

# V.N.16 Fundamentals of Hydroxide Conducting Systems for Fuel Cells and Electrolyzers

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## Objectives

- Provide fundamental understanding of hydroxide conducting systems
- Explore stability and basicity of cations
- Relate cation chemistry and structure to conductivity
- Elucidate importance of carbonate in hydroxide conducting systems

## Technical Barriers

Alkaline membrane-based electrochemical systems have been limited by: 1) the poor stability of tetraalkyl ammonium ions employed as covalently tethered cations in anion exchange membranes; 2) the decreased conductivity of hydroxide compared to protons; and 3) the role of carbonate/hydroxide equilibrium in these systems. Alkaline systems have shown improved electrocatalysis and the ability to operate without precious metal catalysts (like platinum). If systems based on alkaline membranes could achieve good stability and conductivity, they would play a major role in enabling a hydrogen economy.

## Abstract

The advantages of an alkaline system for fuel cells are improved efficiency, and also the enablement of non-precious metal catalysis, a critical showstopper to widespread implementation of traditional (acidic) fuel cells. Alkaline systems have been largely ignored by the fuel cell community due to concerns with carbonate formation and the inability to produce membranes of acceptable stability. Still, no fundamental investigations

quantifying the role of carbonate formation have been made and investigation of cations other than those based on quaternary ammonium has been very limited. This proposal addresses both of these points, and will probe fundamental aspects of hydroxide conductors for conductivity and stability. We will emphasize the investigation of families of cations that show promise, but have been largely overlooked by the ion exchange community. The project includes molecular dynamics modeling which allow us to probe the chemical stability and conductivity of target cations, the functional component of anion exchange materials. This modeling work will be closely tied to the characterization of traditional cations and the synthesis and characterization of non-traditional cations potentially suitable for incorporation into anion exchange membranes. Finally, the role of carbonate (or bicarbonate) versus hydroxide anion in these systems will be elucidated. The team we have assembled is eminently and uniquely qualified to successfully achieve these goals. The results of the work proposed here will provide a greater understanding of the fundamental aspects of hydroxide conductors for fuel cell and electrolysis applications, and the development of hydroxide-stable cations may lead the way for the next generation of fuel cells and electrolyzers.

## Progress Report

We are finding a connection between the chemical stabilities of the cation, and the extent of interaction between the hydroxide anion and water(s) of hydration. Hydroxides of the family of tris(dialkylamino)sulfonium cations have exhibited considerable stability in water, even at high temperature, but when the water is removed by evaporation they degrade rapidly at room temperature by hydroxide attack at sulfur, a reaction previously unknown for this class of cations. Molecular modeling studies suggest that both hydroxide attack at sulfur and beta-CH-elimination can be facile degradation pathways. It is known that hydroxide becomes more basic in anhydrous media, and these results highlight the effects of such increased basicity when the hydrating waters are removed by evaporation.

It has been known for many years that tetramethyl ammonium hydroxide is stable in aqueous solution at room temperature. However, the solid material decomposes when heated above *ca.*50°C. We observed the decomposition of solid tetramethyl ammonium hydroxide pentahydrate using TGA and analyzed the gases that were evolved using IR spectroscopy and mass spectrometry. Initially, there was loss of water followed by decomposition of the tetramethyl ammonium ion.

The results reveal that contrary to the commonly held belief that this material decomposes solely by nucleophilic attack of hydroxide on the tetramethyl ammonium cation via an  $SN_2$  process,<sup>1</sup> there is a significant degree of deprotonation of the methyl group to form an ylide structure. This was discovered by the observation of deuterium scrambling into the trimethyl amine that was liberated when the reaction was carried out using tetramethylammonium deuterioxide ( $D_2O$ )<sub>5</sub>. There was also a surprisingly large amount of dimethyl ether formed in the decomposition reaction, again consistent with ylide formation.

The results of these experiments are consistent with our computational studies that suggest that both ylide formation and nucleophilic attack are accessible degradation routes for quaternary ammonium. Furthermore, the increase in both nucleophilicity and basicity that is observed in the hydroxide ion as the number of water molecules of hydration is reduced is also predicted by the computational work and is in agreement with the results observed in the stability studies of the sulfonium and phosphazanium cations. All of our results suggest that cation stability in the presence of hydroxide will be highly dependent on the presence of enough water to attenuate the extraordinary nucleophilicity and basicity of hydroxide that develops as hydroxide is dehydrated.

Our computational work has thoroughly investigated the mechanisms of decomposition of tetramethyl ammonium ion ( $TMA^+$ ) on the basis of hydroxide ( $HO^-$ ) attack. Both  $SN_2$  and ylide mechanisms are available and they have been found to have similar activation energies in the range 10–15 kcal/mol, determined on the basis of standard electronic structure methods together with a “polarizable continuum model” of the solution medium. In addition, we have computationally investigated these decomposition routes for a methylated macrobicyclic amine (the “DABCO” headgroup) that literature precedents have suggested to have better stability.<sup>2</sup> We found an activation energy for that case quite similar to that for  $TMA^+$ . The conclusion suggested by this work is that variability in stability of alkyl ammonium head groups is an expression of accessibility of the cations to  $HO^-(aq)$ .

### Future Directions

Two paths are being followed to address the issue of access of  $HO^-(aq)$  to alkyl ammonium head groups. The first is analysis of experimental D/H isotope scrambling by a process that proceeds through the ylide intermediate. The second path to investigate access of  $HO^-(aq)$  to alkyl ammonium head groups is pore-level molecular simulation of these membranes. This requires a practical molecular model of  $HO^-(aq)$  which

hasn't been available. We have, therefore, developed an empirical valence bond (EVB) model of  $HO^-(aq)$  that permits realistic proton exchange events. Work is in progress to validate this model, and results will be reported in due course.

In the coming year (FY 2008), we will complete the validation of the EVB model of  $HO^-(aq)$ , and pore-level simulation of hydration membranes with  $TMA^+$  headgroups and  $HO^-$  counter-ions. We will combine the simulation results with available experimental data to characterize access of  $HO^-(aq)$  to alkyl ammonium head groups. We will continue studying the rates and mechanisms for degradation of hydroxides of quaternary ammonium, sulfonium, phosphazanium and guanidinium cations. We will be working toward the development of next-generation cations, in one or more of these families that show improved resistance to these chemical degradation processes. By using molecular modeling and conductivity and mobility measurements we will determine the extent and consequences of cation-hydroxide (hydrate) interactions, and use these findings to guide the development of better-conducting, degradation-resistant cation-hydroxides.

In later years we expect to begin incorporating these cation-hydroxides into membranes for more detailed study and possible application, and to determine the nature and effects of carbonate inclusion.

### References

1. K. Kneifel and K. Hattenbach, “Properties and Long-term Behavior of Ion Exchange Membranes,” *Desalination*, 34, **1980**, 77.
2. B. Bauer, H. Strathmann and F. Effenberger, “Anion-Exchange Membranes with Improved Alkaline Stability,” *Desalination*, 79, **1990**, 125.

### Publications (Including Patents) Acknowledging the Grant or Contract

1. “*Non-van-der-Waals* treatment of the hydrophobic solubilities of  $CF_4$ ,” D. Asthagiri, H. S. Ashbaugh, A. Piryatinski, M. E. Paulaitis, L. R. Pratt (LA-UR-07-0811) submitted to *J. Am. Chem. Soc.* (2007).“
2. “Simulation of the hydration of tetramethyl ammonium ion in water,” (LA-UR-06-) S. Chempath, L. R. Pratt, and B. Pivovar.
3. “Alkaline Anion Exchange Membranes for Fuel Cell Applications,” B. Einsla, B. Pivovar, invited article for *PCCP*, (in preparation).
4. Provisional patent, “Anion-Conducting Polymer, Composition and Membrane,” Los Alamos National Laboratory and the University of California, B. Pivovar, D. Thorn, filed 2005.