

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

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widespread implementation of traditional (acidic) fuel cells. Alkaline systems have seen much less research interest by the fuel cell community compared to competing technologies 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 project addresses both of these points, and probes 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 quantum mechanics (QM) and molecular dynamics (MD) 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.

Objectives

- Provide fundamental understanding of hydroxide conducting systems.
- Explore stability and basicity of cations.
- Relate cation chemistry and structure to stability and 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 current 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 commercial competitiveness of fuel cell systems.

Abstract

The advantages of an alkaline system for fuel cells are improved efficiency, and the enablement of non-precious metal catalysis, a critical showstopper to

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The lifetimes of anion exchange membranes and the covalently tetherable cations that make them possible have historically been perceived to be inadequate by the research community.¹ The studies we have performed in this project have allowed for better quantification of cation degradation rates, and have found that cation stability is meaningfully higher than what is generally perceived (and likely acceptable for some applications).^{2,3} Our results are consistent with other results in the literature⁴ and seem reasonable when compared with recent membrane durability studies.^{5,6} These reflect significant improvements over systems studied earlier that had been developed largely for ion exchange applications.⁷ These findings suggest that in current state of the art materials, the primary durability limitation is cation stability, the primary focus of this project. To date we have quantified improved durability with 3 cation systems compared to the standard benzyl

trimethylammonium (BMTA) cation. The best of these, an ether-linked ammonium showed more than a 3x improvement in stability, a meaningful increase when considering applications.

Significant advances in this project have come from studies of cation stability and center on the role of water and solvation in cation stability. In hindsight, the fact that water availability (eg., # of waters per hydroxide) would play a role in cation stability seems fairly obvious, yet this phenomenon had been only minimally reported in the literature^{8,9}, and not in the context of membranes (although many vendors of these materials ship them hydrated with instructions to keep wet). Our results demonstrate that the impact of solvation is greater than what many would have expected, and show that under many conditions hydration is far more important than temperature for degradation. The importance of ylide formation (which may also be related to water content and solvation) as a degradation pathway has been highlighted by our chemical and computational studies.

Our studies have involved both experimental and computational studies of cation degradation. In our computational work, all reaction energies and free energies of reaction barriers for transition states were estimated by Gaussian 03 software, with B3LYP/6-311++G(2d,p) level of theory and the polarizable continuum model (PCM) to account for the solvent. We have also made qualitative and quantitative findings from ab-initio MD simulations performed with VASP software and the rPBE functional. These studies have shown that by treating the water molecules in the hydroxide solvation shell explicitly and the bulk water molecules implicitly, the calculated reaction barrier free energies are in much better agreement with experimental values.¹⁰ We have recently demonstrated the utility of a QM-molecular mechanics (MM) hybrid algorithm and umbrella sampling technique for faster calculation of reaction energy barriers, and shown that in carbonate or bicarbonate form, reaction barriers for decomposition are significantly (>10kcal/mol) higher than in hydroxide form.

Our thermal analyses of crystalline TMAOH pentahydrate used EGA (evolved gas analysis) to probe degradation chemistry.³ The results from these studies have allowed us to benchmark mechanistic details and correlate the results with our computational studies. The identity and quantities of the gases that were evolved upon decomposition of TMAOH pentahydrate were analyzed by a combination of thermogravimetry (TG), FT-IR spectroscopy and mass spectrometry (TG-FTIR and/or TG-MS). We have focused primarily on ammonium based cations: BMTA, tetramethyl ammonium, ethyltrimethyl ammonium and phenyltrimethyl ammonium have received the most attention. Mechanistic studies using partially deuterated or judiciously substituted alkyl ammonium cations has allowed us to study the interplay of the various

decomposition mechanisms; Hoffman degradation, nucleophilic attack and ylide formation. Furthermore, an ether linked ammonium¹¹, and two other literature referenced nitrogen-centered cations have shown increased stability compared to BMTA.^{4,12}

Future Directions

Our primary focus remains on fundamental investigations into the mechanisms and reaction barriers associated with cation degradation. This involves both quantifying and understanding the rates of current materials, and the pursuit of advanced cations with improved durability. Additional studies will include investigation into conductivity (basicity) and the role of carbonate. We have already begun modeling studies of carbonate and bicarbonate solutions of the cations under investigation and will use these alternate salt-forms to better probe stability and durability experimentally. Now that we have verified our ability to quantitatively assess cation stability under well hydrated conditions, we can and will include many other cations, including phosphonium, and expand our studies of phosphazenium and sulfonium which had been limited due to the surprisingly high stability we had observed with ammonium based cations. The calculations on reaction energies and free energies of reaction barriers for these cations are already under the way based on our established computational models. Preliminary result shows that the degradation of trimethyl amino sulfonium by hydroxide has a more negative reaction energy than ammonium cations such as TMA or BMTA (-48 kcal/mol vs. -25~29 kcal/mol). We have already received other advanced cations that have been shown to have good performance and durability in fuel cell applications¹⁵ in a collaborative agreement from Yushan Yan's group.

Our experimental studies will incorporate fixed humidity into our thermal gravimetric analysis (TGA) studies. To date we have focused either on liquid based cation degradation (primarily in NMR tubes at elevated temperatures) or decomposition under drying conditions where degradation of cations is greatly impacted by the loss of water (typical TGA). As water content is critical in the degradation of cations, by including controlled humidity in our studies we will be more able to probe the sensitivity of durability on water content and better isolate degradation products.

Our synthesis of novel cations will focus on triaminosulfonium, triaminosulfoxonium and phosphazenium derivatives because these materials have demonstrated the potential to be much more stable to attack by hydroxide ion than the more conventional trialkyl ammonium ions. We will also expect to expand our studies to include oligomers and polymers such that we can study the stability of the cation tether, the role of polymer architecture on properties and durability,

and the role of carbonate/bicarbonate on the stability and conductivity of these systems. Advanced NMR techniques, including magic-angle spinning (MAS), ^1H - ^{13}C cross polarization, nuclear spin-relaxation time, and two-dimensional NMR techniques will be utilized to obtain information about the ionic structure, mobility of the charge carriers (conductivity), and polymer – cation interactions.

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