
Lab Call FY18 (Membrane): Stable Alkaline Membrane Based on Proazaphosphatranes Organic Super Base

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Overall Objectives

- Synthesize and characterize alkaline ion conducting polymers for alkaline membrane fuel cell applications.
- Develop alkaline membranes based on the super base.
- Evaluate the performance of the membranes.

Fiscal Year (FY) 2019 Objectives

- Synthesize and characterize the proazaphosphatranes super base grafted polymers.
- Develop alkaline membranes based on the super base.
- Evaluate the stability and performance of the polymers and membranes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Performance
- Durability
- Cost

Technical Targets

This is a focused one-year proof-of-concept study on a new class of ultra-stable and high pH proazaphosphatranes super bases for application in alkaline membranes for alkaline membrane fuel cell applications. The DOE fuel cell membrane targets are:

- Initial conductivity should be >100 mS/cm fully hydrated at 30°C, better than the quats hydroxyl system.
- Membrane stability should be >2,000 hours of membrane electrode assembly operation with less than 20% performance degradation.
- Initial performance in an H₂/O₂ fuel cell similar to a KOH-based system (film at 40 μm) at 50°C of $i = 620 \text{ mA/cm}^2$ at $V_{\text{cell}} = 0.60 \text{ V}$, cost: \$4/kW net.

FY 2019 Accomplishments

- Quantified the thermal stability of three proazaphosphatranes and the derivative super bases in 2 M KOH at 75°C fuel cell fast aging condition.
- Identified the most stable polymer backbone structure to be used in alkaline membranes.
- Synthesized proazaphosphatranes grafted polymer.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

INTRODUCTION

Alkaline membrane fuel cells have demonstrated the application of platinum-group-metal-free (PGM-free) catalyst and facile oxidation kinetics. However, stable, high-ion-conductive and low-swelling membranes for room temperature alkaline polymer electrolyte membrane (PEM) fuel cell applications that meet both life and performance targets remain elusive. Proazaphosphatranes super bases have superior stability and high alkalinity. The OH^- based membrane of super base can potentially be processed similarly to commercial ion exchange membranes in aqueous solution, with precise control of alkalinity and swelling. Membrane electrode assemblies may be fabricated in a facile manner with a PGM-free catalyst. A new class of ultra-stable and high pH proazaphosphatranes super bases has been investigated as a potential candidate for alkaline membranes in this project.

APPROACH

This project used synthetic chemistry to develop new alkaline membranes with superb stability and performance to enable a PGM-free alkaline membrane-based fuel cell. Lawrence Berkeley National Laboratory aimed to perform proof-of-concept work on a new class of ultra-stable and high-pH proazaphosphatranes super bases for application in alkaline membranes, with an ultimate goal of developing high-performance alkaline membranes and a fuel cell system that rivals the performance of current Nafion membrane and PEM fuel cell systems.

RESULTS

The most investigated and highly commercially developed alkaline membrane is the organic quaternary ammonium (quats) hydroxyl functionalized polymer membrane, used in, for example, water purification applications. However, membrane degradation due to the Hoffmann elimination of the quaternary ammonium group is the major issue limiting the practical application of this type of alkaline membrane. The pH (~11) of the quats hydroxyl is also low for the optimum alkaline fuel cell application. Although other approaches using mineral base (e.g., KOH) functionalization can achieve a higher pH, lack of membrane stability, leakage of mineral base over time, and carbonate formation and precipitation prevent successful implementation of the mineral bases in PEM fuel cell applications. There are very few organic bases being explored for alkaline fuel cell membrane application except the quats system [1].

One of the major developments beyond the amine and quats base is the phosphonium-based proton sponge and proazaphosphatranes super base (Figure 1), mainly as a catalyst for organic synthesis. The proazaphosphatranes super base has a pH over 26 in organic solvent, stronger than mineral bases such as KOH [2–3]. Proazaphosphatranes are used as a catalyst in organic base reactions at high pH and have a turnover rate of more than 10,000. These above-mentioned examples demonstrate the superb stability of the proazaphosphatranes organic super base compounds [4]. Noticeably, the super base is synthesized by reacting its salt precursor with very strong *t-buOK* base in high yield (~97%) (Figure 2).

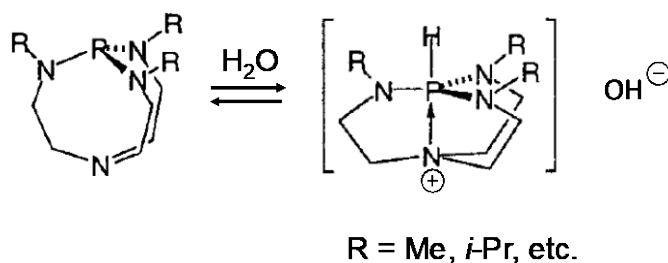


Figure 1. Proazaphosphatranes organic super base and its transformation in OH^- base in aqueous solution

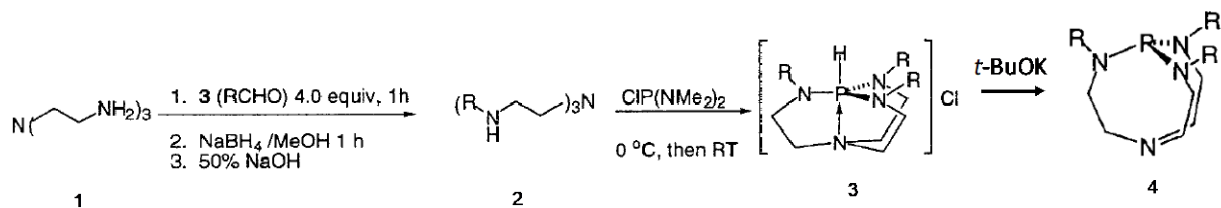


Figure 2. General synthetic procedure of the proazaphosphatranes organic super base

A proof-of-concept investigation was conducted to answer three key issues:

1. Does the new base derivative have superb stability suitable for alkaline fuel cell applications?
2. What is a good polymer matrix to host this base?
3. What areas need further improvement: membrane stability, swelling, or kinetics?

Based on preliminary results, we will decide the research focus for the next phase.

1. Alkaline Stability of the Proazaphosphatranes Organic Super Base and Its Derivative

The stability of two types of the proazaphosphatranes organic super base was investigated in various conditions, including mild conditions (pH=13 and at 25°C and 70°C) and accelerated aging test conditions (2 M KOH at 75°C for extended period). Some of the samples were tested up to 8 months, and the super bases showed little degradation. The sample stability was tracked by nuclear magnetic resonance (NMR) spectroscopy technique. The most stable super base structure was R = methyl group, which showed no degradation at pH=13 at 70°C for the 8-month period. However, the super base of R = isopropyl group tended to degrade due to the tertiary carbon on the isopropyl groups.

The R = methyl group (Figure 1) was chosen to be synthesized into a model compound with a connection on the phosphorus group to the benzoic (Bz) moiety. This model compound structure mimics the end polymer structure. This model compound was subjected to a 2 M KOH and 75°C fuel cell membrane accelerated aging condition. The model compound showed about 5% degradation after 2 weeks of aging (Figure 3).

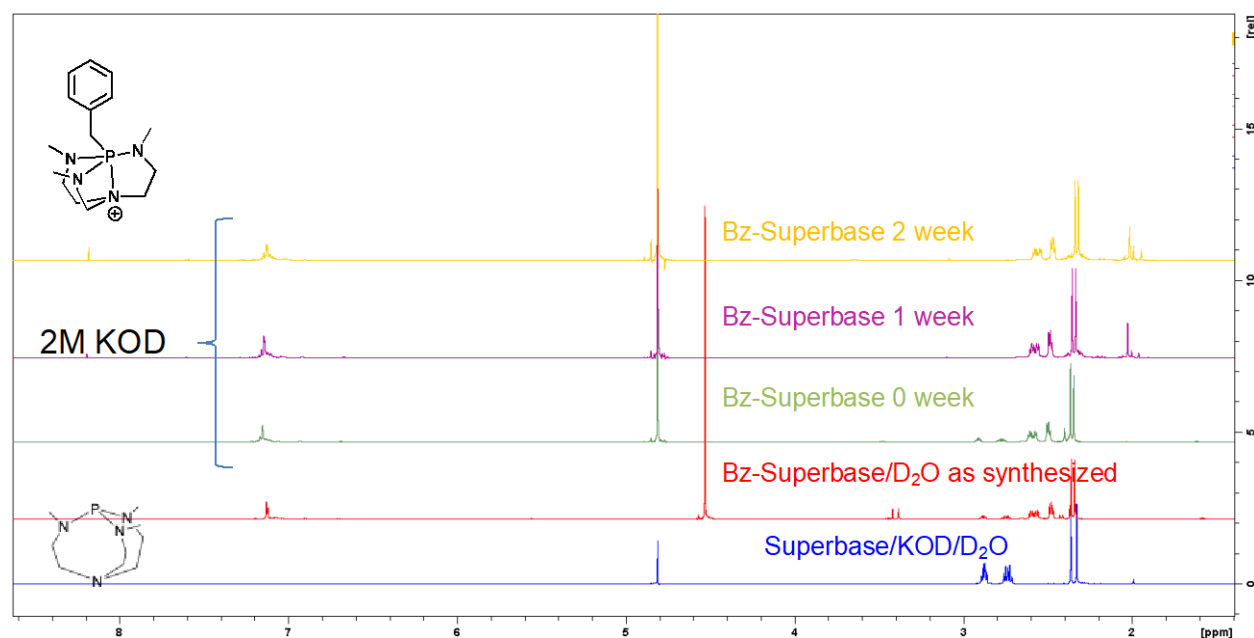


Figure 3. Accelerated aging stability by ^1H NMR of the Bz-super base in 2 M KOD at 75 °C.

2. Selection of Polymer Matrix

Polystyrene-based copolymers exhibit superb base stability. In this project, hydrogenated polystyrene-co-isoprene was used as the polymer backbone structure. We chose to study the long-term stability of hydrogenated polystyrene-co-isoprene in 2 M NaOH in H₂O at 75°C. The polymer showed no sign of degradation after 1-month exposure in the base solution at 75°C. This hydrogenated polystyrene-co-isoprene backbone polymer was chosen to be modified and grafted with super base.

3. Synthesis of the Proazaphosphatranes Organic Super Base Grafted Polymer

The super base grafted polystyrene-co-isoprene based on hydrogenated sample was successfully synthesized (Figure 4). However, the grafting rate was only 12% per repeating unit. When the based polymer possesses higher chloro moiety, the super base tends to crosslink the polymer backbone structure.

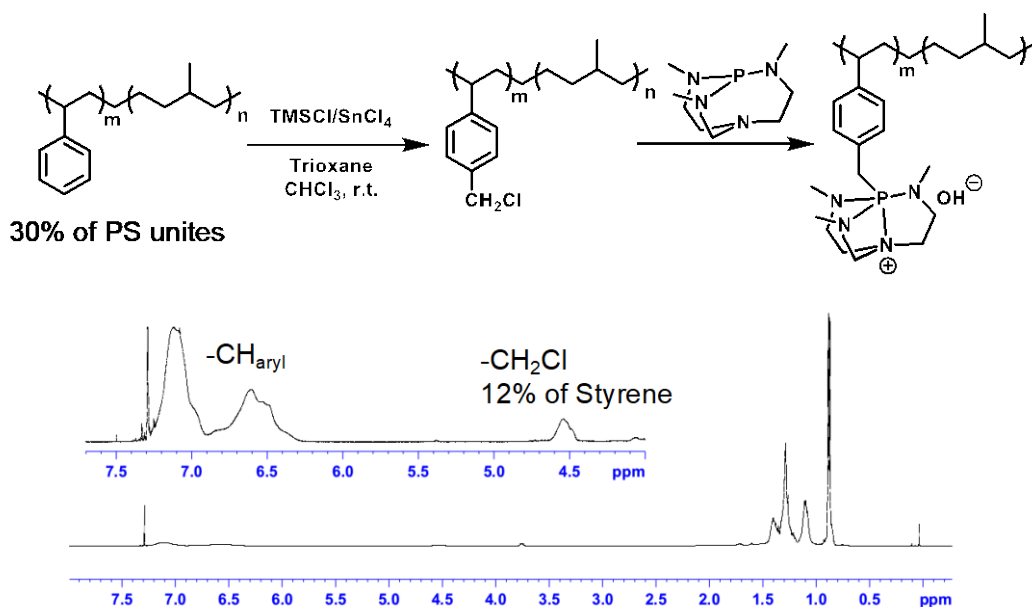


Figure 4. The synthesis of super base grafted polymer

CONCLUSIONS AND UPCOMING ACTIVITIES

In this project, a new alkaline base-proazaphosphatranes organic super base was identified as an alternative base functional group to synthesize alkaline membranes. The stability of the base was investigated through multiple methods. The proazaphosphatranes organic super base has better stability at high alkaline condition compared to other organic bases. Hydrogenated polystyrene-co-isoprene tends to have better high alkaline stability compared to other type of polymer backbone materials. The alkaline polymer was successfully synthesized and characterized. The main drawback of this class of polymer is that the base content is low due to the large volume of proazaphosphatranes super base moiety and synthetically low grafting density of the super base moiety onto the polymer.

This is a one-year project.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Gao Liu, "Stable Alkaline Membrane Based on Proazaphosphatranes Organic Super Base," DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Washington, DC, May 1, 2019.

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