Chemical Structure and Morphological Considerations for Designing Direct Methanol Fuel Cell Proton Exchange Membranes

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A large fraction of performance loss in direct methanol fuel cells is related to methanol “crossover” as determined by the proton exchange membrane’s methanol permeability. Much new research has focused on creating new proton exchange membranes with comparable conductivity and lower methanol permeability than Nafion, the current state of the art. It is proposed in this work that the chemical structure may only provide part of the equation when designing polymers with inherently low methanol permeability. The methanol permeability is directly related to the confinement of water within the polymer matrix. Just as important as the polymer chain’s chemical structure is the final hydrophilic/hydrophobic matrix or microphase separated morphology. If morphologies can be created that promote stronger association between the polymer chain and the water molecules, the inherent methanol permeability of the resulting membrane should be decreased.

For instance, Nafion, which has a high methanol permeability, has a large amount of relatively loosely bound water as indicated by its high electro-osmotic drag coefficient, long ^{1}H NMR T1 and T2 relaxation time, and large limiting current convective velocities. Conversely, sulfonated arylene ether sulfone copolymers have low methanol permeabilities and show decreased electro-osmotic drag coefficients, relaxation times, and convective velocities. Nafion and sulfonated arylene ether sulfone copolymers have similar protonic conductivity and water uptake, but their other transport properties are markedly different. This difference is accounted for by considering the stiffness of the polymer backbone and the arrangement of polymer and ionic groups within the hydrophilic domains where transport primarily occurs.

It is noted that one of the routes to manipulating the membrane morphology is by changing the polymer chemical structure. However, other processing parameters or could be developed to improve existing membranes materials. Similar morphologies as measured by the relaxation times of water should yield similar transport properties even if the chemical composition of the matrix may be different.