Modeling of proton transfer in alternative non-teflonated PEMFC membranes for elevated temperature operation.

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Proton exchange membranes operating at elevated temperatures (<100-130°C) are expected to diminish problems of system integration and water management in the current state of the art PEMFCs stacks. Since the current state of the art low temperature proton conductor (Nafion, from Dupont) requires greater than 80 percent relative humidity for maintaining proton conductivity, alternative approaches for elevated temperature are required. One approach under active consideration is the use of Nafion membrane composites containing inorganic oxide gels. This approach relies on the ability of the composite on maintaining higher levels of hydration within the membrane structure at lower relative humidities. On the other end of the spectrum, alternative membrane chemistries are being investigated in order to enable sufficient proton conductivity at lower relative humidity such as at 50% level. Ongoing studies at our laboratory have shown promising results with conductivity at low relative humidity.

Proton ion transfer in Nafion-like membranes (perfluorosulfonic acid ionomers membranes) is generally controlled by both the microstructure of the polymer and the charge & water distribution in the hydrated polymer. In this study a series of candidate membranes (1) Sulfonated Poly (Arylene Ether Sulfone) BPSH-40, (2) Sulfonated Poly (Phenyl Sulfone) Radel R and (3) Polysulfidesulfone are modeled for their proton transport characteristics. A proper model for proton transport will help in understanding: (a) effect of the teflonated *vs.* non-teflonated backbone of the polymeric structure, (b) difference in the hydrogen bonding and finally (c) how the sulfonated groups, located on the polymer chain, affects the performance of the PEMFC.

Stokes law [1] molecular-based non-equilibrium statistical mechanical models have proved the important predictive behavior of such membranes is strictly dependent upon the porosity and the hydration level. Moreover, one-dimensional steady state modeling of a polymer electrolyte fuel cell has shown the effect of water content on the overall performance of PEMFC. Particularly a net flux ratio of 0.2 (H_2O:H^+) was both predicted and experimentally observed [2] with an increase in the membrane resistance as a function of charge density.

The main focus of this work is to understand proton transport as a function of site selected sulfonation. Ab-initio Hartree-Fock theory with second order electron correlation correction to the energy and density functional theory is used to understand and optimize the sulfonic acid fragments of interest. In-plane rotational potential energy surfaces are also estimated in order to calculate and evaluate the chain flexibility as well as the proton accessibility.

References:

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