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## BESH2019 Hydroxide Conductors for Energy Conversion Devices

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### Program Scope

The present lack of stable, high performance, hydroxide conducting anion exchange membranes (AEMs) is a key limitation for several extremely promising energy conversion and storage systems and development of such materials is critical if the true potential of these technologies is to be realized. The main goal of this project is to evaluate and understand the factors that govern the stability of quaternary ammonium cationic group, linkage, and tether components of polymer electrolyte anion exchange membranes towards development of novel AEM materials with improved stability. Degradation routes and stability of quaternary ammonium cationic groups bound to perfluorinated polymer backbones are of particular interest. Our previous work within this space focused on evaluating the stability of benzyltrimethylammonium and imidazolium cationic groups as well as establishment of an applied and novel method to evaluate and quantify cation stability under conditions representative of those experienced by AEM materials during device operation. We have since expanded our focus to include not only the stability of cationic groups themselves but also their linkage and tether structure. The stability of AEM materials depends on several factors including the structure of cationic groups as well as tethers and covalent linkages. Using a combined experimental and computational approach we have been developing structure-function-property relationships that have resulted in notable increases in stability and development of improved AEM materials. More specifically, by preparing a series of model ammonium cations with varying linkage, tether, and cationic group structure and evaluating their stability using our established method, we have identified key degradation routes and problematic structures as well as key structural features that perturb degradation and improve stability. Computational modeling focused on our library of model cations has afforded further understanding of relevant degradation methods. Overall, our work represents a systematic progression of identification of optimized covalent linkage, tether, and cationic group structure for improved stability.

### FY 2016 Highlights

- Synthesis and evaluation of several model cationic compounds in terms of their stability towards hydroxide has resulted in notable improvements in stability.
- We have developed structure-function-property relationships relevant to AEM stability by preparing series of model cationic compounds with varying covalent linkages, tether lengths, and cationic groups and evaluating the hydroxide stability of these compounds using our established method. Modulation of covalent linkage, tether length and structure, and cationic functional groups followed by analysis of degradation routes and breakdown products has resulted in emergence of trends that are currently being applied to develop AEM materials with improved stability.
- We have demonstrated a strong correlation between acidity of hydrogen in  $\beta$  position to quaternary ammonium cation and the rate of the cation degradation (Hoffman elimination).

- We have established that  $\beta$ -hydrogen acidity is strongly influenced by the length of the aliphatic tether and properties of alkyl group (aliphatic vs. perfluoroalkyl) detached to sulfonamide functionality.
- For a particular series of model compounds representing AEM materials with perfluorinated polymer backbones containing cationic functionality bound via sulfonamide linkages, we have demonstrated significant increases in stability ( $\sim 30x$ ). By varying tether length/structure we have perturbed certain key degradation methods and identified tethers optimized for maximum stability.
- We have identified optimal tether structure and length for elimination of unfavorable interactions between polymer backbone/covalent linkage that result in degradation.
- By applying trends and information obtained from our series of degradation studies we identified new model cation targets that have been designed to perturb key degradation methods.
- We have extended our previous computational modeling research to investigate the stability of substituted phosphonium cations and cyclic quaternary ammonium cations, and then compared our calculation results with the experimental measurements from our collaborators.
- For the substituted phosphonium, the major degradation pathways are the nucleophilic addition pathway and the  $S_N2$  pathway. Our calculation results have good correlation with the experimental data for both pathways.
- For the cyclic quaternary ammonium cations, major degradation pathways are the  $S_N2$  pathway and  $E2$  pathway. Our computational results show some correlation with the experimental data for the  $S_N2$  pathway but underestimate the reaction barriers for the  $E2$  pathway. Our current computational works are aimed to understand why the density functional theory calculation resulted in underestimated  $E2$  reaction barriers.