

Modified imidazolium functionalized AEM and investigation of influences on the conductivity
Ye Liu, Junhua Wang, Yushan Yan, Matthew W. Liberatore, Andrew M. Herring

Colorado School of Mines, Department of Chemical & Biological Engineering, Golden, Co 80401
University of Delaware, Department of Chemical & Biomolecular Engineering, Newark, De 19716

Alkaline fuel cell (AFC) is widely investigated recently as a promising alternative for the well-established proton exchange membrane fuel cell (PEMFC) due to its advantages of high efficiency and low cost. In order to prevent leakage and component corrosion problem, anion exchange membrane (AEM) was used to substitute its original liquid potassium hydroxide electrolyte. Up to date, relative low conductivity and chemical stability when works under alkaline condition are two main limitations for AEM. There are a large amount of investigations focusing on widening cation selection [1-5] for better AEM performance besides most frequently used quaternary ammonium.

Imidazolium was received intensive investigations since 2010 due to its intrinsic beneficial properties. For example, its five ring conjugated structure helps to delocalize positive charge [6], synthesis chemistry is more in favor of generating phase-separated morphology via pre-functionalized strategy [7] and its thermal stability is higher than quaternary ammonium [8]. Zhang [9] and Guo [10] investigated on the identical imidazolium AEM with different backbones. There is a great difference on their chemical stability. Deavin [11] made a comparison of benzyltrimethylammonium and benzylmethylimidazolium cation with the same backbone AEM. It is found that imidazolium functionalized AEM shows comparable conductivity, but lower stability compared with ammonium functionalized AEM. Later, Page [12] modified the imidazolium by attaching another methyl group on the carbon between two nitrogen and found chemical stability was improved. In our investigation, 1,4,5-trimethyl-2-(2,4,6-trimethoxyphenyl) imidazolium functionalized polyphenylene oxide (PPO-TMIM) was studied with the structure shown in Fig. 1. It is expected that the membrane performance could be modified by the contribution from strong electron donating functional groups as well as increased steric effect.

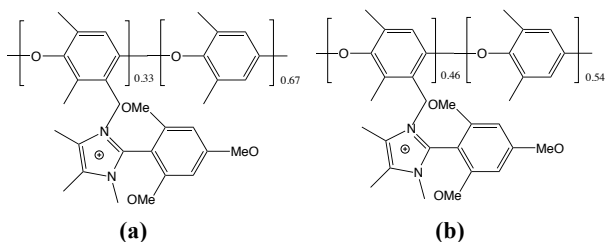


Fig.1 Structure of PPO-TMIM1 (a) and PPO-TMIM2 (b)

Chemical stability was tested by immersing the membrane into 1 M NaOH solution under room temperature for 60 days. The conductivity does not show reduction after was treated under base. Conductivity with different counter ions were tested under 95%RH, from 50C to 90C. The results are shown in Fig. 2. Conductivity of PPO-TMIM2 with larger IEC is higher than that of PPO-TMIM1, but PPO-TMIM2 turns up to degradation at higher temperature. In addition, conductivities with different counter ions for PPO-TMIM1 and PPO-TMIM2 do not show the same trend. In order to better explain the conductivity performance, water uptake from DVS

technique, glass transition temperature from DSC measurement, morphology determination from SAXS technology, anion diffusion coefficient were further investigated. Based on both independent analysis of the influences above and their comprehensive effect on conductivity performance, the dominant influence factor would be determined.

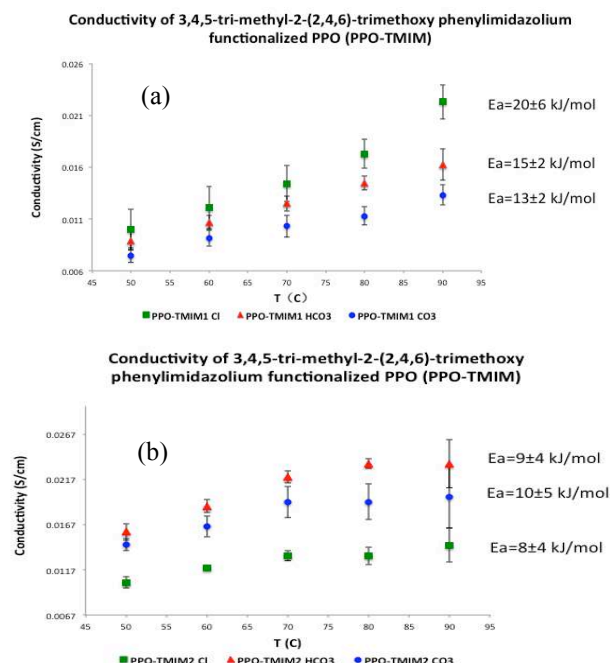


Fig.2 Conductivity of PPO-TMIM1 (a) and PPO-TMIM2 (b)

Reference

- [1] V. Neagu, I. Bunia, I. Plesca. Polymer Degradation and Stability. 2000, 70, 463-468.
- [2] S. Gu, R. Cai, T. Luo, et al. Angew. Chem, Int. Ed. 2009, 48, 6499-6502.
- [3] J. T. Kevin, Noonan, M. Kristina, et al. Journal of American Chemistry Society. 2012, 134, 18161-18164.
- [4] B. Z. Zhang, S. Gu, J. H. Wang, et al. RSC Advances. 2012, 2, 12683-12685.
- [5] J. H. Wang, S. H. Li, S. B. Zhang. Macromolecules. 2010, 43, 3890-3896.
- [6] Y. S. Ye, Y. A. Elabd. Macromolecules. 2011, 44, 8494-8503.
- [7] J. Ran, L. Wu, R. John, et al. Journal of Membrane Science. 2012, 415-416, 242-249.
- [8] W. H. Awad, J. W. Gilman, M. Nyden, et al. Thermo chimica Acta. 2004, 409, 3-11.
- [9] F. X. Zhang, H. M. Zhang, C. Qu. Journal of Materials Chemistry. 2011, 21, 12744.
- [10] M. L. Guo, J. Fang, H. K. Xu, et al. Journal of Membrane Science. 2010, 362, 97-104.
- [11] O. I. Deavin, S. Murphy, A. L. Ong, et al. Energy & Environmental Science. 2012, 5, 8584.
- [12] O. M. M. Page, S. D. Poynton, S. Murphy, et al. RSC Advances. 2013, 3, 579-587.

Acknowledgments

The authors would like to thank the Army Research Office for support of this research under the MURI #W911NF-10-1-0520. The authors would also like to thank the rest of the MURI team members.