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Design strategies to overcome performance limitations in hydrocarbon-based Polymer Electrolyte Membranes

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Hydrocarbon PEM materials are being widely studied as replacements for commercial Nafion-type perfluorinated polymeric materials in polyelectrolyte membrane fuel cells (PEMFC) and methanol crossover in the direct methanol fuel cell (DMFC) application. There are several reasons for this, among which are: (a) cost reduction (b) FC operation at higher temperatures to improve kinetics and reduce the sensitivity of catalyst poisoning by fuel impurities, and (c) reduction in fuel crossover from anode to cathode.

Commercial Nafion-type PEMs owe their chemical stability, high proton conductivity and good dimensional stability to several important structural design features such as: (a) 'super-acidic' fluoro-sulfonic acid groups that require only a low concentration or ion exchange capacity (IEC) to achieve good conductivity (b) flexible ionic side chains, allowing the formation of ionic clusters and (c) highly hydrophobic backbone combined with hydrophilic side chains leads to phase-separated morphology and the formation of proton-conducting channels.

Hydrocarbon PEMs have the potential to be cheaper and easier to make, operate at higher temperatures, and have less environmental impact. In addition, they have lower fuel permeability due to the more rigid polymer backbone. However, hydrocarbon-sulfonic acids have intrinsically lower acidity and therefore proton conduction. Increasing the IEC to levels that give similar conductivity to Nafion typically results in polymers that swell excessively in a humidified environment, leading to a severe loss of mechanical integrity. In addition, since fuel cell membrane electrode assemblies are almost universally constructed by using Nafion ionomer as a glue to bind the catalyst to the PEM, a dimensional mismatch and mechanical failure leading to electrode delamination will occur when there are significant differences in swelling behaviour over a temperature range.

Our research has investigated several structural design strategies for PEM materials, particularly for DMFC, which can lessen the undesirable trade-off behavior of water and methanol swelling associated with increased proton conductivity, brought about by increasing the IEC. Constraining high IEC polymer electrolyte membranes by non-bonding interactions has been effective in significantly increasing fuel cell performance in DMFC. Alternatively, self-organization of polymers into

hydrophilic proton-conducting domains and hydrophobic domains allows good proton conduction to be achieved at lower IEC values, which can be accomplished by structural side-chains. Work on designing PEMs containing segmented structures with high ionic concentrations in the ionic block is also under investigation as possible materials for intermediate temperature PEMFC. The lecture will summarize some of the progress made so far.