Dynamic Studies of Sulfonated Ionic Salt
Composites for High Temperature Fuel Cells

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Proton exchange membranes fuel cells (PEMFCs) use Nafion as an electrolyte. Nafion is the most widely used due to its chemical resistance, durability and high proton conductivity.[1] However, conductivity dramatically decreases above 80°C due to its dependence on water to be proton conductive.[2,3] Higher operational temperatures (>120°C) would be ideal to reduce catalyst poisoning.[4,5] Alternative materials for an electrolyte would be ionic salts. Ionic salts are chemically, thermally and electrochemically stable and proton conductive under anhydrous conditions. [6-8] Previous ionic salts studied contained phosphate functional groups where it was shown that these systems have good conductivity in anhydrous conditions.[9] Phosphates possess substantial proton conductivity; however high temperatures can promote an irreversible condensation into pyrophosphates, which lowers conductivity. Sulfonated ionic salts are ideal for PEMCs due to higher thermal stability as well as promising conductivities in anhydrous conditions.[6,8] Sulfonated ionic salts of interest here are prepared with methanesulfonic acid paired with heterocyclic cations such as imidazole and benzimidazole. Although these salts are good proton conductors at high temperatures, they require a membrane support to be fully applicable for fuel cells. Currently, porous Teflon is chosen as the host material from previous studies determining homogenous loading throughout the polymer.[10] Salts are characterized by themselves as well in a polymer host to observe host-salt interactions.

Fast magic angle spinning solid state ^{1}H NMR is used to study local mobility in electrolytes in their intended state. Double quantum filter (DQF) NMR methods will be used to determine proton mobility by filtering out signals of mobile species. With higher temperatures the hydrogen bonded proton (A) becomes more mobile due to additional attenuation compared to the other protons as seen in Figure 1. Attenuation throughout DQF VT for the salt was 32% and the composite was 38% which indicates an increase in local dynamics in the composite, attributed to polymer backbone motions. Spin lattice relaxation time (T_1) were determined to be shorter in the composite than the salt itself. With IMSA salt (2.1 s) and for composite (300 ms) indicates higher mobility in the composite than the salt. This reflects macroscale proton conductivity within the composite membrane. Local mobility will be compared to bulk conductivity measurements by electrochemical impedance spectroscopy.
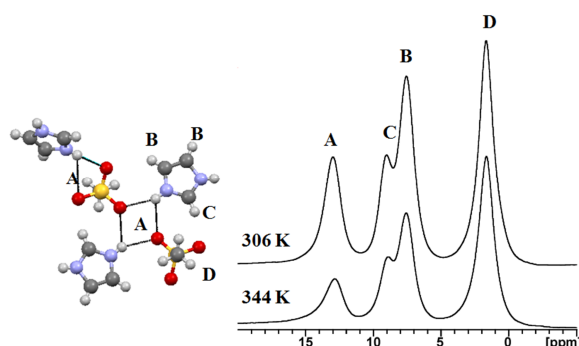

Figure 1: Variable Temperature DQF of Imidazolemethanesulfonate Salt, 500 MHz, 2.5 mm, 25 kHz

References

(1)   Mauritz, K. A.; Moore, R. B. *Chemical Reviews* **2004**, *104*, 4535.
(2)   Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Chemistry of Materials* **2003**, *15*, 4896.
(3)   Jung, D. H.; Cho, S. Y.; Peck, D. H.; Shin, D. R.; Kim, J. S. *Journal of Power Sources* **2002**, *106*, 173.
(4)   Baschuk, J. J.; Li, X. **2001**, *- 25*.
(5)   Hwang, K. S.; Yang, M. C.; Zhu, J.; Grunes, J.; Somorjai, G. A. *J. Mol. Catal. A-Chem.* **2003**, *204*, 499.
(6)   Noda, A.; Susan, A. B.; Kudo, K.; Mitsushima, S.; Hayamizu, K.; Watanabe, M. *Journal of Physical Chemistry B* **2003**, *107*, 4024.
(7)   Sekhon, S. S.; Park, J. S.; Cho, E.; Yoon, Y. G.; Kim, C. S.; Lee, W. Y. *MACROMOLECULES* **2009**, *42*, 2054.
(8)   Watanabe, M.; Tsurumi, K.; Mizukami, T.; Nakamura, T.; Stonehart, P. *Journal of The Electrochemical Society* **1994**, *141*, 2659.
(9)   Traer, J. W. *Journal of Physical Chemistry B* **2007**, *111*, 5602.
(10)   Traer, J., McMaster University, 2008.