^{19}F and ^{13}C PGSTE-NMR Diffusion Study to Understand Ion Transport in Alkaline Anion Exchange Membranes

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Understanding transport in Anion exchange membranes is important from the point of view of fuel cells. Higher transport properties will result into increased fuel cell performance. Here we report a novel Pulse Gradient Stimulated Echo (PGSTE) NMR based technique to understand ion transport in AEMs.

The primary goal of AEMs in fuel cells is to transport hydroxide (OH^-) ions from cathode to anode. OH^- being highly caustic and detrimental to the membrane is usually substituted with less caustic ions like halides, carbonate and bicarbonate. In this study we have substituted the usual halides like Cl^- or Br^- with F^- ion. Fluoride ion offers few advantages for being used as a substitute for hydroxide like same size, nonreactive and NMR active. Also It is practically impossible to keep CO_2 from reacting with hydroxide in the AMEs which results in formation of bicarbonate/carbonate mixtures in AEMs. Thus it becomes important to see the transport of bicarbonate/carbonate ions in the membranes.

PGSTE-NMR tells us about restrictions in the membranes on micrometer length scale by changing diffusion times.

We have studied anion diffusion in various AEM materials like block copolymers of Poly (vinyl benzyl trimethyl ammonium) and poly (methylbutylene), Poly (vinyl benzyl trimethyl ammonium) and Polyethylene, and polyphenylene based[1] polymers which employ various synthesis routes and film casting techniques, thus giving different morphological structures. These different morphological structures result in different ion channels which are being investigated using the PGSTE-NMR technique.

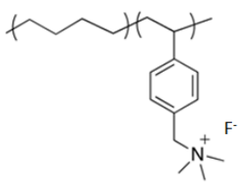

Figure 1. Structure of PE-b-PVBTMA based AEMs

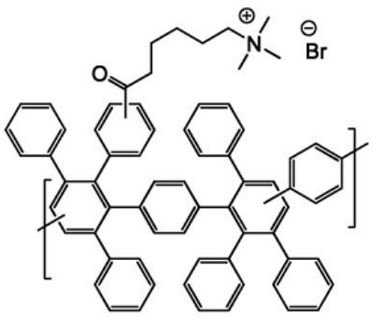

Figure 2. Poly(phenylene) based AEMs[1] (TMAC6PP)

We probe fluoride ($^{19}F^-$), ^{13}C enriched carbonate ($^{13}CO_3^{2-}$) and enriched bicarbonate ($H^{13}CO_3^-$) diffusion in the above mentioned AEMs to get insight into anion self diffusion coefficients.

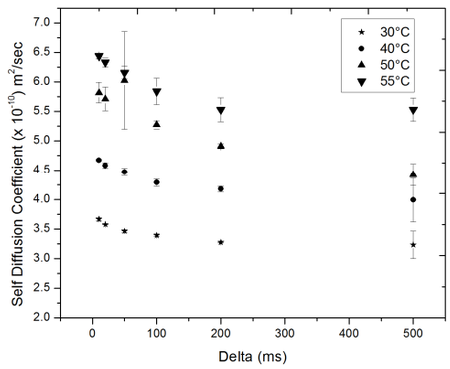

Figure 3. Fluoride Self Diffusion as a function of diffusion Time Delta (Δ) for TMAC6PP type of membrane.

Figure 3 shows a typical self diffusion curve for fluoride ion in the poly(phenylene) based membranes showing the effect of restricted diffusion at short diffusion times which diminishes as the diffusion time is increased. Also it is worth noticing that effect of restricted diffusion is prominent at higher temperatures (55°C) when the ions are much more mobile compared to the lower temperature. (30°C)

This transport study reports an entirely new approach to understanding ion transport by studying fluoride, bicarbonate, carbonate ion diffusion in AEMs.

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We would like to thank the Army Research Office for funding this Multidisciplinary University Research Initiative under contract #W911NF-10-1-0520 and the Colorado School of Mines NMR facility, funded by National Science Foundation under the grant CHE-0923537. We would like to thank Yifan Li, D M Knauss, J R Varcoe, Michael R. Hibbs, Tsunghan Tsai E. Bryan Couglin for providing with AEMs for this study and Yuan Yang from CSM for helping with the NMR facility at CSM.

References:

(1) Hibbs, M. R. ***Journal of Polymer Science Part B: Polymer Physics*** **2012, in press, available online**: **10.1002/polb.23149**