscopic models of fuel cell power generation treat proton transport across the electrode/electrolyte interface with a mass transfer coefficient; however, this approach is generally lacking in predictive capabilities. The technical barrier to generating a fuel cell model with predictive capabilities of interfacial transport has been our ignorance regarding the nanoscale structure of the electrode/electrolyte interface. The use of molecular simulation, coupled with experiment, allows us to examine the electrode/electrolyte interface in detail and observe

the fundamental physical mechanisms that allow or prevent protons adsorbed to platinum-alloy catalyst nanoparticles on the surface of the electrode from being transported into the hydrated polymer electrolyte membrane.

Abstract

We report on a combined computational and experimental project investigating the transport of protons across the electrode/electrolyte interface of hydrogen PEM fuel cells. Our molecular simulations of the bulk hydrated membrane show a morphology of the aqueous nanophase within the system that loses connectivity at low humidity, leading to a drop in vehicular diffusion of protons. Structural analysis of the degree of hydration of protons indicates a drop in structural diffusion as well at low humidity. At the membrane/vapor interface, we do not observe significant additional mass transfer resistance. At the membrane/vapor/electrode interface, we do not observe any wetting. At the membrane/vapor/catalyst interface, we observe significant wetting. Experimentally, we observe a positive relationship between feed-gas humidity and power production. We can attribute this behavior to the presence of water in the membrane, facilitating proton transport. This response agrees with the decreased vehicular and structural proton diffusion found in molecular modeling at low membrane hydration levels. We have also observed that high pressure at the cathode inhibits power production; this is believed to be a result of water condensation affecting catalyst performance. Low temperature slightly inhibits power production. Taken as a whole, this data suggests that the placement of catalyst particles and the degree of humidity is crucial to optimizing the proton transport across the electrode/electrolyte interface. We draw connections between our molecular-level understanding and implications for fuel cell design.

Progress Report

The Model

The composite model of the electrode/electrolyte interface is shown in Figure 1. We perform molecular dynamics (MD) simulations on four regions of a model fuel cell pore/membrane: (i) bulk hydrated membrane, (ii) the hydrated membrane/vapor interface, (iii) the hydrated membrane/vapor/electrode interface, and

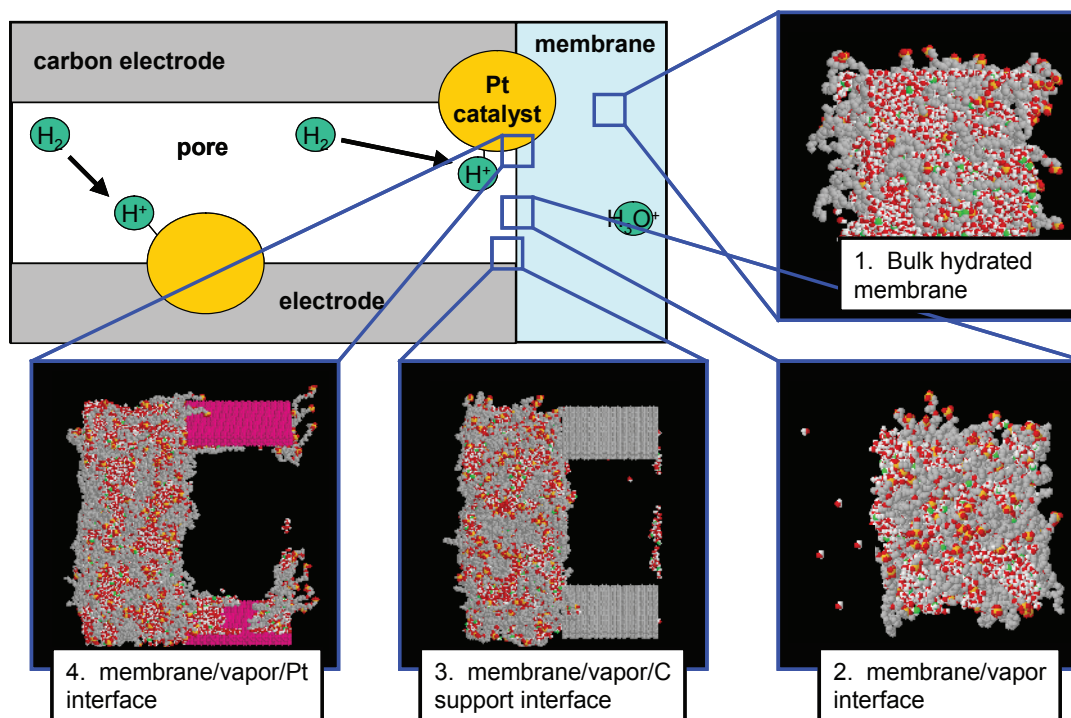


FIGURE 1. Connection between the molecular simulation systems and the macroscopic electrode/electrolyte interface.

(iv) the membrane/vapor/catalyst interface. In our simulations the polyelectrolyte is Nafion[®], the electrode is graphite and the catalyst is platinum.

Bulk Hydrated Membrane Studies

We have simulated the bulk hydrated membrane using MD simulations at 5%, 10%, 15% and 20% water by weight. This is an interesting range of water contents because Nafion[®] loses most of its proton conductivity as one moves from 20% to 5% water. This work is now published. There are numerous detailed observations one can make from studying the structure and dynamics of the hydrated Nafion[®] membrane as a function of water content, but we limit ourselves to the three most important conclusions in this report. First, the nanoscale morphology of the aqueous nanonetwork shows that the water clusters are not spherical, but rather form a tortuous network of thin strings of water molecules. This morphology matches experimental scattering data, with characteristic dimensions of the water network on the order of 2.5 nm. Second, a water cluster analysis shows breakdown of the continuous aqueous nanophase as one decreases the water content from 10% to 5%. Thus at low humidity levels, there is a hindrance to vehicular diffusion of the protons. Third, at low water content, a majority of hydronium

ions are not sufficiently hydrated to form the Eigen ions that are necessary to contribute to proton conduction. Therefore, low humidity also hinders the structural diffusion of protons. In short, both mechanisms of diffusion of protons are hindered at low humidity for two different reasons.

Hydrated Membrane/Vapor Interface Studies

We have completed simulation on the hydrated membrane/vapor interface. We have generated a complete suite of structural, thermodynamic and transport properties. At the interface, we find an increase in both the parallel and perpendicular components of the vehicular diffusivity of the hydronium ion, which can be attributed to the decrease in membrane density near the interface. At the interface, we observe a small decrease in the number of waters hydrating hydronium ions, which is expected to slightly lower the structural diffusivity. However, taken together, we do not observe a strong intrinsic resistance to mass transfer in the interface beyond that of the bulk hydrated membrane. If, as has been suggested, the electrode/electrolyte interface is indeed a bottleneck in the total proton conductivity of the fuel cell, we must probe deeper into the underlying physical mechanisms of this process.

Hydrated Membrane/Vapor/Electrode Interface

We are currently performing simulations of the hydrated membrane/vapor/electrode interface. We see essentially no wetting of the graphite electrode by the water stored in the hydrated membrane. The implication of this finding is that catalyst particles must be located in immediate proximity to the hydrated membrane in order for those particles to contribute to the total proton conductivity of the fuel cell. A sizeable gap between catalyst and membrane can result in catalyst particles that are “too dry”. A quantitative determination of the critical size of the gap between catalyst and membrane that can support proton conduction is underway.

Hydrated Membrane/Vapor/Catalyst Interface

We are currently performing simulations of the hydrated membrane/vapor/catalyst interface. We see very significant wetting of the platinum catalyst by the water stored in the hydrated membrane. At high humidity levels, our preliminary results suggest that a platinum nanoparticle can be completely covered in an aqueous film, resulting in the “too wet” condition which significantly slows diffusion of H_2 to the surface and the adsorption rate of H_2 onto the catalyst. A quantitative determination of the degree of wetting of the catalyst as a function of hydration level is underway.

Experimental Work

We have completed the assembly of a fully functional fuel cell. Experiments thus far have explored the effect of many operating parameters on the fuel cell's power production. We have observed that high feed-gas humidity, atmospheric cathode pressure, and moderately high temperature increase the cell's performance. Increasing circuit resistance inhibits power production (Figure 2). Upon completing these experiments, we can

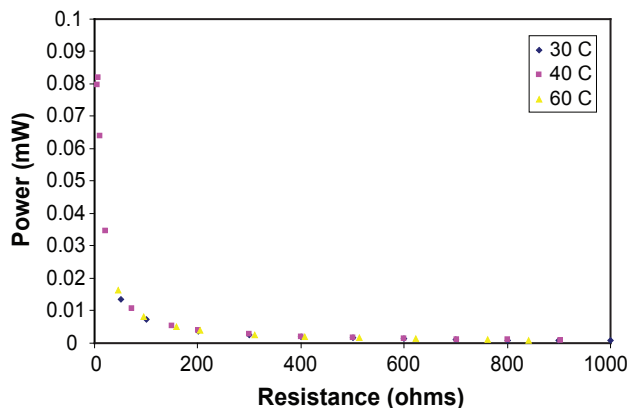


FIGURE 2. Power developed by the fuel cell as a function of circuit resistance; in addition to decreased power at high resistance, we observed decreased H_2 flow through the system.

operate the fuel cell sufficiently well to obtain useful data via other analytical methods.

We have also conducted preliminary experiments using electrochemical impedance spectroscopy (EIS). Preliminary EIS experiments (Figure 3) indicated that our catalyst acts more as a porous surface rather than a planar surface. We are currently preparing to perform equivalent circuit modeling using EIS on the fuel cell to assign resistance values to various resistance mechanisms taking place in the fuel cell. These measurements will allow a qualitative comparison with molecular modeling. A quantitative comparison may also be possible by relating the membrane's ionic resistance with proton diffusivity.

Our group at Georgia Tech presented a poster at the 2006 Imaging and Neutrons meeting at the Spallation Neutron Source at ORNL. Neutron imaging is currently being pursued as a method to further investigate the presence and transport of water in the fuel cell during its operation. This is important since the presence of water plays a key role in understanding the cell's operation.

Future Directions

For the computational work, we are currently pursuing four directions. First, a quantitative determination of the critical size of the gap between catalyst and membrane that can support proton conduction is underway. Second, a quantitative determination of the degree of wetting of the catalyst as a function of hydration level is underway. Third, a reactive algorithm to incorporate structural diffusion in these models is under development. Fourth, we are communicating the implications of these findings with experimentalists in order to gain valuable feedback on guiding the fundamental work.

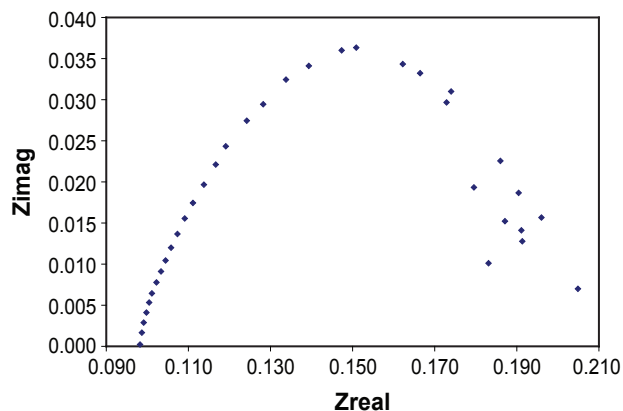


FIGURE 3. Nyquist plot showing the imaginary impedance as a function of real impedance in the fuel cell. This spectrum was obtained by performing potentiostatic EIS. The scatter at higher Z_{real} (real impedance) is a result of the EIS settings; this will be minimized with further refinement of the EIS procedure.

For the experimental work, we are currently focusing on the use of EIS to better understand the various resistance mechanisms in different regions of the fuel cell. We intend to relate resistance to diffusivity at the various parts of the cell. We are also pursuing the use of neutron imaging to visually detect the presence of water in various regions of the fuel cell. It is our goal to experimentally estimate the amount of water at various regions in the fuel cell for comparison with the measured resistances from EIS, as well as with molecular-modeling results.

Publications (Including Patents) Acknowledging the Grant or Contract

1. Cui, S.T., Liu, J., Esai Selvan, M., Keffer, D.J., Edwards, B.J., Steele, W.V., "A Molecular Dynamics Study of a Nafion Polyelectrolyte Membrane and the Aqueous Phase Structure for Proton Transport", *J. Phys. Chem. B*, accepted, 01/2007.
2. Gabitto, J., and C. Tsouris, "Hydrogen Transport in Composite Inorganic Membranes," *J. Membrane Sci.*, submitted (2007).
3. Aaron, D., Yiaccoumi, S., Tsouris, C., Cui, S.T., Liu, J., Esai Selvan, M., Keffer, D.J., Edwards, B.J., Steele, W.V., "Interfacial Phenomena in Proton-Exchange Membrane Fuel Cells", Proceedings of the ACS Colloid and Surface Science Symposium, Newark, DE, June, 2007.
4. Esai Selvan, M., Liu, J., Keffer, D.J., Edwards, B.J., Cui, S.T., Steele, W.V., "A Molecular-Level Reaction Algorithm for Proton Transport Consistent with Quantum Mechanical Transition State Theory and Macroscopic Conductivity", Proceedings of the ECS Annual Meeting, Chicago, IL, May, 2007.
5. Cui, S.T., Liu, J., Esai Selvan, M., Keffer, D.J., Edwards, B.J., Steele, W.V., "A Molecular Dynamics Study of Nafion Polyelectrolyte Membrane and the Aqueous Phase Structure for Proton Transport", Proceedings of the AIChE Annual Meeting, San Francisco, CA, November, 2006.
6. Keffer, D. J., Cui, S.T., Edwards, B.J., Steele, W.V., "The Molecular Structure of Hydrated Nafion Membrane Interfaces: Developing a Model for Proton Transport", Proceedings of the Electrochemical Society Annual Meeting, Denver, CO, May, 2006.