

# V.N.7 Polymer Functionalized Zeolite Proton Exchange Membrane (PFZ-PEM) for Medium Temperature (> 120°C) Fuel Cells from Theory, Simulation, and Experiment

William A. Goddard III (Primary Contact),  
Mark E. Davis (co-PI), Seung Soon Jang  
Mail Code (139-74) (400 South Wilson Ave.)  
California Institute of Technology  
1200 East California Blvd.  
Pasadena, California 91125 USA  
Phone: (626) 395-2731 (wag), 395-2730 (Sec),  
Fax: (626) 585-0918  
E-mail: wag@wag.caltech.edu

DOE Program Officer: William S. Millman  
Phone: (301) 903-5805  
E-mail: William.Millman@science.doe.gov

## Subcontractor:

Yushan Yan (co-PI)  
A235 Bourns Hall  
University of California  
Riverside, CA 92521  
Phone: (951) 827-2068; Fax: (951) 827-5696  
E-mail: yushan@engr.ucr.edu

## Objectives

The overall objective of the proposed project is to simulate, design, and fabricate a novel proton exchange membrane that can operate over the range from -30°C to 200°C. The new membrane is to have higher proton conductivity and lower permeability to H<sub>2</sub> and O<sub>2</sub> than Nafion® and to be lower cost.

In order to determine the basic understanding of the chemical and physical properties of the membrane such as micro/nano structures, proton/water diffusion, gas permeability, mechanics properties, we combine multi-scale simulations to select the most reasonable candidates and to carry out experiments on the more promising cases while also validating the theory on specific cases. This strategy dramatically reduces the number of experiments required to find the optimum materials.

## Technical Barriers

The current best materials for PEM FC are perfluorosulfonic polymers such as Nafion®. Due to its Teflon-like backbone, Nafion® has outstanding chemical and thermal stability and is an excellent proton conductor but only when fully hydrated. Unfortunately, pure Nafion® PEM PEMFC is limited to operate at

around 85°C because it dehydrates at higher temperature with a decrease in proton conductivity by orders of magnitude. Moreover, below 0°C pure Nafion® PEM loses its proton conductivity as well because the water as proton carrier inside freezes.

Our new materials should solve these problems while also decreasing the costs.

## Abstract, Progress Report and Future Directions

Based on our previous studies, we hypothesized that maintaining the water channels in liquid form inside membrane is the key to obtaining high proton conductivity at temperature above 100°C and at temperatures below 0°C. If the water is kept in liquid form, it can serve as proton carrier to transfer protons well above its boiling temperature 100°C. Davis had made a breakthrough in synthesizing the organic functionalized zeolites in which an aryl sulfate acid site is retained inside Beta zeolite, so we started with this class of systems, manipulating the hydrophilicity by modifying the tetrahedral framework atoms.

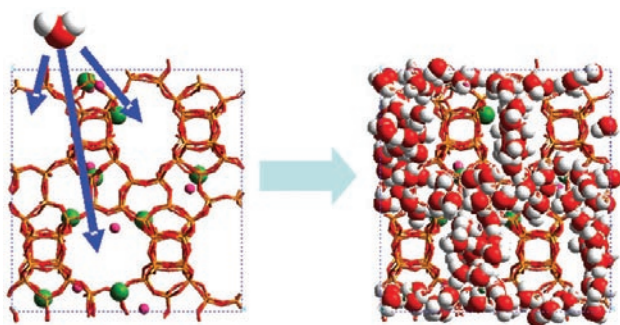
To predict the properties of these systems, we carried out grand canonical Monte Carlo calculations using Force Fields (FF) optimized from Quantum Mechanics (QM) to predict the water uptake of Al-doped zeolite BEA structures with various amount of doped Al,

$$P_{add} = \min \left[ \frac{1}{(N+1)} \frac{PV}{kT} \exp \left( \frac{-\Delta U}{kT} \right); 1 \right]$$
$$P_{sub} = \min \left[ \frac{NkT}{PV} \exp \left( \frac{-\Delta U}{kT} \right); 1 \right]$$

where  $P_{add}$  and  $P_{sub}$  denotes the probability of adding and subtracting one water molecule into the system of interest, respectively.

We validated our simulation protocol and the accuracy of the force field by comparing our simulated water uptake with the experimental data from the Davis Lab as shown in Figure 2. Indeed the simulations capture the temperature dependency of water uptake as a function of the amount of Al:

- first, as the amount of Al increases, the water uptake increases at the same temperature;
- second, the water uptake decreases with increasing temperature.



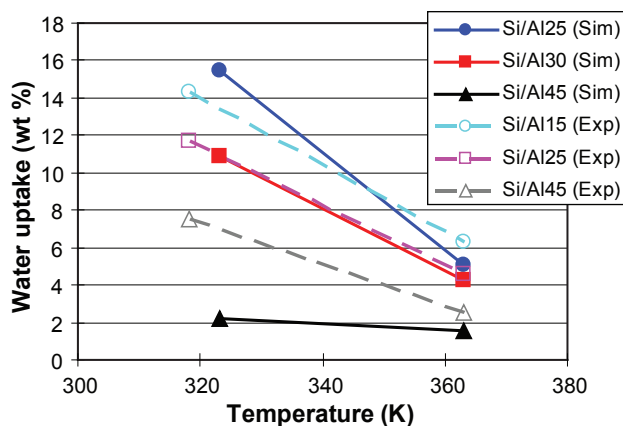
**FIGURE 1.** Simulation of water uptake of zeolite BEA (Si/Al 30) using grand canonical Monte Carlo method.

For zeolites with high amounts of Al, we obtain good agreement between theory and experiment. For the case of Si/Al 45, our simulations are in qualitative accordance. The simulations also describe very well the water sorption by zeolite over a broad range of temperature.

Temperature dependent, proton conductivity measurements have been obtained on molecular sieves that have the zeolite beta topology. Our results demonstrate clearly that acid sites generated via the framework positioning of aluminum do participate in proton conduction and increasing amounts enhance the conductivity. Additionally, initial results using other element substitutions such as zinc, show that conductivity does correlate with acid strength; the stronger the acid the better the conductivity. These studies are confirming our hypotheses that number density and strength of acid centers in the molecule sieve do influence conductivity.

In attempts to synthesize materials with lower dependence on water for proton conductivity, we prepared organic-inorganic hybrid solids which we showed to contain only one water molecule per acid site. The proton conductivity of one of these materials was evaluated and shows that the conductivity can proceed at a fairly high level in the absence of bulk water (2). Current studies are aimed at fundamental understanding of this conduction mechanism.

UCR has been participating and supporting the simulation and modeling efforts at Caltech to identify the best zeolite structure and the best organic functional



**FIGURE 2.** Comparison of simulated water uptake at Various Si:Al ratios to our experimental results.

groups. In addition, we are exploring new zeolites such as titanosilicates, which, in their unfunctionalized form, may have superior proton conductivity than aluminosilicates. We have also explored the preparation of composite membranes based on Nafion® and our current acid functionalized beta zeolites. This membrane has shown excellent methanol fuel cell performance (see publication). The demonstration for high temperature use is in progress. In the future, we will continue to work with Caltech in determining the ideal zeolite structure and the ideal organic functional groups. Once we have them decided, we will perform the synthesis and characterizations of the materials first in powder form and then in the form of composite membranes.

### Publications (Including Patents) Acknowledging the Grant or Contract

1. Z. Chen, B. A. Holmberg, W. Li, X. Wang, W. Deng, R. Munoz, Y. Yan **2006**. Nafion/Zeolite Nanocomposite Membrane by In-situ Crystallization for Direct Methanol Fuel Cell, *Chem. Mater.*, 18:5669-5675.
2. C. A. Alabi and M. E. Davis, "Proton Conducting Solid Electrolyte via Ozonolysis of Cationic Ammonium Organoalkoxysilane Surfactant Templated MCM-41," *Chem. Mater.*, 18, 5634 (2006).