Abstract #1438, 223rd ECS Meeting, © 2013 The Electrochemical Society

A Tutorial on Alternate Proton Conducting Membranes

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Proton-conducting membranes serve as the electrolyte and separator in numerous electrochemical technologies such as fuel cells, electrolyzers, redox flow batteries, electro-winning, electrosynthesis, and sensing. To date the most widely used proton-conducting membrane is the perfluorinated sulfonic acid polymer, Nafion® that was introduced by Du Pont in the late 1960s. While Nafion has extraordinary chemical stability and excellent proton conductivity, it relies on it high water content to be useful in the above-listed applications.

This presentation will review the properties of the Nafion and Nafion-like materials and elaborate on the specific factors that determine their unique performance. The presentation will also describe the limitation of Nafion that have necessitated the search for alternate membranes. The use of Nafion at temperature greater than 100^{o}C and relative humidity less than 50% results in water loss and substantial reduction in conductivity. Further, the manufacturing of Nafion membranes uses expensive fluorinated monomers and processes that make the final product often uneconomical for large-scale applications. Therefore, there has been an unfulfilled and relentless quest for alternative membranes that can offer comparable chemical stability and conductivity over a range of temperatures at a relatively lower cost compared to Nafion.

The advances made with many different approaches to develop alternate proton conducting membranes will be reviewed. Among these widely researched approaches include, (a) polymeric sulfonated acid membranes and composite membranes with additives that help to retain water can provide sufficient proton conductivity at temperatures up to 120 ^{o}C and relative humidity higher than 25%, (b) membranes based on phosphoric acid-doping that conduct protons over a limited range of 160^{o} - 200 ^{o}C, (c) membranes using imidazole side groups as proton "carriers" are promising anhydrous proton conductors, (d) aprotic non-aqueous liquids as proton carriers and (e) non-polymeric inorganic membranes based on cesium hydrogen phosphate exhibit impressive proton conductivity at 230 ^{o}C under anhydrous conditions.

Membranes that have shown significant improvements over Nafion for reducing methanol crossover in direct methanol fuel cells will also be reviewed. The importance of retaining proton conductivity while reducing methanol crossover poses a challenge to the development of such membranes. In this regard, interpenetrating polymer networks offer tunable properties that can be of benefit.

We will also discuss studies by us and other groups on polymeric quaternary ammonium salts that can conduct protons in the absence of water or any other liquid-phase "proton-carrier". The proton transport in these polymer salts occurs by the ionization of the quaternary ammonium groups followed by proton transfer to the anionic groups and reorganization of the polymer backbone by flexing. The proton conductivity correlates with the acid-base properties of the amine and the anion. The bisulfates and dihydrogen phosphates of poly-2-vinylpyridine (P2VP) and poly-4-vinylpyridine (P4VP) were investigated up to temperatures as high as 180^{o}C. We have fabricated membranes and membrane-and-electrode assemblies using this type of membrane. We have also verified the proton-conducting properties of such membranes through steady-state electrochemical hydrogen pumping experiments.

Acknowledgement

The authors acknowledge the Loker Hydrocarbon Research Institute of the University of Southern California for financial support.

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